Franklinphilite, the manganese analog of stilpnomelane, from Franklin, New Jersey

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ABSTRACT

Franklinphilite, the manganese analog of stilpnomelane, ideally $K_4Mn_{48}(Si,Al)_{72}(O,OH)_{216} \cdot nH_2O$ (with $n \simeq 6$), is triclinic, space group P1 or $P\overline{1}$; the pseudo-orthohexagonal unit cell has parameters a = 5.521(4), b = 9.560(6), and c = 36.57(5) Å, with V = 1930.2(5) Å³, and Z = 3/8. Holotype material, with 54 mol % of the endmember, is dark brown, occurs in radial aggregates of platy crystals, has a density of 2.66 g/cm³, and is biaxial, negative, with $\alpha = 1.545(5)$, $\beta = 1.583(3)$, and $\gamma = 1.583(3)$; pleochroism is distinct with X = pale yellow and Y = Z = deep brown. In the holotype specimen, franklinphilite occurs in a centimeter-wide vein intimately associated with friedelite, and crosscutting a breccia of aegirine, calcite, chamosite and interlayered 7-Å and 14-Å phyllosilicates. It also occurs with nelenite, rhodonite and tirodite in another assemblage. Both occurrences are from Franklin, Sussex County, New Jersey.

INTRODUCTION

During the course of an extensive investigation of layer silicates from Franklin and Sterling Hill, Sussex County, New Jersey, we noted a specimen of stilpnomelane from Franklin with an anomalously high Mn content. Manganoan stilpnomelane has been identified before, and reported previously on a sample from Franklin which was Mndominant (Dunn *et al.*, 1984). However, that material contained only 35 mol % of the theoretical manganese end-member, being Mn-dominant by a plurality; accordingly, we deferred naming it then. Newly discovered manganese-dominant material has now been characterized; it contains 54 mol % of the end-member and its description follows.

We have named this mineral *franklinphilite* using the locality-name root *Franklin* and the Greek word $\phi_i\lambda\delta\varsigma$ (*philos*) for "friend." The name is in allusion to its chemical composition; it contains the elements which contribute to the uniqueness of the chemical relations of Franklin and Sterling Hill. The name also honors the many geologists, mineralogists and collectors who have been *friends of Franklin* and who have contributed to our understanding of the deposit. The new species and the name have been approved by the IMA Commission on New Minerals and Mineral Names. The holotype specimen is deposited in the Smithsonian Institution under catalogue # NMNH 167390.

Parsettensite has informally been considered a possible Mn-analog of stilpnomelane and the status of this mineral has long been ambiguous. Recently, Guggenheim (1986), Ozawa *et al.* (1986), and Guggenheim and Eggleton (1987, 1988) have investigated parsettensite and found it to have a unique modulated structure, distinct from that of stilpnomelane.

OCCURRENCE

Franklinphilite is known from two distinct assemblages at Franklin, Sussex County, New Jersey. Given the large number of secondary manganese silicates at this locality, it is probable that other franklinphilite assemblages exist.

Franklinphilite was found on the Buckwheat dump; nothing is known of its original mine location or of its geological setting. Although the specimen is of anomalous appearance, it is assuredly from the Franklin mine. The original massive specimen was from a lowtemperature assemblage which probably occurred as a cavity filling or vein filling; it was about 30 cm in size. Hand-specimens derived from this original specimen vary substantially in appearance and in the relative proportions of the principal minerals.

One hand-specimen obtained from the larger original specimen is the type specimen for baumite (Frondel and Ito, 1975). Baumite was discredited by Guggenheim and Bailey (1989, 1990), who reported it to be a coherent intergrowth of 7Å and 14Å phases related to greenalite-caryopilite and chlorite, respectively. They also provided information on the phases associated with baumite and the difficulty of characterizing them.

Another hand-specimen from the original specimen is the holotype



specimen for franklinphilite. This is a breccia consisting of abundant calcite, franklinite fragments, fine-grained friedelite, chamosite (the "brunsvigite" of Frondel and Ito, 1975), aegirine, the dense fine-grained mixture formerly known as baumite, and 1 x 3-cm broken fragments of crude willemite crystals. This breccia is crosscut by a 3-cm wide vein composed of fine-grained, medium brown, impure friedelite, which contains a central 1-cm zone of impure, fine-grained, dark brown franklinphilite (Fig. 1). This zone is composed of small radiating clusters of platy crystals; euhedral crystals were not observed, but franklinphilite is more coarsely crystallized, and darker brown at the vein margins where it is in contact with impure friedelite. Figure 2 shows an intergrowth of franklinphilite and friedelite.

Franklinphilite is also known from a second assemblage from Franklin, described by Dunn *et al.* (1984). In this assemblage, franklinphilite is black, nearly opaque, and associated with nelenite, rhodonite and tirodite. Descriptive data are given by Dunn *et al.* (1984) as an adjunct to the description of lennilenapeite and are therefore not repeated here; the specimens are in the Harvard Mineralogical Museum collection (specimens #89999, #89365 and #92791-b).

PHYSICAL AND OPTICAL PROPERTIES

The holotype franklinphilite is very dark brown with a light brown streak and a vitreous to slightly resinous luster. The hardness is approximately 4 (Mohs); cleavage on {001} is imperfect; fracture was not observed; franklinphilite is brittle. The density of fragments varies, due both to impurities and incipient cleavages; the range of observed values is 2.6 to 2.8 g/cm³ compared with the calculated value of 2.66 g/cm³.

Optically, franklinphilite is transparent to translucent, and biaxial with 2V (meas) = $10(3)^{\circ}$, 2V (calc) = 0° . The indices of refraction, measured in white light, are $\alpha = 1.545(5)$, $\beta = 1.583(3)$, and $\gamma = 1.583(3)$. Because of the poor quality of the material, orientation of the indicatrix was incompletely determined; only the angle between X and (001), approximately 6° , could be measured. Pleochroism is distinct with X = pale yellow, Y = Z = deep brown; dispersion was not detected. Franklinphilite is not discernibly fluorescent in ultraviolet radiation.

rigure 1. Drawing depicting the frankmiphilte assemblage. The groundmass is a serpentinecalcite-friedelite-"baumite" breccia; the dark band (1) is coarsely crystallized franklinphilite; the lighter-colored, wider band (2) is an impure mixture of franklinphilite and friedelite. Drawing by Mary A. Parrish.

CRYSTALLOGRAPHIC DATA

Several cleavage fragments were mounted for single-crystal X-ray diffraction studies, but all specimens gave precession photographs with diffuse and broad reflections. This occurred in part because of curvature that inevitably was created during cleavage, but also was apparently caused by original defects. The unit cell and space group could therefore not be unambiguously determined using only such photographs. However, the photographs were directly compared with corresponding photographs of lennilenapeite and other stilpnomelanes; these were found to be nearly identical, insofar as could be judged given the imperfect nature of the franklinphilite photographs, implying that franklinphilite is isostructural with stilpnomelane.



Figure 2. Back-scattered electron image of a thin-section showing blades of dark franklin-philite and light friedelite.

In order to obtain higher quality diffraction patterns, electron diffraction patterns were obtained by spreading crushed fragments on holey carbon films, and using a Phillips CM-12 scanning transmission electron microscope (STEM) fitted with a Kevex solid state detector. Sharp, well-defined hk0 single-crystal patterns were preferentially obtained as grains were oriented with the {001} cleavage (indexed relative to the orthohexagonal cell: see below) normal to the electron beam. Such patterns were of two types, duplicating the examples of hk0 patterns of stilpnomelane and friedelite, respectively, as illustrated by Guggenheim and Eggleton (1988). Grains for which [001] was parallel to the electron beam displayed diffraction patterns typical of those obtained by Crawford et al. (1977) for stilpnomelane, with alternate rows of reflections parallel to the c-axis displaying sharp and diffuse reflections, respectively, with the diffuse streaking parallel to c^* . Qualitative energy-dispersive X-ray analyses were obtained for grains exhibiting diffraction patterns; those grains showing the typical stilpnomelane-like diffraction patterns gave data consistent with compositions identical within error to that obtained by electron microprobe analysis; those having the friedelite-like pattern contained only Mn, Si, O and Cl in amounts corresponding to friedelite.

Powder X-ray diffraction data (Table 1) were obtained using a 114.6mm diameter Gandolfi camera, polycrystalline specimen, FeKa radiation, and Si as an internal standard. Because franklinphilite is, by analogy, isostructural with stilpnomelane and thus triclinic, but pseudo-hexagonal, observed *d*-values for non 00*l* reflections may be indexed with more than one choice of pseudosymmetrically related indices. Powder diffraction data therefore cannot be used to refine the cell parameters for the triclinic cell. However, Eggleton and Chappell (1978) recommended using an orthohexagonal cell. The cell parameters were therefore refined by least-squares using such a cell, utilizing indices as given for corresponding reflections by Guggenheim and Eggleton (1988) for lennilenapeite and stilpnomelane. The resultant lattice parameters are a = 5.521(4), b = 9.560(6), c = 36.57Å, and V = 1930.2(5) Å³. Z = 3/8 for this cell; the non-integral value derives from the fact that the pseudo-orthohexagonal cell is a subcell of the true triclinic cell, for which Z = 1. Table 1 contains a list of the powder X-ray diffraction data, with reflections indexed on the orthohexagonal cell. The lattice parameters for the pseudotrigonal cell are a = 22.08(1) and c = 12.19(2) Å. These compare with values of 22.05 and 12.19 Å, as reported by Guggenheim and Eggleton (1988) for lennilenapeite, and 22.11 and 12.14 Å for manganoan stilpnomelane.

CHEMICAL COMPOSITION

Because of the presence of numerous fine inclusions, franklinphilite could not be analyzed by wet-chemical methods; electron microprobe wavelength-dispersive analysis was employed. The analytical data were obtained utilizing an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a sample current of 0.025 µA, measured on brass. Standards used were hornblende (Si,Al,Fe,Mg,K,Na), ZnO (Zn), and manganite (Mn); the data were corrected using standard Bence-Albee correction factors. Due to impurities, the concentration of water could not be measured directly and it was calculated by difference; the value so obtained (8.1 weight % H₂O) compares very favorably with that (8.4 weight % H₂O) for other franklinphilite samples from Franklin (previously described as manganese-dominant stilpnomelane) for which water was directly determined (Dunn et al., 1984). Franklinphilite is homogeneous. The resultant analysis yielded: SiO₂ 44.0, Al₂O₃ 3.6, Fe₂O₃ 7.8, MgO 6.4, K₂O 1.5, Na₂O 0.4, ZnO 5.9, MnO 22.3, H_2O [8.1], total = 100%. Total iron is assumed to be ferric iron, in part based on the associated aegirine.

The empirical formula, calculated on the basis of 120 total tetrahedral plus octahedral cations, as is the convention for stilpnomelane, is $(K_{2.64}Na_{1.07})_{\Sigma 2.71}(Mn_{26.08}Mg_{13.18}Zn_{6.02}Fe_{2.72}^{+3})_{\Sigma 48}(Si_{60.77}Al_{5.86}Fe_{5.38}^{+3})_{\Sigma 72}$ $(O_{163.23}(OH)_{52.77})_{\Sigma 216} \cdot nH_2O$, with Mn >> Mg > Zn in holotype franklinphilite. There is extensive solid solution with lennilenapeite, the

Table 1. Powder X-ray diffraction data for franklinphilite
compared with data for lennilenapeite. Data for friedelite that
occurs intimately intergrown with franklinphilite are also listed

Franklinphilite*			Lennilenapeite [†]		
<i>I</i> / <i>I</i> _o	$d_{\rm obs}(\mathbf{\ddot{A}})$	$d_{ m calc}({ m \AA})$	hkl**	I/I。	$d_{\rm obs}({ m \AA})$
100	12.3	12.2	003	100	12.11
30	7.27f				
				2	6.09
5	5.54			2	5.50
20	4.79	4.78	110	5	4.76
		4.78	020		
10	4.40			2	4.39
20	4.08	4.06	009	20	4.07
2	3.83				
30	3.61f			5	3.67
2	3.18				
20	3.06	3.05	0,0,12	20	3.04
20	2.881f				
30	2.737	2.729	202	30	2.734
40	2.583	2.582	205	40	2.582
5	2.553f				
2	2.449	2.441	207	2	2.439
10	2.405f				
30	2.362	2.363	208	30	2.365
10	2.201	2.203	2,0,10	2	2.204
20	2.120f			10	2.125
10	1.968f			1	1.965
2	1.897	1.897	2,0,14		
10	1.730f				
5	1.694	1.697	2,0,17	1	1.695
5	1.677f				
2	1.623f				
30	1.594	1.593	060	30	1.593
30	1.580	1.580	063	30	1.578
5	1.541	1.542	066	10	1.542
2	1.520f				
				1	1.413
2	1.376	1.376	402	1	1.373

*Data for reflections from friedelite are listed in italics and with the letter f appended to the *d*-value.

**Indices based on orthohexagonal cell with a = 5.521, b = 9.560, c = 36.57 Å.

†Dunn et al., 1984.

Mg-analog of stilpnomelane, as shown by the data of Dunn et al. (1984).

ACKNOWLEDGMENTS

The authors are indebted to Mr. John L. Baum, curator of the Franklin Mineral Museum, for his donation of the type specimen, to Mr. John Cianciulli for assistance with museum specimen research, to Ms. Mary Parrish for the specimen drawing, and to Mr. Herb Yeates who suggested the Greek suffix in the mineral name.

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