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Penkvilksite, a new kind of silicate structure: OD character, X-ray single-crystal (1*M*), and powder Rietveld (2*O*) refinements of two MDO polytypes

Stefano Merlino, Marco Pasero
Department of Earth Sciences, University of Pisa, Via S. Maria 53, I-56126 Pisa, Italy
Gilberto Artioli
Department of Earth Sciences, University of Milano, Via Botticelli 23, I-20133 Milano, Italy
Alexander P. Khomyakov
Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Russian Academy of Sciences, Veresaev Street 15, 121357 Moscow, Russia

Abstract

The nomenclature of the mineral species penkvilksite, $Na_4Ti_2Si_8O_{22}\cdot 4H_2O$, has been revised, after the second finding in nature of the mineral, which has been demonstrated to occur in two polytypic modifications: the earlier-described orthorhombic (penkvilksite-2*O*) and the present monoclinic (penkvilksite-1*M*). Penkvilksite-2*O* is found in the Lovozero alkaline massif, Kola Peninsula, Russia, with space group *Pnca*, $a = 16.3721(5)$, $b = 8.7492(3)$, $c = 7.4020(2)$ Å; its structure was refined by X-ray powder diffraction with the use of full-profile Rietveld technique, $R_p = 0.076$, $R_{wp} = 0.098$. Penkvilksite-1*M* is found in the Khibina alkaline massif, Kola Peninsula, Russia, with space group $P2_1/c$, $a = 8.956(4)$, $b = 8.727(3)$, $c = 7.387(3)$ Å, $\beta = 112.74(3)°$; its structure was refined by single-crystal X-ray diffraction on 1174 independent reflections, $R = 0.045$, $R_w = 0.047$. Penkvilksite represents a novel kind of silicate structure, characterized by the occurrence of alternating clockwise- and counterclockwise-growing spirals of corner-sharing SiO_4 tetrahedra, whose periodicity corresponds to six tetrahedral units. The 2*O* and 1*M* polytypes of penkvilksite are also described, according to the OD theory, as two out of the four possible maximum degree of order (MDO) polytypes within a family of OD structures formed by two layers.

Introduction

Penkvilksite was originally described as a new titanium sodium hydrosilicate from the Yubileynaya pegmatoid vein of the Lovozero alkaline massif, Kola Peninsula, Russia (Bussen et al., 1975). Its ideal chemical formula was given as $Na_4Ti_2Si_8O_{22}\cdot 5H_2O$, with minor substitutions of Ca, Zr, and Al for Na, Ti, and Si, respectively. Bussen et al. (1975) described the new mineral as follows: "Porous lumps of penkvilksite are as much as 3 cm in diameter and consist of fine-grained fibrous-radial and spherulitic aggregates. Such aggregates are white, opaque, and dull at the surface, but in freshly fractured chips they exhibit a pearly or silky luster. They consist of subparallel intergrowths of minute transparent, colorless flakes, no larger than tenths of a millimeter." Penkvilksite was assigned to the orthorhombic or monoclinic systems on the basis of its optical properties.

Starting from the cell parameters $a = 7.48$, $b = 8.77$ Å, $\gamma = 90°$, determined from electron diffraction patterns (Bussen et al., 1975), Khalilov et al. (1977) derived through the Ito method the following unit-cell parameters from the powder pattern (diffractometer data, Cu$K\alpha$ radiation): $a = 8.72(2)$, $b = 7.38(2)$, $c = 16.33(2)$ Å. Moreover, Khalilov et al. indicated, on the basis of the systematic absences in the powder diffraction pattern, *Pmmn* as the space group for penkvilksite (we shall comment later on this).

Since then, the occurrence of penkvilksite has been reported from Mont Saint-Hilaire, Québec, Canada (Chao and Baker, 1979; Horváth and Gault, 1990). More recently, some crystals of an unknown phase (phase B in what follows) were found in Khibina, Kola Peninsula. A new chemical analysis was carried out that closely matches that of penkvilksite (phase A in what follows), apart from the small Zr substitution in the latter. The occurrence of well-developed crystals of phase B enabled us to obtain a full crystallographic characterization: phase B is monoclinic, space group $P2_1/c$, with $a = 8.956(4)$, $b = 8.727(3)$, $c = 7.387(3)$ Å, $\beta = 112.74(3)°$.

The similar chemical composition and the relationships between the unit-cell parameters pointed to a close structural relationship between phase A and phase B. The recognition of the OD character of penkvilksite was the key element leading to the successful description of both phases.

Following the guidelines on the nomenclature of polytype structures stated by the Ad-Hoc Committee of the

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Table 1. Electron microprobe analyses (wt%) of penkvilksite polytypes

	1*M*	2*O*
SiO_2	55.21	54.69
TiO_2	17.70	15.91
ZrO_2	<0.1	2.17
Al_2O_3	<0.1	0.76
Fe_2O_3	0.20	0.19
MnO	<0.1	0.01
CaO	<0.1	1.60
SrO		0.01
Na_2O	14.39	13.13
K_2O	<0.05	0.09
Nb_2O_5	0.73	1.08
Ta_2O_5		0.06
P_2O_5		0.02
F		0.05
H_2O	8.29*	8.33*
Sum		98.10
O = F		−0.02
Total	96.52	98.08

Note: penkvilksite-1*M*, Khibina massif (this study; anal.: G. N. Nechelyustov) $Na_{4.04}(Ti_{1.93}Nb_{0.05}Fe_{0.02})Si_{7.99}O_{22}\cdot 4H_2O$ (based on O = 22). Penkvilksite-2*O*, Lovozero massif (recalculated from Bussen et al., 1975) $(Na_{3.66}Ca_{0.25}K_{0.02})(Ti_{1.72}Zr_{0.15}Nb_{0.07}Fe_{0.02})(Si_{7.87}Al_{0.13})O_{21.98}F_{0.02}\cdot 4H_2O$ (based on O + F = 22).

* Computed assuming $4H_2O$ pfu.

International Union of Crystallography (Guinier et al., 1984), we submitted to the Commission on New Minerals and Mineral Names of the International Mineralogical Association a proposal to revise the nomenclature of penkvilksite and apply polytype suffixes. The proposal has been accepted. Therefore, it is appropriate now to indicate phase A (namely, penkvilksite, the mineral originally defined by Bussen et al., 1975) as penkvilksite-2*O* and to introduce in the mineralogical literature the new name penkvilksite-1*M* to refer to the newly discovered polytype.

Selected mineralogical data

Whereas penkvilksite-2*O* was thoroughly described as the new mineral penkvilksite by Bussen et al. (1975), penkvilksite-1*M* has never been properly characterized, and essential mineralogical data are presented here in detail.

Penkvilksite-1*M* was found in the drill core from Mount Restinyun, in the northeastern part of the Khibina alkaline massif, Kola Peninsula, Russia. The mineral occurs as very small anhedral crystals, 0.1–1 mm in length, and it is associated with calcite, elpidite, lorenzenite, phlogopite, barite, and sphalerite. It crystallized from residual peralkaline salt-silicate liquids. Crystals of penkvilksite-1*M* are transparent, colorless, with white streak and vitreous luster. The measured density is 2.63(5) g/cm³; the calculated value is 2.61 g/cm³.

Optical data (λ = 5890 Å): biaxial (+), α = 1.640(2), β = 1.646(2), γ = 1.675(2), $2V_{meas}$ = 50(1)°, $2V_{calc}$ = 50°, dispersion $r < \nu$ strong.

Five chemical analyses were carried out by means of a Camebax electron microprobe (operating conditions: 20 kV, 20 nA). The following standards were used: chkalovite (Na,Si), almandine (Fe), anatase (Ti), synthetic $LiNbO_3$ (Nb). The average analytical data for penkvilksite-1*M* are presented in Table 1 and compared with those for penkvilksite-2*O*, taken from Bussen et al. (1975).

The X-ray powder pattern of penkvilksite-1*M* (Gandolfi technique) is shown in Table 2, compared with that of penkvilksite-2*O*. It seems proper to remark that the powder patterns of the two phases exhibit close analogies, together with minor, although significant, differences.

Single-crystal analysis of penkvilksite-1*M*

A crystal measuring 0.25 × 0.2 × 0.15 mm, previously examined by Weissenberg photographs, was chosen for the intensity data collection, which was carried out on an Ital Structures four-circle automatic diffractometer, using graphite-monochromated Mo$K\alpha$ radiation (γ = 0.71069 Å). The following unit-cell parameters were derived through the least-squares fitting of 2θ values of 28 reflections (20° < 2θ < 30°): monoclinic, space group $P2_1/c$, a = 8.956(4), b = 8.727(3), c = 7.387(3) Å, β = 112.74(3)°. The data collection was performed in a ω-2θ scan mode, with scan width 1.6° + 0.3° tan θ and scan speed 1.5° min^{-1}, proportionally increased on the basis of the intensity of a prescan of the peaks. The reflections up to 2θ = 25° were measured at two equivalent positions, whereas all the independent reflections were measured to 2θ = 60°. Of the 1811 measured intensities, those having $I > 3\sigma_I$ were considered observed and were used in the least-squares calculations after correction for Lorentz and polarization factors. Equivalent reflections were merged (R_{symm} = 0.048), thus obtaining a set of 1174 independent structure factors.

The crystal structure of penkvilksite-1*M* was solved by direct methods using the SHELXS86 (Sheldrick, 1986) and refined using the SHELX76 (Sheldrick, 1976) computer program packages. The most intense maxima of the *E*-map were easily interpreted, on the basis of their heights and of the bonding distances, as due to Ti, two Si and five O atoms. A subsequent Fourier synthesis revealed the positions of Na and two more O atoms. Neutral atomic scattering factors f, f', and f'' were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). According to the chemical data for penkvilksite-1*M*, very minor substitution of Nb and Fe for Ti occurs, but such substitutions were not taken into account during the structural refinement. An empirical correction for the absorption effects was performed by DIFABS (Walker and Stuart, 1983). The correction factors for F ranged from 0.89 to 1.09, and the value of R_{symm} from merging equivalents dropped from 0.048 to 0.034. The positional parameters of the two H atoms, corresponding to the positive maxima of the difference-Fourier synthesis, were refined by taking into account the bond-valence balance and constrained to chemically reasonable H bonding distances and angles by means of the DFIX instructions in the SHELX76 program. The final reliability indices were R = 0.045 and R_w = 0.047 $\{w = 1/[\sigma^2(F_o) + 0.00047(F_o)^2]\}$ for all 1174 observed reflec-

TABLE 2. Powder X-ray diffraction patterns of penkvilksite polytypes

Penkvilksite-1*M**				Penkvilksite-2*O***			
I	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}	*hkl*
S	8.290	8.280	100	100	8.2118	8.1861	200
mw	6.020	6.005	$\bar{1}10$	35	5.9878	5.9776	210
				13	5.6551	5.6510	011
mS	5.300	5.307	$\bar{1}11$	62	5.3441	5.3417	111
				30	4.6526	4.6505	211
				16	4.3770	4.3746	020
vw	4.140	4.140	200	20	4.0949	4.0930	400
mS	3.990	3.988	111	14	3.9269	3.9256	311
				5	3.8592	3.8582	220
w	3.674	3.675	021	9	3.7034	3.7074	410
		3.653	$\bar{1}21$			3.7010	002
				8	3.6116	3.6099	102
mw	3.393	3.406	$\bar{1}12$	29	3.4224	3.4214	221
S	3.339	3.344	$\bar{2}02$	69	3.3727	3.3723	202
				49	3.3123	3.3149	411
m	3.130	3.126	121	12	3.1477	3.1467	212
				48	3.1003	3.0996	321
				56	3.0621	3.0631	302
				3	2.9901	2.9888	420
S	2.884	2.883	211	5	2.8802	2.8910	312
				43	2.8326	2.8331	511
				7	2.7853	2.7843	122
w	2.723	2.722	$\bar{3}02$	24	2.7464	2.7473	230
						2.7452	402
w	2.689	2.688	022	22	2.7134	2.7134	031
w	2.658	2.666	$\bar{1}31$	56	2.6759	2.6769	131
		2.653	$\bar{2}22$				
				5	2.6166	2.6193	412
				28	2.5761	2.5756	231
				12	2.5094	2.5091	322
				14	2.4715	2.4710	521
				19	2.4553	2.4572	611
						2.4524	502
				7	2.4295	2.4296	331
w	2.358	2.359	$\bar{1}13$	12	2.3594	2.3614	512
		2.355	122				
				7	2.2811	2.2807	213
				6	2.2661	2.2686	132
vw	2.197	2.202	013	13	2.1874	2.1873	040
		2.198	311				
vw	2.160	2.160	$\bar{3}13$				
				3	2.1135	2.1132	240
				2	2.0805	2.0806	141
				7	2.0544	2.0540	413
w	2.015	2.015	321	6	2.0327	2.0320	241
		2.014	410				
				10	1.9885	1.9869	721
				4	1.9590	1.9580	341
				7	1.9220	1.9242	811
						1.9240	631
						1.9224	513
w	1.872	1.873	$\bar{1}33$	2	1.8711	1.8713	133
		1.870	420			1.8707	142
				4	1.8515	1.8537	820
						1.8505	004
w	1.827	1.828	302	8	1.8357	1.8357	233
						1.8351	242
w	1.792	1.792	033	9	1.7917	1.7913	613
						1.7909	802
mw	1.772	1.769	$\bar{3}33$	15	1.7801	1.7806	333
						1.7800	342
				7	1.7681	1.7677	214
				3	1.7540	1.7546	812
						1.7544	632
				5	1.7297	1.7316	911
mw	1.704	1.703	$\bar{2}24$	24	1.7050	1.7067	640
						1.7043	024
						1.7029	051
				4	1.6853	1.6862	404
				5	1.6675	1.6685	224
						1.6672	251
						1.6664	713
				5	1.6555	1.6574	822
						1.6557	414
mw	1.621	1.621	$\bar{4}33$	5	1.6325	1.6328	533
				4	1.6100	1.6100	504
						1.6093	10.1.0
						1.6090	450
				8	1.5713	1.5725	10.1.1
						1.5723	451
				12	1.5493	1.5503	813
						1.5502	633
						1.5498	642
mw	1.528	1.527	402	10	1.5306	1.5333	10.2.0
						1.5315	604
						1.5295	922
						1.5262	832
				9	1.4968	1.4973	10.0.2
						1.4944	840
w	1.480	1.480	152	1	1.4745	1.4758	10.1.2
						1.4756	452
				3	1.4539	1.4539	115

* Gandolfi camera, diameter 114.6 mm, Fe$K\alpha$ radiation, λ = 1.93728 Å; a = 8.979(3), b = 8.721(6), c = 7.403(3) Å, β = 112.75(3)°.

** Philips diffractometer, Cu$K\alpha$, λ = 1.54178 Å; a = 16.3721(5), b = 8.7492(3), c = 7.4020(2) Å.

tions, using anisotropic atomic displacement parameters for all atoms with the exception of the H atoms, whose isotropic displacement parameters were forced to be identical. The maximum Δ/σ for non-H atoms in the last least-squares cycle was −0.28; maximum and minimum heights in the final difference-Fourier synthesis were +1.1 and −0.9 e/Å^3, respectively.

The final atomic fractional coordinates and equivalent isotropic displacement parameters for penkvilksite-1*M* are reported in Table 3, and bond distances are listed in Table 4. Anisotropic displacement parameters and observed and calculated structure factors are listed in Table 5.[1] A drawing of the structure of penkvilksite-1*M* as seen along **b** is presented in Figure 1.

RELATIONSHIPS BETWEEN PENKVILKSITE-2*O* AND PENKVILKSITE-1*M*

The solution of the crystal structure of penkvilksite-1*M* by single-crystal X-ray diffraction measurements, together with the metric relationships with penkvilksite-2*O*, provided the clue for understanding the relationship between the two phases. Starting from the structure of penkvilksite-1*M*, it is possible to build a reliable structural model for penkvilksite-2*O*. In penkvilksite-1*M*, the O atoms labeled O6 (shared between two Si2-centered tetrahedra) lie on inversion centers at ½00 and ½½½. A new structure can be obtained, given the assumption of twofold axes passing through O6 atoms. The new struc-

[1] For a copy of Tables 5 and 6, order Document AM-94-568 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

Table 3. Final positional and displacement parameters (Å²) for penkvilksite polytypes

Penkvilksite-1*M*					Penkvilksite-2*O*				
Atom	*x*	*y*	*z*	*U**	Atom	*x*	*y*	*z*	*U*
Ti	0	½	0	0.0072(3)	Ti**	0	½	0	0.0310(8)
Si1	0.1598(1)	0.1599(1)	0.1981(2)	0.0081(4)	Si1	0.0825(2)	0.1613(4)	0.1247(5)	0.0312(11)
Si2	0.3138(1)	0.4423(1)	0.4067(2)	0.0082(3)	Si2	0.1567(1)	0.4399(3)	0.2603(4)	0.0161(9)
Na	0.1928(3)	0.6912(2)	0.7136(3)	0.0266(7)	Na	0.1023(3)	0.6911(5)	0.6220(8)	0.063(2)
O1	0.3136(3)	0.2621(3)	0.3462(4)	0.0124(10)	O1	0.1599(3)	0.2612(5)	0.2006(10)	0.025(3)
O2	0.1032(3)	0.0379(3)	0.3202(4)	0.0118(10)	O2	0.0501(4)	0.0372(7)	0.2695(8)	0.028(2)
O3	0.0207(3)	0.2781(3)	0.0677(4)	0.0119(10)	O3	0.0074(4)	0.2704(6)	0.0633(10)	0.025(2)
O4	0.2347(4)	0.0519(4)	0.0704(4)	0.0126(10)	O4	0.1162(3)	0.0507(6)	−0.0389(6)	0.033(2)
O5	0.2091(4)	0.5387(3)	0.2153(4)	0.0109(10)	O5	0.1115(3)	0.5394(6)	0.1052(7)	0.021(2)
O6	½	0	0	0.0142(16)	O6	¼	½	0.2705(9)	0.016(3)
OW	0.3696(5)	0.6888(6)	0.2086(6)	0.0451(16)	OW	0.1954(6)	0.6844(8)	−0.1548(12)	0.049(3)
H1	0.330	0.605	0.093	0.17(4)	H1	0.173	0.586	−0.108	0.10(5)
H2	0.488	0.667	0.066	0.17(4)	H2	0.242	0.650	−0.232	0.14(5)

* The equivalent isotropic displacement was converted from the anisotropic parameters (with the exception of the H atoms).
** Site occupancy is 90% Ti + 10% Zr.

ture has space group *Pnca,* and unit-cell parameters a = 16.33, b = 8.72, and c = 7.38 Å, identical to those given by Khalilov et al. (1977) for penkvilksite, except for the space group, given as *Pmmn* by the latter authors on the basis of the systematic absences in the powder pattern ($hk0$ with $h + k$ odd). However, additional systematic absences can be assumed, namely, $h0l$ with l odd and $0kl$ with k odd; all the exceptions reported in the powder pattern by Khalilov et al. (1977) (203, 105, 031, 038, etc.) correspond to multiply indexed reflections. In this way, the resulting space group is not *Pmmn* but *Pbcn* or *Pnca* in our setting (our choice of axes for the orthorhombic structure is consistent with the standard orientation of axes in the monoclinic structure with space group $P2_1/c$).

Table 4. Selected interatomic distances (Å) and angles (°) for penkvilksite polytypes

	1*M*	2*O*
Si1-O1	1.651(3)	1.639(6)
-O2	1.599(3)	1.615(7)
-O3	1.617(3)	1.621(7)
-O4	1.648(4)	1.645(6)
Av.	1.629	1.630
O1-Si1-O2	110.6(2)	112.6(4)
O1-Si1-O3	107.7(1)	111.6(3)
O1-Si1-O4	105.6(2)	107.9(3)
O2-Si1-O3	114.9(2)	109.4(4)
O2-Si1-O4	103.3(2)	101.7(3)
O3-Si1-O4	114.4(2)	113.2(3)
Av.	109.4	109.4
Si2-O1	1.635(3)	1.625(5)
-O4	1.621(4)	1.645(6)
-O5	1.600(3)	1.620(6)
-O6	1.619(1)	1.617(2)
Av.	1.619	1.627
O1-Si2-O4	106.2(2)	108.0(3)
O1-Si2-O5	109.0(1)	109.8(3)
O1-Si2-O6	107.9(1)	107.2(2)
O4-Si2-O5	111.5(2)	115.7(3)
O4-Si2-O6	110.4(1)	109.0(2)
O5-Si2-O6	111.6(1)	106.9(2)
Av.	109.4	109.4
Na-O2	2.398(4)	2.431(8)
-O3	2.340(3)	2.364(8)
-O3′	2.954(4)	2.961(9)
-O4	2.463(4)	2.438(7)
-O5	2.361(3)	2.366(7)
-OW	2.252(4)	2.249(11)
-OW′	2.673(6)	2.776(10)
Av.	2.492	2.512
Ti-O2 (× 2)	1.917(3)	1.921(6)
-O3 (× 2)	1.991(3)	2.066(5)
-O5 (× 2)	1.962(3)	2.014(5)
Av.	1.957	2.000
Ow-H1	1.00	1.00
OW···O5	2.686(6)	2.683(10)
OW-H1-O5	152	131
OW-H2	1.00	1.00
OW···O1	2.699(5)	2.685(11)
OW-H2-O1	142	129
H1-OW-H2	105	103

A conclusive test of the correctness of the structural hypothesis for penkvilksite-2*O* has been carried out by means of Rietveld analysis of the model using powder diffraction data, since no single crystal of suitable size is available for the orthorhombic phase.

Powder Rietveld analysis of penkvilksite-2*O*

A polycrystalline aggregate of the penkvilksite-2*O* was repeatedly hand-ground in an agate mortar, and the powder was then side-loaded in an Al flat-plate holder. The X-ray powder data were collected in the conventional Bragg-Brentano parafocusing geometry, using unfiltered Cu$K\alpha$ radiation and a diffracted-beam pyrolitic graphite crystal monochromator. A step-scan mode was employed, with steps of 0.02°, a counting time of 15 s for each step, and a total 2θ angular scan range from 8 to 140°. The data treatment and the Rietveld structure analysis were carried out using the GSAS computer program package (Larson and Von Dreele, 1992). The 1003 independent reflections in the powder pattern were treated as $K\alpha_1,\alpha_2$ doublets in the fixed intensity ratio 2:1. A total of 6600 observed intensity points were used in the refinement; the peak profiles were modeled using a pseudo-Voigt function, and the background intensity was fitted by a cosine Fourier series with three coefficients.

The hypothetical structural model for penkvilksite-2*O* discussed above, with 11 independent atoms (one Ti, two Si, six O, one Na, and one O in H_2O) in space group *Pnca,* was fixed in the initial stages of the refinement. The adjustment of the lattice parameters, of the coefficients of the peak profile, and of background functions was suf-

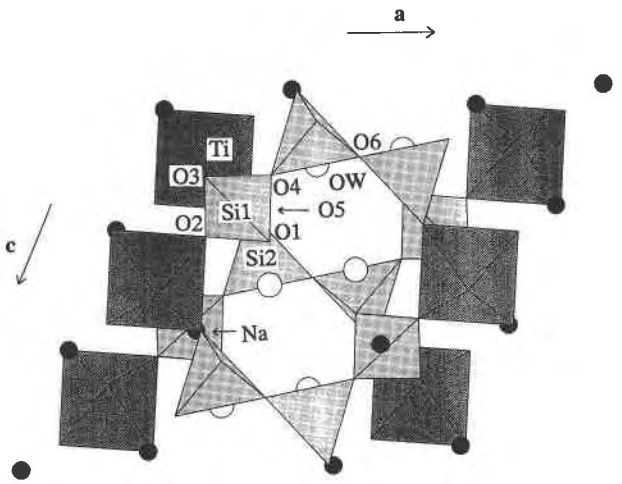

Fig. 1. The crystal structure of penkvilksite-1*M*, as seen along [010], featuring SiO_4 tetrahedra and TiO_6 octahedra.

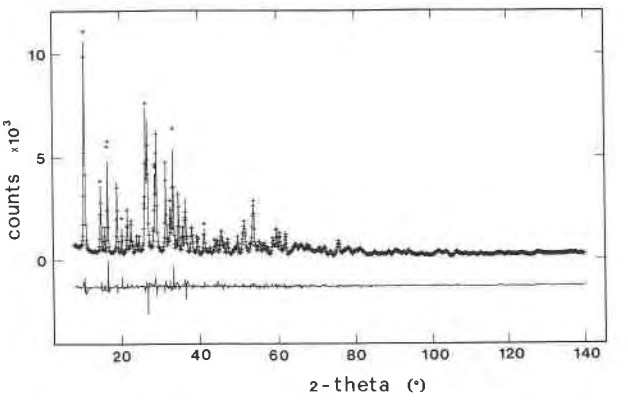

Fig. 2. The full range of observed (plus signs), calculated (solid curves), and difference (lower curve) profiles for the multiphase Rietveld refinement (penkvilksite-2*O* 95.9%, penkvilksite-1*M* 4.1%).

ficient to make the refinement converge readily to profile-agreement factors of $R_p = \Sigma|I_o - I_c|/\Sigma I_o = 0.18$ and $R_{wp} = \{\Sigma[w(I_o - I_c)^2]/\Sigma[wI_o^2]\}^{1/2} = 0.21$, confirming that the model is essentially correct. Successive refinement of the atomic coordinates and isotropic displacement parameters further reduced the agreement indices to $R_p = 0.08$ and $R_{wp} = 0.11$. Attempts to refine the occupancy parameters for all atomic sites indicated full occupancy for all atoms within the standard deviation, except for the Ti site, for which the occupancy factors was significantly larger than 1.0. We interpreted this overestimation as due to the Zr substitution in the octahedral Ti site.

At this stage, the structural analysis was completed by (1) allocation of 10% Zr in the Ti site according to the results of the chemical analysis, (2) addition of the monoclinic penkvilksite-1*M* as an impurity, to account for a few low-intensity diffraction peaks in the powder pattern that were shifted with respect to the Bragg peak positions of orthorhombic phase, and (3) insertion of the two theoretical H atom positions in the structure, with soft constraints on H bonding distances and angles.

During the refinement, the atomic coordinates for the atoms of the penkvilksite-1*M* resulting from the single-crystal study were kept fixed. Furthermore, the coefficients of the peak profile functions for both phases were constrained to the same since the small quantity of the monoclinic phase in the powder mixture and the strong peak overlap between the two phases did not allow independent refinement of the profile parameters for penkvilksite-1*M*.

The multiphase refinement successfully converged to final agreement factors of $R_p = 0.076$, $R_{wp} = 0.098$, $GOF = \{\Sigma[w(I_o - I_c)^2]/(N_{obs} - N_{var})\}^{1/2} = 5.29$, $R_{Bragg} = \Sigma|I'_o - I'_c|/\Sigma I'_o = 0.071$, $R_F = \Sigma|F_o - F_c|/\Sigma F_o = 0.052$. [In these expressions, I_o and I_c are the observed and calculated step intensities, and I'_o and I'_c are the observed (i.e., decomposed using the fitted peak profile function) and calculated integrated peak intensities.] The final cycles refined 56 parameters for penkvilksite-2*O* and five parameters for penkvilksite-1*M*. The refined cell constants for the orthorhombic phase are $a = 16.3721(5)$, $b = 8.7492(3)$, $c = 7.4020(2)$ Å. The relative proportions of the two phases in the powder mixture are 95.9(1) wt% for penkvilksite-2*O* and 4.1(1) wt% for penkvilksite-1*M*, estimated from the refined phase scale factors by standard Rietveld quantitative analysis (Hill, 1991; Snyder, 1992).

Final atomic fractional coordinates and displacement factors are listed in Table 3, and selected bond distances and angles are reported in Table 4. The intensity values of the observed and calculated profiles are given in Table 6.[1] Figure 2 shows the observed, calculated, and difference powder profiles for the final multiphase refinement.

Description of the structure

Despite the different space group symmetries, the two polytypes of penkvilksite, penkvilksite-2*O* and penkvilksite-1*M*, have the same atoms, labeled in the same way, in the asymmetric unit. Actually, they merely differ in the stacking of the same building blocks. Therefore the following description holds for both polytypes, unless otherwise stated.

The two independent tetrahedra play different roles in the structure of penkvilksite. Si1-centered tetrahedra share two corners with other tetrahedra and two corners with TiO_6 octahedra. Si2-centered tetrahedra share three corners with tetrahedra and one corner with a TiO_6 octahedron.

Penkvilksite displays a new kind of connection among SiO_4 tetrahedra. Spirals of corner-sharing tetrahedra develop along [010]. The periodicity of the spirals corresponds to six tetrahedral units. Si2-centered tetrahedra are shared between adjacent spirals, which are oriented in an alternate clockwise and counterclockwise fashion. The stacking of the spirals along [001] gives rise to tetrahedral layers parallel to (100). The connection of neigh-

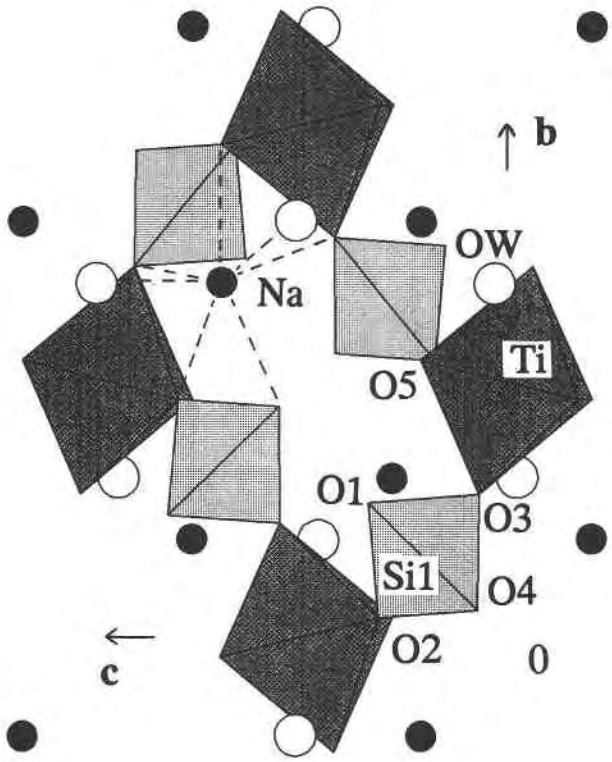

Fig. 3. The octahedral layers in penkvilksite, as seen along [100], featuring the sevenfold-coordinated Na cations (solid circles) and the H_2O molecules (open circles).

boring layers of tetrahedra is due to Ti^{4+} cations in octahedral coordination.

An alternate way of describing the structure of penkvilksite is based on the fundamental blocks formed by TiO_6 octahedra and Si1-centered tetrahedra. The connection between octahedra and tetrahedra—through the sharing of corners—is illustrated in Figure 3. Neighboring blocks along (100) are linked through Si_2O_7 groups.

The coordination polyhedron around Ti^{4+} is almost regular, with similar Ti-O distances. This is related to the observation that the O atoms belonging to the TiO_6 octahedron display very similar environments. Indeed, each of these O atoms is linked, besides Ti, to one Si and one Na atom (O3 is actually linked to two Na atoms, and consequently it displays the greatest Ti-O distance, but the second neighbor Na is farther apart, being Na-O3 = 2.96 and 2.95 Å for penkvilksite-2*O* and penkvilksite-1*M*, respectively). Significant distortions of the TiO_6 octahedra have been observed, for instance, in lintisite (Merlino et al., 1990), another sodium titanosilicate found in the Lovozero alkaline massif. However in lintisite, in contrast to the present case, the O atoms belonging to the TiO_6 octahedra display unequal bonding with the other cations.

Na cations are placed on both sides of the octahedral layers and are sevenfold coordinated by five O atoms and two H_2O molecules (Fig. 3).

Table 7. Bond valence sums (vu) for penkvilksite polytypes

	Ti*	Si1	Si2	Na	H bonds	$\Sigma_c\nu$
O1		0.930	0.971		0.227	2.128
		0.960	0.997		0.234	2.191
O2	0.759	1.070		0.199		2.028
	0.780	1.025		0.182		1.987
O3	0.621	1.019		0.232 + 0.044		1.916
	0.527	1.008		0.218 + 0.043		1.796
O4		0.937	1.008	0.167		2.112
		0.945	0.945	0.178		2.068
O5	0.672		1.067	0.219	0.234	2.192
	0.607		1.011	0.217	0.236	2.071
O6			1.014			2.028
			1.019			2.038
OW				0.295 + 0.094	−0.461	−0.072
				0.297 + 0.071	−0.470	−0.102
$\Sigma_a\nu$	4.104	3.956	4.060	1.250		
	3.828	3.938	3.972	1.206		

Note: penkvilksite-1*M* (first rows); penkvilksite-2*O* (second rows).
* Occupancy (90% Ti + 10% Zr) for penkvilksite-2O.

A total of four H_2O molecules (OW atoms) are present in the unit cell. The OW atoms are linked only to Na^+ and form H bonds with O1 and O5 atoms. This has been assumed on the basis of both metrical and crystal chemical considerations. The bond-valence calculations (Table 7), computed using the parameters of Brese and O'Keeffe (1991), indicate for both refinements an undersaturation for O1, O3, and O5 (Table 7). As the bond-valence balance for O1 and O5 is increased because of the contribution of O-H···O bonding (Ferraris and Ivaldi, 1988), a minor undersaturation for O3 atoms still occurs. However, the position of the H_2O molecules indicated as highly unlikely a H···O bond toward O3. Because of the large OW-O3 distance (3.30 and 3.41 Å for penkvilksite-2*O* and penkvilksite-1*M*, respectively), this would bring a negligible contribution to the bond-valence sums for O3.

The lack of recognizable peaks in the final difference-Fourier map for penkvilksite-1*M* led us to exclude the occurrence of more than four H_2O molecules. Actually, the chemical analysis of Bussen et al. (1975) indicated 4.9 H_2O molecules per unit cell, taking into account both H_2O^+ and H_2O^-. Besides the crystallographic evidence, it does not seem possible for additional H_2O to occur in the structure of penkvilksite, as the only suitable site—the channel externally delimited by the tetrahedral spirals—is already filled.

The structure of penkvilksite bears some resemblance to that of lemoynite, $(Na,K)_2CaZr_2Si_{10}O_{26}\cdot 5$–$6H_2O$ (Le Page and Perrault, 1976). In the structure of lemoynite, layers of ZrO_6 octrahedra occur, which are similar to the layers of TiO_6 octahedra in penkvilksite. However, the layers in lemoynite are connected to each other by means of layers formed by six-membered rings of SiO_4 tetrahedra instead of spirals of tetrahedra parallel to [010] as in penkvilksite. Moreover, the way the octahedra are connected by corner-sharing SiO_4 tetrahedra is different in the two structures.

More recently, another structure characterized by alternating octahedral and tetrahedral layers, the latter of

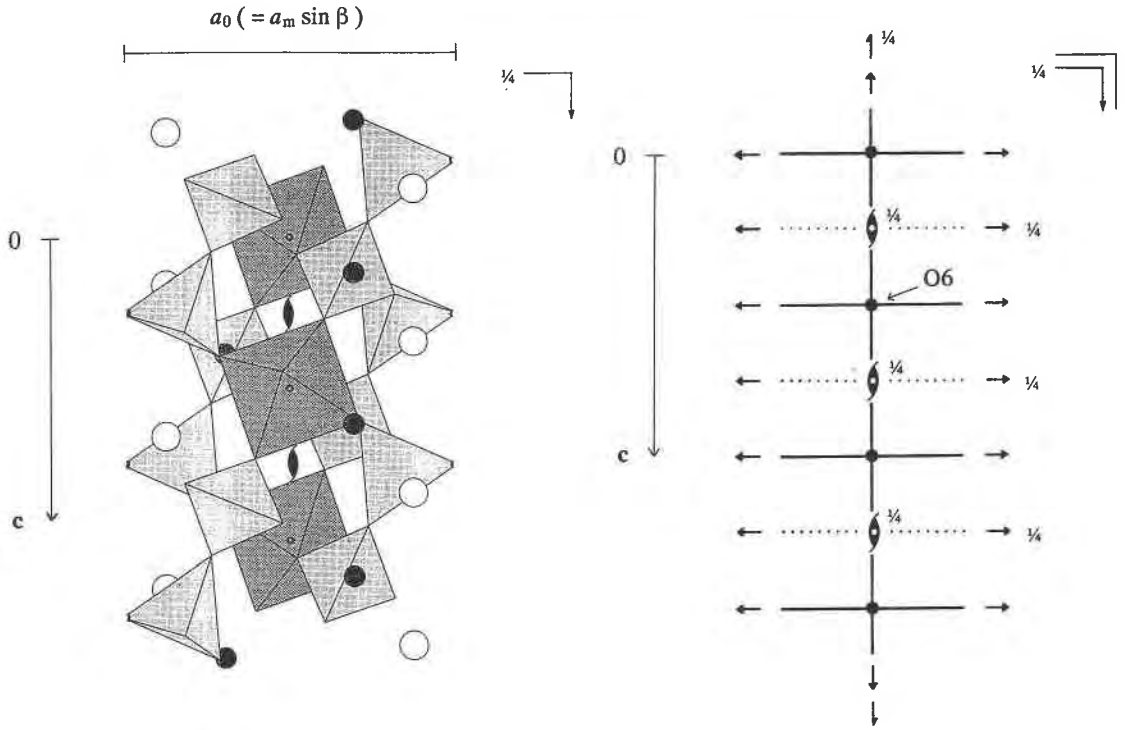

Fig. 4. The two OD layers in penkvilksite, L_{2n} (**A**) and L_{2n+1} (**B**), as seen along [010]. The layer-group symmetry is given for each.

which contain six-membered rings of tetrahedra, has been reported for the synthetic magnesium ultraphosphate, MgP_4O_{11} (Yakubovich et al., 1993).

OD CHARACTER OF PENKVILKSITE

The above-discussed polytypes of penkvilksite, penkvilksite-2*O* and penkvilksite-1*M*, represent two maximum degree of order (MDO) polytypes within a family of OD structures built up from two kinds of layer. The OD approach to the polytypic relationships between penkvilksite-1*M* and penkvilksite-2*O* was fundamental to the development of a reliable structural model for the latter polytype. Otherwise, because of the lack of suitable single crystals, it might have been exceedingly difficult to perform an ab initio determination of the structure. For an appraisal of the OD theory, the reader is directed to Dornberger-Schiff (1966, 1979), and Ďurovič and Weiss (1986).

The OD-groupoid symbol, which comprises the layer-group symbol of the two constituting layers, as well as the positional relationships between them (Grell and Dornberger-Schiff, 1982), is the following:

$$P(1)2_1/c1 \qquad A(m)mm$$
$$[0,-¼].$$

The first OD layer, L_{2n}, with layer-group symmetry $P(1)2_1/c1$ (Fig. 4A), comprises almost entirely the unit-cell content of the monoclinic penkvilksite, with only the exception of the O atoms—O6—shared by two Si2-centered tetrahedra. These O atoms constitute the second OD layer, L_{2n+1}, with layer-group symmetry $A(m)mm$ (Fig. 4B). The higher symmetry and the structural simplicity of the L_{2n+1} layers allow for the existence of four distinct MDO polytypes within this family, as L_{2n} layers on the opposite sides of the L_{2n+1} layer may be related in four ways through four pairs of symmetry operations of the L_{2n+1} layer (Dornberger-Schiff and Grell, 1982). These symmetry operations and the space groups of the resulting MDO polytype are as follows:

MDO1: $\bar{1}$ at 00 and 2_1 parallel to **b** ($P2_1/c$);
MDO2: $\bar{1}$ at ¼¼ and 2 parallel to **b** ($I2/c$);
MDO3: *n* perpendicular to **a** and 2 parallel to **c** (*Pnca*);
MDO4: *m* perpendicular to **a** and 2_1 parallel to **c** (*Pmcn*).

The polytypes of penkvilksite found so far are MDO1 (namely, penkvilksite-1*M*, $P2_1/c$, formerly referred to as phase B) and MDO3 (namely penkvilksite-$2O_1$, *Pnca*, formerly referred to as phase A). The other two MDO polytypes should be called penkvilksite-2*M* (MDO2) and

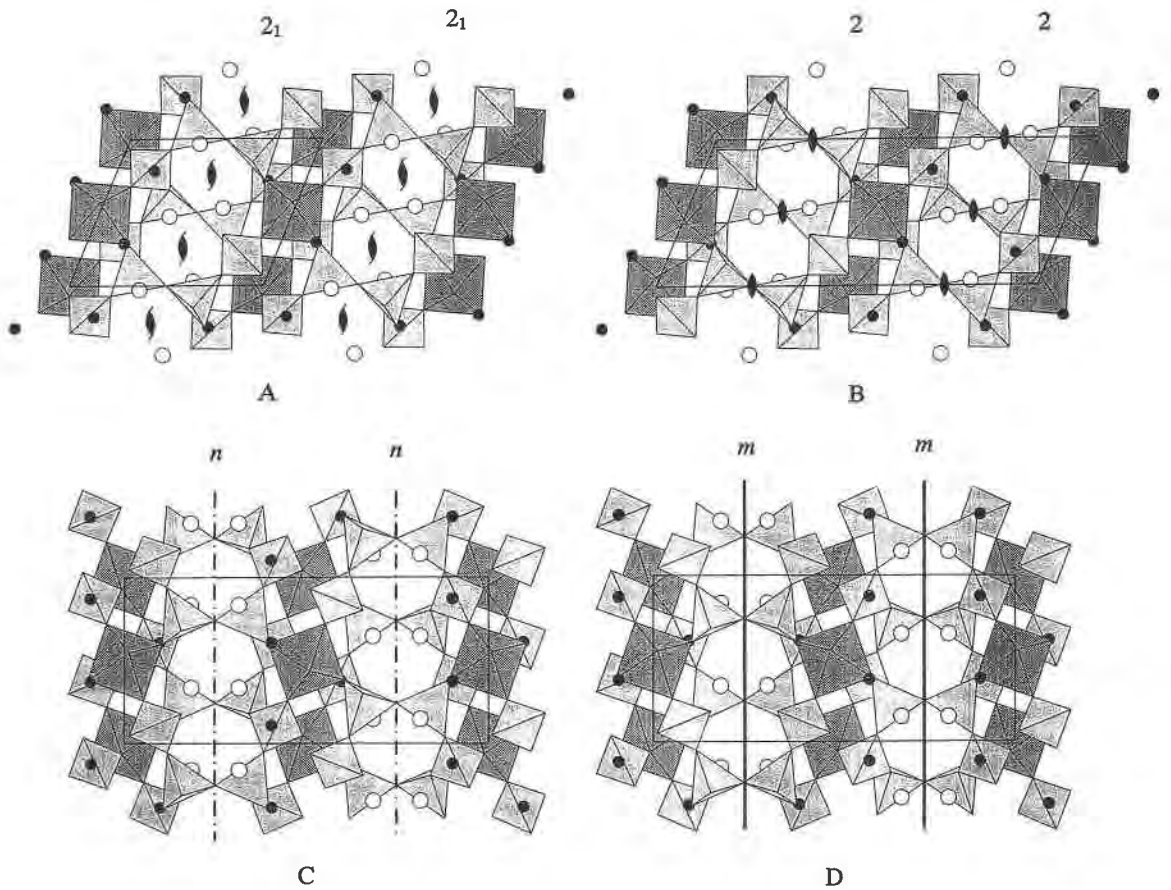

Fig. 5. The four MDO polytypes of penkvilksite, as seen along [010]: (**A**) MDO1, penkvilksite-1*M*, space group $P2_1/c$; (**B**) MDO2, penkvilksite-2*M*, space group *I*2/*c*; (**C**) MDO3, penkvilksite-2O_1, space group *Pnca*; (**D**) MDO4, penkvilksite-2O_2, space group *Pmcn*. For each of them, the symmetry operations active in L_{2n+1} layers are indicated, and the unit cell is outlined.

penkvilksite-2O_2 (MDO4). Drawings of the four MDO polytypes are shown in Figure 5.

As far as we can foresee, the subscript 1, used to define the orthorhombic polytype of penkvilksite, seems unnecessary. Indeed, although a second polytype with orthorhombic symmetry and with two layers of each kind within the unit cell has been enumerated (MDO4, space group *Pmcn*, penkvilksite-2O_2), its occurrence in nature is unlikely because of crystal chemical constraints. Even if one accepts the possibility of structural desymmetrization (i.e., the possibility for OD layers to undergo more or less pronounced distortions, depending on the particular structure in which they occur: Ďurovič, 1979), the H_2O molecules would be too close to each other, resulting in O-O distances of about 2.2–2.3 Å. Moreover, the two structures MDO4 and MDO2 display a noticeably different structural arrangement with respect to MDO1 and MDO3, as the former do not contain spirals of SiO_4 tetrahedra. Because of the presence of either twofold axes along [010] or mirrors normal to [100] in place of 2_1 or glides, spirals degenerate into close six-membered rings of tetrahedra.

Acknowledgments

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References cited

Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Bussen, I.V., Men'shikov, Yu.P., Mer'kov, A.N., Nedorezova, A.P., Uspenskaya, Ye.I., and Khomyakov, A.P. (1975) Penkvilksite, a new titanium-sodium hydrosilicate. Doklady Earth Science Section, 217, 126–129 (translated from Doklady Akademii Nauk SSSR, 217, 1161–1164, 1974).

Chao, G.Y., and Baker, J. (1979) What's new from Mont St. Hilaire. Mineralogical Record, 10, 99–101.

Dornberger-Schiff, K. (1966) Lehrgang über OD-Strukturen, 135 p. Akademie Verlag, Berlin.

——— (1979) OD structures: A game and a bit more. Kristall und Technik, 14, 1027–1045.

Dornberger-Schiff, K., and Grell H. (1982) Geometrical properties of MDO

polytypes and procedures for their derivation. II. OD families containing OD layers of M > 1 kinds and their MDO polytypes. Acta Crystallographica, A38, 491–498.

Ďurovič, S. (1979) Desymmetrization of OD structures. Kristall und Technik, 14, 1047–1053.

Ďurovič, S., and Weiss, Z. (1986) OD structures and polytypes. Bulletin de Minéralogie, 109, 15–29.

Ferraris, G., and Ivaldi, G. (1988) Bond valence vs bond length in O···O hydrogen bonds. Acta Crystallographica, B44, 341–344.

Grell, H., and Dornberger-Schiff, K. (1982) Symbols for OD groupoid families referring to OD structures (polytypes) consisting of more than one kind of layer. Acta Crystallographica, A38, 49–54.

Guinier, A., Bokij, G.B., Boll-Dornberger, K., Cowley, J.M., Ďurovič, S., Jagodzinski, H., Krishna, P., de Wolff, P.M., Zvyagin, B.B., Cox, D.E., Goodman, P., Hahn, Th., Kuchitsu, K., and Abrahams, S.C. (1984) Nomenclature of polytype structures: Report of the International Union of Crystallography Ad-Hoc Committee on the Nomenclature of Disordered, Modulated and Polytype Structures. Acta Crystallographica, A40, 399–404.

Hill, R.J. (1991) Expanded use of the Rietveld method in studies of phase abundance in multiphase mixtures. Powder Diffraction, 6, 74–77.

Horváth, L., and Gault, R.A. (1990) The mineralogy of Mont Saint-Hilaire, Québec. Mineralogical Record, 21, 281–359.

Ibers, J.A., and Hamilton, W.C., Eds. (1974) International tables for X-ray crystallography, vol. IV, 366 p. Kynoch, Birmingham, U.K.

Khalilov, A.D., Dzhafarov, N.K., and Khomyakov, A.P. (1977) Electron microscopic and X-ray investigation of the framework Ti-silicate penkvilksite. In G.A. Sidorenko, Ed., X-ray investigation of raw materials, p. 114–119. All-Union Institute of Mineral Resources, Moscow (in Russian).

Larson, A.C., and Von Dreele, R.B. (1992) GSAS general structure analysis system. Report LAUR-86-748. Los Alamos National Laboratory, New Mexico, U.S.A.

Le Page, Y., and Perrault, G. (1976) Structure cristalline de la lemoynite, $(Na,K)_2CaZr_2Si_{10}O_{26}\cdot 5–6H_2O$. Canadian Mineralogist, 14, 132–138.

Merlino, S., Pasero, M., and Khomyakov, A.P. (1990) The crystal structure of lintisite, $Na_3LiTi_2[Si_2O_6]_2O_2\cdot 2H_2O$, a new titanosilicate from Lovozero (USSR). Zeitschrift für Kristallographie, 193, 137–148.

Sheldrick, G.M. (1976) SHELX76. Program for crystal structure determination. University of Cambridge, England.

——— (1986) SHELXS86. Program for the solution of crystal structures. University of Göttingen, Germany.

Snyder, R.L. (1992) The use of reference intensity ratios in X-ray quantitative analysis. Powder Diffraction, 7, 186–193.

Walker, N., and Stuart, D. (1983) An empirical method for correcting diffractometer data for absorption effects. Acta Crystallographica, A39, 158–166.

Yakubovich, O.V., Dimitrova, O.V., and Vidrevich, A.I. (1993) Magnesium ultraphosphate MgP_4O_{11}: Growth and crystal structure. Crystallography Reports, 38, 176–180 (translated from Kristallografiya, 38, 77–85, 1993).

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