Refinement of the crystal structure of cyrilovite from Cyrilov, Western Moravia, Czech Republic

Krystalová struktura cyrilovitu z Cyrilova na západní Moravě v České republice (Czech summary)

(1 text-fig., 6 tabs)

MARK A. COOPER[1] – FRANK C. HAWTHORNE[1] – PETR ČERNÝ[1]

[1] *Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2*

The crystal structure of cyrilovite from Cyrilov, western Moravia, Czech Republic, ideally Na $[Fe^{3+}_3 (PO_4)_2 (OH)_4 (H_2O)_2]$, tetragonal, *a* 7.3255(4), *c* 19.328(2) Å, *V* 1037.2(2) Å^3, *Z* = 4, was refined to an *R*-index of 1.4 % for 1532 unique reflections measured with Mo*K*α X-radiation on an automated four-circle diffractometer. Cyrilovite crystallizes in the enantiomorphic space group $P4_12_12$ and refinement of a twin model shows that both enantiomers, $P4_12_12$ and $P4_32_12$, are present as a 1:1 mixture; thus cyrilovite is racemically twinned. The structure consists of intersecting corner-sharing chains of $Fe^{3+}\phi_6$ (ϕ = unspecified anion) octahedra that form sheets parallel to (001). These sheets are linked into a framework of octahedra and tetrahedra by PO_4 tetrahedra, with [8]-coordinated Na and H_2O in the interstices of the framework. Consideration of local bond-valence requirements suggests that a small amount of Ca is incorporated into the cyrilovite structure *via* the substitution $^{Na}Ca + {}^{M(1)}Fe^{2+} \rightarrow {}^{Na}Na + {}^{M(1)}Fe^{3+}$. Cyrilovite is isostructural with wardite, Na $[Al_3 (PO_4)_2 (OH)_4 (H_2O)_2]$. Cyrilovite has no cleavage, as suggested by the pattern of bond valence throughout the structure. However, wardite is listed in standard reference works as having perfect {001} cleavage. Examination of wardite shows it to have no cleavage, as suggested by its structural arrangement.

Key words: cyrilovite, crystal structure, chemical composition

Introduction

Cyrilovite, ideally Na $Fe^{3+}_3 (PO_4)_2 (OH)_4 (H_2O)_2$, was described as a new mineral by Novotný – Staněk (1953) from a phosphate-bearing pegmatite at Cyrilov, western Moravia, Czech Republic. It has been discovered at several additional localities over the past 45 years ("avelinoite" of Lindberg – Pecora 1954, see Strunz 1956, Kasymov 1966, Correia Neves 1966, Fontan et al. 1981, Cozzupoli et al. 1987); however, it is still a quite rare phosphate which requires, for its formation, high activity of Na in a highly oxidizing environment.

The crystal structure of cyrilovite was refined by Cozzupoli et al. (1987) but some aspects of the structure were not addressed. Novák et al. (2000) re-investigated cyrilovite from the type locality, under the aegis of the IMA Museum Commission program of upgrading the understanding of poorly characterized type-specimens. We used this opportunity for re-examination of the crystal structure of this cyrilovite, and report our results here.

Experimental

Collection of X-ray data

Zero- and first-level X-ray precession photographs showed sharp circular diffraction spots consistent with tetragonal symmetry and the enantiomorphic space groups $P4_12_12$ and $P4_32_12$. The crystal used in the collection of the X-ray intensity data was an equidimensional fragment (Table 1) of high optical clarity. It was mounted on a Siemens *P*4 automated four-circle diffractometer. Twenty-five reflections were centred in the range 7–32°2θ using graphite-monochromated Mo*K*α X-radiation; the resulting cell dimensions are given in Table 1. A total of 12,172 reflections was measured ($4 \le 2\theta \le 60°$) with index ranges $\overline{10} < h < 10$, $\overline{10} < k < 10$, $\overline{27} < l < 27$) according to the method described by Burns et al. (1994). The intensity data were corrected for absorption (psi-scan method), Lorentz, polarization and background effects, and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of five standard deviations based on counting statistics. Of the 1532 unique reflections, 1495 were considered as observed.

Electron-microprobe analysis

Subsequent to the collection of the diffraction data, the crystal used for this procedure was mounted in epoxy, polished, carbon coated and analyzed with a CAMECA SX-50 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15kV, a specimen current of 20 nA, a beam size of 10 μm, and

Table 1. Miscellaneous information for cyrilovite.

a (Å)	7.3255(4)	crystal size (mm)	0.14 x 0.15 x 0.19
c	19.3278(18)	radiation/mon	Mo*K*α/Graphite
V (Å^3)	1037.16(15)	Total no. of I	12172
Sp. Gr.	$P4_12_12/P4_32_12$	No. of F_o^2	1532
$P4_12_12$ fraction	0.47(1)	No. of $\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$	1514
$P4_32_12$ fraction	0.53(1)	scale factor (k)	0.3260(5)
μ (mm^{-1})	4.59	extinction (x)	0.0031(4)
$D_{calc.}$ (gcm^{-3})	3.106	weights a,b	0.0274, 0.19
Z	4	*R* (azimuthal) %	1.7 → 0.9
		R (merge) %	1.7
		R_1 ($\lvert F_o \rvert > 4\sigma$) %	1.4
		wR_2 (F_o^2) %	4.4

counting times on peak and background of 20 and 10 s, respectively. The following standards were used: Na, P, Fe (maricite), Al (kyanite), Ca (diopside); Mg, Mn, Ti and K were not detected. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou – Pichoir (1984, 1985). The chemical composition (mean of 11 points) is given in Table 6, together with the unit formula calculated on the basis of 12 anions.

Refinement of the crystal structure

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were used with the Siemens SHELXTL PLUS (PC version) system of programs. Refinement of the structure was initiated in the space group $P4_12_12$ using the coordinates of Cozzupoli et al. (1987) for all sites except those for H, and converged rapidly to an R value of 2.3 %. At this stage, site-population refinement indicated complete occupancy of the M(1) + M(2) and Na sites by Fe and Na, respectively; these results are in accord with the formula unit derived from the electron-microprobe analysis, and hence the site populations of the M(1), M(2) and Na sites were fixed at Fe, Fe and Na in all subsequent refinement cycles.

Previous refinements of wardite (Fanfani et al. 1970) and cyrilovite (from Bosa, Sardinia, Italy; Cozzupoli et al. 1987) were reported in the space group $P4_12_12$, and no attempt was made to distinguish between the two possible enantiomorphic structures ($P4_12_12$ and $P4_32_12$). With an entire sphere of data, we ran a series of refinements (based on both F and F^2) to try and identify the correct enantiomorphic structure. These results are summarized in Table 2.

Table 2. R-indices for various enantiomers and twin model for cyrilovite.

	$P4_12_12$	$P4_32_12$	Twin
F refinement			
R %	2.3	2.3	–
$w R$%	3.1	3.1	–
F^2 refinement			
R_1 %	2.2	2.1	1.6
wR_2 %	6.3	6.2	5.4

In all refinements, an isotropic-extinction parameter was refined; it is small but significant in each case. A fixed weight of $1/\sigma^2 F$ was included. The R values for both enantiomers are the same (Table 2). To test for absolute configuration, the Rogers parameter (η) was refined (Rogers 1981). If this parameter refines to +1 with a small e. s. d., the current configuration is correct; a value of –1 indicates that the structure should be inverted. A value near zero may indicate racemic twinning. For our F refinements in $P4_12_12$ and $P4_32_12$, the Rogers parameter refined to –0.05(5) and 0.05(5), respectively, suggesting racemic twinning.

For the refinements based on F^2, all 1532 unique data were used, together with weighting parameters indicated by the refinement. Again, the R values for both enantiomers are essentially the same (Table 2). The Flack (Flack 1983) parameter (x) refines to 0.53(2) and 0.47(2) for the $P4_12_12$ and $P4_32_12$ structures, respectively. Ideally, the Flack parameter should refine to zero if the absolute structure is correct, and to +1 if it needs to be inverted. It will refine somewhere between 0 and 1 if racemic twinning is present. Both the Rogers's parameter [F] and Flack parameter [F^2] refine to values with small estimated standard deviations, suggesting racemic twinning; we therefore refined the structure as a twin using the twin matrix ($\bar{1}00$ / $0\bar{1}0$ / $00\bar{1}$) with the fractional contribution of the twin component as variable. The refined value of 0.53(2) indicates a twin consisting of 47 % of the $P4_12_12$ structure and 53 % of the $P4_32_12$ structure. The R_1 and wR_2 values for the twin model are 1.6 % and 5.4 %, respectively (Table 2). In the final refinement, peaks from the difference-Fourier corresponding to sensible H-positions were incorporated into the refinement model with the soft constraint that the H-positions lie ~0.98 Å from the donor anion; final indices are R_1 = 1.4 %, wR = 4.4 %. Final atom positions and displacement parameters are given in Table 3, and selected interatomic distances and angles are given in Table 4.

The crystal structure of cyrilovite

General topology

The cyrilovite (and wardite) structure has been described and illustrated previously (Cozzupoli et al. 1987; Fanfani et al. 1970) and we present only a complementary structural account here. The main structural slab (001) of cyrilovite is shown in Figure 1. The principal structural motif in cyrilovite is the [Mϕ_5] chain (ϕ = unspecified anion) that is decorated by PO_4 tetrahedra arranged in a staggered fashion at the periphery of the chain. These chains extend parallel to the ***a***-axes to form an octahedral-tetrahedral slab (Fig. 1). The tetrahedral vertices that project out of the plane of the slab link to octahedra of the adjacent slabs (atoms indicated by large black circles in Fig. 1). Eight-coordinated Na occupies the interstices within the resulting octahedral-tetrahedral framework, and additional intra- and inter-slab linkage is provided by H-bonds. The H-bonds to acceptors within the structural slab are shown as dashed lines; other H-bonds (not shown) are to H-bond acceptors above and below the slab. The H(1) and H(4) positions associated with the two OH groups are alternatively above and below the octahedral chains. Two H_2O groups occur as neighbouring ligands on one side of each Na site. Along two opposing edges of the Naϕ_8 polyhedron are edge-sharing PO_4 tetrahedra that point in opposite directions. In 90° opposition to the pair of PO_4 groups about Na are two criss-crossing sets of H-bonds that provide structural cohesion between Na–M(1) and M(1)–M(2) vertices.

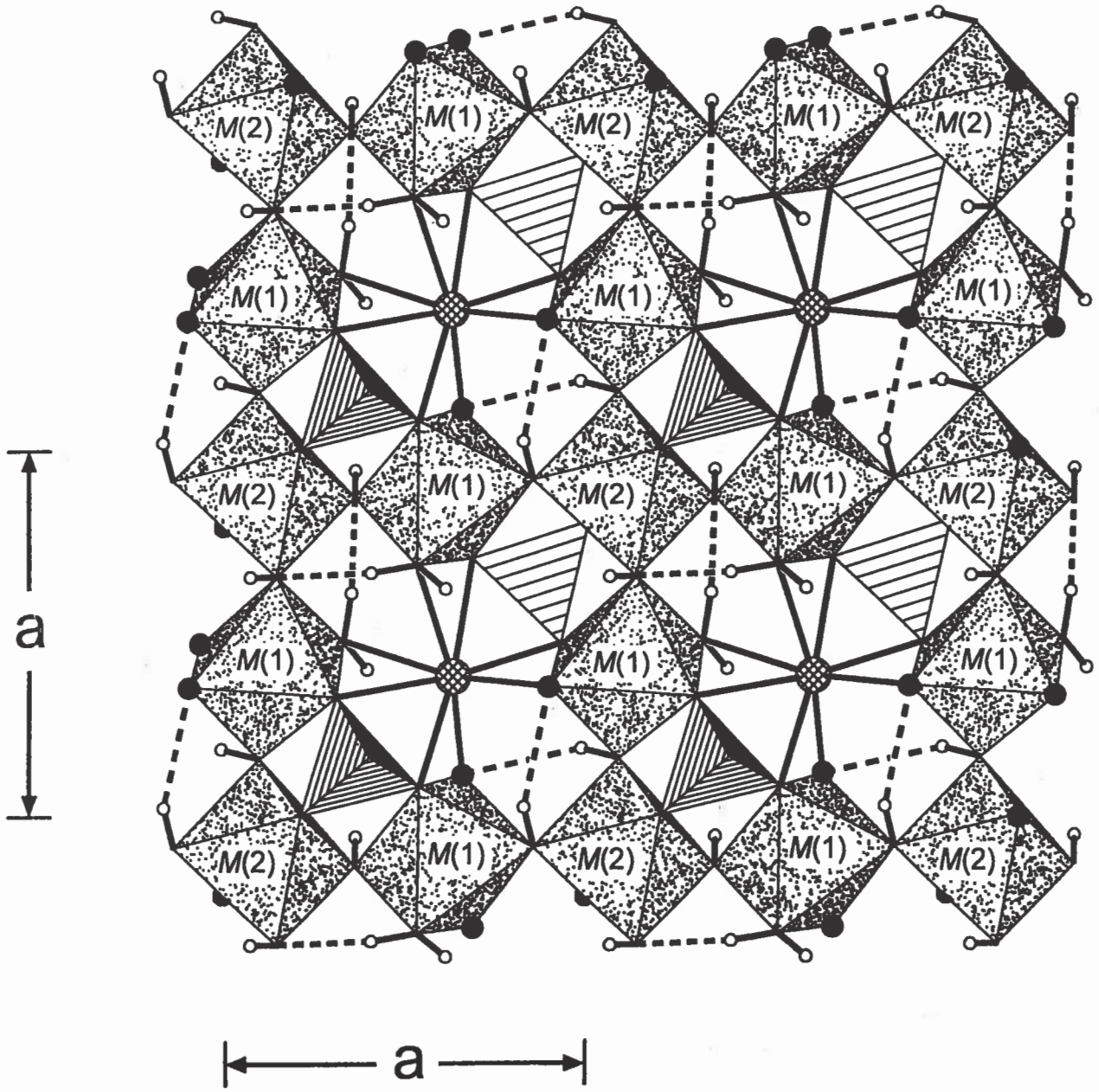

Fig. 1. The crystal structure of cyrilovite viewed down [001]; PO_4 groups are line-shaded, Na atoms are shown as trellis-shaded circles, H atoms are shown as small open circles, Na–ϕ and O–H bonds are shown as heavy black lines, H-bonds are shown as broken lines; the black circles are O atoms that link to tetrahedra of adjacent slabs.

Table 3. Final positional and displacement parameters for cyrilovite. $U_{ij}=U_{ij}x10^4$

Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0.14038(5)	0.36596(5)	0.35039(2)	73(1)	72(2)	81(2)	65(1)	4(1)	6(1)	3(1)
M(1)	0.39492(3)	0.10846(3)	0.25769(1)	81(1)	91(1)	71(1)	82(1)	–3(1)	5(1)	5(1)
M(2)	0.10351(3)	0.10351(3)	0	79(1)	74(1)	74(1)	91(1)	–6(1)	6(1)	1(1)
Na	0.3743(1)	0.3743(1)	1/2	198(2)	197(3)	197(3)	200(5)	22(3)	–22(3)	16(4)
O(1)	–0.0338(2)	0.4281(2)	0.31393(6)	154(2)	104(5)	218(6)	138(5)	88(4)	–22(4)	14(4)
O(2)	0.2958(2)	0.5056(2)	0.33954(6)	115(2)	125(5)	124(5)	96(5)	–3(4)	12(4)	–42(4)
O(3)	0.1967(2)	0.1809(2)	0.32056(6)	147(2)	158(6)	104(5)	178(5)	–42(4)	67(4)	–9(4)
O(4)	0.1056(2)	0.3471(2)	0.42845(5)	121(2)	116(5)	178(5)	70(4)	17(4)	15(4)	10(4)
O(5)	0.1384(2)	0.3533(2)	–0.04307(5)	114(2)	151(5)	85(5)	105(4)	–5(4)	–15(4)	1(4)
O(6)	0.1779(2)	0.0272(2)	0.18970(7)	185(3)	227(6)	149(6)	179(5)	20(5)	–103(5)	–32(5)
O(7)	0.4100(2)	0.3503(2)	0.21191(6)	116(2)	148(5)	77(5)	124(5)	8(4)	29(4)	15(4)
H(1)	0.064(3)	0.355(4)	–0.085(1)	500						
H(2)	0.113(4)	0.106(3)	0.157(1)	500						
H(3)	0.156(4)	–0.102(1)	0.179(2)	500						
H(4)	0.516(3)	0.323(4)	0.183(1)	500						

Table 4. Selected interatomic distances (A) and angles (°) in cyrilovite.

P–O(1)	1.527(1)	M(1)–O(1)a	1.974(1)	
P–O(2)	1.545(1)	M(1)–O(3)	1.967(1)	
P–O(3)	1.530(1)	M(1)–O(4)b	2.003(1)	
P–O(4)	1.536(1)	M(1)–O(5)c	2.005(1)	
<P–O>	1.535	M(1)–O(6)	2.147(1)	
		M(1)–O(7)	1.983(1)	
Na–O(1)b,g	2.624(1) x2	<M(1)–O>	2.013	
Na–O(3)b,g	2.757(1) x2			
Na–O(4),f	2.413(1) x2	M(2)–O(2)c,d	2.013(1)	x2
Na–O(6)b,g	2.613(2) x2	M(2)–O(5),e	2.027(1)	x2
<Na–O>	2.602	M(2)–O(7)c,d	1.998(1)	x2
<M(2)–O>	2.013			
H–bonding				
O(5)–H(1)	0.98(1)	H(1)....O(1)j	2.53(2)	
O(6)–H(2)	0.98(1)	H(2)....O(2)d	1.68(1)	
O(6)–H(3)	0.98(1)	H(3)....O(5)h	1.98(2)	
O(7)–H(4)	0.98(1)	H(4)....O(3)i	2.49(1)	
		H(4)....O(4)i	2.48(2)	
O(5)–O(1)j	3.285(2)	O(5)–H(1)–O(1)j	134(2)	
O(6)–O(2)d	2.650(2)	O(6)–H(2)–O(2)d	168(3)	
O(6)–O(5)h	2.876(2)	O(6)–H(3)–O(5)h	151(3)	
O(7)–O(3)i	3.394(2)	O(7)–H(4)–O(3)i	154(3)	
O(7)–O(4)i	3.283(2)	O(7)–H(4)–O(4)i	139(2)	
H(2)–H(3)	1.61(2)	H(2)–O(6)–H(3)	110(3)	

Symmetry operators: a: $\bar{y}$+1, $\bar{x}$, $\bar{z}$+½; b: x+½, $\bar{y}$+½, $\bar{z}$+¾; c: $\bar{x}$+½, y–½, $\bar{z}$+¼; d: y–½, $\bar{x}$+½, z–¼; e: y, x, $\bar{z}$; f: y, x, $\bar{z}$+1; g: $\bar{y}$+½, x+½, z+¼; h: $\bar{y}$+½, x–½, z+¼; i: y+½, $\bar{x}$+½, z–¼; j: $\bar{x}$, $\bar{y}$+1, z–½

Hydrogen bonding

The O-atom at O(6) is bonded to H-atoms at H(2) and H(3), forming the H_2O group in cyrilovite. Strong H-bonds are directed toward the O-acceptor atoms at O(2) and O(5) (Table 4). Cations at the Na and M(1) sites also bond to O(6), and in accordance with the valence-sum rule, the M(1)–O(6) bond is elongated to 2.147 Å (Table 4) so that the donor O-atom at O(6) maintains a valence of 2 *vu*. The O-atoms at O(5) and O(7) are bonded to the H-atoms at H(1) and H(4), respectively, to form the two OH groups in cyrilovite. Both donor oxygen atoms corner share to M(1) and M(2) octahedra. The acceptors atoms O(1), O(3) and O(4) are all situated far away (Table 4), and the H-bonds associated with the OH groups are therefore weak.

The chemical formula of cyrilovite

The ideal end-member formula of cyrilovite is Na $[Fe^{3+}_3 (PO_4)_2 (OH)_4 (H_2O)_2]$. There are two significant chemical variations that occur in the cyrilovite-wardite series. The first involves homovalent $Fe^3 \rightleftharpoons Al$ substitution over the M sites that is the basis for the name difference. Most of the chemical data from the literature is consistent with near end-member compositions (Al: wardite; Fe^{3+}: cyrilovite) (Cozzupoli et al. 1987, Lindberg 1957, Hurlbut 1952); however, Fontan et al. (1981) report an intermediate composition ($Fe^{3+}_{2.31}$ $Al_{0.69}$). There is no accompanying structure refinement for this aluminous cyrilovite, so it remains unknown as to whether Al and Fe^{3+} show any preference for either of the two available M sites.

The second chemical variation involves Ca substitution into the structure. Modern microprobe techniques on well-formed cyrilovite crystals have clearly shown significant Ca (0.80 wt. % CaO: Cozzupoli et al. 1987; 0.53 wt. % CaO: Table 6). The 3 wt. % CaO reported for Fairfield wardite (Larsen – Shannon 1930) is most likely too high due to impurities (Hurlbut 1952). The extent of Ca substitution seems to be limited, probably <1 wt. % CaO in all cases thus far characterized. However, substitution of Ca for Na must be accompanied by another polyvalent substitution in order to maintain electroneutrality. It has been suggested that vacancies may be present at the [8]-coordinated Na-site (Cozzupoli et al. 1987). Two other possibilities must also be considered: $OH^- \rightarrow H_2O$ and $Fe^{2+} \rightarrow Fe^{3+}$. Let us consider each of these mechanisms from a bond-valence perspective.

$Ca + OH^- \rightarrow Na + H_2O$

In addition to H-atoms at H(2) and H(3), the O-atom of the H_2O group also coordinates the Na and M(1) sites (Table 4). If Ca^{2+} were to occupy the Na-site, O(6) would receive additional bond-valence (relative to Na at the Na-site), but not enough to offset the loss from losing one H-atom. The loss of one of the H-atoms would also mean that one of the current acceptors [O(2) or O(5)] would be bond-valence deficient. Substitution of H_2O by OH, associated with Ca → Na substitution, does not seem plausible.

$Ca + \square \rightarrow 2Na$

With Na occupying the Na site and Fe^{3+} residing at M(1), the bond-valence sums at O(1), O(3) and O(4) are all 2 *vu* (Table 5). If the cyrilovite structure incorporates Ca^{2+} *via* the substitution Ca + □ → 2Na, locally there will be instances where O(1), O(3) and O(4) receive no additional bond-valence (Na-site = □) and instances where the

Table 5. Bond-valence table for cyrilovite. Calculated from the parameters of Brown – Altermatt (1985), values in *vu* (valence units).

	Na	M(1)	M(2)	P	H(1)	H(2)	H(3)	H(4)	Σ
O(1)	0.109↓x2	0.559		1.275	0.1				2
O(2)			0.503↓x2	1.215		0.25			2
O(3)	0.076↓x2	0.57		1.265				0.05	2
O(4)	0.192↓x2	0.517		1.245				0.05	2
O(5)		0.514	0.485↓x2		0.9		0.15		2.1
O(6)	0.112↓x2	0.35				0.75	0.85		2.1
O(7)		0.546	0.524↓x2					0.9	2
Σ	0.98	3.06	3.02	5	1	1	1	1	

Table 6. Chemical composition (wt. %) and unit formula (*apfu*)* for cyrilovite.
* Calculated on the basis of 12 anions, including OH = 4 *apfu*;
** Calculated for OH = 4, H_2O = 2 *apfu*.

P_2O_5	28.76 (26)	P	2
Fe_2O_3	48.44 (23)		
Al_2O_3	0.05 (1)	Fe^{3+}	3
FeO	0.44	Fe^{2+}	0
CaO	0.40 (9)	Σ	3
Na_2O	6.19 (7)		
(H_2O)**	14.68	Na	1
Total	98.96	Ca	0
		Σ	1
		OH	4
		H_2O	2

valence will be substantial (Na-site = Ca^{2+}). This large range in bond-valence contribution to O(1), O(3) and O(4) must be compensated by substantial bond-length adjustments to the coordinating M(1) and P cations. The extent to which the structure can deform to accommodate these changes is unknown. For this reason, we do not favor this substitution, although we recognize that it cannot be refuted by the refinement and microprobe results given here. Perhaps a substantially more calcic cyrilovite (or wardite) will someday clarify this matter.

$Ca + Fe^{2+} \rightarrow Na + Fe^{3+}$

If Fe^{2+} were to substitute for Fe^{3+} at the M(1) site when Ca^{2+} is present at the Na site, the resulting offset in incident valence at O(1), O(3) and O(4) would locally maintain the required incident bond-valence at these O-atoms without any need for large structural deformation.

The radii for Ca and Na in [8]-coordination are 1.12 and 1.18 Å, respectively, and the radii for Fe^{3+} and Fe^{2+} in octahedral coordination are 0.645 and 0.78 Å, respectively (Shannon 1976). When Ca substitutes for Na, we anticipate a slight contraction of the coordinating anions inward toward the central cation; when Fe^{2+} substitutes for Fe^{3+}, an expansion of the octahedron will occur. The Na site is surrounded by four edge-sharing M(1) octahedra (Fig. 1). It is easy to envision a slight contraction about the Na site ($Ca^{2+} \rightarrow$ Na) coupled to a mutual expansion of the surrounding M(1) octahedra ($Fe^{2+} \rightarrow Fe^{3+}$).

From a crystal-chemical standpoint, we favour [$^{Na}Ca + {}^{M(1)}Fe^{2+} \rightarrow {}^{Na}Na + {}^{M(1)}Fe^{3+}$] to explain the incorporation of Ca into the cyrilovite structure, and present our chemical data (Table 6) in accord with this proposition.The general formula of cyrilovite can therefore be written as (Na, Ca) $[(Fe^{3+}, Fe^{2+})_3 (PO_4)_2 (OH)_4 (H_2O)_2]$.

Cleavage in the wardite-cyrilovite minerals

There is an interesting quandary regarding the cleavage reported for cyrilovite and the isostructural wardite. Cyrilovite from Italy has no cleavage and breaks easily along conchoidal fractures (Cozzupoli et al. 1987). The cyrilovite of the present work behaves in the same manner, as noted by Novotný – Staněk (1953) and Staněk (1971). However, wardite from Fairfield, Utah, is described as having perfect basal {001} cleavage (Larsen – Shannon 1930). Palache et al. (1951) also describe wardite as having perfect {001} cleavage, and in addition, the {001} growth face is usually present as a small brilliant face. How is it possible that cyrilovite and wardite are isostructural, and possess *no* cleavage and *perfect* cleavage, respectively? To help resolve this issue, we examined a high quality wardite sample from Rapid Creek, Yukon, Canada, containing numerous crystals several millimetres in size. No cleavage was observed.

We evaluated the cyrilovite/wardite structure for planes of weak bonding that might be responsible for possible cleavage. It should be noted that Fanfani et al. (1970) attributed the perfect {001} cleavage in wardite to the alternating (Al + Na) and (PO_4 + H-bonds) layers along [001]. To help simplify analysis of directional strengths of bonds, we can limit the discussion to the stronger bonds present. From inspection of the bond valences (Table 5), these strong interactions belong to the M^{3+}–O (0.5 *vu*) and P^{5+}–O (1.25 *vu*) bonds. In Figure 1, we see that a grid pattern of strong M^{3+}–O bonds results from the orthogonally intersecting corner-sharing chains of $M^{3+}\phi_6$ octahedra. The PO_4 tetrahedra lying above and below the octahedral sheet bind adjacent octahedral vertices within the octahedral sheet shown, as well as neighbouring octahedral vertices in the layers above and below (Fig. 1). We have emphasized this strong bonding along [001] associated with P^{5+}–O interactions, by marking with black circles the octahedral vertices that bond to PO_4 tetrahedra belonging to neighbouring slabs. Thus, the cyrilovite/wardite structure is a three-dimensional network of strong M^{3+}–O and P^{5+}–O bonds, and the weaker Na–O and H-bonds provide additional cohesion. This assessment of bonding is in agreement with the lack of cleavage observed for both cyrilovite and wardite. Perhaps, the brilliant {001} growth face usually seen on wardite (Palache et al. 1951) has been at times mistaken for a {001} basal cleavage.

Acknowledgments. We thank Mati Raudsepp and Milan Rieder for their comments on this paper. This work was supported by Natural Sciences and Engineering Research Council of Canada Major Equipment, Major Facilities Access and Research Grants to FCH and Major Installation plus Research Grants to PČ.

Submitted December 20, 1999

References

Brown, I. D. – Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. – Acta Crystallogr., B41, 244–247.

Burns, P. C. – MacDonald, D. J. – Hawthorne, F. C. (1994): The crystal chemistry of manganese-bearing elbaite. – Can. Mineral., 32, 31–41.

Correia Neves, J. M. (1966): Cyrilovite, fosfosiderite, rockbridgeite e entros minerais dos pegmatitos de Vermilhas (Vouzela, Portugal). – Revista Est. Gerais. Univ. Moçambique 3, fasc. II, Ciencias Geol., 41–60.

Cozzupoli, D. – Grubessi, O. – Mottana, A. – Zanazzi, P. F. (1987): Cyrilovite from Italy: Structure and crystal chemistry. – Mineral. Petrol., 37, 1–14.

Fanfani, L. – Nunzi, A. – Zanazzi, P. F. (1970): The crystal structure of wardite. – Mineral. Mag., 37, 598–605.

Flack, H. D. (1983): On enantiomorph-polarity estimation. – Acta Crystallogr., A39, 876–881.

Fontan F. – Permingeat, F. – Pillard, F. (1981): An aluminous cyrilovite, first link of a possible solid solution series between cyrilovite and wardite. – Bull. Minéral., 104, 785–792.

Hurlbut, C. S., Jr. (1952): Wardite from Beryl Mountain, New Hampshire. – Amer. Mineral., 37, 849–852.

Kasymov, A. K. (1966): Cyrilovite from central Kyzyl-Kum. – Geol. J. Uzbekistan, 1, 26–32. (in Russian)

Larsen, E. S. – Shannon, E. V. (1930): The minerals of the phosphate nodules from near Fairfield, Utah. – Amer. Mineral., 15, 307–337.

Lindberg, M. L. (1957): Relationship of the minerals avelinoite, cyrilovite and wardite. – Amer. Mineral., 42, 204–213.

Lindberg, M. L. – Pecora, W. T. (1954): Avelinoite, a new hydrous sodium ferric phosphate mineral from Minas Gerais, Brazil. – Science, 120, 1074–1075.

Novák, M. – Sejkora, J. – Cooper, M. A. (2000): Cyrilovite from Cyrilov, western Moravia, Czech Republic; new data on the type material. – J. Czech Geol. Soc. (in press).

Novotný, M. – Staněk, J. (1953): A new mineral, the phosphate cyrilovite. – Acta Acad. Morav., Sci. Nat., 25, 325–336. (in Czech).

Palache et al. (1951): Dana's System of Mineralogy, 7th ed., V. II, New Work, Wiley, 940 pp.

Pouchou, J. L. – Pichoir, F. (1984): A new model for quantitative analysis I. Application to the analysis of homogeneous samples. – La Recherche Aerospatiale, 3, 13–38.

Pouchou, J. L. – Pichoir, F. (1985): "PAP" $\phi(\rho Z)$ procedure for improved quantitative microanalysis. – Microbeam Anal., 104–106.

Rogers, D. (1981): On the application of Hamilton's ratio test to the assignment of absolute configuration and an alternative test. – Acta Crystallogr., A37, 734–741.

Shannon, R. D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. – Acta Crystallogr., A32, 751 pp.

Staněk, J. (1971): Investigation of secondary iron-manganese phosphates from the pegmatite near Cyrilov – Folia Fac. Sci. Nat. Univ. Purkynianae Brunensis XII, Geol. 22, Op. 9, 25–48 (in Czech).

Strunz, H. (1956): Identität von Avelinoit und Cyrilovit. Neues Jahrb. Mineral., Monatsh. 8, 187–189.

Krystalová struktura cyrilovitu z Cyrilova na západní Moravě v České republice

Krystalová struktura cyrilovitu z Cyrilova na zapadní Moravě v České republice, s ideálním chemickým složením Na $[Fe^{3+}_3 (PO_4)_2 (OH)_4 (H_2O)_2]$, tetragonální symetrií, a 7.3255(4), c 19.328(2) Å, V 1037.2(2) Å^3, a $Z = 4$ byla vypřesněna k R-indexu 1.4 % na základě 1532 reflexí získaných s MoKα zářením na automatizovaném čtyřkruhovém difraktometru. Cyrilovit krystaluje v enanciomorfní prostorové grupě $P4_12_12$ a vypřesnění dvojčatného modelu ukazuje, že oba enanciomery, $P4_12_12$ a $P4_32_12$, jsou zastoupeny v poměru 1:1; cyrilovit je tudíž racemicky zdvojčatěn. Struktura je tvořena z navzájem se protínajících řetězců rohy propojených oktaedru $Fe^{3+}\phi_6$ (ϕ = nespecifikovany aniont), které skládají vrstvy paralelní s (001). Tyto vrstvy jsou spojeny do trojrozměrné struktury tetraedry PO_4; [8]-koordinovaný Na a molekuly H_2O jsou situovány v intersticích. Posouzení lokálních požadavků na valence vazeb ukazuje, že malé množství Ca může být vázano ve strukture cyrilovitu díky substituci $^{Na}Ca + {}^{M(1)}Fe^{2+} \rightarrow {}^{Na}Na + {}^{M(1)}Fe^{3+}$. Cyrilovit je isostrukturní s warditem, Na $[Al^3 (PO_4)_2 (OH)_4 (H_2O)_2]$. Cyrilovit nemá žádnou štěpnost, jak napovídá systém vazebných sil v celé struktuře. Warditu je však ve standardních příručkách přisuzována dokonalá štěpnost podle (001). Přezkoumání warditu ukazalo, že nemá žádnou štěpnost, v souhlase s jeho strukturním uspořádáním.