SAMFOWLERITE, A NEW Ca Mn Zn BERYLLOSILICATE MINERAL FROM FRANKLIN, NEW JERSEY: ITS CHARACTERIZATION AND CRYSTAL STRUCTURE[1]

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ABSTRACT

Samfowlerite, ideally $Ca_{14}Mn_3Zn_2(Zn,Be)_2Be_6(SiO_4)_6(Si_2O_7)_4(OH,F)_6$, is monoclinic, $P2_1/c$, with a 9.068(2), b 17.992(2), c 14.586(2) Å, β 104.86(1)°, and $Z = 2$. It occurs as colorless 0.05-mm-diameter crystals in andradite-lined vugs in franklinite – willemite ore from Franklin, Sussex County, New Jersey. Electron- and ion-microprobe analyses yielded CaO 34.1, MgO 0.2, MnO 9.3, ZnO 9.5, BeO 5.6, SiO_2 36.9, F 1.0, H_2O (by difference) 3.8, less O=F 0.4, total 100 wt%. Optically, it is biaxial negative, $2V$ 29.0(1)°, with α 1.674(3), β 1.680(3), and γ 1.681(3). The measured and calculated densities are 3.28 ± 0.05 and 3.31 g/cm³, respectively. The strongest powder X-ray-diffraction lines are [d in Å(I)(hkl)]: 2.863(100)($\overline{3}$21,053), 2.653(50)(251), 2.388(50)($\overline{3}$34,$\overline{1}$72), 2.771(40)($\overline{1}$25), 2.272(30)(172,234,$\overline{4}$02,$\overline{1}$55), 1.832(30)($\overline{3}$74), 1.860(20)($\overline{3}$27,$\overline{4}$06,066), and 1.803(20)($\overline{3}$81,0·10·0,$\overline{3}$82). The crystal structure has been solved and refined to an unweighted residual of 0.043 for 2495 observed reflections. Although samfowlerite is, strictly speaking, a mixed-anion (SiO_4 and Si_2O_7) silicate, the structure may be viewed as being composed of layers of vertex-sharing TO_4 tetrahedra (T = Si,Be,Zn) alternating with layers of vertex- and edge-sharing CaO_8 bicapped trigonal prisms and MnO_6 octahedra, the layers being parallel to (102). The TO_4 groups and $CaO_8–MnO_6$ groups share vertices with one another across the layer boundaries to form the three-dimensional structure. Within the layers of tetrahedra, the TO_4 groups form a network of 4-, 5-, and 8-membered rings. The apparent substitution of Be for Zn in the ratio ⅝ to ⅜ on one of the T sites suggests that the space group $P2_1/c$ is only that of an average structure, and that the true structure is of lower symmetry, with ordering of Zn and Be on separate sites.

Keywords: samfowlerite, new mineral species, crystal structure, beryllosilicate of calcium, manganese and zinc, Franklin, New Jersey.

SOMMAIRE

La samfowlerite, de composition idéale $Ca_{14}Mn_3Zn_2(Zn,Be)_2Be_6(SiO_4)_6(Si_2O_7)_4(OH,F)_6$, est monoclinique, $P2_1/c$, a 9.068(2), b 17.992(2), c 14.586(2) Å, β 104.86(1)°, avec Z égal à 2. Les cristaux, incolores et 0.05 mm de diamètre, tapissent avec l'andradite des cavités dans le minerai à franklinite + willemite de la mine Franklin, comté de Sussex, au New Jersey. Les analyses aux microsondes électronique et ionique indiquent CaO 34.1, MgO 0.2, MnO 9.3, ZnO 9.5, BeO 5.6, SiO_2 36.9, F 1.0, H_2O (par différence) 3.8, moins O=F 0.4, pour un total de 100% (par poids). Il s'agit d'un minéral biaxe négatif, $2V$ 29.0(1)°, avec α 1.674(3), β 1.680(3), et γ 1.681(3). La densité mesurée est de 3.28 ± 0.05, tandis que la densité calculée est de 3.31. Les huit raies les plus intenses du cliché de diffraction (méthode des poudres) [d en Å(I)(hkl)] sont: 2.863(100)($\overline{3}$21,053), 2.653(50)(251), 2.388(50)($\overline{3}$34,$\overline{1}$72), 2.771(40)($\overline{1}$25), 2.272(30)(172,234,$\overline{4}$02,$\overline{1}$55), 1.832(30)($\overline{3}$74), 1.860(20)($\overline{3}$27,$\overline{4}$06,066), et

1.803(20)($\overline{3}$81,0·10·0,$\overline{3}$82). Nous avons affiné la structure cristalline jusqu'à un résidu non pondéré de 0.043 pour 2495 réflex-ions observées. Quoique la samfowlerite est, *sensu stricto*, un silicate à trame mixte (SiO_4 et Si_2O_7), on peut considérer sa structure en termes de couches de tétraèdres TO_4 à coins partagés (T représente Si, Be et Zn) d'une part, en alternance avec des couches de polyèdres CaO_8 en forme de prismes trigonaux biterminés et d'octaèdres MnO_6 qui partagent coins et arêtes d'autre part, ces couches étant parallèles à (102). Les groupes TO_4 et les polyèdres CaO_8 et MnO_6 partagent des atomes d'oxygène apicaux pour former une charpente tridimensionnelle. Dans les couches de tétraèdres, les groupes TO_4 sont articulés en anneaux de 4, 5 et 8 membres. La substitution apparente de Be pour Zn dans une proportion de ⅚ à ⅜ dans un des sites T fait penser que le groupe spatial $P2_1/c$ s'applique seulement à une structure moyenne, et que la structure possède en fait une symétrie plus basse, avec mise en ordre de Zn et de Be dans des sites séparés.

<div align="right">(Traduit par la Rédaction)</div>

INTRODUCTION

During an examination of late-stage minerals occurring in vugs in ore from Franklin, New Jersey, the properties of one of the minerals found could not be identified with those of any known species. Although it occurs in exceedingly minute quantities, precluding the measurement of some properties, we have nevertheless been able to characterize the miner-al and to define it as a new species. We have named it *samfowlerite* in honor of Dr. Samuel Fowler, M.D. (1779–1844), the pre-eminent figure in the history of the Franklin mining district. Dr. Fowler, a physician, scientist, industrialist, and entrepreneur, was instru-mental in bringing most of the great American natu-ralists and scientists of his time to Franklin and encouraging mineralogists in Europe and elsewhere to study the zinc deposits at Franklin. *Fowlerite*, now known to be a zincian variety of rhodonite, had previ-ously been named for Dr. Fowler. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. The holo-type specimen is deposited in the Smithsonian Institution under catalogue number M04254.

OCCURRENCE

Samfowlerite was originally found on only one small specimen from the Franklin mine, in Franklin, Sussex County, New Jersey. The holotype material occurs in a vug in granular willemite – franklinite – andradite ore. The vug is partly lined with massive white garnet of the andradite – grossular series, the surfaces of the garnet crystals being light orange-pink in color. The single cluster of samfowlerite crystals in the specimen occurs on the garnet. The holotype specimen is a micromount and is part of a famous Franklin cahnite assemblage found in 1927 and described by Palache (1935).

Subsequent to IMA–CNMMN approval of sam-fowlerite, an additional specimen was found, and this permits a more detailed description of the assemblage. The specimen consists of franklinite – willemite – andradite granular ore, which has vuggy areas. These vugs are lined with various minerals, including sparse 2-cm crystals of willemite and barite. Garnet (andradite – grossular solid solution), which crystallized contemporaneously with and sub-sequent to the barite crystals, also lines the vugs. Minor johnbaumite is included in the garnet. Indeed, garnet is the most notable feature of the assemblage, varying in color and texture from yellow-brown granular material, to whitish, fine-grained, zoned material forming dodecahedra, to a thin pinkish orange outer zone. Of particular interest are very small, submillimeter-sized crystals that occur as late-stage crystallites on the pinkish orange material. These crystals are euhedral, twinned, colorless cahnite, pseudohexagonal light brown clinochlore [called biotite by Palache (1935)], thin druses of very pale pink leucophoenicite, and euhedral crystals of colorless samfowlerite (Fig. 1). Although only a very few specimens are available for study, it can be said that samfowlerite tends to occur alone in vugs, with or without clinochlore, and also occurs interstitially to platy crystals of barite.

Inasmuch as cahnite and associated barite are colorless to white, other specimens of samfowlerite may exist unrecognized and perhaps mislabeled as cahnite in systematic collections.

PHYSICAL AND OPTICAL PROPERTIES

The holotype material is a 0.5-mm-diameter group of crystals, with each crystal being approximately 0.05 mm in diameter. On that specimen, and on the small number of specimens subsequently discovered, the crystals form aggregates like that shown in Figure 1. Single crystals of samfowlerite have very smooth, highly reflective faces and are colorless, with a vitreous luster and white streak; they may appear white in the aggregate. No cleavage was observed, but the amount of material studied was so small that cleavage, if present, could well have gone undetected. The hardness was not directly determined, but the mineral is very soft, the estimated Mohs hardness

FIG. 1. A cluster of typical crystals of samfowlerite. The field of view is *ca*. 0.7 μm in maximum dimension.

being no more than 3. The density, measured using heavy liquid techniques, is 3.28 ± 0.05 g/cm^3, compared with calculated values of 3.29 g/cm^3 (based on the cell volume obtained from least-squares refinement using the powder-diffraction data) and 3.31 g/cm^3 (based on the cell volume obtained from refinement using the data obtained by single-crystal diffraction). Both values are calculated from the "final" unit-cell contents given in a subsequent section. There is some similarity in appearance between samfowlerite and some nontypical crystals of clinohedrite.

Optically, samfowlerite is biaxial, negative, with $2V$ 29.0(1)°, α 1.674(3), β 1.680(3), and γ 1.681(3). Dispersion was not observed. The orientation is $Y = b$, $X \wedge a = 44°$, and $Z \wedge c = 29°$. Samfowlerite fluoresces with a very weak red color in both longwave and shortwave ultraviolet radiation.

X-RAY CRYSTALLOGRAPHY

Single crystals were studied by both precession and Weissenberg techniques. Some precession photographs were obtained using CuKα radiation in order to prevent overlap of reflections from different levels caused by the relatively large unit-cell translations. A study of the systematic extinctions led to the unambiguous determination of the space group as $P2_1/c$. The cell parameters measured from the precession photographs are a 9.10, b 18.06, and c 14.64 Å, β 104.8°. Powder X-ray-diffraction data (Table 1) were obtained using a 114.58-mm-diameter Gandolfi powder camera, Ni-filtered CuKα radiation, a polycrystalline specimen, and NBS Si (a 5.43088 Å) as an internal standard. A least-squares refinement of the cell parameters using nine unambiguously indexable powder-diffraction lines yielded a 9.090(7),

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR SAMFOWLERITE

I_{obs}	d_{obs}	d_{cal}	hkl	I_{obs}	d_{obs}	d_{cal}	hkl
2	7.735	7.689	$\bar{1}11$	2	2.184	2.177	351
		4.919	102			2.175	323
5	4.923	4.907	$\bar{1}31$	2	2.132	2.139	106
		4.526	$\bar{1}13$			2.134	420
2	4.515	4.507	040			2.129	164
5	4.228	4.250	$\bar{2}02$	2	2.064	2.075	$\bar{2}46$
		3.844	$\bar{2}22$			2.058	155
2	3.827	3.807	132	2	2.036	2.036	421
		3.609	$\bar{1}04$			1.967	027
		3.594	221	2	1.959	1.959	174
10b	3.570	3.546	004				
		3.527	004	20	1.860	1.863	$\bar{3}27$
		3.362	202			1.861	$\bar{4}06$
2	3.336	3.323	142			1.852	066
2	3.239	3.245	$\bar{1}43$	30	1.832	1.832	$\bar{3}74$
2	3.054	3.042	034			1.807	$\bar{3}81$
		2.869	$\bar{3}21$	20	1.803	1.803	0·10·0
100	2.863	2.861	053			1.800	$\bar{3}82$
40	2.771	2.772	$\bar{1}25$	5	1.744	1.743	138
50	2.653	2.653	251	5	1.721	1.720	$\bar{4}46$
		2.590	$\bar{2}53$			1.693	1·10·2
10	2.582	2.579	$\bar{3}14$	20	1.689	1.692	038
		2.492	$\bar{3}42$			1.688	$\bar{3}28$
5	2.492	2.488	302			1.687	530
		2.460	204			1.611	$\bar{5}51,502$
10	2.459	2.456	340	5	1.613	1.610	$\bar{1}19$
		2.454	$\bar{2}62$			1.609	$\bar{1}·11·1$
		2.390	$\bar{3}34$	10	1.526	1.521	$\bar{5}64$
50	2.388	2.387	$\bar{1}72$			1.520	257
		2.338	$\bar{2}06$	2	1.504	1.508	208
20	2.329	2.337	$\bar{3}15$			1.502	0·12·0,523
		2.336	341	5	1.458		
		2.318	$\bar{3}51$	5	1.432		
		2.282	172	2	1.407		
30	2.272	2.276	234	2	1.384		
		2.269	$\bar{4}02$	5	1.303		
		2.266	$\bar{1}55$				

114.6 mm. diameter Gandolfi camera, CuKα radiation, b = broadened line, visually estimated intensities. Indexed with the aid of the single-crystal diffractometer intensity data on a cell having a 9.090(7), b 18.028(9), c 14.598(12) Å, and β 104.86(5)°.

b 18.028(9), c 14.598(12) Å, β 104.86(5)°, and V 2312(4) Å^3. A second set of refined parameters was obtained using 23 reflections between 13° and 29° 2θ measured during a 4-circle diffractometer study of the crystal chosen for measurement of intensity data. These are a 9.068(2), b 17.992(2), c 14.586(2) Å, β 104.86(1)°, and V 2300.1(7) Å^3.

CHEMICAL COMPOSITION

Owing to the extreme paucity of material, samfowlerite could be analyzed only by microbeam methods, and water was therefore calculated by difference. Operating conditions used for the electron-microprobe analysis included an operating voltage of 15 kV, a sample current of 0.025 μA, and a beam spot of 20 μm for the final analysis that followed tests for homogeneity with a small-diameter beam. The following standards were used: wollastonite (Ca,Si), hornblende (Mg), manganite (Mn), and synthetic ZnO (Zn). The resulting analysis yielded SiO$_2$ 36.9, MgO 0.2, CaO 34.1, ZnO 9.5, and MnO 9.3 wt%. An analysis for light elements with an ion microprobe (SIMS) yielded BeO 5.6 and F 1.0 wt%. With 3.8 wt% H$_2$O by difference, less O = F 0.4, these total 100 wt%. The colorless nature of the crystals suggests that Mn is present as Mn^{2+}, and this is confirmed by the results of the crystal-structure analysis. The unit-cell contents calculated from the combined analytical data, the measured density, and the unit-cell volume derived from the cell-parameter refinement using the powder-diffraction data are Ca$_{27.8}$Mg$_{0.2}$Mn$_{6.0}$Zn$_{5.3}$Be$_{10.2}$Si$_{28.0}$O$_{113.0}$F$_{2.4}$H$_{19.3}$, which may be simplified to the charge-balanced formula Ca$_{28}$Mn$_6$Zn$_6$Be$_{10}$Si$_{28}$O$_{96}$(OH)$_{18}$F$_2$. However, the results of the crystal-structure analysis show that this formula is significantly in error due to an erroneously low analytical value for BeO from the ion probe and consequently an erroneously high assumed value for H$_2$O. The final unit-cell contents yielded by the structure analysis are Ca$_{28}$Mn$_6^{2+}$Zn$_4$(Zn$_{1.5}$Be$_{2.5}$)Be$_{12}$(SiO$_4$)$_{12}$ (Si$_2$O$_7$)$_8$(OH)$_{12}$, where the F indicated by the chemical analyses is assumed to be disordered over the OH sites, since no evidence of ordering was found, and the Si atoms are divided between ortho- and disilicate groups.

STRUCTURE SOLUTION AND REFINEMENT

A subhedral crystal of dimensions 0.08 × 0.09 × 0.15 mm was selected for the measurement of intensity data, after a quality check with the precession method, and mounted on an Enraf–Nonius CAD4 4-circle diffractometer controlled by a MicroVAX 3100 computer. The intensities of 5608 reflections in one asymmetric unit (including symmetry-equivalents $hk0$ and $h\bar{k}0$) having 2θ ≤ 54.9° were then measured and reduced to structure-factor amplitudes by correction for Lorentz-polarization and absorption effects. The latter correction was applied by the psi scan method of North et al. (1968). After elimination of symmetry-equivalent reflections, systematically extinct reflections, and one very low-theta reflection (100), which had a grossly asymmetrical background, a data set of 5237 reflections remained, of which 2496 were considered "observed" using the criterion I_{obs} > 3σ(I_{obs}). Additional information concerning intensity measurement and reduction appears in Table 2. All computations involving data reduction and the solution and refinement of the structure were carried out using the Enraf–Nonius crystallographic software system MolEN. The structure of samfowlerite was solved using the MULTAN11/82 direct methods package incorporated in MolEN, supplemented by a series of difference-Fourier syntheses. The structure (excluding the H atoms, which had yet to be located) refined to an unweighted residual of 0.072 using isotropic tempera-

TABLE 2. EXPERIMENTAL DETAILS

Crystal size	0.08 X 0.09 X 0.15 mm
Radiation	Monochromatized MoKα (λ – 0.7107 Å)
Maximum 2θ	54.90°
Reflection scans	
Scan type	ω/2θ
Scan rates	Between 0° and 7°/min in ω
Scan widths	0.7 + 0.350tanθ
Absorption	
Coefficient (μ₁)	42.0 cm⁻¹
Corrections	Psi scan using 6 reflections and "Fourier" (Walker & Stuart 1983)
Refinement	
Type	Full-matrix least-squares
Function minimized	$\Sigma w(|F_{obs}|-|F_{cal}|)^2$
Weights	$4F^2_{obs}/\sigma^2(F^2_{obs})$
Anomalous disp.	For all atoms except H
Observations	2495 reflections with $I_{obs} > 3\sigma(I_{obs})$
Variables	442 parameters
R (obs. data)	0.043
Rw (obs. data)	0.049
R (all data)	0.182
Esd obs. of unit wt.	1.335
Largest shift/error	0.08
Largest Δρ(x,y,z)	0.95 e/Å³ (on final map)
Diffractometer	Enraf-Nonius CAD4
Computer hardware	MicroVAX 3100
Computer software	MolEN system

TABLE 3. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (Å²) IN SAMFOWLERITE

	x	y	z	B_{eq} or B_{iso}
Ca(1)	0.3391(2)	0.1902(1)	0.3203(1)	0.75(3)
Ca(2)	0.6542(2)	0.1005(1)	0.1731(1)	0.70(4)
Ca(3)	0.9429(2)	0.1852(1)	0.0317(1)	0.70(4)
Ca(4)	0.7377(2)	0.1899(1)	0.6241(1)	1.32(4)
Ca(5)	0.0524(2)	0.1136(1)	0.4621(1)	0.76(4)
Ca(6)	0.2282(2)	0.0994(1)	0.8885(1)	0.70(3)
Ca(7)	0.4747(2)	0.0922(1)	0.7523(1)	0.86(4)
Mn(1)	0.2826(2)	0.0030(1)	0.3548(1)	0.87(3)
Mn(2)	0	0	0	0.90(4)
Zn(1)	0.3555(1)	0.2475(1)	0.0798(1)	0.65(2)
Zn(2)	0.6715(3)	0.0551(1)	0.4198(2)	0.69(5)
Be(1)	0.9596(13)	0.2434(7)	0.7971(8)	0.7(2)
Be(2)	0.0376(14)	0.0514(7)	0.2157(9)	0.8(2)
Be(3)	0.6507(13)	0.0454(7)	0.9426(8)	0.5(2)
Si(1)	0.2903(3)	0.0886(1)	0.1404(2)	0.46(4)
Si(2)	0.1207(3)	0.1862(1)	0.6657(2)	0.56(4)
Si(3)	0.8730(3)	0.0936(1)	0.8392(2)	0.50(4)
Si(4)	0.4687(3)	0.0910(1)	0.5446(2)	0.61(5)
Si(5)	0.1120(3)	0.0169(1)	0.6612(2)	0.62(5)
Si(6)	0.7158(3)	0.2016(1)	0.3633(2)	0.73(5)
Si(7)	0.5374(3)	0.1889(1)	0.9532(2)	0.55(5)
O(1)	0.3322(7)	0.0955(4)	0.4497(4)	0.8(1)
O(2)	0.2689(6)	0.1827(3)	0.7539(4)	0.6(1)
O(3)	0.7430(6)	0.0924(3)	0.7422(4)	0.7(1)
O(4)	0.2521(7)	0.0182(3)	0.7523(4)	0.8(1)
O(5)	0.1474(6)	0.2208(3)	0.5693(4)	0.6(1)
O(6)	0.6414(7)	0.0838(4)	0.5299(5)	1.2(1)
O(7)	0.2197(7)	0.0792(3)	0.2327(4)	0.8(1)
O(8)	0.9173(7)	0.1113(3)	0.1668(4)	0.8(1)
O(9)	0.1547(6)	0.0946(3)	0.0429(4)	0.7(1)
O(10)	0.0347(6)	0.0291(3)	0.3243(4)	0.6(1)
O(11)	0.4776(7)	0.1636(3)	0.6125(4)	0.8(1)
O(12)	0.8505(8)	0.0181(4)	0.4324(4)	1.9(1)
O(13)	0.5737(7)	0.0174(4)	0.0476(4)	0.7(1)
O(14)	0.9792(7)	0.2322(3)	0.6872(4)	0.8(1)
O(15)	0.6610(7)	0.1971(3)	0.0529(4)	0.8(1)
O(16)	0.8385(7)	0.1989(3)	0.4625(4)	0.9(1)
O(17)	0.0924(7)	0.2017(3)	0.3526(4)	0.6(1)
O(18)	0.7869(7)	0.2214(4)	0.2752(5)	1.1(1)
O(19)	0.4052(7)	0.0200(3)	0.1369(4)	0.7(1)
O(20)	0.0540(7)	0.1026(4)	0.6326(5)	1.3(1)
O(21)	0.9796(7)	0.1667(3)	0.8568(4)	0.8(1)
O(22)	0.5833(7)	0.2356(4)	0.8680(4)	1.0(1)
O(23)	0.9917(6)	0.0240(3)	0.8502(4)	0.5(1)
O(24)	0.3950(7)	0.1626(3)	0.1627(4)	0.8(1)
O(25)	0.5079(7)	0.1045(3)	0.9148(4)	0.7(1)
O(26)	0.6195(8)	0.1255(4)	0.3362(5)	1.5(1)
O(27)	0.8090(7)	0.0844(3)	0.9351(4)	0.7(1)
O(28)	0.3687(7)	0.2201(3)	0.9526(4)	0.7(1)
O(29)	0.4615(7)	0.0203(3)	0.6150(4)	0.8(1)
H(1)	0.948(10)	0.145(5)	0.195(6)	1.0
H(2)	0.148(10)	0.229(5)	0.390(6)	1.0
H(3)	0.597(10)	0.009(5)	0.050(6)	1.0

All of the atoms except Be and H were refined using the anisotropic temperature factors (U_{ij}); the B_{iso} of H(1) through H(3) were held constant at 1.0 Å². The contents of the Zn(2) site are assumed to be ($Zn_{1.53}Be_{2.47}$), as indicated by the site occupancy factor refinement. Esd's are in given parenthesis.

ture-factors and the site contents $Zn_{1.5}Be_{2.5}$ for Zn(2). The latter were obtained from a refinement of the site-occupancy factor, which yielded 1.53(2) Zn + 2.47 Be atoms. Discussion of the rationale for assuming the crystal-chemically improbable solid-solution (Zn,Be) and the deficiencies in the alternative explanations is deferred until a later section of this report.

Introduction of anisotropic temperature-factors for all atoms except Be reduced the residual to 0.053, but temperature factors of 8 of the 29 anions were found to be nonpositive definite, and the thermal ellipsoids of most of the atoms were found to be markedly elongate parallel to [010]. Assuming that this resulted from the inadequacy of the psi scan absorption correction (which is only an approximation), a second, supplementary correction for absorption was applied to the structure-factor data using the empirical method of Walker & Stuart (1983). This produced reasonable thermal ellipsoids for all atoms except O(13), which remained nonpositive definite, and reduced the residual to 0.043. A difference synthesis revealed the probable positions of the three H atoms associated with those anions, namely O(8), O(13), and O(17), known from their bond-valence sums to be part of hydroxyl groups. It proved possible to refine the coordinates of the H atoms successfully, but not their temperature factors, and the latter were therefore fixed at B = 1.0 Å² for the remainder of the refinement. A listing of the 50 reflections having the largest values of w(|F|obs – |F|cal) showed only one, 3·7·18, with a strikingly large disparity between |F|obs and |F|cal, and this reflection was therefore deleted from the data set.

The final values of the residuals are 0.043 (unweighted) and 0.049 (weighted) for the 2495 observed reflections and 0.182 (unweighted) for all

5236 reflections. Table 3 contains the refined atomic coordinates and equivalent isotropic temperature-factors, Table 4 the anisotropic temperature-factors, Table 5 the structure-factor amplitudes, Table 6 some selected interatomic distances and angles, and Table 7 the empirical bond-valences calculated using the parameters of Brese & O'Keeffe (1991). Copies of Tables 4 and 5 have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 6.   SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)
IN SAMFOWLERITE

TABLE 6 — (Cont'd.)

CaO₈ Polyhedra

Ca(1)-O(17)	2.410(7)		Ca(4)-O(14)	2.277(6)
O(7)	2.466(6)		O(15)	2.307(6)
O(28)	2.476(6)		O(11)	2.369(7)
O(2)	2.502(6)		O(6)	2.383(7)
O(22)	2.526(6)		O(3)	2.449(7)
O(24)	2.527(7)		O(18)	2.664(7)
O(1)	2.554(7)		O(16)	2.743(7)
O(26)	2.752(7)		O(20)	3.245(7)
Mean	2.527		Mean	2.555

Ca(2)-O(13)	2.406(6)		Ca(5)-O(17)	2.344(7)
O(8)	2.419(7)		O(12)	2.466(7)
O(4)	2.447(6)		O(16)	2.475(7)
O(15)	2.481(7)		O(20)	2.490(7)
O(26)	2.518(8)		O(10)	2.491(6)
O(24)	2.572(7)		O(5)	2.493(6)
O(19)	2.620(6)		O(1)	2.610(7)
O(18)	2.735(7)		O(12)	2.838(7)
Mean	2.525		Mean	2.526

Ca(3)-O(16)	2.402(6)		Ca(6)-O(13)	2.377(6)
O(27)	2.424(6)		O(25)	2.467(6)
O(8)	2.438(7)		O(23)	2.477(6)
O(5)	2.465(6)		O(21)	2.496(6)
O(9)	2.493(6)		O(9)	2.509(7)
O(14)	2.659(6)		O(4)	2.520(7)
O(15)	2.661(7)		O(28)	2.570(6)
O(21)	2.678(7)		O(2)	2.570(7)
Mean	2.528		Mean	2.498

Ca(7)-O(25)	2.322(6)
O(29)	2.361(7)
O(11)	2.415(7)
O(4)	2.419(7)
O(3)	2.475(6)
O(2)	2.481(6)
O(19)	2.640(6)
O(22)	3.102(7)
Mean	2.527

MnO₆ Octahedra

Mn(1)-O(1)	2.138(6)		Mn(2)-O(9)	2.192(6)
O(3)	2.199(6)		O(9)	2.192(6)
O(7)	2.205(6)		O(23)	2.210(6)
O(10)	2.227(6)		O(23)	2.210(6)
O(6)	2.267(7)		O(27)	2.315(6)
O(29)	2.287(6)		O(27)	2.315(6)
Mean	2.220		Mean	2.239

ZnO₄ Tetrahedra

Zn(1)-O(24)	1.924(6)	O(5)-Zn(1)-O(11)	105.1(3)
O(11)	1.934(6)	O(11)-Zn(1)-O(28)	105.8(3)
O(5)	1.940(6)	O(5)-Zn(1)-O(28)	107.1(2)
O(28)	1.953(6)	O(5)-Zn(1)-O(24)	107.7(3)
Mean	1.938	O(24)-Zn(1)-O(28)	110.5(3)
		O(11)-Zn(1)-O(24)	119.9(2)
		Mean	109.4

Zn(2)-O(12)	1.720(8)	O(6)-Zn(2)-O(29)	103.1(3)
O(26)	1.738(7)	O(12)-Zn(2)-O(29)	106.5(3)
O(6)	1.775(8)	O(26)-Zn(2)-O(29)	108.1(3)
O(29)	1.799(7)	O(6)-Zn(2)-O(26)	110.2(3)
Mean	1.758	O(6)-Zn(2)-O(12)	112.1(3)
		O(12)-Zn(2)-O(26)	115.9(4)
		Mean	109.3

BeO₄ Tetrahedra

Be(1)-O(17)	1.61(1)	O(14)-Be(1)-O(18)	101.0(6)
O(21)	1.62(1)	O(17)-Be(1)-O(21)	106.7(7)
O(18)	1.64(1)	O(14)-Be(1)-O(17)	107.9(8)
O(14)	1.67(1)	O(14)-Be(1)-O(21)	113.0(8)
Mean	1.64	O(18)-Be(1)-O(21)	113.8(8)
		O(17)-Be(1)-O(18)	114.5(8)
		Mean	109.5

Be(2)-O(8)	1.57(1)	O(7)-Be(2)-O(10)	100.9(6)
O(10)	1.64(1)	O(8)-Be(2)-O(23)	108.2(7)
O(23)	1.64(1)	O(10)-Be(2)-O(23)	108.8(8)
O(7)	1.68(1)	O(7)-Be(2)-O(23)	109.7(8)
Mean	1.63	O(7)-Be(2)-O(8)	113.8(8)
		O(8)-Be(2)-O(10)	115.2(9)
		Mean	109.4

Be(3)-O(13)	1.57(1)	O(19)-Be(3)-O(25)	102.1(6)
O(27)	1.63(1)	O(13)-Be(3)-O(27)	107.7(7)
O(19)	1.64(1)	O(13)-Be(3)-O(25)	110.3(8)
O(25)	1.64(1)	O(25)-Be(3)-O(27)	111.0(8)
Mean	1.62	O(19)-Be(3)-O(27)	112.3(8)
		O(13)-Be(3)-O(19)	113.4(8)
		Mean	109.5

SiO₄ Tetrahedra

Si(1)-O(24)	1.620(7)	O(7)-Si(1)-O(24)	104.5(3)
O(19)	1.624(7)	O(19)-Si(1)-O(24)	106.5(3)
O(9)	1.627(6)	O(7)-Si(1)-O(19)	109.6(3)
O(7)	1.642(6)	O(7)-Si(1)-O(9)	110.9(3)
Mean	1.628	O(9)-Si(1)-O(19)	111.7(3)
		O(9)-Si(1)-O(24)	113.2(3)
		Mean	109.4

Si(2)-O(2)	1.606(6)	O(5)-Si(2)-O(20)	102.9(4)
O(5)	1.611(7)	O(14)-Si(2)-O(20)	105.9(4)
O(14)	1.624(7)	O(5)-Si(2)-O(14)	105.9(3)
O(20)	1.645(7)	O(2)-Si(2)-O(20)	111.6(3)
Mean	1.622	O(2)-Si(2)-O(14)	113.9(3)
		O(2)-Si(2)-O(5)	115.6(3)
		Mean	109.3

Si(3)-O(3)	1.594(6)	O(23)-Si(3)-O(27)	101.9(3)
O(21)	1.614(7)	O(21)-Si(3)-O(23)	104.9(3)
O(23)	1.632(6)	O(21)-Si(3)-O(27)	105.9(3)
O(27)	1.654(7)	O(3)-Si(3)-O(23)	113.3(3)
Mean	1.624	O(3)-Si(3)-O(27)	114.2(3)
		O(3)-Si(3)-O(21)	115.3(3)
		Mean	109.3

Si(4)-O(1)	1.605(6)	O(6)-Si(4)-O(29)	102.3(3)
O(11)	1.628(7)	O(6)-Si(4)-O(11)	104.1(3)
O(6)	1.639(7)	O(11)-Si(4)-O(29)	104.1(4)
O(29)	1.647(7)	O(11)-Si(4)-O(11)	113.0(4)
Mean	1.630	O(1)-Si(4)-O(29)	115.6(3)
		O(1)-Si(4)-O(6)	116.3(4)
		Mean	109.2

Si(5)-O(4)	1.586(6)	O(10)-Si(5)-O(12)	105.5(4)
O(12)	1.617(8)	O(12)-Si(5)-O(20)	105.9(4)
O(10)	1.626(7)	O(10)-Si(5)-O(20)	106.9(3)
O(20)	1.648(7)	O(4)-Si(5)-O(20)	109.5(3)
Mean	1.619	O(4)-Si(5)-O(10)	113.8(4)
		O(4)-Si(5)-O(12)	114.6(4)
		Mean	109.4

Si(6)-O(16)	1.584(6)	O(22)-Si(6)-O(26)	103.6(4)
O(26)	1.617(7)	O(18)-Si(6)-O(26)	107.0(4)
O(18)	1.618(8)	O(18)-Si(6)-O(22)	108.8(4)
O(22)	1.663(7)	O(16)-Si(6)-O(22)	109.2(3)
Mean	1.620	O(16)-Si(6)-O(18)	113.7(4)
		O(16)-Si(6)-O(26)	114.0(4)
		Mean	109.4

Si(7)-O(15)	1.599(6)	O(22)-Si(7)-O(28)	103.9(3)
O(25)	1.617(6)	O(25)-Si(7)-O(28)	104.5(3)
O(28)	1.627(7)	O(22)-Si(7)-O(25)	105.6(4)
O(22)	1.640(7)	O(15)-Si(7)-O(22)	112.8(3)
Mean	1.621	O(15)-Si(7)-O(28)	114.4(4)
		O(15)-Si(7)-O(25)	114.6(4)
		Mean	109.3

H-O and O-H-O

H(1)-O(8)	0.74(9)	O(8)-H(1)-O(14)	144(9)
O(14)	2.24(9)	O(8)-H(1)-O(18)	122(9)
O(18)	2.50(10)	O(8)-H(1)-O(17)	149(9)
O(17)	2.55(9)		
O(8)-O(14)	2.872(9)		
O(18)	2.964(10)		
O(17)	3.211(8)		

H(2)-O(17)	0.80(8)	O(17)-H(2)-O(28)	153(10)
O(28)	2.18(9)		
O(17)-O(28)	2.916(8)		

H(3)-O(13)	0.72(9)	O(13)-H(3)-O(25)	130(9)
O(25)	2.36(9)	O(13)-H(3)-O(19)	147(9)
O(19)	2.41(10)	O(13)-H(3)-O(13)'	145(9)
O(13)'	2.54(8)		
O13-O(25)	2.879(9)		
O(19)	3.042(10)		
O(13)'	3.162(11)		

TABLE 6 — (Cont'd.)

Shared Vertex T–T

Zn(1)–Si(7)	2.967(3)		Zn(2)–Si(6)	2.821(4)
Si(2)	2.982(3)		Si(5)	2.849(4)
Si(1)	3.095(3)		Si(4)	2.972(4)
Si(4)	3.166(3)		Si(4)	3.022(4)
Mean	3.052		Mean	2.916
Be(1)–Si(6)	2.81(1)		Be(2)–Si(5)	2.80(1)
Si(2)	2.88(1)		Si(1)	2.86(1)
Si(3)	2.92(1)		Si(3)	2.91(1)
Mean	2.87		Mean	2.86
Be(3)–Si(7)	2.80(1)		Si(1)–Be(3)	2.810(13)
Si(1)	2.81(1)		Be(2)	2.863(14)
Si(3)	2.94(1)		Zn(1)	3.095(3)
Mean	2.85		Mean	2.923
Si(2)–Be(1)	2.881(14)		Si(5)–Be(2)	2.797(14)
Zn(1)	2.982(3)		Zn(2)	2.849(4)
Si(5)	3.046(4)		Si(2)	3.046(4)
Mean	2.970		Mean	2.897
Si(3)–Be(2)	2.905(13)		Si(6)–Be(1)	2.810(13)
Be(1)	2.915(13)		Zn(2)	2.821(4)
Be(3)	2.941(13)		Si(7)	3.050(4)
Mean	2.920		Mean	2.894
Si(4)–Zn(2)	2.972(4)		Si(7)–Be(3)	2.798(12)
Zn(2)	3.022(4)		Zn(1)	2.967(3)
Zn(1)	3.166(3)		Si(6)	3.050(4)
Mean	3.053		Mean	2.938

Esd's are in parenthesis. Distances and angles are based on the cell parameters a 9.0677(18), b 17.992(2), c 14.586(2), and β 104.86(1)°.

DESCRIPTION OF THE STRUCTURE

The structural description of the samfowlerite may be simplified by treating it as a structure composed of layers of vertex-sharing TO_4 tetrahedra (T = Si,Be,Zn) alternating with layers of vertex- and edge-sharing CaO_8 bicapped trigonal prisms and MnO_6 octahedra, the octahedron being a special case of the trigonal antiprism. The layering is parallel to (102). Polyhedra in the two types of layers share vertices and edges across the interlayer boundaries to form the three-dimensional network that constitutes the entire structure. These cross-boundary linkages are so numerous as to prevent samfowlerite from being considered a true layer structure, a fact made clear by the absence of the perfect cleavage normally associated with such structures. However, as noted previously, both the number and size of crystals available for study are very small, and thus an inferior cleavage (perhaps on {102}) could easily have escaped notice.

The detailed configuration of the layer of tetrahedra can be understood with the aid of a diagram showing the tetrahedral nodes (Fig. 2), which shows a continuous network of 4-, 5-, and 8-membered rings. The environments of the divalent cations are uniform, all Zn atoms being 4-connected to four Si, and all Be atoms being 3-connected to three Si, but, whereas the Si atoms are also all 3-connected, their T–T linkages

are of different types. That is, Si(1) is connected to two Be plus one Zn, Si(3), to three Be, Si(4), to three Zn, and Si(2), Si(5), Si(6), and Si(7) each to one Be, one Zn, and one Si. The layers of tetrahedra thus contain both ortho- and disilicate groups in the ratio 3:2, the dimers being $Si(2)Si(5)O_7$ and $Si(6)Si(7)O_7$. An alternative representation of the layers of tetrahedra appears in Figure 3, which shows an edge-view of three such layers, the SiO_4 and Si_2O_7 groups being drawn as solid polyhedra, and the BeO_4 and ZnO_4 groups as skeletal tetrahedra to improve clarity.

An edge-view of the prismatic layers appears in Figure 4. In the edge-view, neighboring CaO_8 bicapped trigonal prisms are linked in two ways. For Ca(1) through Ca(5), one capping ligand is shared with one adjacent CaO_8 group, and the second capping ligand is shared with the other adjacent CaO_8 group, i.e., the capping O atoms of one group are simultaneously vertex O atoms of the prisms of the two adjacent groups. In the case of Ca(6) and Ca(7) (upper right corner in Fig. 4), the method of linking adjacent prisms is quite different, with the $Ca(6)O_8$ and $Ca(7)O_8$ groups sharing one prism edge and one capping ligand (which is not a vertex atom for either). However, the linkage of $Ca(6)O_8$ and $Ca(7)O_8$ to the neighboring groups, $Ca(3)O_8$ and $Ca(4)O_8$, respectively, is of the normal type. If the edge-view of any layer shown in Figure 4 is extended in the third dimension along [010] into a full layer, the CaO_8 polyhedra are seen to share prism vertices and edges with one another and with the MnO_6 octahedra, the latter groups being centered at $y \approx 0$ and ½. The CaO_8 bicapped prisms are quite distorted, with many of their lateral edges having very different lengths within the same polyhedron. The $Mn(1)O_6$ and $Mn(2)O_6$ octahedra are more nearly regular.

The presence of three hydroxyl groups [O(8)–H(1), O(13)–H(3), and O(17)–H(2)] in the structure of samfowlerite, together with the conspicuously low bond-valence sums for some of the anions (Table 7), suggests the existence of hydrogen bonding. A survey of the O–H distances and O–H–O angles in Table 6, combined with the bond-valence data, suggests two possible hydrogen-bonded configurations involving H(1), namely O(8)–H(1)...O(18) and O(8)–H(1)...O(14). The distances and angles for the latter are more reasonable than those for the former, but the valence sums in Table 7 give a contrary indication. That is, O(18), with a sum of 1.79 v.u., is conspicuously underbonded and is therefore in need of an additional valence-contribution by way of a hydrogen bond, but the sum for O(14) already equals its ideal value of 2.0 v.u. On this basis, O(18) would seem to be the more probable choice for a hydrogen bond receptor. There is no similar ambiguity involving H(2) and H(3), however. The distance and angle data in Table 6 are all in accord with the existence of hydrogen-bonded configurations O(17)–H(2)...O(28) and
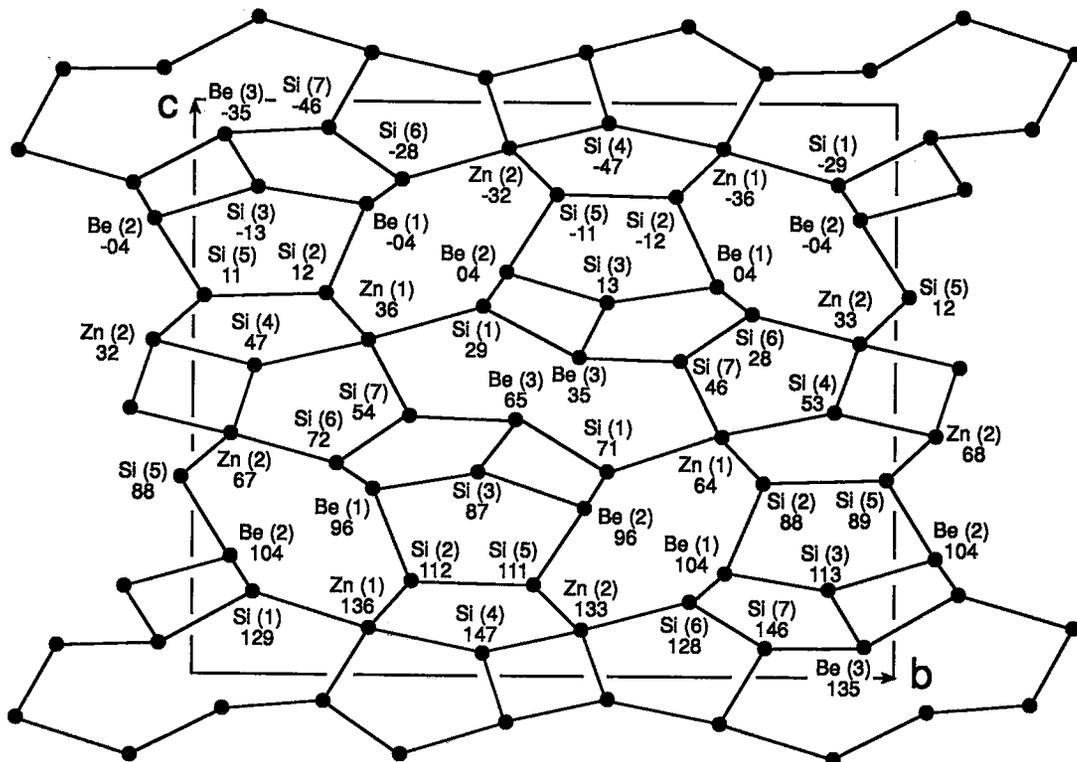
FIG. 2. One layer of tetrahedra in samfowlerite viewed in projection down [100] and represented as a tetrahedral node diagram. Numbers beneath atomic symbols are x coordinates ×100.

O(13)–H(3)...O(19), and this is supported by the valence sums of 1.95 v.u. for O(28) and 1.83 v.u. for O(19). The possibility of a hydrogen bond between H(3) and O(25) is unlikely given the low value of the O(13)–H(3)–O(25) angle (130°) and the fact that O(25) is already overbonded, with a valence sum of 2.15 v.u.

As to the remaining O^{2-} anions with valence sums less than 1.90 v.u., namely O(1), O(2), O(9), O(15), and O(16), it is not possible to invoke hydrogen bonding as a source for the additional valence needed, as none of the H atoms makes a sufficiently close approach for such bonding to occur. Bond-valence considerations do, however, provide a simple explanation for the two Ca–O distances of extraordinary length, namely 3.245(7) Å for Ca(4)–O(20) and 3.102(7) Å for Ca(7)–O(22). [These fall outside of the range of Ca–O bond distances given by Baur (1970), 2.25 to 2.96 Å, but O(20) and O(22) must be assumed to be bonded to Ca(4) and Ca(7), respectively, to complete the CaO_8 coordination that is the rule in this structure.] Atoms O(20) and O(22) are both coordinated to (2Si+2Ca) and are, respectively, the bridging anions in the two disilicate groups Si(2)Si(5)O$_7$ and

Si(6)Si(7)O$_7$. The Pauling bond strengths to both O(20) and O(22) are an excessive 2 ½ v.u., but the observed Ca–O lengthening reduces their empirical valence-sums to more reasonable values of 2.16 and 2.13 v.u., respectively.

DISCUSSION

We have already briefly noted the apparent existence of solid solution involving Zn and Be on the Zn(2) site of samfowlerite and the probability that this anomalous situation exists only in the average structure of the mineral, the real structure having symmetry lower than $P2_1/c$ as a result of ordering of Zn and Be onto separate structural sites. Four lines of evidence support the existence of apparent (Zn,Be) solid solution in the average structure: the observed Zn(2)–O interatomic distances, the isotropic temperature-factors of the anions coordinating the Zn(2) site, the results of the electron-microprobe analysis, and charge-balance considerations affecting the choice of an appropriate chemical formula.

Refinement of the site-occupancy factor of Zn(2), assuming simultaneous occupancy by both species,
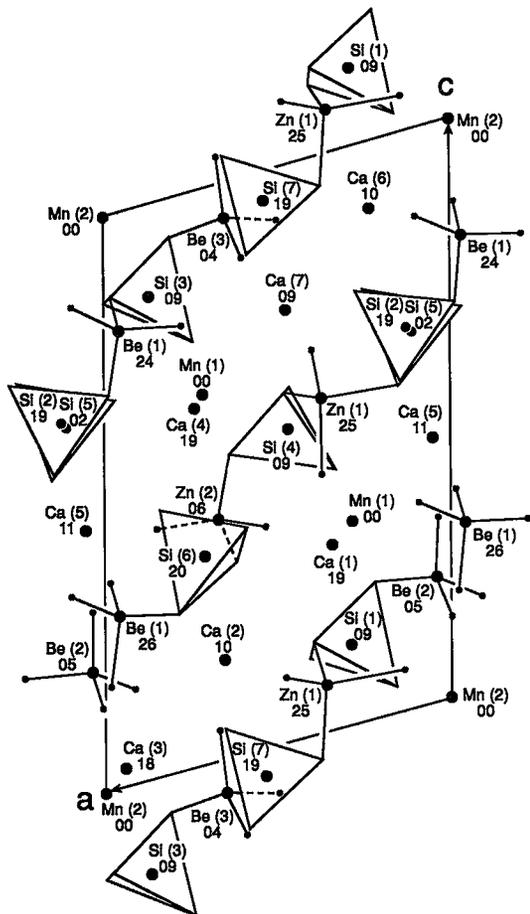
FIG. 3. An edge-view of three layers of tetrahedra in samfowlerite from $y = 0$ to $\frac{1}{4}$ in projection on (010). To reduce polyhedral overlap and improve clarity, the BeO_4 and ZnO_4 groups are shown as skeletal tetrahedra, and only the cation positions in the neighboring layers of prisms are shown. Numbers beneath atomic symbols are y coordinates $\times 100$. The $Si(2)Si(5)O_7$ dimer appears at the upper right of the cell, the shared anion O(20) being situated at (0.05,0.10,0.63). The $Si(6)Si(7)O_7$ dimer (considered as a whole) is outside the range of the diagram along y, the shared anion O(22) being located nearly on the glide plane at (0.58,0.24,0.87).

FIG. 4. An edge-view of two layers of CaO_8 bicapped prisms in samfowlerite from $y = 0$ to $\frac{1}{4}$ in projection on (010). To improve clarity, only the cation positions in the neighboring layers of tetrahedra are shown. Numbers beneath atomic symbols are y coordinates $\times 100$. In most cases, the two capping ligands of one CaO_6 prism are simultaneously vertex ligands for the two neighboring CaO_6 prisms, as shown (on the lower left of the figure) for $Ca(2)O_6$, for which the two capping ligands (marked with asterisks) are shared with $Ca(1)O_6$ and $Ca(3)O_6$.

yielded 38.3% ($\sim\frac{3}{8}$) Zn and 61.7% ($\sim\frac{5}{8}$) Be. Using this Zn/Be ratio and the grand mean values of 1.958 Å and 1.634 Å for ^{IV}Zn–O and ^{IV}Be–O, respectively, from the survey paper by Baur (1981), the mean bond-length for the Zn(2) site is predicted from a simple weighted average to be 0.383(1.958) + 0.617(1.634) = 1.758 Å. This result is the same as the observed mean value of 1.758 Å for Zn(2)–O in Table 6, the observed

range being 1.720(8) to 1.799(7) Å. Alternatively, using Baur's method, which involves equations of the form $d(A–X) = [d(A–X)_{mean} + b\Delta p(X)]$ Å, and the observed Zn/Be ratio yields the same result. This is so because the parameter b is 0.18 for both $(Be–O)_{mean}$ and $(Zn–O)_{mean}$ and because, of the four O atoms coordinated to Zn(2), two have $\Delta p(X) = -0.04$ and the other two $\Delta p(X) = +0.04$. Thus, the $b\Delta p(X)$ terms cancel one another, and the expression for the predicted mean bond-length of the (Zn,Be) site reduces to the simple weighted average. The point, of course, is that regardless of the method of calculation, the predicted value for the mean Zn(2)–O distance derived from the refined contents of the site is the same as the observed value.

TABLE 7. EMPIRICAL BOND-VALENCES (V.U.) FOR SAMFOWLERITE

	Ca1	Ca2	Ca3	Ca4	Ca5	Ca6	Ca7	Mn1	Mn2	Zn1	Zn2	Be1	Be2	Be3	Si1	Si2	Si3	Si4	Si5	Si6	Si7	ΣVₐ
O1	0.21				0.18													1.05				1.83
O2	0.24					0.20	0.25									1.05						1.74
O3				0.27			0.25	0.33									1.08					1.93
O4		0.27				0.22	0.30												1.11			1.90
O5			0.26		0.24					0.53						1.04						2.07
O6				0.33				0.28			0.48							0.96				2.05
O7	0.26							0.33					0.44		0.95							1.98
O8			0.30	0.28									0.60									1.18
O9			0.24			0.23			0.34 (x2)							0.99						1.80
O10					0.24			0.31				0.50								1.00		2.05
O11				0.34				0.30		0.54									0.99			2.17
O12					0.26,0.10						0.56									1.02		1.94
O13		0.31				0.33								0.59								1.23
O14			0.15	0.43								0.46				1.00						2.04
O15			0.25	0.15	0.40																1.07	1.87
O16				0.31	0.12	0.25														1.11		1.79
O17	0.30				0.36							0.54										1.20
O18		0.13		0.15									0.49								1.02	1.79
O19		0.17					0.16							0.50		1.00						1.83
O20				0.03	0.24												0.95		0.94			2.16
O21			0.15			0.24						0.53						1.03				1.95
O22	0.22						0.05													0.90	0.96	2.13
O23						0.25			0.32 (X2)					0.49					0.98			2.04
O24	0.22	0.20								0.55						1.01						1.98
O25						0.26	0.38						0.49								1.02	2.15
O26	0.12	0.23									0.53									1.02		1.90
O27			0.29						0.24 (X2)					0.52			0.92					1.97
O28	0.25					0.20				0.51											0.99	1.95
O29							0.35	0.26			0.45								0.94			2.00
ΣVc	1.82	1.86	1.83	2.07	1.87	1.93	2.04	1.90	1.80	2.13	2.02	2.02	2.03	2.10	3.95	4.04	4.01	3.94	4.07	4.05	4.04	

The bond valences for Zn(2) are calculated assuming 38.3% Zn and 61.7% Be, as indicated by the site occupancy factor refinement. Atoms O(18), O(19), and O(28) receive an additional valence contribution from H(1), H(3), and H(2), respectively, through hydrogen bonds from the hydroxyl oxygens O(8), O(13), and O(17).

If two cations as different in size as Be^{2+} and Zn^{2+} simultaneously populate the same set of structural sites, then there must be at least a small variation in site environment as the positions of the coordinating anions adjust to accommodate the larger or the smaller cation. Such positional disorder should manifest itself in temperature-factors for the anions that are conspicuously higher than those of other anions in the structure. An examination of the equivalent isotropic temperature-factors of the anions coordinated to Zn(2) shows the expected effect for three out of four of them. The Zn(2)–O bond distances (in Å) and equivalent isotropic temperature-factors (in Å²) are 1.720(8) and 1.9(1) for O(12), 1.738(7) and 1.5(1) for O(26), 1.775(8) and 1.2(1) for O(6), and 1.799(7) and 0.8(1) for O(29). The remaining 25 anion sites in the asymmetric unit have an average equivalent B_{iso} of 0.78 Å², and only two have values greater than 1.0 Å², those being 1.1(1) Å² for O(18) and 1.3(1) Å² for O(20). The average B_{iso} value for the anions coordinated to Zn(2) is 1.4 Å² compared to 0.74 Å² for the eight TO_4 groups that do not share any vertices with Zn(2)O₄. Clearly, the temperature-factors associated with the Zn(2)O₄ tetrahedron are anomalous relative to those of the other tetrahedral groups in the structure. An exception is B_{iso} of Zn(2), itself, which is normal and equal to that of Zn(1) within one esd. This implies that, whereas the positions of the coordinating anions are correlated with the identity of the cation occupying Zn(2), the position of the cation is not, and remains unchanged regardless of whether T is Zn^{2+} or Be^{2+}. Note also that there is an inverse correlation between Zn(2)–O bond length and the B_{iso} values of the O ligands. The significance of this, if any, is unknown, but it is clear that the relatively large temperature-factors of the anions predicted by the (Zn,Be) solid-solution model do, in fact, occur in the Zn(2)O₄ tetrahedron.

The empirical unit-cell contents of samfowlerite derived from the results of the electron- and ion-microprobe analyses before the solution of the crystal structure became available are $(Ca_{27.8}Mg_{0.2})_{\Sigma 28.0}Mn_{6.0}Zn_{5.3}Be_{10.2}Si_{28.0}O_{113.0}H_{19.3}F_{2.4}$. Except for Zn and Be, the coefficients of all of the metal and Si atoms have integral values that are nicely consistent with the ranks of the available equipoints in space group $P2_1/c$. The value for Be was obtained from the ion microprobe and has a large uncertainty associated with it; indeed, the crystal-structure analysis showed that it is much too small, but the value for Zn was obtained from the same electron-microprobe analysis that produced the "good" values for (Ca,Mg), Mn, and Si. A value of 5.3 Zn per cell made it difficult to derive an acceptable chemical formula; i.e., assuming five Zn per cell produced a formula that was charge-balanced but inconsistent with the 2- and 4-fold

equipoints of $P2_1/c$, whereas an assumption of six Zn produced the opposite problem. Once the structure solution was obtained and the anomalous character of the Zn(2) site was noted, an occupancy-factor refinement for Zn(2) assuming Zn as the sole species on the site produced a value of 1.76(2) atoms, but this also is inconsistent with a charge-balanced formula. However, when the possibility of (Zn,Be) solid solution on Zn(2) was recognized and a second occupancy-factor refinement produced the site contents 1.53(2) Zn + 2.47 Be, the problem with charge balance was resolved. The (Zn,Be) solid-solution model and the electron-microprobe analysis are therefore essentially in agreement both on the number of Zn atoms per cell (5.5 *versus* 5.3, respectively) and the fact that this number is nonintegral.

Two objections to the foregoing interpretation of the anomalous character of the Zn(2) site are (1) that the proposed complete order of Zn and Be atoms in the true (as opposed to the average) structure should produce a superstructure, but none is observed in the diffraction patterns, and (2) that the Zn(2) site may indeed be occupied in a completely normal fashion by a single atomic species other than Zn^{2+} or Be^{2+}. Taking the second of these first, the obvious candidates for the "unknown" cation are Al^{3+} and Si^{4+}. The former has an X-ray scattering power similar to that observed for the site and the right bond-distance to oxygen [1.752 Å according to Baur (1981)], but its presence is ruled out by results of the chemical analysis. The latter is likewise excluded by the chemical data, which indicate only 28.0 Si per cell, and by the observed mean Zn(2)–O distance of 1.758 Å, which is too long to represent ^{IV}Si–O.

The other objection, which concerns the absence of a superstructure, is less easily dismissed, as the large difference in scattering power between Zn and Be should produce such a feature in the diffraction patterns of samfowlerite. A possible explanation is that the crystals are composed of domains, each domain possessing an ordered arrangement of Zn and Be atoms and a symmetry lower than the observed $P2_1/c$, but that the average structure, summed over all domains, has the observed monoclinic space-group and apparent (Zn,Be) solid solution on the Zn(2) site. This hypothesis could be checked in a study using electron microscopy, but this is not possible at present owing to the lack of sufficient available material.

Finally, there is the question of the relationship of samfowlerite to other silicate structures. The presence of mixed ortho- and disilicate ions places samfowlerite with the epidote group, the pumpellyite group, and vesuvianite in the classification of Strunz (1970),

and Table 11.1 of Liebau (1985) lists several synthetic species containing the same mixed anions. Other than this, however, samfowlerite shows no great structural affinities to any of them, and it would seem, therefore, that the new mineral represents a new and unique structural type.

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