

Wawayandaite, a new calcium manganese beryllium boron silicate from Franklin, New Jersey

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ABSTRACT

Wawayandaite, a new mineral from Franklin, New Jersey, is found associated with willemite, friedelite, and numerous other minerals. It is monoclinic, space group $P2/c$ or Pc , with $a = 15.59(2)$, $b = 4.87(1)$, $c = 18.69(4)$ Å, $\beta = 101.84(15)^\circ$, $Z = 1$. Chemical analyses yielded BeO 17.6, MgO 1.9, CaO 24.8, MnO 9.8, ZnO 1.1, B₂O₃ 3.8, SiO₂ 28.2, H₂O 9.6, Cl 3.0, less O = Cl 0.7, total = 99.1 wt%. The idealized chemical formula is $\text{Ca}_{12}\text{Mn}_4\text{B}_2\text{Be}_{18}\text{Si}_{12}\text{O}_{46}(\text{OH},\text{Cl})_{30}$.

Wawayandaite occurs as colorless platy crystals with a pearly luster; many are strongly curved. Cleavage is perfect on {010}, $D_{\text{meas}} \approx 3.0$, $D_{\text{calc}} = 2.98$ g/cm³. It is biaxial, negative, with $2V = 85^\circ$, $\alpha = 1.619$, $\beta = 1.631$, and $\gamma = 1.641$.

INTRODUCTION

Our preliminary investigation of the mineral described here indicated it was a species new to science, and our subsequent detailed study has borne out this initial finding. We have named this mineral *wawayandaite* in allusion to the grossly curved and winding habit of the preponderance of its crystals. The word “wawayanda,” in the language of the early inhabitants of the Franklin area, the Lenni Lenape Indians, means “many or several windings.” The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Cotype specimens are in the Smithsonian Institution collection under catalogue numbers NMNH 93391 and NMNH R5869. A small amount of powdered wawayandaite, the remainder of the thermoanalytical sample, is in the Royal Ontario Museum collection under catalogue number M44227.

DESCRIPTION

Wawayandaite occurs rarely in sharp, platy, 0.1-mm-diameter, very thin crystals, tabular on {100}, and twinned on (100); other forms are indiscernible. Such crystals are exceedingly rare. The majority of wawayandaite crystals are grossly curved in all dimensions and are exceedingly thin, resembling diaphanous, warped, and freely formed

barysilite; some Franklin prehnite is slightly similar. Wawayandaite also occurs as exceedingly fine-grained aggregates, similar to a clay.

Wawayandaite is colorless and transparent; fine-grained aggregates are white and opaque, and the few known platy, flat crystals are decidedly turbid. An intense pearly luster, very obvious on the grossly curved thin crystals, is not clearly discernible on the flat platy crystals. The claylike, fine-grained aggregates have a variable pearly-to-dull luster. The streak is white. Wawayandaite platy crystals are brittle, but the thin curved crystals are quite flexible. An apparent cleavage is perfect on {100}. The hardness (Mohs') is near 1 for the aggregate, but the best platy crystals are too small for testing. The density of the aggregates is less than 1.0 g/cm³. The density of crystal clusters, measured with heavy-liquid techniques, varies substantially from 2.4 to 3.0 g/cm³. Since this variation is likely due to trapped air, we have adopted the highest value, which is close to the calculated density, 2.98 g/cm³.

Optically, wawayandaite is biaxial, negative, $2V_{\text{obs}} = 85.2(2.6)^\circ$; the indices of refraction in Na light are $\alpha = 1.619$ (calc.), $\beta = 1.631(1)$, and $\gamma = 1.641(1)$; dispersion is strong, $r < v$. The orientation is $X \wedge a = 11.5^\circ$ within the obtuse β angle, $Y \parallel b$, $Z \parallel c$. Wawayandaite shows no observable pleochroism or discernible fluorescence in ultraviolet radiation.

TABLE 1. X-ray powder diffraction data for waywayandaite

d_{obs}^*	d_{obs}	d_{calc}^{**}	hkl	d_{obs}^*	d_{obs}	d_{calc}	hkl
90	15.1	15.3	100†	20	2.330	2.337	416
30	9.2	9.1	002†			2.333	108
20	8.6	8.7	102†			2.329	602
20	7.65	7.63	200†			2.328	216
5	7.20	7.22	102†			2.327	504
						2.325	208
5	6.56	6.56	202†				
20	4.61	4.64	110	50	2.249	2.254	610
		4.57	004			2.252	613
		4.57	111			2.245	513
2	4.33	4.33	204†	5	2.225	2.225	702
		4.30	012			2.219	117
2	4.11	4.11	210	20	2.179	2.181	322
		4.11	211			2.179	700†
		4.10	302			2.174	406
2	3.819	3.814	400†	20	2.104		
2	3.501	3.519	310	10	2.053		
2	3.365	3.368	311	10	1.990		
		3.365	114	5	1.953		
10	3.244	3.244	213	1	1.870		
		3.239	214†	2	1.782		
100	3.157	3.161	114†	2	1.730		
70	3.001	3.004	410	5	1.712		
		3.002	314	20	1.684		
		3.001	412†				
				30	1.632		
5	2.902	2.901	214	2	1.611		
		2.895	215	15	1.560		
60	2.718	2.726	412	2	1.516		
		2.720	414†	5	1.441		
70	2.626	2.625	116†				
		2.625	511	2	1.389		
30	2.581	2.586	510	2	1.337		
		2.585	016	5	1.315		
				2	1.289		
				2	1.269		

Note: Data were obtained using a 114.6-mm-diameter Gandolfi camera with $\text{CuK}\alpha$ radiation and Si standard.

* Intensities visually estimated.

** Interplanar spacings calculated with lattice parameters $a = 15.586$, $b = 4.874$, $c = 18.690$ Å, $\beta = 101.84^\circ$.

† Reflection indices used in least-squares refinement. Choices of indices in part based on intensities observed on single-crystal diffraction patterns.

CHEMICAL COMPOSITION

Due to the paucity of material, wawayandaite could not be analyzed using classical wet-chemical methods. Accordingly, a number of different analytical procedures were utilized. Wavelength-dispersive electron-microprobe scans and ion-microprobe scans failed to reveal measurable quantities of elements other than those reported here.

Microprobe analysis was employed for the determination of Si, Mg, Ca, Zn, Mn, and Cl, utilizing an ARL-SEM-Q electron microprobe. The operating conditions were: 15-kV accelerating voltage, 0.025- μ A. A sample current measured on brass, and a 10- μ m beam that was moved over the surface during analysis to minimize loss of volatiles. The standards used were wollastonite (Ca,Si), hornblende (Mg), zincite (Zn), manganite (Mn), and chlorapatite (Cl); the data were corrected using a modified version of the MAGIC-4 program (Colby, 1980).

Water and other volatiles were determined using a Mettler TA-1 thermoanalyzer coupled to an Inficon IQ200

quadrupole mass spectrometer for thermogravimetric analysis (TGA) and the identification of the evolved gas species (EGA). Minor visible impurities were removed from the sample prior to TGA-EGA analysis by hand picking under the microscope. Following weighing at 40% relative humidity at 23 °C a sample of 729 ± 10 μ m was placed in a Pt₉₀Rh₁₀ crucible and allowed to stabilize in the thermoanalyzer for 2 h at 20 °C at an ultimate vacuum of 1×10^{-7} torr. The small sample size (near instrumental limits) limited the accuracy of the analysis. During the two-hour period in vacuum the sample lost approximately 1 wt% of volatiles (presumably H₂O), but when one considers the standard error for this analysis is ± 2 wt%, this loss is not significant. The sample was heated in a quartz-glass furnace at a rate of 10 °C/min to a maximum temperature of 1050 °C. A loss of 9.6 (± 2) wt% H₂O occurred between 330 and 650 °C, with maximum losses at 580 and 614 °C (measured on the total evolved gas pressure curve). A loss in this temperature range suggests that the H₂O is present in the wawayan-

daite structure as OH ion. A further 3% weight loss followed between 670–790 °C with a maximum at 700 °C. The volatile responsible for this second loss was not detected by the mass spectrometer, presumably because it condensed on the surfaces of the vacuum column before it reached the detector. Very minor amounts of CO₂ and CO were detected in this temperature range, probably originating from minor calcite impurities in the sample.

B and Be were determined by ion-microprobe mass spectrometry utilizing a Cameca IMS-3F ion microanalyzer. The primary beam of negative O ions had a 100 nA current and a net impact energy of 14.0 keV on the specimen. The beam was focused and rastered on a 250 μm × 250 μm square area. Positive secondary ions of B-11, Be-9, Si-30, and Ca-40 were collected in a circular area 60 μm in diameter centered at the square raster area, and the signals were detected by an electron multiplier. A sample voltage of 30 V was applied to suppress the molecular ion signals. Standard uvite (B) and berylite (Be) and wawayandaite were measured under identical conditions. For each standard, a sensitivity factor was generated based on the stated weight percentages of the constituents. These sensitivity factors were then used to determine the concentration of B and Be in wawayandaite. The results are (using uvite) B/Si = 0.886, (using berylite) Be/Ca = 0.358, yielding, respectively, 3.8 wt% B₂O₃ and 17.6 wt% BeO. There is only a small body of data on the accuracy of ion microprobe determinations for B and Be in minerals. The data for Be obtained using this technique in the original description of ehrlite (Robinson et al., 1985) were found by Hawthorne and Grice (1987) to be in error on the high side, so the potential for error exists here as well. The combined analyses yield: SiO₂ 28.2, MgO 1.9, CaO 24.8, ZnO 1.1, MnO 9.8, B₂O₃ 3.8, BeO 17.6, H₂O 9.6, Cl 3.0, less O ≡ Cl 0.7, total = 99.1 wt%. The empirical formula, calculated on the basis of 76 O + Cl atoms, is (Ca_{11.12}Mn_{3.48}Mg_{1.19}Zn_{0.34})_{216.13}B_{2.75}Be_{17.71}Si_{11.81}(OH)_{26.80}Cl_{2.12}O_{47.08}. This is idealized as Ca₁₂Mn₄B₂Be₁₈Si₁₂O₄₆(OH,Cl)₃₀, with Z = 1.

The formula is consistent with the equipoint rank requirements of the space group, but the poor quality of the twinned crystals precludes a crystal-structure determination that would permit determination of site occupancies. We note the discrepancy between the determined and theoretical B values, but have no explanation for this other than analytical error. The possible space groups have equipoint ranks of only 2 or 4, and we have chosen 2 B atoms per unit cell because that value is closer than 4 to the observed value (2.75) and because it provides better agreement with the analytical total. Solid solution of OH and Cl has been inferred. The numbers of Ca and Mn atoms are idealized as 12 and 4, respectively, because there is generally a high degree of order of Ca and Mn where more than one site is available in Franklin minerals.

X-RAY CRYSTALLOGRAPHY

Wawayandaite was studied using the Weissenberg and precession methods. Single-crystal diffraction patterns

showed Laue symmetry 2/m. There is no extinction rule for 0k0 reflections, but all of the h0l reflections having $l = 2N + 1$ are unobserved. The space group is therefore *Pc* or *P2/c*. Those general reflections having $l = 2N + 1$ are commonly weak, implying that there is a superstructure with periodicity $c/2$. The crystals that were studied exhibit twinning on {100}, precluding the measurement of intensities for a structure determination. Corresponding reflection intensities from both twin orientations appear to be equal, consistent with, but not proving, that the twin domains are small, randomly distributed, and of equal volume. This implies that untwinned crystals may be rare or nonexistent.

Powder X-ray diffraction data (Table 1) were obtained using a 114.6-mm diameter Gangolfi camera, CuK α radiation (Ni-filtered), Si as an internal standard, and a sample consisting of several small crystals. Separate patterns were obtained in which Si was not present in order to record reflections that overlapped those of Si. Where multiple indexing of reflections was indicated, specific indices were chosen, where possible, on the basis of visibly observed intensities from single-crystal patterns. Care should be used in interpreting wawayandaite X-ray diffraction patterns, as willemite can be so abundant and intimately mixed that strong reflections of willemite may be present, resulting in some ambiguity in identification. Least-squares refined lattice parameters are $a = 15.59(2)$, $b = 4.87(1)$, $c = 18.69(4)$ Å, $\beta = 101.84(15)^\circ$, corresponding to a unit cell with $Z = 1$.

OCCURRENCE AND PARAGENESIS

Wawayandaite was found on museum specimens from the Franklin Mine, Franklin, Sussex County, New Jersey. It is a late-stage vein mineral, occurring with superb, 6 × 1 mm, prismatic willemite crystals, the best ever found at Franklin, and with 5 mm, equant, rhombic, calcite crystals; both of which occur on a vein surface of andradite on calcite-poor, willemite-franklinite ore. Pink hodgkinsonite and colorless, twinned cahnite crystals also are on the specimen. These minerals are partially coated with a druse of dull reddish brown friederite. Wawayandaite occurs last in this sequence, forming platy crystals, warped crystals, and clay-like aggregates coating the earlier formed minerals.

Although crystal habits and textures vary, the host assemblage and matrix is invariant, and there is no doubt that these specimens all came from one isolated occurrence. It was found prior to 1923 because specimens were in collectors' hands by then, having surely been retained for their superb willemite crystals. Thus, like the specimens in which a number of Franklin minerals were discovered, wawayandaite specimens also were preserved by serendipity.

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