

THE CRYSTAL STRUCTURE OF WOOLDRIDGEITE, $\text{Na}_2\text{CaCu}^{2+}_2(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, A NOVEL COPPER PYROPHOSPHATE MINERAL

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ABSTRACT

The crystal structure of wooldridgeite, $\text{Na}_2\text{CaCu}^{2+}_2(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, orthorhombic, a 11.938(1), b 32.854(2), c 11.017(1) Å, V 4321.2(8) Å³, Z = 8, was solved by direct methods in the space group $Fdd2$ and refined by a full-matrix least-squares method to an R index of 3.4% for 1649 observed ($|F_o| > 5\sigma |F_o|$) reflections. There are two distinct P sites, each tetrahedrally coordinated by four O atoms; the resulting phosphate tetrahedra link through a common anion to form a $[\text{P}_2\text{O}_7]$ group. There is one unique Cu site octahedrally coordinated by four O atoms and two (H_2O) groups, with typical Jahn–Teller distortion [$1.94 \leq \text{Cu}-(\text{O}, \text{H}_2\text{O}) \leq 3.39$ Å]. There is one unique Ca site octahedrally coordinated by four O atoms and two (H_2O) groups, and one unique Na site octahedrally coordinated by two O atoms and four (H_2O) groups. The $(\text{Cu}\phi_6)$ (ϕ : unspecified anion) octahedra each share two *trans* vertices to form a $[\text{Cu}\phi_5]$ chain of corner-sharing octahedra that is decorated with flanking (P_2O_7) groups to form a $[\text{Cu}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})]$ chain. These chains are arranged parallel in layers orthogonal to $[010]$, and the chains in adjacent layers are mutually orthogonal. This array of chains is held together by interstitial Ca and Na, and a network of H bonds.

Keywords: wooldridgeite, crystal structure, phosphate, hydrogen bonds, pyrophosphate.

SOMMAIRE

Nous avons résolu et affiné la structure cristalline de la wooldridgeite, $\text{Na}_2\text{CaCu}^{2+}_2(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, orthorhombique, a 11.938(1), b 32.854(2), c 11.017(1) Å, V 4321.2(8) Å³, Z = 8, par méthodes directes dans le groupe spatial $Fdd2$ sur matrice entière et moindres carrés jusqu'à un résidu R de 3.4% en utilisant 1649 réflexions observées ($|F_o| > 5\sigma |F_o|$). La structure contient deux sites P distincts, chacun ayant une coordinence tétraédrique avec quatre atomes d'oxygène. Les tétraèdres sont liés en partageant un anion pour former un groupe $[\text{P}_2\text{O}_7]$. Il y a un seul site Cu , à coordinence octaédrique avec quatre atomes d'oxygène et deux groupes (H_2O); ces octaèdres font preuve d'une distorsion typique de Jahn–Teller [$1.94 \leq \text{Cu}-(\text{O}, \text{H}_2\text{O}) \leq 3.39$ Å]. Il y a un seul site Ca , à coordinence octaédrique avec quatre atomes d'oxygène et deux groupes (H_2O), et un site Na , à coordinence octaédrique avec deux atomes d'oxygène et quatre groupes (H_2O). Les octaèdres $(\text{Cu}\phi_6)$ (ϕ : anion non spécifié) partagent deux de leurs anions en position *trans* pour former une chaîne d'octaèdres $[\text{Cu}\phi_5]$ à coins partagés; celle-ci est décorée avec des groupes (P_2O_7) latéraux pour former une chaîne $[\text{Cu}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})]$. Ces chaînes sont disposées de façon parallèle dans des couches perpendiculaires à $[010]$, et les chaînes des niveaux adjacents sont mutuellement orthogonales. Cet agencement de chaînes est consolidé par des cations Ca et Na interstitiels et un réseau de liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: wooldridgeite, structure cristalline, phosphate, liaisons hydrogène, pyrophosphate.

INTRODUCTION

Wooldridgeite is a hydrated sodium–calcium–copper pyrophosphate mineral, $\text{Na}_2\text{CaCu}^{2+}_2(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, described from the Judkins quarry, Nuneaton, Warwickshire, England, by Hawthorne *et al.* (1999). Judkins quarry exposes a well-defined unconformity between Precambrian igneous basement and overlying Cambrian sedimentary rocks, and there are minor sulfide and supergene minerals within 10–20 m of the unconformity. The quarry has been worked for many

years for roadstone. Wooldridgeite is only the second pyrophosphate mineral known, and hence the structure is of considerable interest, particularly as the rarity of condensed-phosphate minerals has not yet been explained satisfactorily.

EXPERIMENTAL

The crystal used in this work is from the type locality. A fragment was mounted on a Siemens P4 automated four-circle diffractometer equipped with a Mo

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X-ray tube. Twenty-eight reflections were measured on a random-orientation photograph and aligned automatically on the diffractometer. From the resulting setting-angles, least-squares refinement gave the cell dimensions listed in Table 1, together with the orientation matrix. Intensity data were collected according to the procedure of Hawthorne & Groat (1985). A total of 1323 reflections was measured out to a maximum 2θ angle of 55° ($0 \leq h \leq 15$, $0 \leq k \leq 42$, $0 \leq l \leq 14$). A fixed scan-speed of $0.75^\circ 2\theta \text{ min}^{-1}$ was used. Twelve strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of Ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector). These data were used to calculate an absorption correction, with the crystal modeled as an ellipsoid, which reduced the azimuthal R index from 1.5% to 1.3%; this correction was then applied to the normal intensity data. Data were corrected for Lorentz and polarization effects, averaged and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of five standard deviations on the basis of counting statistics. Miscellaneous information pertaining to data collection and structure refinement is given in Table 1.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from the *International Tables for X-ray Crystallography*, Vol. 4 (Ibers & Hamilton 1974). R and wR indices are of the conventional form and are given as percentages.

The structure was solved by direct methods using the SHELXTL PC Plus system of programs. The E -statistics indicated that the structure is non-centrosymmetric, and we found a solution in the space-group $Fdd2$. The solution with the highest combined figure-of-merit refined to an R index of 3.4% for a model with anisotropic displacements; the absolute configuration of the

TABLE 1. MISCELLANEOUS INFORMATION FOR WOOLDRIDGEITE

a (Å)	11.938(1)	Crystal Size (mm)	$0.04 \times 0.06 \times 0.08$
b	32.854(4)	radiation	Mo K α /Gr
c	11.017(1)	No. of intensities	1323
V (Å ³)	4321.2(8)	No. of $ F_o > 5\sigma(F_o)$	649
Sp. Gr.	$Fdd2$	R (azimuthal) %	1.5 - 1.3
Z	8	R (obs) %	3.4
$m\mu$ (mm ⁻¹)	2.65	wR (obs) %	4.0
D_c (g.cm ⁻³)	2.279		
Cell content: $8[\text{CaNa}_2\text{Cu}_2(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}]$			
$R = \Sigma(F_o - F_c)/\Sigma F_o $			
$wR = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$, $w = 1$			

structure was established. Final atomic positions and displacement parameters are given in Table 2, and selected interatomic distances in Table 3. The observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2. Empirical bond-valence values are shown in Table 4.

DISCUSSION

Cation coordination

There are two crystallographically distinct P sites, each coordinated by four O atoms in a tetrahedral arrangement. One O atom, O(1), is bonded to both distinct P atoms, forming a $[\text{P}_2\text{O}_7]$ dimer. Each P atom has three short terminal bonds of ~ 1.52 Å and one long bridging bond to O(1) of ~ 1.63 Å. The elongation of the bridging bonds to O(1) is a result of the bond-valence requirements of O(1); as O(1) bonds to two P atoms with a Pauling bond-strength of 1.25 vu (valence units) each, the P -O(1) bonds must elongate to produce the required bond-valence incident at O(1) (Table 5). In accord with simple molecular-orbital arguments (Lager & Gibbs

TABLE 2. FINAL PARAMETERS FOR WOOLDRIDGEITE

Site	x	y	z	U_{02}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0	0	0	15(1)	15(2)	17(2)	14(2)	0	0	3(2)
Na	0.2143(6)	0.0974(2)	0.0959(8)	49(2)	64(4)	62(4)	22(3)	-7(4)	17(4)	-34(4)
Cu	0.1201(2)	0.13964(6)	0.6000(4)	19(1)	20(1)	21(1)	17(1)	9(1)	7(1)	10(1)
P(1)	0.0457(3)	0.1811(1)	0.3560(5)	18(1)	20(2)	21(2)	15(2)	0(2)	4(2)	-4(1)
P(2)	0.1413(3)	0.0705(1)	0.8009(5)	17(1)	18(2)	18(2)	17(2)	3(1)	3(2)	0(2)
O(1)	0.1986(7)	0.0470(3)	0.685(1)	18(3)	17(5)	23(5)	13(5)	-2(4)	-3(4)	0(4)
O(2)	0.0870(8)	0.2128(3)	0.268(1)	21(3)	19(5)	26(6)	18(5)	6(4)	-1(4)	-6(4)
O(3)	0.1374(8)	0.1687(3)	0.445(1)	27(3)	24(6)	39(6)	19(5)	6(5)	5(5)	14(5)
O(4)	0.2401(9)	0.1045(3)	0.544(1)	31(3)	34(6)	35(6)	25(6)	16(5)	17(5)	23(5)
O(5)	0.0916(8)	0.1096(3)	0.751(1)	27(3)	36(6)	22(5)	22(5)	11(5)	17(5)	8(5)
O(6)	0.2355(8)	0.0781(3)	0.893(1)	28(3)	27(6)	35(6)	22(5)	-8(5)	-2(5)	-9(5)
O(7)	0.0555(7)	0.0412(3)	0.847(1)	22(3)	25(5)	25(5)	17(4)	-1(5)	3(5)	-12(4)
OW(1)	0.0840(7)	0.0437(3)	0.158(1)	24(3)	19(5)	27(6)	25(6)	-4(5)	3(5)	-2(4)
OW(2)	0.042(1)	0.1388(4)	0.046(1)	50(4)	61(8)	54(8)	38(6)	-4(7)	11(6)	-8(7)
OW(3)	0.129(1)	0.2119(4)	0.924(1)	44(4)	42(6)	45(7)	45(7)	-14(6)	-6(6)	3(6)
OW(4)	0.230(1)	0.1869(5)	0.710(1)	72(6)	59(9)	108(12)	45(9)	-29(8)	20(7)	-46(9)
OW(5)	0.1562(8)	0.0125(3)	0.376(1)	35(4)	28(6)	38(6)	38(7)	-4(5)	-10(5)	-2(5)

$U_i \times 10^3$

TABLE 3. continued

Cu octahedron			
OW(4)—O(3)	3.17(2)	OW(4)—Cu—O(3)	93.8(5)
OW(4)—O(4)	3.27(2)	OW(4)—Cu—O(4)	98.3(5)
OW(4)—O(5)	3.06(2)	OW(4)—Cu—O(5)	89.7(5)
OW(4)—O(6)a	3.05(2)	OW(4)—Cu—O(6)a	88.8(5)
OW(4)a—O(3)	3.95(2)	OW(4)a—Cu—O(3)	90.9(5)
OW(4)a—O(4)	3.51(2)	OW(4)a—Cu—O(4)	77.1(5)
OW(4)a—O(5)	3.79(2)	OW(4)a—Cu—O(5)	85.8(5)
OW(4)a—O(6)a	4.10(2)	OW(4)a—Cu—O(6)a	96.0(5)
O(3)—O(4)	2.67(1)	O(3)—Cu—O(4)	86.3(4)
O(4)—O(5)	2.89(1)	O(4)—Cu—O(5)	95.6(4)
O(5)—O(6)a	2.89(1)	O(5)—Cu—O(6)a	85.9(4)
O(6)a—O(3)	<u>2.83(1)</u>	O(6)a—Cu—O(3)	<u>91.7(4)</u>
<O—O>	3.25	<O—Cu—O>	90
P(1) tetrahedron			
O(1)a—O(2)	2.50(1)	O(1)a—P(1)—O(2)	106.0(5)
O(1)a—O(3)	2.52(1)	O(1)a—P(1)—O(3)	106.6(6)
O(1)a—O(4)a	2.49(1)	O(1)a—P(1)—O(4)a	105.8(5)
O(2)—O(3)	2.51(1)	O(2)—P(1)—O(3)	111.5(6)
O(2)—O(4)a	2.51(1)	O(2)—P(1)—O(4)a	112.8(7)
O(3)—O(4)a	<u>2.54(1)</u>	O(3)—P(1)—O(4)a	<u>113.6(6)</u>
<O—O>	2.51	<O—P(1)—O>	109.4
P(2) tetrahedron			
O(1)—O(5)	2.53(1)	O(1)—P(2)—O(5)	106.1(6)
O(1)—O(6)	2.54(1)	O(1)—P(2)—O(6)	106.4(5)
O(1)—O(7)	2.48(1)	O(1)—P(2)—O(7)	104.3(6)
O(5)—O(6)	2.54(1)	O(5)—P(2)—O(6)	112.9(6)
O(5)—O(7)	2.52(1)	O(5)—P(2)—O(7)	113.5(5)
O(6)—O(7)	<u>2.52(1)</u>	O(6)—P(2)—O(7)	<u>112.7(7)</u>
<O—O>	2.52	<O—P(2)—O>	109.3
P(1)—P(2)	2.830(7)	P(1)—O(1)—P(2)	120.6(6)

TABLE 4. BOND-VALENCE TABLE FOR WOOLDRIDGEITE (vii)

[illegible]

TABLE 5. PROPOSED H-BONDING FOR WOOLDRIDGEITE

OW(1)...O(3)a	2.68(1)	[H1]	O(3)a-OW(1)-OW(5)	108.2(5)
OW(1)...OW(5)	2.75(2)	[H2]		
OW(2)...O(4)a	2.81(2)	[H3]	O(4)a-OW(2)-OW(3)d	117.3(5)
OW(2)...OW(3)d	2.94(2)	[H4]		
OW(3)...O(7)g	2.84(2)	[H5]	O(7)g-OW(3)-O(1)h	103.9(5)
OW(3)...O(1)h	2.95(2)	[H6]	O(7)g-OW(3)-OW(4)	103.6(5)
OW(3)...OW(4)	2.78(2)	[H6]'	O(1)h-OW(3)-OW(4)	116.9(6)
OW(4)...OW(5)g	2.83(2)	[H7]	OW(5)g-OW(4)-OW(3)	115.1(6)
OW(4)...OW(3)	2.78(2)	[H8]		
OW(5)...O(2)g	2.78(1)	[H9]	O(2)g-OW(5)-OW(4)a	102.9(5)
OW(5)...OW(4)a	2.83(2)	[H10]		

1973), the O–P–O(1) angles are all significantly smaller ($\sim 106^\circ$) than the mean value of the O–P–O angles (109.4°).

There is one crystallographically distinct Cu site surrounded by six O atoms in a very distorted octahedral arrangement. The coordination polyhedron shows considerable Jahn–Teller distortion, with $\langle \text{Cu–O(meridional)} \rangle = 1.96 \text{ \AA}$ and $\text{Cu–O(apical)} = 2.37$ and $3.39 \text{ \AA}$. The $\langle \text{Cu–O} \rangle$ distance of $2.27 \text{ \AA}$ is in accord with the high degree of distortion of the polyhedron (Burns & Hawthorne 1995).

There is one crystallographically unique Ca site octahedrally coordinated by four O atoms and two (H_2O) groups, and one crystallographically unique Na site octahedrally coordinated by two O atoms and four (H_2O) groups (Fig. 1).

Structure topology

Each ($\text{Cu}\phi_6$) octahedron (ϕ : unspecified ligand) links through one *trans* pair of vertices to other ($\text{Cu}\phi_6$) octahedra to form a [$\text{Cu}\phi_5$] chain of the type discussed by Moore (1970). This chain is decorated by [P_2O_7] groups to form a [$\text{Cu}(\text{P}_2\text{O}_7)\phi$] chain of octahedra and tetrahedra (Fig. 2). These chains extend along [101] (and $[10\bar{1}]$) and are linked into sheets by ($\text{Na}\phi_6$) and ($\text{Ca}\phi_6$) octahedra; the pattern of chains extending along [101] is shown in Figure 3. Each chain is flanked (to the right in Fig. 3) by a chain of corner-sharing ($\text{Na}\phi_6$) octahedra in which the Na– ϕ –Na linkage is through *cis* vertices (as compared with the Cu– ϕ –Cu linkage, which is through *trans* vertices). Each ($\text{Na}\phi_6$) octahedron shares an edge with a ($\text{Cu}\phi_6$) octahedron. The double chains thus formed are linked in the $[101]$ direction into a sheet (Fig. 3) by ($\text{Ca}\phi_6$) octahedra. These sheets stack along the [010] direction, with each sheet rotated 90° with respect to the adjacent sheets (Fig. 4), the linkage between sheets involving Ca–O and Na–O bonds. The orthogonal nature of the [$\text{Cu}(\text{P}_2\text{O}_7)\phi$] chains is well illustrated in Figure 5, and shows that the overall structure is best described as an array of parallel and orthogonal [$\text{Cu}(\text{P}_2\text{O}_7)\phi$] chains linked by interstitial Ca and Na cations.

Hydrogen bonding

The bond-valence table of woolldridgeite (Table 4) indicates that five of the twelve crystallographically distinct anions are (H_2O) groups. The H atoms were not

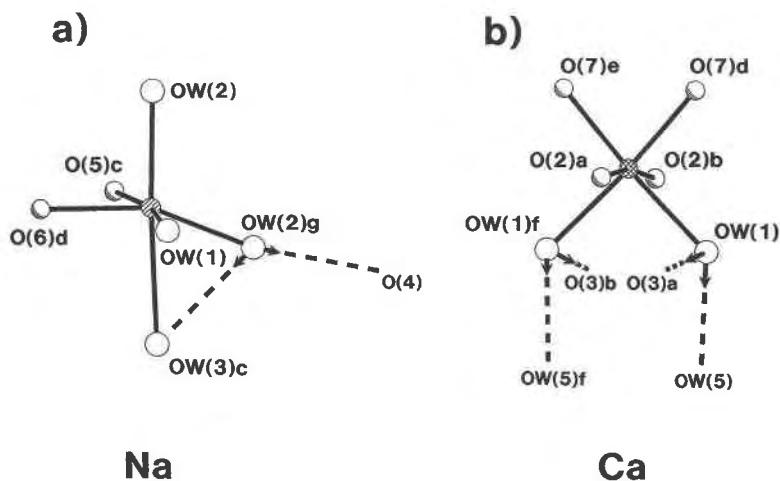


FIG. 1. The coordination of the interstitial-cation sites: (a) Na (diagonal-shaded circles); (b) Ca (cross-hatched circles); highlighted circles are O atoms, larger unshaded circles are (H_2O) groups, donor $\rightarrow$ H bonds are shown as arrows, H $\rightarrow$ acceptor bonds are shown as broken lines.

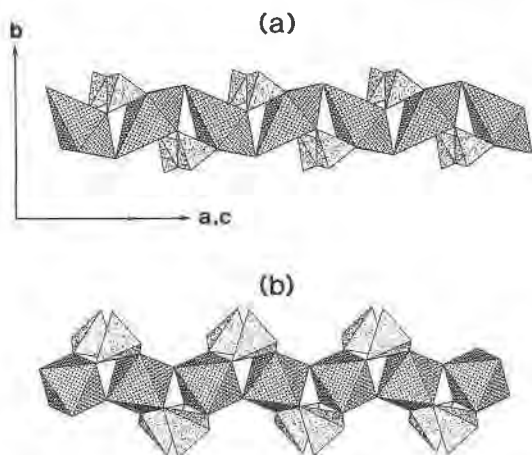


FIG. 2. (a) Perspective view of the $[\text{Cu}(\text{P}_2\text{O}_7)\phi]$ chain in wooldridgeite; (b) perspective view of the type-VI $[\text{Al}(\text{PO}_4)_2(\text{OH})]$ chain in sinkankasite; (PO_4) tetrahedra are irregularly dot-shaded, and $(\text{Cu}\phi_6)$ octahedra are dash-shaded, and $(\text{Al}\phi_6)$ tetrahedra are cross-shaded.

located in final difference-Fourier maps, but a sensible scheme of H bonding was developed on the basis of appropriate stereochemistry (Table 5). The resulting distribution of bond valences (Table 5) leads to near-ideal incident-bond-valence sums at all of the anions in the structure. The H-bond network in wooldridgeite is shown in Figure 6. There are three different types of (H_2O) groups in this structure (Hawthorne 1992): (1) the OW(4) group bonds to two Cu^{2+} cations and hence is part of the structural unit; (2) the OW(1), OW(2) and OW(3) groups bond only to interstitial cations, and (3) the OW(5) group is held in the structure only by H bonds. Inspection of Figure 6 shows that OW(4) bridges the $[\text{Cu}\phi_5]$ chain along its length, and the low incident bond-valence required for an (H_2O) group is in accord with the long $\text{Cu}-\phi$ (apical) bonds bridging the chain (Table 4). The rest of the (H_2O) groups occupy positions interstitial to the $[\text{Cu}\phi_5]$ chains (Fig. 6), increasing interchain linkage and, most important of all, catering to the coordination requirements of the interstitial cations and moderating their Lewis acidity.

There are some unusual features of the H-bonding scheme derived here. First, the OW(2) group H bonds to OW(3) along the edge of an $(\text{Na}\phi_6)$ octahedron; this

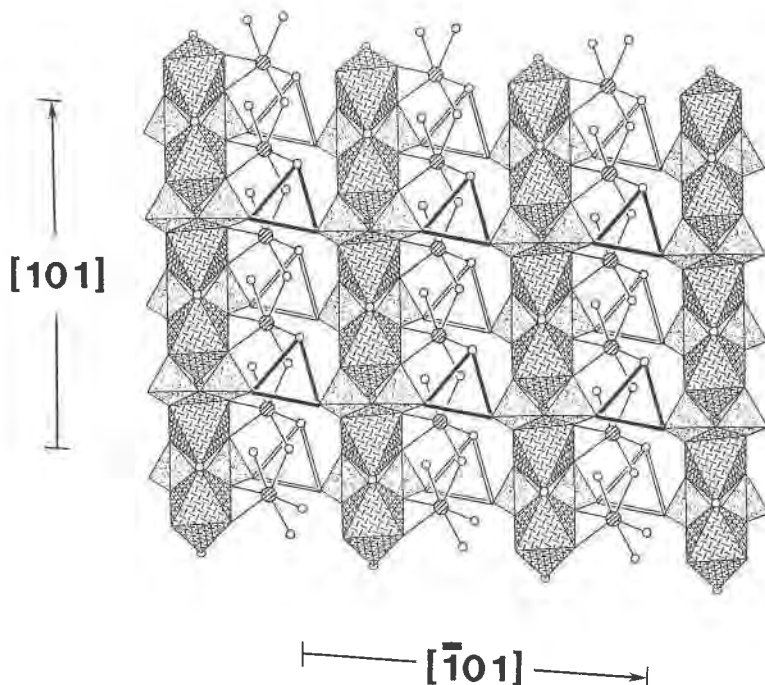


FIG. 3 Linkage of $[\text{Cu}(\text{P}_2\text{O}_7)\phi]$ chains along $[\bar{1}01]$ in wooldridgeite (projected down $[010]$); polyhedral shading as in Figure 1, small unshaded circles are (H_2O) groups, and $\text{Na}-\text{O}$ bonds are shown as thin lines, the heavily drawn triangles are faces of $(\text{Ca}\phi_6)$ octahedra above the plane of the sheet, and the double-line triangles are faces of $(\text{Ca}\phi_6)$ octahedra below the plane of the sheet.

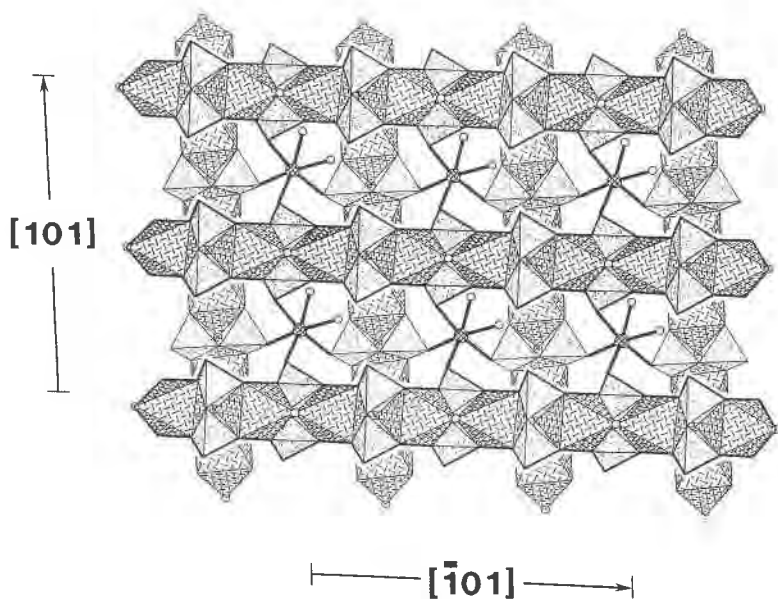


FIG. 4. The relation between adjacent sheets in wooldridgeite, omitting the Na atoms for clarity; polyhedron shading as in Figure 2, and Ca- ϕ bonds shown as heavy lines.

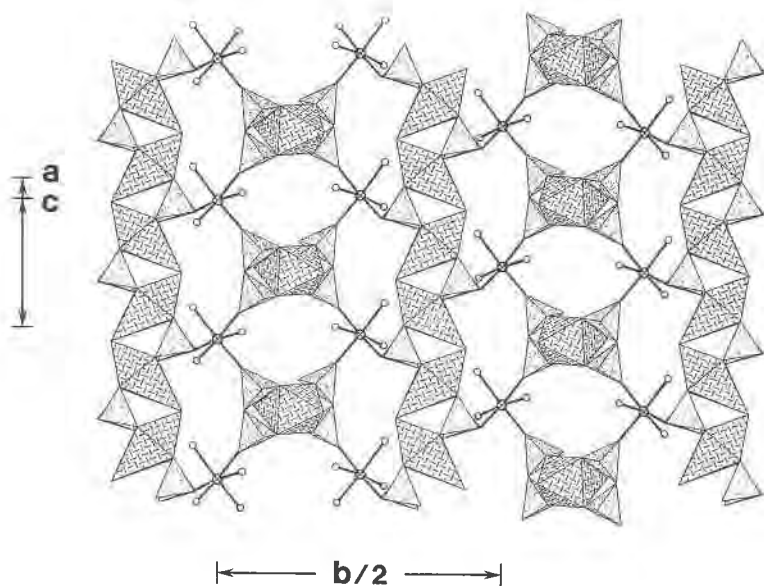


FIG. 5. The structure of wooldridgeite projected onto (101), legend as in Figure 3; Na atoms (omitted for clarity) occur in the interstices between chains adjacent along [101]

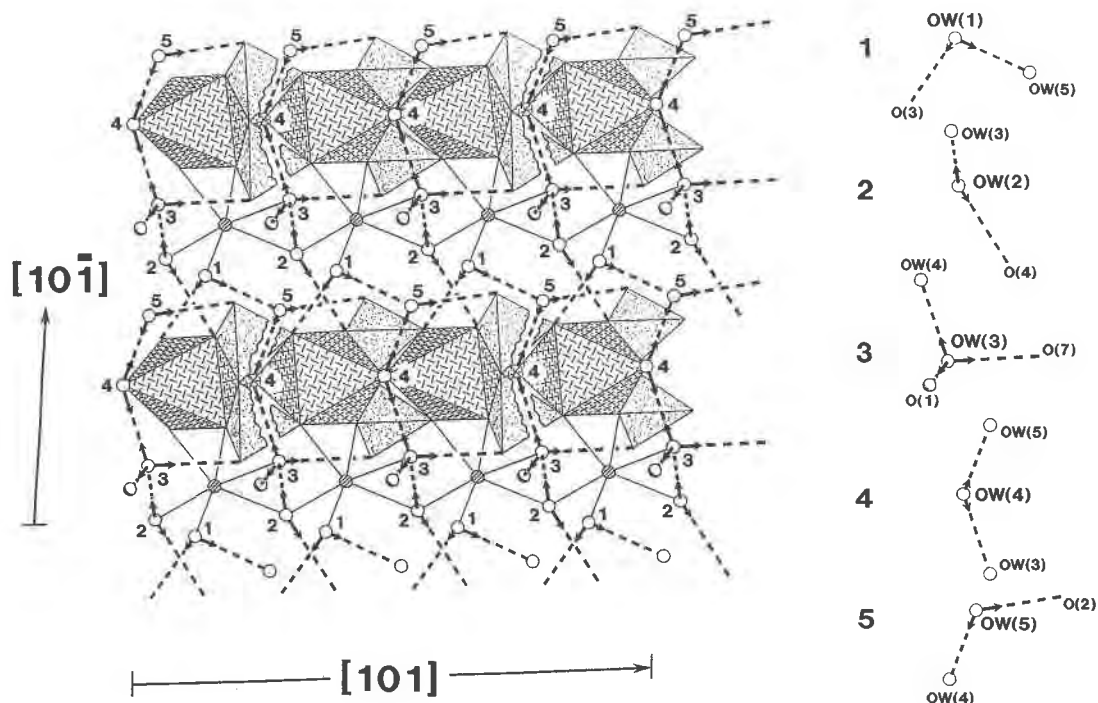


FIG. 6. The structure of woolldridgeite projected down $[010]$ and showing the network of H-bonds; donor $\rightarrow$ acceptor bonds are shown as heavy broken lines. Local details of each (H_2O) group are shown to the right of the figure.

is unusual, but the $\text{Na}-\text{O}(3)$ bond is much longer ($2.90 \text{ \AA}$) than the other Na -bonds ($<2.42 \text{ \AA}$). Second, one of the H bonds involving the $\text{Ow}(3)$ group is bifurcated, and hence there are three donor-acceptor interactions shown in Figure 6.

Related structures

The principal structural motif in woolldridgeite is the $[\text{Cu}^{2+}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})]$ chain that can be generalized to the form $[M(\text{T}_2\text{O}_7)\phi]$, where M is an octahedrally coordinated cation and T is a tetrahedrally coordinated cation. Moore (1970) considered the structural hierarchy of chains of octahedra and tetrahedra based on an $[M\phi_5]$ backbone. He developed a hierarchy of possible arrangements with a chain-repeat distance of $\sim 7.2 \text{ \AA}$, and showed that there is a relatively large family of minerals based on these chains. Although none of these chains contain condensed tetrahedral groups, they are similar to the $[\text{Cu}^{2+}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})]$ chain in woolldridgeite; they are all $[M\phi_5]$ chains decorated by (TO_4) groups. As far as octahedron-octahedron and octahedron-tetrahedron linkages are concerned, woolldridgeite has the type-VI chain of Moore (1970), designated as the *tancoite chain* by Hawthorne (1985). This chain occurs in a number of structures (Table 6), all of which show the typical ~ 7.2

$\text{\AA}$ repeat ($6.9\text{--}7.3 \text{ \AA}$), except for *tancoite*, which has a doubled repeat-distance of $14.07 \text{ \AA}$. The only topological difference between the woolldridgeite chain (Fig. 2a) and the type-VI chain (Fig. 2b) is the cooperative rotation and fusion of the phosphate groups (that are isolated in the type-VI chain) to form the $[\text{P}_2\text{O}_7]$ linkage in woolldridgeite. Interestingly, this tetrahedron-tetrahedron linkage does not seem to affect the articulation of the rest of the chain of octahedra and tetrahedra.

In the $7 \text{ \AA}$ structures of Table 6, the $[M(\text{TO}_4)_2\phi]$ chains link through $(M\phi_6)$ octahedra to form dense slabs that link, usually through alkali or alkaline-earth cations, to form the complete structure. The arrangement of chains and interstitial cations is very different in woolldridgeite; here, the chains extend in two directions (as compared to one direction in the structures of Table 6), and there is no further linkage into sheet-like structural units, as is the case for many of the $7 \text{ \AA}$ structures.

Other condensed-phosphate minerals

Canaphite, $\text{Na}_2\text{Ca}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})_4$, is the only other mineral known to contain (P_2O_7) groups (Rouse *et al.* 1988). However, there are three natural materials that contain $[\text{P}_2\text{O}_7]$ groups:

TABLE 6. MINERALS BASED ON THE TYPE VI $[M(T\Phi)_2\Phi]$ CHAIN OF FIG. 2B.

Mineral	Formula	a (Å)	b (Å)	c (Å)	β (°)	Sp. Gr.	Ref.
Tancoite	$Na_2LiH[Al(PO_3)_2(OH)]$	6.948(2)	14.089(4)	14.065(3)		Pbcb	(1)
Sideronatrite*	$Na_2[Fe^{3+}(SO_4)_2(OH)](H_2O)_3$	7.29(1)	20.56(2)	7.17(2)		Pnn2	(2)
Jahnsite	$CaMnMg_2Fe^{3+}(PO_3)_2(OH)_2(H_2O)_8$	14.94(2)	7.14(1)	9.93(1)	110.16(8)	P2/a	(3)
Whiteite	$CaFe^{2+}Mg_2Al(PO_3)_2(OH)_2(H_2O)_8$	14.90(4)	6.98(2)	10.13(2)	113.11(9)	P2/a	(4)
Lun'okite	$Mn_2(Mg, Fe^{2+}, Mn)_2Al(PO_3)_2(OH)_2(H_2O)_8$	14.95	18.71	6.96		Pbca	—
Overite	$Ca_2Mg_2Al(PO_3)_2(OH)_2(H_2O)_8$	14.72(1)	18.75(2)	7.107(4)		Pbca	(5)
Segelerte	$Ca_2Mg_2Fe^{3+}(PO_3)_2(OH)_2(H_2O)_8$	14.826(5)	18.751(4)	7.307(1)		Pbca	(5)
Wilhelmierlingite	$Ca_2Mn_2Fe^{3+}(PO_3)_2(OH)_2(H_2O)_8$	14.80(5)	18.50(5)	7.31(2)		Pbca	—
Sinkankasite	$Mn^{2+}(H_2O)_4[Al(PO_3)_2(OH)](H_2O)_2$	9.590(2)	9.818(2)	6.860(1)	99.63(3)	***P1	(6)
Guildite	$Cu^{2+}[Fe^{3+}(SO_4)_2(OH)](H_2O)_4$	9.786(2)	7.134(1)	7.263(1)	105.38(1)	P2/m	(7)
Yttisite	$Y_4Ti(SiO_4)_2O(F, OH)_8$	14.949(4)	10.626(2)	7.043(2)		Cmcm	(8)

References: (1) Hawthorne (1983); (2) Scordari (1981); (3) Moore & Araki (1974); (4) Moore & Ito (1978); (5) Moore & Araki (1977); (6) Burns & Hawthorne (1995); (7) Wan *et al.* (1978); (8) Balko & Bakakin (1975)

*structure not definitively established

*** $\alpha = 108.04(3)$, $\gamma = 98.87(3)$

"pyrocoprite" $(K, Na)_2 Mg (P_2O_7)$
 Martini (1997)
 "pyrophosphate" $K_2 Ca (P_2O_7)$ Martini (1994)
 "arnhemite" $(K, Na)_4 Mg_2 (P_2O_7)_2 (H_2O)_5$
 Martini (1994).

All of these were formed in caves containing burning bat guano.

Apart from the presence of (P_2O_7) groups, there is no close structural relation between canaphite and wooldridgeite; the structure of wooldridgeite is dominated by the $[Cu^{2+} (P_2O_7) (H_2O)]$ chain, whereas canaphite does not have an octahedrally coordinated medium-sized divalent cation that could form such a chain.

It has been argued that condensed phosphates will not occur as minerals (Liebau 1970, Byrappa 1983). The discovery of canaphite (Peacor *et al.* 1985) and wooldridgeite (Hawthorne *et al.* 1999) has disproved this contention.

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