

Miguelromeroite, the Mn analogue of sainfeldite, and redefinition of villyaellenite as an ordered intermediate in the sainfeldite-miguelromeroite series

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ABSTRACT

Based on single-crystal structure refinements, miguelromeroite, $\text{Mn}_3(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$, from the Ojuela mine, Mapimi, Durango, Mexico, is described as a new species corresponding to the Mn-dominant member of a series with sainfeldite, $\text{Ca}_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$, and type villyaellenite, $(\text{Mn,Ca})\text{Mn}_2\text{Ca}_2(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$, from Sainte-Marie aux Mines, Alsace, France, is redefined as an ordered intermediate species in the series.

Miguelromeroite is monoclinic, $C2/c$, $a = 18.030(1)$, $b = 9.2715(5)$, $c = 9.7756(5)$ Å, $\beta = 96.266(2)^\circ$, $V = 1624.4(2)$ Å³, $Z = 4$. At the Ojuela mine, miguelromeroite occurs as a compact spray of orange-pink, prismatic crystals up to 4 cm in length. Crystals are elongate on [001] with forms {100}, {110} and {10 $\bar{1}$ }. Physical properties: pale pink streak, transparent, vitreous luster, brittle, good {100} cleavage, conchoidal fracture, Mohs hardness ~4, measured density 3.69(3) g/cm³, and calculated density 3.714 g/cm³. Optical properties: biaxial (-), $n_\alpha 1.713(2)$, $n_\beta 1.723(2)$, $n_\gamma 1.729(2)$, $2V_{\text{meas}} 70(5)^\circ$, $2V_{\text{calc}} 75^\circ$, orientation $X = b$, $Z \wedge c = 40^\circ$ in obtuse β , pleochroic pale pink, $Z \gg X > Y$. Miguelromeroite is named for Miguel Romero Sanchez (1926–1997) in recognition for his dedication to documenting and preserving Mexico's rich mineral heritage.

Miguelromeroite also occurs at the Veta Negra mine, Tierra Amarilla, Copiapó Province, Chile, at Sterling Hill, Ogdensburg, Sussex County, New Jersey, and at the Gozaisho mine, Iwaki, Fukushima Prefecture, Honshu Island, Japan. Some material from the Gozaisho mine may correspond to another ordered species in the series with the formula $(\text{Ca,Mn})\text{Mn}_2\text{Ca}_2(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$.

Keywords: Miguelromeroite, new mineral, villyaellenite, redefinition, crystal structure, cation ordering, Mapimi (Mexico), Sainte-Marie aux Mines (France)

INTRODUCTION

Sarp (1984) described villyaellenite from Sainte-Marie aux Mines, Alsace, France, as the Mn-dominant member of a series with sainfeldite, $\text{Ca}_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$. Prior to publication of the description, Kampf submitted a proposed new mineral “romeroite” from the Ojuela mine, Mapimi, Durango, Mexico (IMA 1984-37). Voting on the mineral from Mapimi was suspended when its identity with villyaellenite was recognized, although the material from Mapimi is close to the Mn end-member, whereas that from Sainte-Marie aux Mines is near the midpoint in the series with $\text{Mn}/(\text{Mn}+\text{Ca}) = 0.57$.

Subsequently, Kampf and Ross (1988) published the structure of villyaellenite based on the material from Mapimi. That study included a distance-least-squares (DLS) simulation of the structure of villyaellenite from Sainte-Marie aux Mines that showed its octahedral sites to vary significantly in size and suggesting that Mn and Ca are very likely to be ordered in those sites. Because the evidence was indirect, it was not considered conclusive enough to define the Mapimi and Sainte-Marie aux Mines material as a distinct species.

In the current study, the direct determination of the structure

of type villyaellenite from Sainte-Marie aux Mines was undertaken and, as reported herein, it confirms the earlier evidence that the structure of type villyaellenite from Sainte-Marie aux Mines exhibits ordering of Mn and Ca in the octahedral sites. Type villyaellenite is, therefore, determined to be an ordered intermediate species in the series between the Ca end-member sainfeldite and the Mn end-member, described herein under the name miguelromeroite.

Miguelromeroite is named for Miguel Romero Sanchez (1926–1997; Fig. 1) in recognition of his dedication to documenting and preserving Mexico's rich mineral heritage. Detailed information on Dr. Romero's background and his contributions to Mexican mineralogy is provided by Wallace (2008). The compound (first + last) name was chosen because of the similarity of the originally proposed “romeroite” to the existing mineral names romeite and römerite. The mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification (IMA). The holotype is deposited in the Natural History Museum of Los Angeles County (catalog number: 25414).

OCCURRENCE

The type locality for miguelromeroite is the San Judas Chimney, Ojuela mine, Mapimi, Durango, Mexico (25°47'37"N, 103°47'28"W). Other occurrences of the new mineral, pre-

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FIGURE 1. Miguel Romero Sanchez.

viously reported under the name villyaellenite, include the Veta Negra mine, Tierra Amarilla, Copiapó Province, Chile (chemistry verified by semi-quantitative EDS); Sterling Hill, Ogdensburg, Sussex County, New Jersey (Dunn 1995); and the Gozaisho mine, Iwaki, Fukushima Prefecture, Honshu Island, Japan (Matsubara et al. 1996). The latter locality has yielded material near the Mn end-member (miguelromeroite), as well as material with $Mn/(Mn+Ca) = 0.44$ (Matsubara, pers. comm.). Villyaellenite is also reported from Jáchymov, Bohemia, Czech Republic (Hloušek and Tvrđý 2002); however, specific details of its chemistry were not provided.

The mineral was found on a single specimen collected in 1981 during mining for specimens that also produced remarkable purple Mn-rich adamite crystals (Moore and Megaw 2003). A compact spray of miguelromeroite crystals to 4 cm in length mostly fills a vug in a secondary oxidation zone assemblage. The walls of the vug and some surfaces of the miguelromeroite are coated with alternating layers of cryptocrystalline arseniosiderite and bladed ogdensburgite (Kampf and Dunn 1987). An aureole of massive chalcophanite surrounds the vug and extends into the host rock, a limonitic gossan. Subhedral to euhedral crystals and stringers of colorless to pale green adamite are embedded in the limonite, chalcophanite, and layered arseniosiderite-ogdensburgite (Fig. 2).

APPEARANCE AND PHYSICAL PROPERTIES

At the Ojuela mine, miguelromeroite occurs as a compact spray of orange-pink, prismatic crystals up to 4 cm in length. Crystals are elongate on $[001]$ and exhibit the forms $\{100\}$, $\{110\}$, and $\{10\bar{1}\}$ (Fig. 3). No twinning was observed. At Sterling

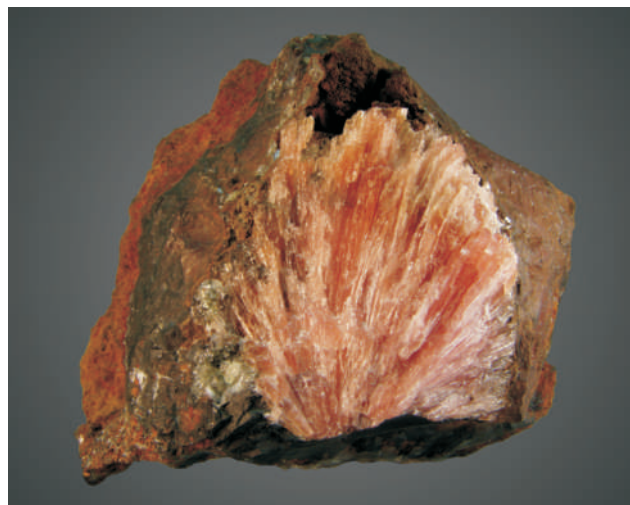


FIGURE 2. Holotype specimen of miguelromeroite from Mapimi. Crystals of miguelromeroite in spray are up to 4 cm in length.

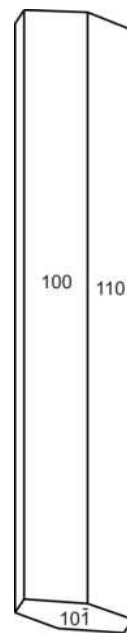


FIGURE 3. Crystal drawing of miguelromeroite (clinographic projection).

Hill (New Jersey), the mineral occurs as transparent orange-pink crystals in flattened, circular, radial (7 mm diameter) aggregates. At the Veta Negra mine (Chile), the source of most specimens on the mineral collector market, the mineral occurs as sprays and divergent aggregates of transparent pink prisms to several millimeters in length.

The mineral has a very pale pink streak. It is transparent and has a vitreous luster. Crystals are brittle with a good cleavage on $\{100\}$ and conchoidal fracture. The Mohs hardness is about 4. The density measured on a Berman balance is $3.69(3) \text{ g/cm}^3$. The density calculated from the empirical formula and refined cell data is 3.714 g/cm^3 .

Miguelromeroite is biaxial (–) with indices of refraction n_α 1.713(2), n_β 1.723(2), and n_γ 1.729(2), measured in white light.

The $2V$ measured conoscopically is $70(5)^\circ$; the calculated $2V$ is 75° . No dispersion was observed. The optical orientation is $X = b$, $Z \wedge c = 40^\circ$ in obtuse β . The mineral is pleochroic in shades of pale pink, $Z \gg X > Y$.

The Gladstone-Dale compatibility (Mandarino 1981) $[1 - (K_p/K_c)]$ is -0.010 , indicating superior agreement between the chemistry, density, and the average of the indices of refraction.

CHEMICAL COMPOSITION

Quantitative chemical analyses were performed by electron microprobe (WDS mode, 15 kV, 50 nA) using as standards wolastonite for Ca, garnet for Fe and Mn, synthetic ZnO for Zn, and synthetic olivenite for As. Water was determined on a 903-H DuPont moisture-evolution analyzer. In Table 1, the average of five microprobe analyses is compared to that provided by Sarp (1984) for type villyaellenite from Sainte-Marie aux Mines.

The empirical formula of miguelromeroite (based on O = 20 apfu) is: $(\text{Mn}_{4.63}^{2+}\text{Zn}_{0.32}\text{Ca}_{0.08}\text{Fe}_{0.01}^{2+})_{\Sigma 5.04}(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_{1.94}(\text{AsO}_4)_{2.06}$. The simplified end-member formula is $\text{Mn}_5(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2$, which requires MnO 39.22, As_2O_5 50.82, H_2O 9.96, total 100.00 wt%. Miguelromeroite is easily soluble in dilute HCl.

To obtain a reasonable empirical formula for type villyaellenite, it must be assumed that the H_2O determined by TGA (Sarp 1984) is in error. Reducing the H_2O value from 11.42 to 10.7% yields the empirical formula for villyaellenite (based on O = 20 apfu) with 4.00 As apfu: $(\text{Mn}_{2.74}^{2+}\text{Ca}_{2.10})_{\Sigma 4.84}(\text{H}_2\text{O})_4(\text{AsO}_3\text{OH})_{2.31}(\text{AsO}_4)_{1.69}$.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Both powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Spider curved imaging plate micro-diffractometer utilizing monochromatized $\text{MoK}\alpha$ radiation. The powder data for miguelromeroite are presented in Table 2.

The structures of both miguelromeroite (Mapimi) and type villyaellenite (Sainte-Marie aux Mines) were refined in this study. The structure refinement of villyaellenite was performed on a crystal fragment from the holotype specimen obtained from H. Sarp in 1986 (Muséum d'Histoire Naturelle, Genève: 435/77). The Rigaku Crystal Clear software package was used for processing of the structure data. The SHELXL97 software (Sheldrick 1997) was used for the solution and refinement of the structure. Data sets are available on deposit.¹

The occupancies of all three octahedral cation sites (M1, M2, and M3) in the miguelromeroite structure refined best when assigned full occupancy by Mn. During the refinement of the villyaellenite structure, both Mn and Ca were assigned to the octahedral cation sites M1 and M3; however, because most of the

¹ Deposit item AM-09-048, data sets. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

M2-O bond lengths are relatively short for Ca-O bonds, that site was assigned completely to Mn, but its occupancy was refined. The final refined occupancies of these sites are M1: $\text{Mn}_{0.68}\text{Ca}_{0.32}$, M2: $\text{Mn}_{0.95}\square_{0.05}$, M3: $\text{Ca}_{0.85}\text{Mn}_{0.15}$.

The details of the refinements are provided in Table 3, final atomic coordinates and displacement parameters in Table 4, selected interatomic distances in Table 5, and bond valences in Table 6.

DESCRIPTION OF THE STRUCTURE

The structures of miguelromeroite, villyaellenite, and sainfeldite (Fig. 4) are based on an octahedral edge-sharing pentamer. Pentamers are linked into a loose framework by sharing corners with octahedra in adjacent pentamers and are further linked via AsO_4 and AsO_3OH tetrahedra. There are three distinct octahedral sites: M1, M2, and M3. This structure type was originally solved by Moore and Araki (1973) for the PO_4 analogue hureaulite.

In the structure of miguelromeroite, all octahedral sites are

TABLE 1. Microprobe analyses (wt%) for miguelromeroite and villyaellenite

Constituent	Miguelromeroite*	Villyaellenite†
CaO	0.47 (0.43–0.63)	13.58
FeO	0.08 (0.08–0.09)	–
MnO	36.23 (34.85–36.96)	22.40
ZnO	2.85 (2.43–3.84)	–
As_2O_5	50.62 (48.90–51.91)	52.99
H_2O	9.87‡	11.42§
Total	100.12 (98.30–101.93)	100.39

* Averages and ranges for five analyses.

† Sarp (1984).

‡ Water determined by moisture-evolution analysis.

§ Water by TGA.

TABLE 2. X-ray diffraction data for miguelromeroite

l_{obs}	d_{obs}	d_{calc}	hkl	l_{obs}	d_{obs}	d_{calc}	hkl
16	8.994	8.975	200*	4	2.159	2.155	024
28	8.279	8.248	110*	1	2.111	2.115	314
7	6.485	6.455	111			2.062	440
7	6.179	6.142	111	10	2.052	2.047	333
4	4.866	4.866	002			2.047	404
8	4.649	{ 4.646	311*	3	2.020	2.021	424
		{ 4.643	020	5	1.971	1.975	730*
11	4.490	{ 4.489	202*	6	1.876	1.881	912
		{ 4.487	400			1.819	151
5	4.319	4.309	311*	2	1.810	1.811	151
7	4.131	4.124	220*			1.804	822
5	3.876	3.868	221	4	1.777	1.778	334*
15	3.734	3.730	221*	8	1.754	1.752	534
2	3.494	3.495	402			1.680	044
33	3.357	3.359	022*	26	1.680	1.678	931*
100	3.234	3.227	221*	21	1.628	1.627	135*
68	3.074	3.071	222*	5	1.575	1.577	116*
39	2.973	2.969	113*	10	1.552	1.553	535
3	2.849	2.848	313	12	1.535	1.536	10 2 2*
2	2.789	2.792	422	11	1.495	1.496	12 0 0*
21	2.676	2.681	331*	2	1.474	1.474	734
9	2.620	2.612	331	5	1.453	1.458	915
7	2.491	2.578	621*			1.427	716
9	2.433	2.433	004*			1.423	10 4 1
21	2.341	{ 2.344	530	10	1.421	1.420	10 4 0
		{ 2.338	711*			1.420	644
18	2.244	{ 2.244	404				
		{ 2.244	800*				

Notes: Reflection indexing based on intensities from structure data. Cell parameters refined from powder data: $a = 18.058(1)$, $b = 9.286(1)$, $c = 9.7913(7)$ Å, $\beta = 96.29(1)^\circ$.

* Reflections used for powder-cell refinement.

TABLE 3. Data collection and structure refinement details for miguelromeroite and villyaellenite

	Miguelromeroite	Villyaellenite
Diffractometer	Rigaku R-Axis Spider	Rigaku R-Axis Spider
X-ray radiation	MoK α (0.71075 Å)	MoK α (0.71075 Å)
X-ray power	50 kV, 40 mA	50 kV, 40 mA
Temperature	298(2) K	298(2) K
Formula	Mn ₅ (H ₂ O) ₄ (AsO ₃ OH) ₂ (AsO ₄) ₂	(Mn,Ca)Mn ₂ Ca ₂ (H ₂ O) ₄ (AsO ₃ OH) ₂ (AsO ₄) ₂
Space group	C2/c	C2/c
Cell parameters		
	<i>a</i>	18.030(1) Å
	<i>b</i>	9.2715(5) Å
	<i>c</i>	9.7756(5) Å
	β	96.266(2)°
	<i>V</i>	1624.4(2) Å ³
	<i>Z</i>	4
Density (structural formula)	3.698 g/cm ³	3.339 g/cm ³
Absorption coefficient	11.977 mm ⁻¹	10.273 mm ⁻¹
<i>F</i> (000)	1708	1658
Crystal size	0.24 × 0.19 × 0.17 mm	0.12 × 0.05 × 0.01 mm
θ range	3.16–27.48°	3.09–21.96°
Index ranges	–22 ≤ <i>h</i> ≤ 23, –12 ≤ <i>k</i> ≤ 12, –12 ≤ <i>l</i> ≤ 12	–19 ≤ <i>h</i> ≤ 19, –9 ≤ <i>k</i> ≤ 9, –10 ≤ <i>l</i> ≤ 10
Reflections collected/unique	16656/1863 [<i>R</i> _{int} = 0.0434]	10473/1051 [<i>R</i> _{int} = 0.1033]
Reflections [<i>F</i> _o > 4 σ <i>F</i>]	1781	918
Completeness	99.5% (to 27.48°)	99.6% (to 21.96°)
Parameters refined	153	155
GoF	1.044	1.088
Final <i>R</i> indices [<i>F</i> _o > 4 σ <i>F</i>]	<i>R</i> ₁ = 0.0383, <i>wR</i> ₂ = 0.0977	<i>R</i> ₁ = 0.0407, <i>wR</i> ₂ = 0.1023
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0402, <i>wR</i> ₂ = 0.0990	<i>R</i> ₁ = 0.0468, <i>wR</i> ₂ = 0.1067
Largest diff. peak/hole	+2.35/–1.15 e/Å ³	+0.59/–1.14 e/Å ³

Notes: $R_{int} = \sum |F_o^2 - F_c^2(\text{mean})| / \sum F_o^2$. GoF = $S = \{\sum [w(F_o^2 - F_c^2)]^2 / (n - p)\}^{1/2}$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2\}^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where *P* is $[2F_o^2 + \text{Max}(F_o, 0)] / 3$; for miguelromeroite *a* is 0.047 and *b* is 50.001; for villyaellenite *a* is 0.059 and *b* is 8.683.

TABLE 4. Atomic coordinates and displacement parameters (Å²) for miguelromeroite (top) and villyaellenite (bottom)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
M1*	0.5000	0.3942(1)	0.7500	0.0134(3)	0.0136(6)	0.0128(6)	0.0139(6)	0.000	0.0023(5)	0.000
M2*	0.31499(4)	0.0872(1)	0.1880(1)	0.0055(2)	0.0053(4)	0.0054(4)	0.0061(4)	0.0014(3)	0.0017(3)	0.0003(3)
M3*	0.32573(5)	0.4714(1)	0.1376(1)	0.0116(2)	0.0121(4)	0.0114(4)	0.0116(4)	–0.0017(3)	0.0021(3)	–0.0004(3)
As1	0.41668(3)	0.31557(6)	0.41075(6)	0.0124(2)	0.0131(3)	0.0129(3)	0.0113(3)	–0.0004(2)	0.0016(2)	0.0001(2)
As2	0.66118(3)	0.23631(6)	0.62399(6)	0.0115(2)	0.0120(3)	0.0111(3)	0.0114(3)	0.0003(2)	0.0015(2)	0.0001(2)
O1	0.4242(3)	0.4383(5)	0.2882(4)	0.0190(9)	0.021(2)	0.020(2)	0.015(2)	0.007(2)	0.000(2)	–0.003(2)
O2	0.3388(3)	0.2224(5)	0.3621(5)	0.0194(9)	0.019(2)	0.020(2)	0.019(2)	–0.004(2)	0.003(2)	–0.006(2)
O3	0.4153(3)	0.3919(5)	0.5667(5)	0.0196(9)	0.017(2)	0.025(2)	0.016(2)	–0.007(2)	0.000(2)	0.002(2)
O4	0.6650(2)	0.2579(5)	0.4519(4)	0.0153(9)	0.019(2)	0.016(2)	0.010(2)	–0.000(2)	0.002(2)	–0.001(2)
O5	0.7070(2)	0.0866(5)	0.6782(5)	0.0160(9)	0.017(2)	0.013(2)	0.019(2)	0.004(2)	0.004(2)	0.003(2)
O6	0.7036(2)	0.3773(5)	0.7080(5)	0.0164(9)	0.012(2)	0.015(2)	0.023(2)	–0.005(2)	0.004(2)	–0.003(2)
O7	0.5704(2)	0.2280(5)	0.6561(5)	0.0167(9)	0.014(2)	0.017(2)	0.019(2)	–0.001(2)	0.003(2)	0.000(2)
OH	0.4902(3)	0.1977(5)	0.4214(5)	0.0233(10)	0.020(2)	0.025(2)	0.024(2)	–0.005(2)	–0.002(2)	0.012(2)
OW1	0.2418(3)	0.4236(5)	0.4706(5)	0.0197(9)	0.022(2)	0.021(2)	0.018(2)	0.000(2)	0.008(2)	0.001(2)
OW2	0.5840(3)	0.0058(6)	0.8411(5)	0.0260(11)	0.024(3)	0.025(3)	0.029(3)	0.012(2)	0.006(2)	–0.002(2)
HOH	0.508(5)	0.221(10)	0.508(5)	0.04(3)						
HW1A	0.210(4)	0.377(8)	0.521(8)	0.04(3)						
HW1B	0.260(6)	0.357(8)	0.416(9)	0.06(3)						
HW2A	0.571(4)	0.082(6)	0.787(7)	0.02(2)						
HW2B	0.546(4)	–0.056(9)	0.836(12)	0.09(5)						

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
M1*	0.5000	0.3906(2)	0.7500	0.0241(10)	0.0209(15)	0.0318(16)	0.0211(15)	0.000	0.0088(10)	0.000
M2*	0.3166(1)	0.0852(2)	0.1865(1)	0.0237(7)	0.0215(10)	0.0290(11)	0.0220(10)	0.0019(7)	0.0083(7)	0.0005(7)
M3*	0.3257(1)	0.4683(2)	0.1398(2)	0.0238(8)	0.0197(13)	0.0283(13)	0.0254(13)	–0.0039(9)	0.0107(8)	–0.0014(8)
As1	0.41724(5)	0.3158(1)	0.4126(1)	0.0227(4)	0.0184(7)	0.0319(7)	0.0191(6)	0.0001(4)	0.0080(4)	0.0009(5)
As2	0.65970(5)	0.2335(1)	0.6233(1)	0.0213(4)	0.0174(7)	0.0280(7)	0.0196(6)	0.0000(4)	0.0073(4)	–0.0001(4)
O1	0.4267(3)	0.4385(7)	0.2962(6)	0.029(2)	0.025(4)	0.039(4)	0.024(4)	0.012(3)	0.011(3)	0.000(3)
O2	0.3400(4)	0.2278(8)	0.3594(7)	0.033(2)	0.020(4)	0.051(5)	0.029(4)	–0.010(3)	0.006(3)	–0.008(3)
O3	0.4153(4)	0.3866(7)	0.5664(6)	0.028(2)	0.030(4)	0.034(4)	0.022(4)	–0.007(3)	0.009(3)	0.008(3)
O4	0.6631(4)	0.2496(7)	0.4554(6)	0.027(2)	0.025(4)	0.043(4)	0.013(3)	0.003(3)	0.002(3)	–0.001(3)
O5	0.7044(3)	0.0878(6)	0.6799(6)	0.025(2)	0.024(4)	0.020(4)	0.032(4)	0.004(3)	0.012(3)	0.002(3)
O6	0.7018(3)	0.3727(7)	0.6988(6)	0.026(2)	0.026(4)	0.022(4)	0.030(4)	–0.012(3)	0.007(3)	–0.003(3)
O7	0.5710(3)	0.2264(7)	0.6545(6)	0.027(2)	0.011(3)	0.052(5)	0.016(4)	–0.007(3)	0.000(3)	–0.004(3)
OH	0.4879(4)	0.1984(8)	0.4214(7)	0.033(2)	0.028(4)	0.050(5)	0.021(4)	–0.010(4)	0.000(3)	0.011(4)
OW1	0.2391(4)	0.4172(7)	0.4705(7)	0.028(2)	0.025(4)	0.036(4)	0.024(4)	–0.001(3)	0.012(3)	0.002(3)
OW2	0.5802(4)	0.0102(9)	0.8380(8)	0.040(2)	0.031(5)	0.049(6)	0.043(5)	0.015(4)	0.012(4)	–0.001(4)
HOH	0.510(4)	0.209(9)	0.504(4)	0.02(3)						
HW1A	0.208(5)	0.371(9)	0.516(10)	0.06(4)						
HW1B	0.260(6)	0.356(8)	0.418(10)	0.06(4)						
HW2A	0.564(6)	0.068(11)	0.771(10)	0.10(6)						
HW2B	0.547(5)	–0.057(9)	0.845(11)	0.07(4)						

* In miguelromeroite, M1, M2, and M3 are fully occupied by Mn. In villyaellenite, the site occupancies are M1: Mn 0.68(4)/Ca 0.32(4); M2: Mn 0.95(1); M3: Mn 0.15(3)/Ca 0.85(3).

occupied by Mn and the average bond lengths for the sites fall within a relatively narrow range, although the differences in the sites suggest that the small amounts of Zn and Ca are in sites M2 and M3, respectively. Additional insight into the ordering is provided by Stock et al. (2002) who synthesized the pure Mn end-member.

TABLE 5. Selected bond distances (Å) for miguelromeroite and villyaellenite

	Miguelromeroite	Villyaellenite
M1-O1 (x2)	2.128(5)	2.190(7)
M1-O3 (x2)	2.224(4)	2.263(7)
M1-O7 (x2)	2.255(5)	2.306(7)
<M1-O>	2.217	2.266
M2-OW2	2.063(5)	2.144(8)
M2-O6	2.066(4)	2.166(7)
M2-O2	2.120(5)	2.192(7)
M2-O5	2.140(4)	2.174(6)
M2-O4	2.148(4)	2.165(7)
M2-OW1	2.325(5)	2.380(7)
<M2-O>	2.159	2.215
M3-O6	2.168(4)	2.302(6)
M3-O4	2.178(4)	2.298(7)
M3-O1	2.201(5)	2.303(7)
M3-O3	2.222(5)	2.328(7)
M3-O5	2.283(4)	2.372(6)
M3-OW1	2.316(5)	2.437(7)
<M3-O>	2.240	2.438
As1-O1	1.669(4)	1.665(6)
As1-O2	1.673(5)	1.681(7)
As1-O3	1.684(4)	1.676(6)
As1-OH	1.713(5)	1.706(7)
<As1-O>	1.685	1.682
As2-O5	1.672(4)	1.672(6)
As2-O6	1.682(4)	1.665(6)
As2-O7	1.701(4)	1.697(6)
As2-O4	1.703(4)	1.688(6)
<As2-O>	1.690	1.681
H bonds:		
OH...O7	2.591(7)	2.642(7)
OW1A...O2	2.672(7)	2.727(9)
OW1B...O2	2.840(7)	2.892(9)
OW2A...O7	2.735(7)	2.738(10)
OW2B...OH	2.706(7)	2.794(10)

The structure refinement of villyaellenite provides average M-O bond lengths for the M1, M2, and M3 sites (Table 5) that are very close to those predicted by Kampf and Ross (1988) based on DLS analysis and clearly show that the larger Ca²⁺ cation should preferentially occupy the M3 site and the smaller Mn²⁺ cation should preferentially occupy the M2 site. Direct evidence for this is provided by the refined site occupancies (see Table 4 footnote) that clearly indicate that the M2 site is dominated by Mn, the M3 site is dominated by Ca, and the M1 site is occupied by somewhat more Mn than Ca. Considering the refined site occupancies, the structural formula for villyaellenite is (Mn_{0.68}Ca_{0.32})(Mn_{1.90}□_{0.10})(Ca_{1.70}Mn_{0.30})(H₂O)₄(AsO₃OH)_{2.20}(AsO₄)_{1.80}. The total octahedral cation content from the structural formula is Mn_{2.88}Ca_{2.02}, which compares well with that from the empirical formula, Mn_{2.74}Ca_{2.10}.

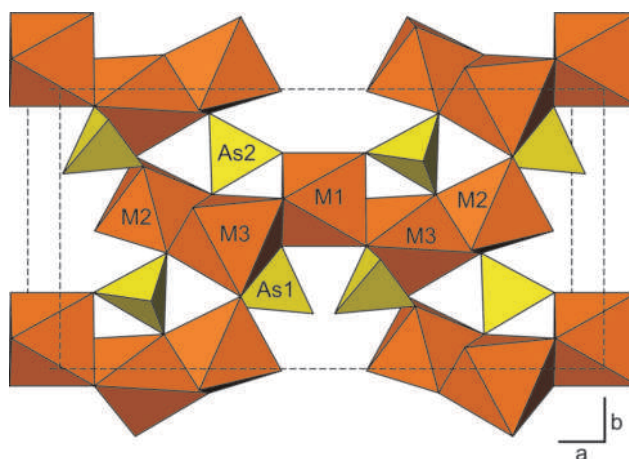


FIGURE 4. Structure of miguelromeroite, villyaellenite, and sainfeldite, viewed parallel to {001}.

TABLE 6. Bond valence summations for miguelromeroite (top) and villyaellenite (bottom)

	O1	O2	O3	O4	O5	O6	O7	OH	OW1	OW2	Σ _v
M1	0.401 (x2→)		0.309 (x2→)				0.285 (x2→)				1.990
M2		0.410		0.380	0.388	0.474			0.236	0.478	2.366
M3	0.329		0.311	0.350	0.264	0.360			0.241		1.856
As1	1.303	1.289	1.251					1.157			5.001
As2				1.189	1.293	1.258	1.195				4.935
HOH							0.294	0.706			1.000
HW1a		0.242							0.758		1.000
HW1b		0.170							0.830		1.000
HW2a							0.210			0.790	1.000
HW2b								0.224		0.776	1.000
Σ _v	2.034	2.111	1.872	1.919	1.945	2.093	1.983	2.087	2.065	2.045	
M1*	0.398 (x2→)		0.327 (x2→)				0.291 (x2→)				2.031
M2*		0.337		0.363	0.354	0.362			0.203	0.384	2.004
M3*	0.403		0.377	0.409	0.335	0.404			0.281		2.209
As1	1.317	1.262	1.279					1.179			5.037
As2				1.238	1.293	1.317	1.208				5.056
HOH							0.257	0.743			1.000
HW1a		0.214							0.786		1.000
HW1b		0.155							0.845		1.000
HW2a							0.209			0.791	1.000
HW2b								0.186		0.814	1.000
Σ _v	2.119	1.968	1.982	2.010	1.982	2.084	1.965	2.108	2.115	1.990	

Note: Non-hydrogen bond strengths from Brese and O'Keeffe (1991); hydrogen bond strengths from Ferraris and Ivaldi (1988), based on O-O distances; valence summations are expressed in valence units.

* Calculated based upon M1 fully occupied by 2/3 Mn²⁺ and 1/3 Ca, M2 fully occupied by Mn²⁺ and M3 fully occupied by Ca.

SAINFELDITE-MIGUELROMEROITE SERIES

As noted by Kampf and Ross (1988), the limited compositional ranges implied by known natural phases in the sainfeldite-miguelromeroite series are consistent with cation ordering in phases with intermediate compositions and with the lack of a continuous solid solution within the series. Notably, miguelromeroite occurs at both Mapimi and Sterling Hill in direct association with minerals containing essential Ca, yet in both cases it contains very little Ca. Also, as noted above, the Gozaisho mine, Honshu Island, Japan, has yielded material near the Mn end-member (miguelromeroite), as well as material with $Mn/(Mn+Ca) = 0.44$.

The compositions of the two known intermediate examples in this series, type villyaellenite with $Mn/(Mn+Ca) = 0.57$ and the material from the Gozaisho mine with $Mn/(Mn+Ca) = 0.44$, suggest that the M1 site is capable of accepting a full range of Ca and Mn occupancies. There would, therefore, appear to be four distinct species in the series (Table 7): the full Ca end-member sainfeldite $Ca_5(H_2O)_4(AsO_3OH)_2(AsO_4)_2$, the full Mn end-member miguelromeroite, $Mn_5(H_2O)_4(AsO_3OH)_2(AsO_4)_2$, and the two end-members of an intermediate solid-solution series between $MnMn_2Ca_2(H_2O)_4(AsO_3OH)_2(AsO_4)_2$ (villyaellenite) and $CaMn_2Ca_2(H_2O)_4(AsO_3OH)_2(AsO_4)_2$ (corresponding to an as yet unnamed species from the Gozaisho mine).

TABLE 7. Minerals in the sainfeldite-miguelromeroite series

	Miguelromeroite	Villyaellenite	Unnamed mineral	Sainfeldite
M1 (1 apfu)	Mn	Mn,Ca	Ca,Mn	Ca
M2 (2 apfu)	Mn	Mn	Mn	Ca
M3 (2 apfu)	Mn	Ca	Ca	Ca
Mn/(Mn+Ca)*	1.0	0.6–0.5	0.5–0.4	0.0

*Assuming complete ordering in the M2 and M3 sites and complete solid solution in the M1 site of the intermediate series. Limited solid solution in the M2 and M3 sites would extend and/or shift the Mn/(Mn+Ca) ranges of the intermediate series.

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REFERENCES CITED

- Breese, N.E. and O'Keefe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192–197.
- Dunn, P.J. (1995) Franklin and Sterling Hill, New Jersey: The world's most magnificent mineral deposits. Self-Published; Excalibur Mineral Company, Peekskill, New York.
- Ferraris, G. and Ivaldi, G. (1988) Bond valence vs. bond length in O...O hydrogen bonds. *Acta Crystallographica*, B44, 341–344.
- Hloušek, J. and Tvrđý J. (2002) Interessante Secundärminerale aus Jáchymov. *Lapis*, 27(7/8), 44–66.
- Kampf, A.R. and Dunn, P.J. (1987) Ogdensburgite from Mapimi and new data for the species. *American Mineralogist*, 72, 409–412.
- Kampf, A.R. and Ross, C.R. (1988) End-member villyaellenite from Mapimi, Durango, Mexico: Descriptive mineralogy, crystal structure, and implications for the ordering of Mn and Ca in type villyaellenite. *American Mineralogist*, 73, 1172–1178.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist* 19, 441–450.
- Matsubara, S., Kato, A., Shimizu, M., Sekiuchi, K., and Suzuki, Y. (1996) Romeite from the Gozaisho mine, Iwaki, Japan. *Mineralogical Journal*, 18, 155–160.
- Moore, P.B. and Araki, T. (1973) Hureaulite, $Mn_5^2(H_2O)_4[PO_3(OH)]_2[AsO_4]_2$: Its atomic arrangement. *American Mineralogist*, 58, 302–307.
- Moore, T.P. and Megaw, P.K.M. (2003) Famous mineral localities: The Ojuela mine, Mapimi, Durango, Mexico. *The Mineralogical Record*, 34, 1–91.
- Sarp, H. (1984) Villyaellenite, $H_2(Mn,Ca)_2(AsO_4)_4 \cdot 4H_2O$ un nouveau minéral de Sainte-Marie aux Mines (France). *Schweizerische Mineralogische und Petrographische Mitteilungen*, 64, 323–328.
- Sheldrick, G.M. (1997) SHELXL97. Program for the refinement of crystal structures. University of Göttingen, Germany.
- Stock, N., Stucky, G.D., and Cheetham, A.K. (2002) Synthesis and characterization of the synthetic minerals villyaellenite and sarkinite, $Mn_3(AsO_4)_2(HAsO_4)_2 \cdot 4H_2O$ and $Mn_2(AsO_4)(OH)$. *Zeitschrift für Anorganische und Allgemeine Chemie*, 628, 357–362.
- Wallace, T.C. (2008) Miguel Romero Sanchez (1925–1997). In *The Miguel Romero Collection of Mexican Minerals*. *The Mineralogical Record*, 39 (Supplement), 5–10.

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