

The mineralogy of väyrynenite, $(\text{Mn,Fe})\text{Be}(\text{PO}_4)(\text{OH})^*$

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With 3 figures

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Auszug

Es wird über eine neue chemische Analyse und über die kristallographische Untersuchung an Einzelkristallen des Väyrynenits von Eräjärvi im zentralen Finnland berichtet. Die Analyse ergab: MnO 34,01, FeO 5,92, CaO 0,53, BeO 13,85, Na_2O 0,20, K_2O 0,04, Al_2O_3 0,40, P_2O_5 39,98, $\text{H}_2\text{O} +$ 4,93, $\text{H}_2\text{O} -$ 0,19, unlösl. 0,06. Die Raumgruppe ist $P2_1/a - C_{2h}^5$; die Gitterkonstanten sind $a = 5,41_1 \pm 0,005 \text{ \AA}$, $b = 14,49 \pm 0,02 \text{ \AA}$, $c = 4,73_0 \text{ \AA} \pm 0,005 \text{ \AA}$, $\beta = 102^\circ 45' \pm 5'$. Die Zelle enthält 4 Formeleinheiten $(\text{Mn,Fe})\text{Be}(\text{PO}_4)\text{OH}$. Die nahe Strukturverwandtschaft des Väyrynenits mit dem Euklas $\text{AlBe}(\text{SiO}_4)\text{OH}$ wird diskutiert.

Abstract

A new chemical analysis and x-ray single-crystal study are reported for väyrynenite, originally described by VOLBORTH (1954) from Eräjärvi in central Finland. The analysis gave: MnO 34.01, FeO 5.92, CaO 0.53, BeO 13.85, Na_2O 0.20, K_2O 0.04, Al_2O_3 0.40, P_2O_5 39.98, $\text{H}_2\text{O} +$ 4.93, $\text{H}_2\text{O} -$ 0.19, insol. 0.06; total 100.11. X-ray crystallographic data are: monoclinic, space group $P2_1/a - C_{2h}^5$; $a = 5.41_1 \pm 0.005 \text{ \AA}$, $b = 14.49 \pm 0.02$, $c = 4.73_0 \pm 0.005$, $\beta = 102^\circ 45' \pm 05'$; cell contents, 4 formula units. The first indexed x-ray powder data and new mineralogical observations on the physical properties are given. The close structural relation between väyrynenite, $(\text{Mn,Fe})\text{Be}(\text{PO}_4)(\text{OH})$, and euclase, $\text{AlBe}(\text{SiO}_4)(\text{OH})$, is discussed.

Introduction

The complex granite-pegmatite occurrence at Viitaniemi in the parish of Eräjärvi in central Finland shows a remarkable assemblage of phosphate minerals. There occur here particularly the rare beryllium phosphates, beryllonite $\text{NaBe}(\text{PO}_4)$, hurlbutite $\text{CaBe}_2(\text{PO}_4)_2$, herderite

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$\text{CaBe}(\text{PO}_4)(\text{F},\text{OH})$, and väyrynenite $(\text{Mn},\text{Fe})\text{Be}(\text{PO}_4)(\text{OH})$, all of which have been described recently in great detail by VOLBORTH (1954a, 1954b, 1954c, 1954d). This paper gives additional mineralogical data and a new chemical analysis for väyrynenite (vi'-ri-në-nite) from this same locality. In addition to the phosphate minerals listed by VOLBORTH as occurring at Eräjärvi, eosphorite, fairfieldite, and moraesite have been found and identified by the authors.

The existence of this manganese-iron beryllium phosphate was known to VON KNORRING as early as 1939 when he recognized it as a possible new mineral in several specimens collected by him at that time. In these specimens väyrynenite occurs in the following characteristic associations: 1) pink crystal aggregates up to 5 cm long, resembling rubellite, in a matrix of finely divided greenish-yellow muscovite (gilbertite) with microcline, amblygonite, apatite, and quartz; 2) brownish-pink crystals 1–3 mm long, enclosed in massive pink eosphorite with amblygonite, dark-green tourmaline, topaz, muscovite, cassiterite, and quartz; 3) pale gray crystal aggregates up to 3 cm long, intimately associated with massive pale gray apatite; and 4) partly replacing beryllonite crystals, in wedge-like pockets of quartz with amblygonite, microcline, and muscovite.

X-ray crystallography

A single-crystal x-ray study was made with a euhedral crystal of väyrynenite (about $0.5 \times 0.5 \times 0.75$ mm), mounted at the end of a glass fiber so that the crystallographic c axis was parallel with the fiber length. Zero-level patterns of the $h0l$ and $0kl$ nets as well as first-level patterns of the $h1l$ and $1kl$ nets were taken with a quartz-calibrated Buerger precession camera, using Mo/Zr radiation ($\lambda = 0.7107 \text{ \AA}$) to establish the lattice type and symmetry. These films were measured and corrected for film shrinkage. Systematic extinctions were observed to be of the type $h0l$, with $h \neq 2n$, and $0k0$ with $k \neq 2n$. These criteria led unequivocally to the space group $P2_1/a-C_{2h}^5$.

Complete x-ray crystallographic data for väyrynenite are summarized in Table 1; they are compared with those originally cited by STRADNER in VOLBORTH (1954d). The value for a obtained in the present study differs considerably from that reported by STRADNER. STRADNER's value is almost twice that we obtained in our study. She does not indicate the method by which her crystallographic data were

Table 1. *Crystallographic data for väyrynenite*

	Present study	STRADNER in VOLBORTH (1954d)
Crystal class	Monoclinic; prismatic $-2/m$	Monoclinic
Cell constants		
<i>a</i>	$5.41_1 \pm 0.005 \text{ \AA}$	10.47 \AA
<i>b</i>	14.49 ± 0.02	14.40
<i>c</i>	$4.73_0 \pm 0.005$	4.75
β	$102^\circ 45' \pm 05'$	$102^\circ 49'$
<i>a</i> : <i>b</i> : <i>c</i> (x-ray)	0.3734 : 1 : 0.3264	0.7271 : 1 : 0.3299
Cell contents	4[(Mn,Fe)Be(PO ₄)(OH)]	8[(Mn,Fe)Be(PO ₄)(OH,F?)]
Cell volume	361.7 \AA^3	697.0 \AA^3
Space group	$P 2_1/a - C_{2h}^5$	—
Spec. grav. (calc.)	3.23 (for Mn:Fe = 85:15)	3.35*
Spec. grav. (obs.)	3.215 ± 0.005 (microbalance) 3.22 (suspension method)	3.183 (VOLBORTH)

* Calculated by the present authors on the basis of the cell data and cell contents cited by the original authors.

derived. Also, there is no mention as to whether all the single-crystal x-ray photographs were made from the same crystal or whether several crystals were used for the various orientations. STRADNER's *a* value of 10.47 \AA is in excellent agreement with the 10.45 \AA given for the *a* value for eosphorite from Newry, Maine by HURLBUT (1950). Pink eosphorite was found by us in close association with väyrynenite which it resembles in habit and color; its identity was established optically and by x-ray powder pattern. There thus exists the possibility that STRADNER may have selected an eosphorite crystal in determining her crystallographic *a*.

That the *a* value of STRADNER is in error is borne out further by the fact that the specific gravity calculated by the present authors, using VOLBORTH's formula and STRADNER's cell constants, is far out of line with any of the reported measured values. On the other hand our specific gravity determinations (3.215 by Berman microbalance; 3.22 by suspension method) are in excellent agreement with the calculated value of 3.23 derived from our formula and cell data.

VOLBORTH's powder data for väyrynenite are in good agreement with those obtained in this study (Table 2). His data, however, cannot be indexed in terms of STRADNER's cell, thus further substantiating the fact that one of the cell constants must be in error.

X-ray powder data

X-ray powder patterns were taken with a Debye-Scherrer camera (114.59 mm diameter), using the Straumanis and Wilson techniques, with both Fe/Mn and Cu/Ni radiations ($\lambda = 1.9373 \text{ \AA}$; $\lambda = 1.5418 \text{ \AA}$). The pattern taken in FeK α radiation (film 8762) was so far superior to

Table 2. X-ray powder data for väyrynenite, (Mn,Fe)Be(PO₄)(OH)Monoclinic, $P2_1/a - C_{2h}^5$ $a = 5.41_1 \pm 0.005 \text{ \AA}$, $b = 14.49 \pm 0.02$, $c = 4.73_0 \pm 0.005$, $\beta = 102^\circ 45' \pm 05'$

Volborth (1954a) *		Present study **				Volborth (1954a) *		Present study **			
Measured (analysis material)		Measured (film 8762)		Calculated		Measured (analysis material)		Measured (film 8762)		Calculated	
I	d _{hkl}	I	d _{hkl}	d _{hkl}	hkl	I	d _{hkl}	I	d _{hkl}	d _{hkl}	hkl
		85	7.251	7.245	020					2.132	151
5	4.95	25	4.960	4.958	110			15 B	2.100	2.100	201
				4.613	001					2.085	$\bar{1}$ 32
6	4.44	60	4.399	4.396	011					2.082	$\bar{2}$ 41
		4	4.265	4.266	120					2.082	032
		13	3.890	3.891	021					2.078	211
				3.790	$\bar{1}$ 11	5	2.05	25 B	2.057	2.058	$\bar{1}$ 61
				3.625	040			6	2.019	2.017	221
		4	3.560	3.563	130			9	1.964		
10	3.45	100	3.452	3.454	$\bar{1}$ 21	6	1.94	9	1.944		
		13	3.340	3.336	031			2	1.915		
		13	3.075	3.075	111			3	1.818		
				3.049	$\bar{1}$ 31	5	1.80	4	1.803		
		6	2.991	2.988	140			4	1.784		
10	2.87	85	2.885	2.887	121	4	1.72	9 B	1.726		
		35	2.851	2.849	041			3	1.691		
8	2.67	42	2.662	2.663	$\bar{1}$ 41			4	1.670		
		25 B	2.642	2.639	200			3	1.652		
				2.636	131			3	1.630		
				2.596	210			4	1.597		
		18	2.548	2.545	$\bar{2}$ 01			4	1.584		
				2.541	150	4 D	1.57	9 B	1.570		
				2.508	$\bar{2}$ 11	3	1.51	9 B	1.524		
		6	2.480	2.479	220			3 B	1.498		
				2.455	051			2	1.475		
1	2.41	18	2.413	2.414	060	1	1.46	3	1.462		
				2.402	$\bar{2}$ 21			9	1.427		
				2.376	141			3	1.414		
				2.333	$\bar{1}$ 51			9	1.386		
		6	2.312	2.315	230			3	1.369		
				2.306	002	3	1.35	2	1.345		
		4	2.279	2.280	012			2	1.334		
				2.279	$\bar{1}$ 12			4	1.316		
5	2.25	13	2.253	2.252	$\bar{2}$ 31			4	1.299		
		13	2.202	2.200	$\bar{1}$ 22					Plus additional weak lines.	
				2.198	022						
				2.196	160						
		9	2.140	2.139	061						
				2.133	240						

* D = diffuse. Camera diameter: 56.7 mm. CuK α radiation, Ni filter. Original spacings converted by present authors from kX to \AA units.

** B = broad. Film corrected for shrinkage. Camera diameter: 114.59 mm. FeK α radiation, Mn filter ($\lambda = 1.9373 \text{ \AA}$). Lower limit 2θ measurable: approximately 6.0° (18.5 \AA).

the one taken in CuK α radiation that it was the film measured. Measurements were made with a Hilger-Watts film-measuring rule with a vernier precision of 0.05 mm. These measurements were corrected for film shrinkage; a shrinkage correction of 1.0025 was applied. The lower limit of 2θ measurable on film 8762 was found to be approximately 6.0° (18.5 Å). Intensities were obtained by visual comparison with a calibrated film strip such that successive step line-exposures are related to each other by a factor of $\sqrt{2}$. X-ray powder data for väyrynenite are given in Table 2 which lists both observed and calculated interplanar spacings. Observed spacings of the present study are compared with those reported by VOLBORTH (1954a); VOLBORTH's original spacings have been converted to Ångström units for the convenience of having both sets of data on the same scale. Interplanar spacings were calculated from the x-ray cell constants down to $d_{hkl} \geq 2.000$ Å. No indexed pattern of väyrynenite previously has been available. The agreement between the observed and calculated spacings is excellent; all lines measured on film 8762 are satisfactorily accounted for.

Morphological data

Five crystals, including the one used in the single-crystal x-ray study, were examined with the two-circle optical goniometer. The crystals were found to be rather poorly developed, each showing no more than seven measurable faces giving fair and excellent signals.

Table 3. Comparison of morphological data for väyrynenite

	Present study	VOLBORTH (1954a)
Crystal class	Monoclinic; prismatic $-2/m$	Monoclinic
Elements (from Table 1)		
Axial ratio	$a:b:c = 0.3734:1:0.3264$; $\beta = 102^\circ 45' \pm 05'$	$a:b:c = 0.7271:1:0.3299$; $\beta = 102^\circ 49'$
Projection	$p_0' = 0.8964$, $q_0' = 0.3264$, $x_0' = 0.2263$	$p_0' = 0.4653$, $q_0' = 0.3299$, $x_0' = 0.2275$
Polar	$p_0:q_0:r_0 = 0.8743:0.3184:1$	$p_0:q_0:r_0 = 0.4537:0.3217:1$
Forms observed	c 001 b 010 m 110	c 001 b 010 m 110 113 (?)*
Dominant forms (descending rank)	m, b, c	

* Apparently a misprint for (013) because it lies in zone with (001) and (010) as indicated on VOLBORTH's stereographic projection (Fig. 5, p. 68).

