

Olmsteadite, $K_2Fe_2^{2+}[Fe_2^{2+}(Nb,Ta)_2^{5+}O_4(H_2O)_4(PO_4)_4]$, a new species, its crystal structure and relation to vauxite and montgomeryite

PAUL B. MOORE, TAKAHARU ARAKI, ANTHONY R. KAMPF, AND IAN M. STEELE

Department of the Geophysical Sciences, The University of Chicago
Chicago, Illinois 60637

Abstract

Olmsteadite, $K_2Fe_2^{2+}[Fe_2^{2+}(Nb,Ta)_2^{5+}O_4(H_2O)_4(PO_4)_4]$, a 7.512(1), b 10.000(3), c 6.492(2)Å, $Z = 1$, space group $Pb2_1m$, occurs as lustrous deep brown to black thick prismatic crystals at the Hesnard pegmatite and as thin prismatic crystals at the Big Chief pegmatite, Black Hills, South Dakota. Hardness = 4; specific gravity 3.36(1) (Hesnard), 3.31(1) (Ta-poor: Big Chief); streak olive-green, cleavages good parallel to {100} and {001}. Variable Ta content (to $Nb_{0.71}Ta_{0.29}$) is noted for Big Chief material. Crystals show $c\{001\}$, $a\{100\}$, $p\{111\}$, $p'\{\bar{1}\bar{1}1\}$ (Big Chief) and additional $m\{110\}$, $g\{101\}$ (Hesnard). Biaxial (+); α 1.725(5), β 1.755(5), γ 1.815(5); $2V \sim 60^\circ$; X blue-green, Y yellow, Z brown; absorption $X \gg Z > Y$, $X||c$, $Y||a$, $Z||b$ (Big Chief); α 1.765(4), β 1.775(4), γ 1.835(4), X dark blue, Y light brown, Z dark brown (Hesnard).

Olmsteadite contains the same kind of structural unit as found in montgomeryite and vauxite. It consists of corner-linked octahedral chains of composition $[Fe_2^{2+}(Nb,Ta)_2^{5+}O_4(H_2O)_4(PO_4)_4]^{6-}$ which are oriented parallel to [010]. These chains are in a *cis*- configuration across the *oxo*-bridges. Average interatomic distances are $Nb^{5+}-O$ 1.98, $Fe^{2+}-O$ 2.12, $P(1)-O$ 1.53 and $P(2)-O$ 1.55Å. The K^+ cation occurs in a distorted cube of oxygen atoms affording an average of $K-O$ 3.02Å.

Introduction

In 1973, Mr. W. L. Roberts of Rapid City, South Dakota, sent us thick prismatic crystals of a deep brown to black phosphate culled from the Hesnard pegmatite near Custer, Custer County, South Dakota, which he noted qualitatively contained potassium, niobium, iron, and phosphorus. Preliminary X-ray powder and single crystal study suggested a species new to scientific intelligence. Several months later, Mr. Roberts submitted thin tabular crystals of an unknown brown phosphate collected by Mr. M. Olmstead from the Big Chief pegmatite, near Glendale, Pennington County, South Dakota, which qualitatively revealed the presence of potassium, iron, and phosphorus. Mutual identity of the two materials was not suspected until we compared their X-ray photographs. In this study, we propose the Big Chief crystals as the type since the crystal structure analysis was performed on that material.

Owing to the peculiar chemistry of the new mineral, here named *olmsteadite*, a complete three-dimensional crystal structure analysis was undertaken, the results of which establish the ideal formula

$K_2Fe_2^{2+}[Fe_2^{2+}(Nb,Ta)_2^{5+}O_4(H_2O)_4(PO_4)_4]$. To our knowledge, this is the first known example of a secondary transition-metal phosphate containing essential niobium.

Descriptive mineralogy

Physical properties

Olmsteadite is a product of hydrothermal leaching and corrosion of primary triphylite-lithiophilite and, presumably, columbite-tantalite. Columbite-tantalite occurs in a paragenesis similar to the primary giant phosphate phases and many occurrences show the two in close contact. Although columbite-tantalite is more resistant to corrosion than triphylite-lithiophilite, many examples are known of partly to extensively altered crystals. It was not possible to locate such examples at either of the localities but columbite-tantalite and triphylite do occur at both.

Olmsteadite occurs early in the sequence of late stage products, its crystals being embedded in minerals later in the sequence. At the Hesnard pegmatite, it is embedded in dense aggregates of red-brown botryoidal-platy rockbridgeite. The crystals are thick

prismatic, very lustrous, and attain lengths up to 1 mm. At the Big Chief pegmatite, the mineral occurs as thin tabular crystals embedded in granular siderite and quartz and rarely exceed 0.3 mm in maximum dimension.

The luster is subadamantine, color deep brown, red-brown to black with bronzy surfaces on some crystals. The streak and powder are olive-green, the hardness 4. Material from the Hesnard pegmatite has a specific gravity of 3.36(1) determined by Berman torsion balance on selected crystals, and Big Chief crystals are 3.31(1) by sink-float in methylene iodide-toluene mixtures. These physical properties resemble those for rockbridgeite and mitridatite with which the new species can be easily confused. The cleavages are good parallel to $\{100\}$ and $\{001\}$. The mineral is difficultly soluble in warm 1:1 hydrochloric acid solution, coloring the solution pale green and leaving behind a fine white flocculent residue.

Crystal morphology

Olmsteadite occurs as lustrous well-developed crystals, thin tabular parallel to $\{001\}$ (Big Chief); and thick tabular parallel to $\{100\}$ to prismatic (Hesnard). Crystals from both localities are elongated parallel to $[010]$. Caution was taken to correctly orient the crystals from the two localities and these were checked by oscillation photographs. Their development is reminiscent of childrenite-eosphorite from pegmatites. The Big Chief crystals afford $c\{100\}$, $a\{100\}$, $p\{111\}$ and $p'\{1\bar{1}1\}$ with p and p' evenly balanced. Crystals from the Hesnard pegmatite show in addition to the aforementioned forms, $m\{110\}$ and $g\{101\}$. Typical developments are presented in Figure 1.

Optical properties

Biaxial (+), α 1.725(5), β 1.755(5), γ 1.815(5), $2V \sim 60^\circ$. Pleochroism is marked, with X blue-green, Y yellow, and Z brown, absorption $X \gg Z > Y$. The orientation of the indicatrix is $X||c$, $Y||a$, $Z||b$. The title formula affords $(n) = 1.74$ from the calculations of Gladstone and Dale using the specific refractive energies in Larsen and Berman (1934).

The Hesnard material has significantly higher indices, α 1.765(4), β 1.775(4), γ 1.835(4), with X dark blue, Y light brown, and Z dark brown. Structural evidence, stated further on, suggests that this material contains substantial Fe^{3+} .

Chemical analysis

Several single crystals were submitted to electron probe analysis (Table 1). Owing to the limited amount of material at our disposal, estimated to be

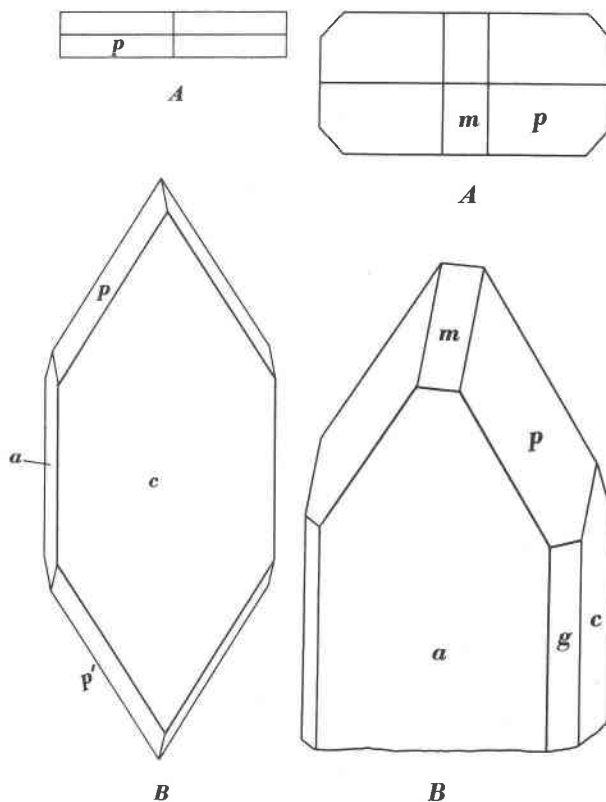


FIG. 1. Crystals of olmsteadite showing the forms $c\{001\}$, $a\{100\}$, $p\{111\}$, $p'\{1\bar{1}1\}$, $m\{110\}$, and $g\{101\}$. (A) Plan. (B) Clinographic projection. The left figure applies to the Big Chief crystals (tabular on $c\{001\}$) and the right figure to Hesnard crystals (tabular on $a\{100\}$).

less than 30 mg, a thorough wet chemical analysis was not possible. The three dimensional crystal structure, however, has been determined to a high level of accuracy, and formal charges and water content can be established with some certainty based on electron densities, bond distances, and electrostatic bond strengths.

A solid state detector with phosphorescent screen permitted routine inspection for elements greater than oxygen in atomic number. Two single crystals from the Hesnard pegmatite and ten grains from the Big Chief pegmatite were examined. The Hesnard material contains but little tantalum, but the Big Chief grains can be divided into tantalum-rich ($>4\%$) and tantalum-poor ($<2\%$) compositions. Manganese substitutes for iron in all grains examined. We employed Mn, Nb, and Ta metal; synthetic magnetite; and natural apatite standards. Corrections, including dead time and background error, were obtained utilizing the ABFAN-2 program of Hadidiacos, Finger, and Boyd (1969). A different correction (Colby, 1968) was applied to the tantalum analysis since our

TABLE 1. Olmsteadite. Refined Electron Probe Analysis

	1	2	3	4	5	6
K ₂ O	8.7	8.5	8.0	7.8	8.9	9.4
MnO	4.8	5.0	2.9	2.9	-	-
FeO	22.7	23.2	24.8	24.6	27.4	28.6
Nb ₂ O ₅	22.7	23.8	23.9	17.8	17.9	26.5
Ta ₂ O ₅ *	0.2	0.2	1.2	7.6	12.2	-
P ₂ O ₅	28.5	28.1	26.2	26.6	26.9	28.3
H ₂ O	-	-	-	-	6.8	7.2
Sum	87.6	88.8	87.0	85.0	100.0	100.0
Specific gravity	3.36		3.31		-	-
Density, gm cm ⁻³	-		-		3.59	3.41

* The Ta correction is somewhat uncertain.
 1,2Hesnard pegmatite. Two single crystals.
 3On a homogeneous grain of Ta-poor material. Big Chief pegmatite.
 4Average over five grains of Ta-rich material. Big Chief pegmatite.
 5Computed for Nb_{0.71}Ta_{0.29} substituted for Nb in (6).
 6Computed for K₂Fe₂²⁺[Fe₂²⁺Nb₂⁵⁺O₄(H₂O)₄(PO₄)₄]

spectrometers were limited to the TaL α spectral line. The correction, however, is uncertain since that correction best applies to metals and alloys. The niobium correction was substantial, amounting to a 33 percent increase beyond the initial ratios. All samples were examined at 15 kV.

Table 1 shows that the agreement between the Hesnard material and the end member composition K₂Fe₂²⁺[Fe₂²⁺Nb₂⁵⁺O₄(H₂O)₄(PO₄)₄] is good if it is assumed that some Fe³⁺ replaces Nb⁵⁺. This is plausible on the grounds of the deep blue color of the Hesnard material and the high indices of refraction. The grains from the Big Chief pegmatite which contain substantial tantalum are believed to represent the composition of the single crystal used in structure analysis since its site occupancy refinement converged to Nb_{0.71}Ta_{0.29}. Excepting Ta₂O₅, whose corrected value is uncertain, the agreement with the computed analysis based on this composition is excellent. Since the density of such a composition is 3.59 g cm⁻³, the specific gravity was apparently determined on the Ta-poor single crystals. It is not surprising that the Ta content varies in the Big Chief sample since several specimens were used to provide enough material for study, and these probably represent slightly different conditions of formation and original fluid composition.

Finally, we remark that even a wet chemical analysis would be incapable of discerning the correct formula since such an analysis cannot distinguish (H₂O) ligands from (OH)⁻ and O²⁻ ligands. The *oxo*-bridge formula proposed here follows from the results of the analysis of the structure.

X-ray crystallography

A single crystal was prepared for three-dimensional structure analysis and the cell parameters were refined directly on the PICKER automated diffractometer yielding *a* 7.512(1)Å, *b* 10.000(3)Å, *c* 6.492(2)Å. Single crystal photographs allow the space groups *Pbmm*, *Pbm2*, or *Pb2₁m*. Structure analysis, including the *N(z)* test on the *hk0* reflections (see Howells, Phillips, and Rogers, 1950) and the *P(y)* test on general reflections (see Srikrishnan and Parthasarathy, 1970), requires the non-centric space group *Pb2₁m*. A section of the crystal used in the structure analysis was prepared for a 114.6 mm Gandolfi camera. The resultant powder data (Table 2) were indexed on the basis of the strong single crystal intensities. Disregarding Ta⁵⁺, the cell contains one end-member formula unit of K₂Fe₂²⁺[Fe₂²⁺Nb₂⁵⁺O₄(H₂O)₄(PO₄)₄] with a computed density of 3.41 g cm⁻³.

Weissenberg photographs of a Hesnard crystal show very weak superstructure reflections, requiring a doubled *c* axis. The space group remains unchanged and the substructure intensities and powder pattern are indistinguishable from the Big Chief crystal. This doubling of *c* plus the invariance of the space group places severe limits on the allowable ordering schemes. The structure analysis shows infinite edge-sharing chains of Fe²⁺-O oxygen octahedra parallel to the *c* axis. We suspect that a weak cooperative ordering of (Fe,Mn)²⁺ and Fe³⁺ along these chains in Hesnard crystals may account for this relationship. It also explains the deep blue pleochroic component parallel to the *c* axis which probably arises from Fe²⁺-Fe³⁺ mixed valence transfer-absorption. Less probable is ordering of minor vacancies or substituting Fe³⁺ over the Nb⁵⁺ sites since this site

TABLE 2. Olmsteadite. Powder Data*

I/Io	d(calc)	d(obs)	hkl	I/Io	d(calc)	d(obs)	hkl
5	7.568	7.512	100	1	2.433	2.429	310
5	6.493	6.492	001	2	2.382	2.385	212
10	6.007	6.006	110	2	2.330	2.327	231
5	4.395	4.409	111	2	2.270	2.275	311
4	4.141	4.162	120	2 brd	2.226	2.239	320
3	3.957	3.961	021			2.228	141
1	3.749	3.756	200	1	2.167	2.164	003
4	3.506	3.504	121	2	2.084	2.081	240
5	3.246	3.251	201	3	1.998	2.002	330
		3.246	002	3	1.981	1.982	241
6	3.045	3.047	130	2	1.944	1.945	312
7	2.990	3.003	220	4	1.912	1.915	142
6	2.856	2.856	112	3	1.873	1.875	203
2	2.749	2.758	131	2	1.844	1.843	322
5	2.717	2.723	022	1	1.764	1.764	133
5	2.560	2.559	122	5	1.749	1.752	242
3	2.498	2.500	040				
1	2.453	2.456	202				
							50 lines, less than 3

*Fe/Mn radiation. 114.6 mm Gandolfi camera diameter. Film corrected for shrinkage and crystal corrected for absorption.
 Indexed for the orthorhombic unit cell: a = 7.512, b = 10.000, c = 6.492.

does not share edges and a cooperative ordering effect is unlikely. The significantly higher indices of refraction and stronger absorption of the Hesnard crystals also support the view that substantial ferric ion is present in the crystal.

These observations add interest to the species since an extensive range of oxidation grade may be possible. A Mössbauer resonance experiment appears to be the best tool to test our suggestions, and if more material comes to light such a study would be practicable.

Name

We honor Mr. Milo Olmstead of Rapid City, South Dakota, an amateur micromounter whose keen judgement led to further examination of specimens which proved to contain an interesting new species. He is typical of the serious-minded amateur mineralogists who have first found and provided many of the new species described in the professional literature, especially over the past ten years.

The name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Olmsteadite: Its crystal structure

Experimental

A single crystal from the Big Chief pegmatite measuring 0.13 mm along *a*, 0.12 mm along *b* and 0.056 mm along *c* was mounted with its *c* axis parallel to the ϕ axis of a PICKER four-circle diffractometer. With graphite-monochromatized MoK α radiation, base scan width of 2.4°, 2 θ scan of 2°/minute and 20

second background counting times, reflections of *hkl* and *h \bar{k} l* were collected up to $\sin\theta/\lambda = 0.75$. Reflections when *I*(obs) were unobserved were set *I*(obs) = 2 σ *I*(obs). The crystal shape can be described by nine faces which provided the information for absorption correction by the Gaussian integral method (Burnham, 1966). Symmetry equivalent reflections of the type *hkl* and *h \bar{k} l* were converted to obtain 1846 *F*(obs) including *hkl* and the *h \bar{k} l* Friedel pairs so that absolute orientation in a polar group could be established. Individual reflections were assigned weights based on long term fluctuation of source intensity and counting statistics.

Solution and refinement of the structure

A full Patterson synthesis, *P*(*uw*), revealed that all heavy atoms were confined to *z* = 0, 1/4, 1/2, and 3/4. The short *c* translation places severe restrictions on the *z* coordinates, and the most plausible distribution of atoms leading to the observed vector densities required a mirror plane normal to this axis. At first, a centrosymmetric model was assumed, but trial β -synthesis (Ramachandran and Srinivasan, 1970) afforded extra densities which necessitated another model. In addition, the *N*(*z*) and *P*(*y*) tests discussed above indicated the noncentric group *Pb2₁m*. Once this was recognized, solution of the structure was rapid. A final γ' -synthesis provided locations of all the remaining non-hydrogen atoms.

Refinement proceeded using scattering factors for Nb⁵⁺, Ta⁵⁺, Fe³⁺, K¹⁺, P⁰ and O¹⁻ from Cromer and Mann (1968), anomalous dispersion corrections for the cations (Cromer and Liberman, 1970), and refinement of the coefficient for secondary extinction (Zachariasen, 1968). Full-matrix scale factor, atomic coordinate and isotropic thermal vibration parameters led to smooth convergence although the Nb site afforded a negative temperature factor. Utilizing scattering curves for Nb and Ta, mixed occupancy refinement was then inaugurated. Finally, the atomic coordinates were inverted and refinement was repeated so that the absolute orientation of the polar structure could be established. The favored model led to an *R* value of 0.037 for all 1846 reflections. The secondary extinction corrections refined to *c*₀ = 2.2(3) × 10⁻⁶.

Final atomic coordinates and isotropic thermal vibration parameters are given in Table 3 and the structure factor data appear in Table 4.¹

¹ For a copy of Table 4, order Document AM-76-012 from the Business Office, Mineralogical Society of America, 1909 K Street, N.W., Washington, D.C. 20006. Please remit in advance \$1.00 for the microfiche.

TABLE 3. Olmsteadite. Atom Coordinates and Isotropic Thermal Vibration Parameters*

Atom	x	y	z	B(Å ²)
Nb	0.27254(5)	0.73837(9)	0	0.44(1)
Fe	.02061(9)	0	0.24183(11)	.77(1)
K	.53021(35)	.97416(28)	½	2.56(4)
P(1)	.1832(2)	.7412(3)	½	.61(2)
O(1)	.0823(8)	.8729(6)	½	.87(9)
O(2)	.0631(11)	.6192(8)	½	1.79(12)
O(3)	.3059(5)	.7376(6)	.3090(6)	1.23(5)
P(2)	.3253(3)	.4149(2)	0	.55(2)
O(4)	.4180(8)	.5547(5)	0	.87(8)
O(5)	.4723(8)	.3067(6)	0	1.04(8)
O(6)	.2138(5)	.3978(4)	.1976(7)	.91(6)
O(7)	.1575(8)	.8999(6)	0	1.16(9)
O(8)	.0735(10)	.6317(7)	0	1.34(9)
OW	.2524(9)	.1117(7)	.2720(12)	2.52(10)

* Estimated standard errors refer to the last digit. The "Nb" refined to 0.709(5)Nb + 0.291(5)Ta.

The best fit led to a distribution of $0.709(5)\text{Nb} + 0.291(5)\text{Ta}$ at the Nb site. The agreement with the probe analysis for all elements except Ta is good; however, the true Ta content is uncertain since the correction for this element is not accurately known. The uncertainty does not affect the following discussion, and we adopt for convenience the ideal end member composition.

Discussion of the structure

Topology of the structure

Olmsteadite consists of cations in octahedral (Nb^{5+} and Fe^{2+}), tetrahedral (P^{5+}) and distorted cubic (K^{1+}) coordination by oxygen atoms. The structure is dominated by the presence of octahedral chains (Fig. 2). The Fe^{2+} -O octahedra share edges to form chains which run parallel to the c axis. These link by corner-sharing to Nb^{5+} -O octahedra and to P(1)- and P(2)-O tetrahedra to form an open framework structure, the K^{1+} cation residing in a large open pocket and coordinating to oxygens in the framework.

We had completed the montgomeryite structure (Moore and Araki, 1974) and shortly thereafter rec-

ognized an uncanny relationship with olmsteadite. If alternate Fe^{2+} -O octahedra along the edge-sharing chain along c in olmsteadite are voided, the resulting corner-linked octahedral chain which runs parallel to the b axis is topologically identical to that in montgomeryite and vauxite! Even more remarkable is the similarity in the disposition of the tetrahedra in all three structures. A direct comparison of all three structures can be made by taking page 849 of Moore and Araki (1974), rotating it $\pi/2$ radians clockwise and placing it adjacent to Figure 2 in this paper. Spatially, all three structures are related such that b 10.0, c 6.5 Å for olmsteadite approximate a 10.0, c 6.2 Å for montgomeryite and a 9.1, c 6.1 Å for vauxite. Olmsteadite differs from the other two structures, however, since all Nb^{5+} -O octahedra are at the same level, so the chain sequence across the *oxo*-bridge is \dots *cis-cis* \dots , whereas in the others it is \dots *cis-trans* \dots across the hydroxyl bridge. We note that the 6.1–6.5 Å repeat in all three structures is roughly twice the Me-O octahedral distances ($2 \times 1.9 = 3.8$ Å) plus the tetrahedral edge distance (2.5 Å). This is clearly seen at the Nb-O and P(1)-O links in olmsteadite.

Bond distances and electrostatic valence balances

The individual bond distances and angles are presented in Table 5. The averages are: Nb^{5+} -O 1.98, Fe^{2+} -O 2.12, P(1)-O 1.53, P(2)-O 1.55 Å. The K^{1+} cation is coordinated to an inner shell (2.85–3.16 Å) of eight oxygens on the vertices of a distorted cube. Three additional oxygens occur at greater distances, $2\text{K}-\text{O}(4)^i$ 3.367(7) Å and $\text{K}-\text{O}(2)^i$ 3.382(9) Å, and constitute the second shell of coordination. The Fe^{2+} -O distance is about 0.02 Å less than the average value of 2.14 Å for $^{16}\text{Fe}^{2+}-\text{O}^{13.5}$ proposed by Shannon and Prewitt (1969).

Two hydrogen bonds are proposed: $\text{OW} \dots \text{O}(6)$ 2.92 Å and $\text{OW} \dots \text{O}(4)^i$ 3.09 Å, with an angle $\text{O}(4)^i-\text{OW}-\text{O}(6)$ 99.5°. These bonds cut across a rather open region in the structure. In the fully assembled structure, the minimum number of broken bonds is parallel to {100}, which is a direction of good cleavage.

To assess the electrostatic bond strength sum, p_x , we adopted $s = +1/6$ for a hydrogen bond acceptor, H_a , and $s = 5/6$ for a hydrogen bond donor, H_d . This procedure follows that of Baur (1970). For these calculations, we adopted $^{16}\text{K}^{1+}$, $^{16}\text{Fe}^{2+}$, $^{16}\text{Ta}^{5+}$, and $^{14}\text{P}^{5+}$ as coordination numbers and charges.

The hydrogen bonds and the coordinating cations (Table 6) suggest that O(7) and O(8) are indeed oxo-

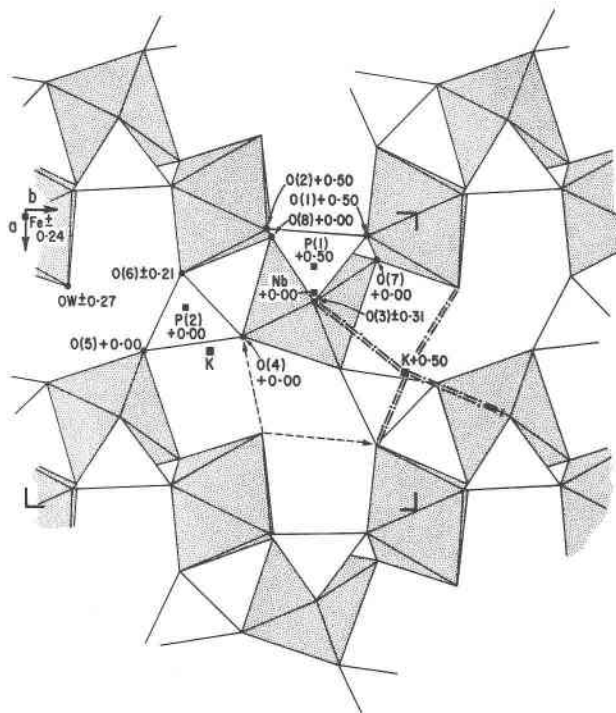


FIG. 2. Polyhedral diagram of the olmsteadite crystal structure down the c axis. The octahedra are stippled and the tetrahedra unshaded. The K-O bonds defining a distorted cube appear as dash-dots and the hydrogen bonds as dashes. Heights are given as fractional coordinates in z .

written in this manner so that a direct comparison can be made with the structurally related montgomeryite, $\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]$; and vauxite, $\text{Fe}_2^{2+}(\text{H}_2\text{O})_4[\text{Al}_4(\text{OH})_4(\text{H}_2\text{O})_4(\text{PO}_4)_4] \cdot 4\text{H}_2\text{O}$.

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