

End-member villyaellenite from Mapimi, Durango, Mexico: Descriptive mineralogy, crystal structure, and implications for the ordering of Mn and Ca in type villyaellenite

ANTHONY R. KAMPF

Mineralogy Section, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, U.S.A.

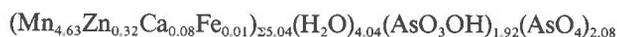
CHARLES R. ROSS II*

Department of Earth and Space Sciences, University of California at Los Angeles, Los Angeles, California 90024, U.S.A.

ABSTRACT

The second occurrence of villyaellenite, at the Ojuela mine, Mapimi, Durango, Mexico, has yielded the nearly pure end member of the species. The mineral occurs as a compact spray of orange-pink prismatic crystals up to 4 cm in length, associated with ogdensburgite, arseniosiderite, adamite, and chalcophanite. Crystals are elongate parallel to [001] with forms {100}, {110}, and $\{\bar{1}01\}$. There is a good {100} cleavage, and the hardness is about 4. Optically, it is biaxial (–) with refractive indices $\alpha = 1.713(2)$, $\beta = 1.723(2)$, and $\gamma = 1.729(2)$; $2V_{\text{meas}} = 70(5)^\circ$ and $2V_{\text{calc}} = 75^\circ$; $X = \mathbf{b}$, $Z \wedge \mathbf{c} = 40^\circ$. Absorption is $Z \gg X > Y$ ($X =$ very pale orange-pink, $Y =$ exceedingly pale orange-pink, $Z =$ pale orange-pink). The specific gravity is 3.69, and the density (calc.) is 3.72 g/cm³.

Chemical analysis by electron microprobe yielded CaO 0.5, MnO 36.2, FeO 0.1, ZnO 2.9, and As₂O₅ 50.6, and moisture evolution analysis gave 9.9 H₂O, total 100.2 wt%. The empirical formula based upon 20 oxygens is



($Z = 4$), close to pure $\text{Mn}_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$.

Single-crystal X-ray precession data indicate space groups Cc or $C2/c$; the latter is confirmed by structure analysis. Cell parameters determined during crystal-structure analysis are $a = 18.015(5)$, $b = 9.261(2)$, $c = 9.770(3)$ Å, $\beta = 96.238(7)^\circ$, $V = 1620.3$ Å³. The strongest lines in the X-ray powder-diffraction pattern (d in Å, I , hkl) are 8.96(50)(200), 8.21(100)(110), 3.243(80)($\bar{5}11$), 3.209(70)($\bar{2}22$), 3.068(70)(222,511), 2.978(50)(600), and 1.678(60)(642).

The refractive indices, specific gravity, chemistry, and cell parameters differ markedly from those of type villyaellenite from Sainte-Marie aux Mines, France, which is near the midpoint of the villyaellenite-sainfeldite series. A third occurrence of villyaellenite at Sterling Hill, New Jersey, consists of material nearly identical chemically to the villyaellenite from Mapimi.

Villyaellenite is isostructural with sainfeldite and hureaulite. The crystal structure of the near end member from Mapimi has been refined by the method of least-squares on the basis of 1183 reflections measured on an automated single-crystal diffractometer to $R = 0.076$ ($R_w = 0.089$). The average Mn–O bond lengths for the three nonequivalent octahedra that make up its five-member edge-sharing chain fragments are Mn(1)–O = 2.21, Mn(2)–O = 2.14, and Mn(3)–O = 2.24 Å. Distance least-squares refinements of the type villyaellenite structure [$\text{Mn}/(\text{Mn} + \text{Ca}) = 0.565$] yield M(1)–O = 2.27, M(2)–O = 2.20, and M(3)–O = 2.36 Å, suggesting the ordering scheme M(1) = Mn + Ca, M(2) = Mn, and M(3) = Ca. The abnormally large a cell parameter in type villyaellenite relative to the Mn and Ca end members of the series and its structural and paragenetic relationships to fluckite further suggest that Mn and Ca are at least partially ordered in type villyaellenite.

INTRODUCTION

Villyaellenite $(\text{Mn,Ca})_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$, was first described by Sarp (1984) from Sainte-Marie aux Mines, France. He noted it to be the Mn-dominant analogue of sainfeldite, a mineral also first described from

this locality. Type sainfeldite is the pure-Ca end member of the series, whereas type villyaellenite has an average cation content of Mn:Ca = 2.69:2.07 [$\text{Mn}/(\text{Mn} + \text{Ca}) = 0.565$]. The second occurrence of villyaellenite, as the nearly pure end member, is described here from the Ojuela mine, Mapimi, Durango, Mexico.

The crystal structures of sainfeldite and hureaulite (the phosphate analogue of villyaellenite) have been determined by Ferraris and Abbona (1972) and Moore and

* Present address: Bayerisches Forschungsinstitut für Experimentelle Geochemie und Geophysik, Universität Bayreuth, Postfach 10 12 51, 858 Bayreuth, Federal Republic of Germany.

Araki (1973), respectively. The Mn and Ca atoms in these minerals are located in three different octahedral sites. The octahedra are joined by sharing edges to form a five-membered chain fragment: M(2)-M(3)-M(1)-M(3)-M(2). Corner sharing between chain fragments and with arsenate or phosphate tetrahedra yields an open three-dimensional framework.

The five-member chain fragments in the sainfeldite-hureaulite structure type closely resemble segments of the octahedral edge-sharing chain found in fluckite, $\text{CaMn}(\text{H}_2\text{O})_2(\text{AsO}_3\text{OH})_2$, a mineral that is intimately associated with villyaellenite at Sainte-Marie aux Mines. Because Ca and Mn have been determined to be completely ordered in fluckite (Catti et al., 1980), it was suspected that they might also be ordered in type villyaellenite.

Unfortunately, the structure of type villyaellenite could not be solved because of the small size and poor quality of its crystals. The determination of the structure of the near end member from Mapimi was undertaken to examine the sizes of its octahedral sites and, in so doing, to investigate the likelihood of Mn and Ca ordering in type villyaellenite. The results of this structure determination then also provided data for a distance least-squares refinement of the structure of type villyaellenite.

OCCURRENCE

Villyaellenite has been identified on a single specimen collected in 1981 from a section of the Ojuela mine known as the San Judas Department. The villyaellenite specimen, provided for study by Mr. John Whitmire, also contains the second occurrence of ogdensburgite, already reported by Kampf and Dunn (1987). The villyaellenite occurs as orange-pink, prismatic crystals up to 4 cm in length that form a compact spray mostly filling a vug. The walls of the vug and some surfaces of this spray are coated with alternating layers of cryptocrystalline arseniosiderite and bladed ogdensburgite. An aureole of massive chalcophanite surrounds the vug and extends from 1 to 3 cm into the host rock, a limonitic gossan. Subhedral to euhedral crystals and irregular stringers of colorless to pale green adamite are imbedded in the limonite, chalcophanite, and layered arseniosiderite-ogdensburgite assemblage. This specimen is preserved in the collection of the Natural History Museum of Los Angeles County (LACMNH 25414).

Villyaellenite has also been found at the Sterling Hill mine, Ogdenburg, New Jersey (P. J. Dunn, pers. comm.), as transparent orange-pink crystals in flattened, circular, radial (7-mm diameter) aggregates. It is found on calcite-bearing willemite-franklinite ore and apparently represents a seam occurrence. Other unusual phases found in the same part of the Sterling Hill deposit include ogdensburgite, sterlinghillite, wallkilldellite, and a Mn-bearing adamite (Dunn, 1981a, 1981b; Dunn and Peacor, 1983).

PHYSICAL AND OPTICAL PROPERTIES

The villyaellenite crystals from Mapimi are elongate on [001] and are tightly intergrown in a slightly divergent

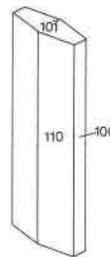


Fig. 1. Crystal drawing of villyaellenite from Mapimi.

spray for most of their lengths. Most of the crystals are slightly curved. Some etching is in evidence, especially toward the end of the spray. Where the spray extends into the small remaining open space of the vug, the euhedral form of some of the crystals has been preserved. These crystals are simple prisms bounded by the forms {100} and {110} and terminated by the pinacoid $\{\bar{1}01\}$. Figure 1 is a crystal drawing of villyaellenite from Mapimi.

Villyaellenite from Mapimi has a good {100} cleavage and a hardness of about 4. It is orange-pink in color and exhibits a nearly white streak and a vitreous luster. It is optically biaxial (-) with refractive indices (measured in white light) $\alpha = 1.713(2)$, $\beta = 1.723(2)$, and $\gamma = 1.729(2)$; $2V_{\text{meas}} = 70(5)^\circ$ and $2V_{\text{calc}} = 75^\circ$. Moderate pleochroism was observed with absorption $Z \gg X > Y$ (X = very pale orange-pink, Y = exceedingly pale orange-pink, Z = pale orange-pink). The optical orientation is $X = \mathbf{b}$, $Z \wedge \mathbf{c} = 40^\circ$.

The specific gravity of villyaellenite from Mapimi, determined on a Berman balance, is 3.69. This value compares favorably to the calculated density of 3.72 g/cm^3 .

CHEMISTRY

Villyaellenite from Mapimi was chemically analyzed with an electron microprobe using the following standards: garnet (Mn and Fe), wollastonite (Ca), ZnO (Zn), and synthetic olivenite (As). In Table 1, the analysis of Mapimi villyaellenite is compared to microprobe analyses by Sarp (1984) for material from Sainte-Marie aux Mines and by P. J. Dunn (pers. comm.) for villyaellenite from the Sterling Hill mine.

Water was directly determined using a 903-H DuPont moisture-evolution analyzer yielding a total of 9.9 wt%, in close agreement with the difference between 100% and the analytical sum from the microprobe analysis of elements with atomic number > 9 .

The empirical formula for villyaellenite from Mapimi (based on 20 oxygen atoms) is $(\text{Mn}_{4.63}\text{Zn}_{0.32}\text{Ca}_{0.08}\text{Fe}_{0.01})_{25.04}(\text{H}_2\text{O})_{4.04}(\text{AsO}_3\text{OH})_{1.92}(\text{AsO}_4)_{2.08}$, which is very near the pure-Mn end member, $\text{Mn}_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$.

X-RAY CRYSTALLOGRAPHY

A single crystal of villyaellenite from Mapimi, studied by precession X-ray single-crystal techniques, confirmed the monoclinic symmetry and indicated the space groups Cc or $C2/c$. The latter was confirmed by the crystal struc-

TABLE 1. Microprobe analyses of villyaellenite

	Mapimi* (This study)	Sterling Hill (Dunn, pers. comm.)	Ste.-Marie aux Mines (Sarp, 1984)
FeO	0.1 (0.1–0.1)	0.3	—
CaO	0.5 (0.4–0.6)	1.0	13.58
ZnO	2.9 (2.4–3.8)	2.8	—
MnO	36.2 (34.9–37.1)	36.0	22.40
As ₂ O ₅	50.6 (48.9–51.9)	50.3	52.99
H ₂ O	9.9**	9.6†	11.42‡
Total	100.2	100.0	100.39

* Average of five points over several crystals; ranges in parentheses.
 ** Water determined by moisture-evolution analysis.
 † Water by difference.
 ‡ Water by TGA.

ture analysis. The cell parameters refined during crystal structure analysis are $a = 18.015(5)$, $b = 9.261(2)$, $c = 9.770(3)$ Å, $\beta = 96.238(7)^\circ$, and $V = 1620.3$ Å³. The X-ray powder diffraction data for d values greater than 1.6 Å are given for the Mapimi material in Table 2.

Sarp (1984) reported the following cell parameters measured from precession photographs: $a = 18.55$, $b = 9.52$, $c = 10.01$ Å, and $\beta = 97^\circ$. In the course of the present study these parameters were refined from the powder diffraction data reported by Sarp by the method of least-squares. The 19 observed d values with intensities greater than 10 were utilized in the refinement, yielding the cell parameters $a = 18.515(37)$, $b = 9.484(9)$, $c = 10.000(7)$ Å, and $\beta = 96.72(7)^\circ$.

CRYSTAL STRUCTURE

Data collection and structure refinement

The villyaellenite crystals from Mapimi exhibit pronounced mosaic spread. Most fragments examined proved to be unsatisfactory for intensity-data collection. The termination of one narrow prism was determined to be of

TABLE 3. Positional and isotropic thermal (Å²) parameters for villyaellenite from Mapimi

Atom	x/a	y/b	z/c	$U \times 10^4$
Mn(1)	0.5	0.3943(4)	0.75	171(14)
Mn(2)	0.3150(1)	0.0874(2)	0.1878(2)	205(12)
Mn(3)	0.3257(1)	0.4713(2)	0.1375(2)	211(14)
As(1)	0.4168(1)	0.3157(2)	0.4109(1)	201(9)
As(2)	0.6611(1)	0.2363(2)	0.6239(1)	192(9)
O(1)	0.4237(6)	0.4360(11)	0.2892(10)	232(61)
O(2)	0.3389(7)	0.2240(12)	0.3631(11)	271(65)
O(3)	0.4150(6)	0.3915(13)	0.5657(11)	297(67)
O(4)	0.6648(6)	0.2574(11)	0.4528(9)	196(59)
O(5)	0.7069(6)	0.0874(11)	0.6788(10)	239(63)
O(6)	0.7040(6)	0.3774(12)	0.7046(11)	265(65)
O(7)	0.5707(6)	0.2276(12)	0.6557(11)	266(64)
OH	0.4897(7)	0.1981(13)	0.4226(11)	322(71)
OW(1)	0.2416(6)	0.4219(12)	0.4702(11)	272(67)
OW(2)	0.5835(7)	0.0053(12)	0.8397(11)	343(74)

Note: Standard deviations are in parentheses. $U_{eq} = [1/(6\pi^2)]\Sigma\Sigma\beta_{ij}a_i a_j$.

adequate quality. This euhedral fragment measured 0.17 × 0.19 × 0.24 mm.

The fragment was mounted on a Huber automated diffractometer employing monochromatized MoK α radiation. A total of 1183 independent reflections was measured to a 2θ limit of 110° using the $\theta/2\theta$ scan method. The data were collected for Lorentz and polarization factors and for absorption.

The space group $C2/c$ was chosen by analogy to sainfeldite, and the atomic positions reported for sainfeldite were utilized to initiate the structure refinement. All computations were done with the UCLA crystallographic computing package. All of the observed structure factors (F_o) were considered nonzero since all exceeded $3\sigma(F_o)$. The structure factors were assigned weights based upon their standard deviations. Scattering factors for neutral atoms and anomalous dispersion coefficients were taken from *International Tables for X-ray Crystallography*

TABLE 2. X-ray powder-diffraction data for villyaellenite from Mapimi

d (Å)*	h_0 *	hkl *	d (Å)**	d (Å)*	h_0 *	hkl *	d (Å)**
8.954	25	200	8.96	2.675	27	331,602	2.674
8.226	53	110	8.21	2.653	7	023	
6.438	14	111	6.41	2.631	8	512	
6.128	11	111	6.13	2.605	13	331	2.610
4.856	7	002	4.84	2.485	9	621	2.487
4.632	25	311,020	4.63	2.428	14	004	2.431
4.477	34	202,400	4.45	2.377	7	621	2.382
4.300	20	311	4.30	2.335	33	711,530	2.337
4.113	7	220	4.11	2.298	8	712	2.302
3.857	10	221	3.851	2.238	24	800,404,133	2.239
3.721	17	221	3.724	2.069	7	713	2.063
3.345	23	022,312	3.345	2.043	11	404,333	2.054
3.262	45	511	3.243	2.016	8	424	2.019
3.219	100	222,420	3.214	1.970	6	730	1.990
3.128	30	421,402	3.131	1.774	8	334	1.778
3.064	71	222,511	3.063	1.747	9	534	1.752
2.973	44	113,600	2.978	1.677	20	931,352	1.678
2.841	11	313		1.640	8	643	1.641
2.785	9	422		1.624	22	135,206,733	1.630
2.742	6	330		1.609	10	153,551	1.614

* Calculated from structure data. The calculated d value has been averaged for multiple lines.

** Interplanar spacings measured from film, 114.6-mm Gandolfi camera, Ni-filtered CuK α radiation.

TABLE 4. Anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for villyaellenite from Mapimi

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	210(20)	240(19)	62	0	11(13)	0
Mn(2)	220(12)	220(12)	170(11)	14(8)	5(8)	9(7)
Mn(3)	218(14)	238(13)	175(13)	-6(9)	15(9)	-21(9)
As(1)	218(9)	236(9)	146(8)	7(7)	5(6)	0(6)
As(2)	198(9)	226(9)	149(8)	-1(6)	1(6)	4(6)
O(1)	224(60)	270(57)	198(55)	38(49)	1(44)	29(45)
O(2)	297(67)	354(64)	156(53)	3(52)	3(47)	-22(46)
O(3)	187(64)	418(67)	263(59)	6(53)	-85(48)	49(51)
O(4)	244(62)	275(58)	73(47)	-31(47)	28(42)	-2(40)
O(5)	272(67)	239(59)	193(52)	-42(48)	-26(46)	104(43)
O(6)	207(64)	317(61)	266(59)	53(50)	2(47)	-134(49)
O(7)	97(54)	396(66)	298(62)	26(50)	-3(46)	-85(51)
OH	257(68)	400(68)	294(64)	87(55)	-43(51)	-69(53)
OW(1)	245(64)	320(65)	236(58)	5(52)	-39(47)	32(47)
OW(2)	393(78)	343(67)	296(64)	11(57)	54(55)	55(52)

Note: The anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Standard deviations are in parentheses.

(1974). The octahedral sites were assumed to be occupied solely by Mn, but the occupancies of these sites were refined, yielding Mn(1) = 0.97(1), Mn(2) = 1.19(1), and Mn(3) = 1.05(1). All other sites were assigned unit occupancies.

The structure refined to $R = 0.076$ and $R_w = 0.089$. The relatively high final R values were probably due, in part, to the large mosaic spread. The positional and isotropic thermal parameters are listed in Table 3, and anisotropic temperature factors are given in Table 4. The observed and calculated structure factors are listed in Table 5.¹

DLS refinement of the type villyaellenite structure

A distance-least-squares (DLS) refinement of the type villyaellenite structure was performed using the OPTDIS program of Dollase (unpub.). The refined cell parameters for type villyaellenite reported above were employed, and starting bond distances were obtained by averaging those of sainfeldite and Mapimi villyaellenite. A total of 67 bond lengths were prescribed and weighted as follows: As-O = 1.0, M-O = 0.14, O-O (<3.2 Å) = 0.07, O-O (>3.2 Å) = 0.04, M-M = 0.04. A total of 43 positional parameters were refined. The refinement converged in three cycles.

A second DLS refinement was performed assuming the ordering scheme implied by the above refinement. In this refinement the initial bond distances were obtained as follows: average values (as determined above) were used for the M(1) site, the M(2) site was modeled after the Mn(2) site in Mapimi villyaellenite, and the M(3) site was modeled after the Ca(3) site in sainfeldite. This refinement also converged in three cycles. The positional parameters for both DLS refinements are provided in Table 6. The octahedral metal-oxygen bond distances from the structure refinement, and the DLS refinements are provided in Table 7.

¹ To receive a copy of Table 5, order Document AM-88-388 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

DISCUSSION

Descriptive mineralogy

Villyaellenite from Mapimi is significantly superior in crystal size and quality to that from Sainte-Marie aux Mines. It is also much closer to the ideal Mn-end member composition. It differs markedly from type villyaellenite in its physical and optical properties and in its cell dimensions. Mapimi villyaellenite is remarkably similar chemically to villyaellenite from Sterling Hill.

The variations in refractive indices, cell parameters, and specific gravity relative to Mn/(Mn + Ca) for sainfeldite, type villyaellenite, and Mapimi villyaellenite are shown in Figure 2. Ideal linear variations between the end members are shown for comparison. The a cell constant and the specific gravity of type villyaellenite differ markedly from the values predicted by these linear variations.

The Gladstone-Dale compatibility index (Mandarino, 1981) calculated for Mapimi villyaellenite is -0.016. This value falls in the range indicating superior compatibility of refractive index, specific gravity, and chemical composition. The compatibility index for sainfeldite is -0.013, also in the superior range, whereas that for type villyaellenite, -0.060, falls in the range of only fair compatibility. It is not clear whether the poorer compatibility seen in type villyaellenite is due to experimental error or to some inherent anomalous Gladstone-Dale behavior. However, it may be noted that, if the cell dimensions of type villyaellenite did not deviate from the linear relationship described above, its calculated specific gravity would be 3.33. This would yield a compatibility index of -0.018, in the range of superior compatibility.

Octahedral bond distances in Mapimi villyaellenite

The average Mn-O distances in Mapimi villyaellenite are Mn(1)-O = 2.21, Mn(2)-O = 2.14, and Mn(3)-O = 2.24 Å. The total octahedral-site content provided by the empirical formula is $\text{Mn}_{4.63}\text{Zn}_{0.32}\text{Ca}_{0.08}\text{Fe}_{0.01}$ [with one Mn(1) site and two each of the Mn(2) and Mn(3) sites represented

TABLE 6. Distance-least-squares positional parameters for type villyaellenite

Atom	DLS no. 1			DLS no. 2		
	x/a	y/b	z/c	x/a	y/b	z/c
M(1)	1/2	0.3929	3/4	1/2	0.3913	3/4
M(2)	0.3158	0.0829	0.1846	0.3240	0.0755	0.1855
M(3)	0.3255	0.4707	0.1387	0.3233	0.4764	0.1367
As(1)	0.4156	0.3192	0.4118	0.4210	0.3172	0.4104
As(2)	0.6602	0.2370	0.6237	0.6629	0.2392	0.6248
O(1)	0.4245	0.4361	0.2824	0.4252	0.4398	0.2942
O(2)	0.3399	0.2286	0.3613	0.3514	0.2131	0.3530
O(3)	0.4146	0.3924	0.5636	0.4146	0.3856	0.5627
O(4)	0.6634	0.2579	0.4565	0.6669	0.2551	0.4573
O(5)	0.7062	0.0903	0.6755	0.7029	0.0856	0.6737
O(6)	0.7030	0.3743	0.7045	0.7122	0.3710	0.7022
O(7)	0.5727	0.2284	0.6565	0.5751	0.2344	0.6565
OH	0.4859	0.2009	0.4238	0.4974	0.2142	0.4238
OW(1)	0.2414	0.4195	0.4691	0.2367	0.4125	0.4570
OW(2)	0.5805	0.0154	0.8400	0.5802	0.0638	0.8072

in the formula unit]. The bond distances and the refined site occupancies suggest that Zn is preferentially contained in the Mn(2) site and Ca in the Mn(3) site, yielding Mn(1) = Mn, Mn(2) = Mn_{0.84}Zn_{0.16}, Mn(3) = Mn_{0.96}Ca_{0.04}. (Note that these site contents were not used in the structure refinement.) Although the crystal used for the structure analysis was not chemically analyzed, microprobe analyses showed the variability of Zn and Ca to be very limited. The point, found to be richest both in Zn and Ca, provided the total octahedral site content Mn_{4.45}Zn_{0.43}Ca_{0.10}Fe_{0.01}, yielding Mn(1) = Mn, Mn(2) = Mn_{0.79}Zn_{0.21}, Mn(3) = Mn_{0.95}Ca_{0.05}. The amount of substitution indicated in these sites is, therefore, relatively small in comparison to the variation in average Mn–O distances.

The average Mn–O distances in hureaulite (Moore and Araki, 1973), Mn(1)–O = 2.188, Mn(2)–O = 2.159, and Mn(3)–O = 2.209 Å, show a similar, though significantly smaller, variation. The AsO₄ tetrahedra in Mapimi vil-

lyaellenite, being significantly larger than the PO₄ tetrahedra in hureaulite, perhaps necessitate adjustments in the octahedral framework, yielding the Mn–O distances observed.

TABLE 7. Octahedral metal–oxygen distances (Å) for villyaellenite

Bond	Mapimi*	DLS no. 1	DLS no. 2
M(1)–O(1)**	2.15	2.22	2.20
M(1)–O(3)**	2.23	2.30	2.31
M(1)–O(7)**	2.26	2.33	2.31
Average	2.21	2.28	2.27
M(2)–O(2)	2.14	2.25	2.14
M(2)–O(4)	2.15	2.24	2.24
M(2)–O(5)	2.14	2.23	2.17
M(2)–O(6)	2.05	2.16	2.16
M(2)–OW(1)	2.33	2.35	2.31
M(2)–OW(2)	2.07	2.18	2.21
Average	2.14	2.23	2.20
M(3)–O(1)	2.20	2.27	2.34
M(3)–O(3)	2.22	2.30	2.33
M(3)–O(4)	2.18	2.25	2.32
M(3)–O(5)	2.29	2.35	2.37
M(3)–O(6)	2.19	2.26	2.32
M(3)–OW(1)	2.33	2.40	2.50
Average	2.24	2.31	2.36

* Estimated standard deviations are ± 0.01 Å.

** Two such bonds for M(1)–O octahedron.

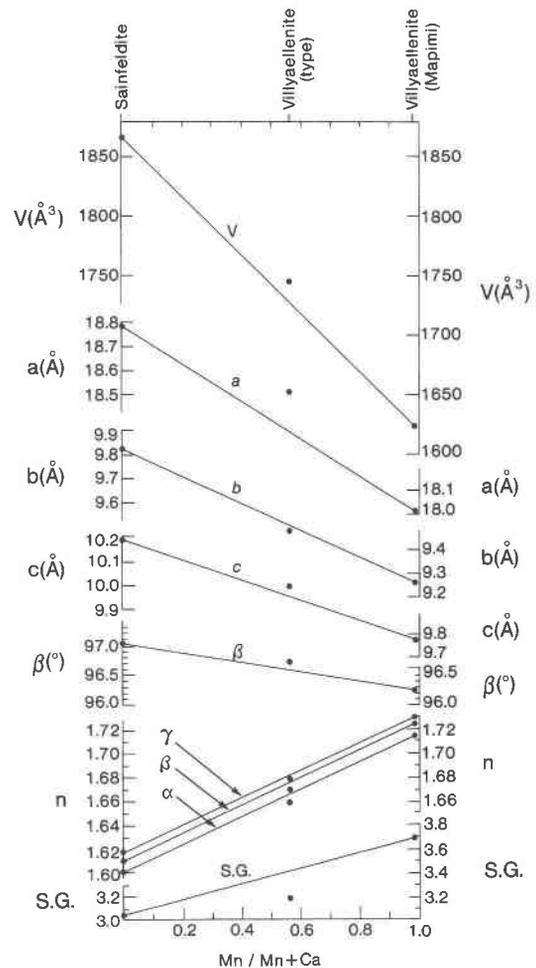


Fig. 2. Variation in cell constants, refractive indices, and specific gravity for the saintfeldite-villyaellenite series. Note that the lines indicate ideal linear variations between the end members.

DLS-refined bond distances in type villyaellenite

The first distance–least-squares (DLS) refinement of the type villyaellenite structure using bond distances averaged from sainfeldite and Mapimi villyaellenite yielded the following average distances: $M(1)–O = 2.28$, $M(2)–O = 2.23$, and $M(3)–O = 2.31$ Å. These values suggest that $M(1) = Mn + Ca$, $M(2) = Mn$, and $M(3) = Ca$, although the average $M(2)–O$ distances are somewhat larger than those observed for $Mn–O$ in hureaulite and fluckite and $M(3)–O$ is somewhat smaller than those observed for $Ca–O$ in sainfeldite and fluckite. The second DLS refinement, assuming this ordering scheme, yielded $M(1)–O = 2.27$, $M(2)–O = 2.20$, and $M(3)–O = 2.36$ Å. These $M(2)–O$ and $M(3)–O$ distances show excellent agreement with distances observed in similar compounds for $Mn–O$ and $Ca–O$, respectively.

Correlation with the fluckite structure

In Figure 3 the octahedral edge-sharing chain portions of the villyaellenite (atomic positions from the second DLS refinement) and fluckite structures are compared. The five-member octahedral chain fragment in villyaellenite and the infinite chain in fluckite are both zig-zag-type chains in which nonopposing edges are shared. In both structures the oxygens of the shared edges also belong to arsenate tetrahedra. The remaining two octahedral corners are each shared with one other octahedron. These corners are either water or arsenate oxygens.

The series $Ca(H_2O)(AsO_3OH)–Mn(H_2O)(AsO_3OH)$ includes the species haidingerite, the Ca end member (Casien et al., 1966), fluckite, with $Ca:Mn = 1:1$, and krautite, the Mn end member (Catti and Franchini-Angela, 1979). Although their symmetries differ (*Pbna*, *P1*, and *P2₁*, respectively), these minerals are structurally similar to one another. Fluckite and krautite are particularly similar, having topologically identical pyroxene-like octahedral chains. The differences observed in their symmetries and structures are not due to ordering per se, but can be attributed to shifts between the chains induced by the difference in size of Ca and Mn.

Two comparisons are of interest in considering the possibility of ordering in villyaellenite. First, the octahedral sites in krautite and Mapimi villyaellenite, the Mn end members of the two series, can be compared. Krautite has four octahedral sites with the average distances $Mn(1)–O = 2.20$, $Mn(1')–O = 2.20$, $Mn(2)–O = 2.17$, $Mn(2')–O = 2.18$ Å. Mapimi villyaellenite exhibits a much larger variation in average $Mn–O$ distances over its three distinct sites. Even without any distortion of the Mapimi villyaellenite structure, some degree of ordering is to be expected.

Second, the cell dimensions parallel to the chains in the structures of the minerals of these two series can be compared. In haidingerite–fluckite–krautite, the octahedral chain is parallel to $[10\bar{1}]$ (The *a* and *c* axes in haidingerite must be interchanged). Although Vegard's law cannot be applied strictly because of the differences in the structures of these minerals, disorder of Ca and Mn over the chain

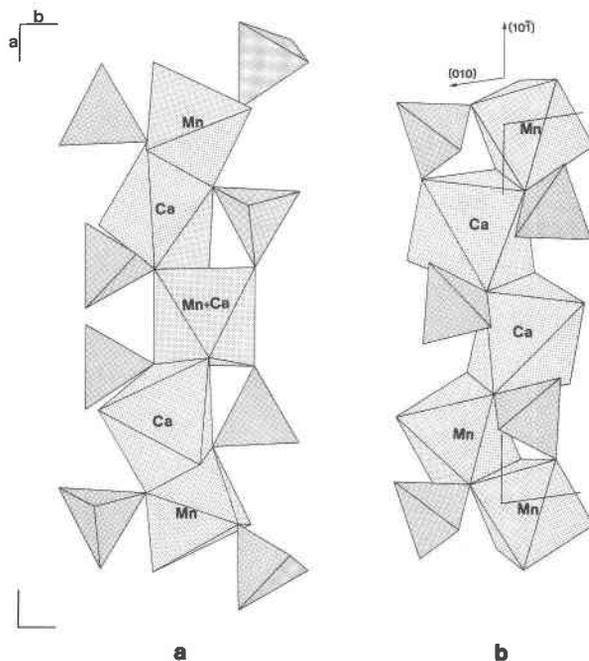


Fig. 3. Comparison of the octahedral edge-sharing chain portions of the (a) villyaellenite and (b) fluckite structures. The atomic positions for the villyaellenite chain are from the second DLS refinement. The fluckite chain is modified from Catti et al. (1980).

sites should yield a $[10\bar{1}]$ dimension for fluckite intermediate between those found in haidingerite and krautite. In fact the $[10\bar{1}]$ cell dimensions are 10.542, 11.706, 11.089 Å for haidingerite, fluckite, and krautite, respectively. This cell dimension for fluckite is greater than it is for either end member, suggesting that the edge-sharing octahedral chain in fluckite may be abnormally lengthened as a result of the ordering of Mn and Ca.

The octahedral chain fragment in sainfeldite and villyaellenite is parallel to the *a* axis. The *a* cell dimension in type villyaellenite is considerably greater than that predicted by Vegard's law. By analogy to fluckite, the lengthening of the octahedral chain fragments in response to the ordering of Mn and Ca is seen as the possible cause.

Paragenetic evidence

Heretofore there have been only two limited composition ranges reported in the series $Ca_5(H_2O)_4(AsO_3OH)_2–(AsO_4)_2–Mn_5(H_2O)_4(AsO_3OH)_2(AsO_4)_2$. These are represented by the types for sainfeldite and villyaellenite, both from Sainte-Marie aux Mines. The nearly pure Mn end member has now been found at both Mapimi, Mexico, and Sterling Hill, New Jersey. At Mapimi, it is in direct association with arseniosiderite and ogdensburgite, minerals that contain essential Ca; at Sterling Hill, it occurs on calcite-bearing willemite–franklinite ore. If Mn and Ca were disordered in intermediate members of this series, then a complete solid-solution series should exist, and it is likely that the villyaellenite from Mapimi and Sterling Hill would contain more substantial amounts of Ca.

Further paragenetic evidence for ordering in type villyaellenite is in association with fluckite reported by Sarp (1984) and observed by us on a sample from Sainte-Marie aux Mines obtained from Sarp via Pete J. Dunn. The minute blades of villyaellenite on this sample project outward from the surface of a crystal of fluckite, and the boundary between the fluckite and villyaellenite crystals is indistinct. This textural relationship suggests that the crystallization of villyaellenite closely succeeded that of fluckite, probably from the same solution and under only slightly differing conditions. Since Ca and Mn are ordered in the fluckite octahedral chain, it is reasonable to suspect that they may also be ordered in the villyaellenite chain.

CONCLUSIONS

The ordering of Mn and Ca in type villyaellenite, although probable, remains unproven. Without evidence from a direct method such as structure analysis, the existence of such ordering can only be inferred. Nevertheless, the evidence at hand suggests that Mn and Ca are at least partially ordered in this mineral.

The octahedral sites in near end-member villyaellenite vary substantially in size, as evidenced by their average metal-oxygen bond distances. The DLS refinements of type villyaellenite generate bond distances appropriate for ordering according to the scheme $M(1) = \text{Mn} + \text{Ca}$, $M(2) = \text{Mn}$, and $M(3) = \text{Ca}$, corresponding to the ideal formula $\text{Ca}_2\text{Mn}_2(\text{H}_2\text{O})_4(\text{Mn,Ca})(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$. The correlation between type villyaellenite and fluckite in terms of paragenesis and structure further supports the likelihood of ordering in type villyaellenite. Finally, the lack of other intermediate members of the sainfeldite-villyaellenite series, despite the occurrence of the nearly pure-Mn end member in relatively Ca-rich associations, suggests that a complete solid solution may not exist and that ordering may set type villyaellenite apart from the two end members.

If direct evidence of the proposed ordering in type villyaellenite is forthcoming, the near end-member villyaellenite from Mapimi and Sterling Hill may qualify as a distinct species.

ACKNOWLEDGMENTS

We wish to thank John Whitmire for providing the only specimen of villyaellenite known from Mapimi, Pete J. Dunn of the U.S. National

Museum of Natural History (Smithsonian Institution) for making available his data on villyaellenite from the Sterling Hill mine, George R. Rossman of the California Institute of Technology for making available the equipment used in the water determination, Charles Strouse of the UCLA Department of Chemistry for assistance in the collection and refinement of the structure data, and Wayne Dollase of the UCLA Department of Earth and Space Sciences for the use of his program ORTRIS and for helpful discussions. The manuscript benefited from reviews by Paul B. Moore of the University of Chicago, Pete J. Dunn, and John M. Hughes of Miami (Ohio) University. One of us (C.C.R.) would like to acknowledge support of NSF grant 4-443875-22146-3 (W. G. Ernst, P.I.).

REFERENCES CITED

- Cassien, M., Herpin, P., and Permingeat, F. (1966) Structure cristalline de la haidingerite. *Bulletin de la Société française de Minéralogie et de Cristallographie*, 89, 18–22.
- Catti, M., and Franchini-Angela, M. (1979) Krautite, $\text{Mn}(\text{H}_2\text{O})(\text{AsO}_3\text{OH})$: Crystal structure, hydrogen bonding and relations with haidingerite and pharmacolite. *American Mineralogist*, 64, 1248–1254.
- Catti, M., Chiari, G., and Ferraris, G. (1980) Fluckite, $\text{CaMn}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a structure related by pseudo-polytypism to krautite, $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$. *Bulletin de Minéralogie*, 103, 129–134.
- Dunn, P.J. (1981a) Ogdensburgite, a new calcium-zinc-ferric iron arsenate mineral from Sterling Hill, New Jersey. *Mineralogical Record*, 12, 369–370.
- (1981b) Sterlinghillite, a new hydrated manganese arsenate mineral from Ogdensburg, New Jersey. *American Mineralogist*, 66, 182–184.
- Dunn, P.J., and Peacor, D.R. (1983) Kittatinnyite and willkilldellite, silicate/arsenate analogues containing calcium and manganese, from Franklin and Sterling Hill, New Jersey. *American Mineralogist*, 68, 1029–1032.
- Ferraris, G., and Abbona, F. (1972) The crystal structure of $\text{Ca}_3(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (sainfeldite). *Bulletin de la Société française de Minéralogie et de Cristallographie*, 95, 33–41.
- International Tables for X-ray Crystallography. (1974) J.A. Ibers and W.C. Hamilton, Eds., vol. 4. Kynoch Press, Birmingham, England.
- Kampf, A.R., and Dunn, P.J. (1987) Ogdensburgite from Mapimi and new data for the species. *American Mineralogist*, 72, 409–412.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441–450.
- Moore, P.B., and Araki, T. (1973) Hureaultite, $\text{Mn}_3(\text{H}_2\text{O})_4[\text{PO}_3(\text{OH})_2]_2[\text{PO}_4]_2$: Its atomic arrangement. *American Mineralogist*, 58, 302–307.
- Sarp, H. (1984) Villyaellenite, $\text{H}_2(\text{Mn,Ca})_3(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ un nouveau minéral de Sainte-Marie aux Mines (France). *Schweizerische Mineralogische und Petrographische Mitteilungen*, 64, 323–328.

MANUSCRIPT RECEIVED JANUARY 11, 1988

MANUSCRIPT ACCEPTED MAY 24, 1988