

## Franklinfurnaceite, a Ca-Fe<sup>3+</sup>-Mn<sup>3+</sup>-Mn<sup>2+</sup> zincosilicate isotypic with chlorite, from Franklin, New Jersey

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

DONALD R. PEACOR

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

ROBERT A. RAMIK

Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, Ontario M5S 2C6, Canada

SHU-CHUN SU\*

Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A

ROLAND C. ROUSE

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

### ABSTRACT

Franklinfurnaceite, ideally Ca<sub>2</sub>Fe<sup>3+</sup>Mn<sub>2</sub><sup>3+</sup>Mn<sup>3+</sup>Zn<sub>2</sub>Si<sub>2</sub>O<sub>10</sub>(OH)<sub>8</sub>, is monoclinic, space group C2, with  $a = 5.483(7)$ ,  $b = 9.39(3)$ ,  $c = 14.51(1)$  Å,  $\beta = 97.04(8)^\circ$ , and  $Z = 2$ . The strongest lines in the X-ray powder-diffraction pattern are ( $d, I/I_0, hkl$ ): 2.305(100)(20 $\bar{4}$ ,22 $\bar{2}$ ,133), 2.707(80)(130,13 $\bar{1}$ ), 2.602(70)(201,13 $\bar{2}$ ), 14.4(50)(001), and 3.35(50)(023). It is dark brown with vitreous luster and perfect {001} cleavage;  $D_{\text{meas}} = 3.66$  and  $D_{\text{calc}} = 3.737$  g/cm<sup>3</sup>. Optically, it is biaxial (-),  $2V = 79^\circ$ ,  $\alpha = 1.792(4)$ ,  $\beta = 1.798(4)$ , and  $\gamma = 1.802(4)$ ; dispersion  $r < v$ , moderate; strongly pleochroic with  $X =$  very dark brown,  $Y =$  brown,  $Z =$  deep brown; orientation is  $Z = \mathbf{b}$ , with  $X$  and  $Y$  in the (010) plane,  $Y \wedge c = 29^\circ$ . Absorption is intense,  $X \gg Z > Y$ . Franklinfurnaceite is associated with hetaerolite, clinohedrite, hodgkinsonite, and willemite from Franklin, Sussex County, New Jersey. Crystal-structure analysis shows it to be a zincosilicate isotypic with minerals of the chlorite group.

### INTRODUCTION

During petrographic studies of zinc silicate assemblages from Franklin, New Jersey, a mineral was found that has an appearance similar to that of bannisterite and ganophyllite, minerals that are known from this deposit but not from the host assemblage. The X-ray powder pattern has similarities to those of the chlorite group of minerals, but it also has distinct differences. Subsequent investigation has verified that it has a structure and composition that are closely related to those of the chlorite group, but with unique characteristics. We have named this new mineral *franklinfurnaceite* after the old name for the community (Franklin, New Jersey) in which the Franklin mine is located. The new species and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Type material is preserved in the National Mineral Collection at the Smithsonian Institution under catalogue no. C6309.

### PHYSICAL AND OPTICAL PROPERTIES

Franklinfurnaceite forms very thin, platy crystals, tabular on {001}, with {001} the dominant form, and a rough face of unknown index subordinate as very thin, serrated edges, as shown in Figure 1. The maximum crystal size is 0.3 mm, but most crystals are considerably smaller. Such crystals are sometimes irregularly intergrown to form polycrystalline aggregates up to 1.0 cm in diameter.

Franklinfurnaceite is dark brown in color, with a vitreous luster and a brown streak. The hardness is estimated to be 3 (Mohs); it is extremely brittle. Cleavage is perfect on {001} and easily produced. The density, measured by heavy-liquid techniques, is 3.66 g/cm<sup>3</sup>, compared with the calculated value of 3.737 g/cm<sup>3</sup>.

Optically, franklinfurnaceite is biaxial negative,  $2V = 79^\circ$  (78.5° calc.); optic axis dispersion is moderate with  $r < v$ . Indices of refraction, determined in Na light, are  $\alpha = 1.792(4)$ ,  $\beta = 1.798(4)$ , and  $\gamma = 1.802(4)$ . The most striking feature of this mineral in thin section is its intense pleochroism with  $X =$  very dark brown,  $Y =$  brown, and  $Z =$  deep brown. Accordingly, the strong absorption is  $X \gg Z > Y$ . The optical orientation is  $Z = \mathbf{b}$ , both  $X$

\* Permanent address: Institute of Geology, Chinese Academy of Sciences, Beijing, China.

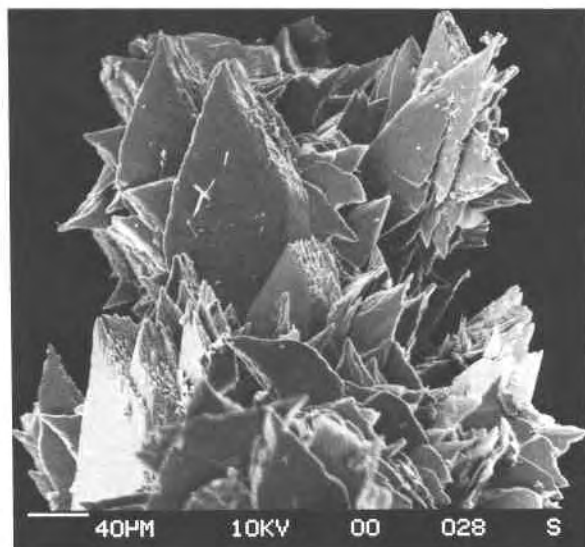


Fig. 1. Cluster of franklinfurnaceite crystals, showing the parallel to subparallel habit of the aggregate. Scale bar is 40  $\mu\text{m}$ .

and  $Y$  are in the (010) plane with  $Y$  in the acute angle between the  $a$  and  $c$  axes, and  $Y \wedge c = 29^\circ$ . Calculation of the Gladstone-Dale relationship (Mandarino, 1981) yields  $K_c = 0.221$  and  $K_p = 0.218$ , yielding superior agreement of the physical and chemical data.

#### CHEMICAL COMPOSITION

Owing to paucity of material, a wet-chemical analysis of franklinfurnaceite could not be carried out. It was chemically analyzed with an ARL-SEM-Q electron microprobe with an operating voltage of 15 kV and a sample current of 0.025  $\mu\text{A}$ , measured on brass. Standards utilized for the compositions given herein were hornblende (Si, Al, Fe, Mg, Ca), manganite (Mn), and synthetic zincite (Zn). A wavelength-dispersive scan gave no indication of the presence of any elements with atomic number greater than 9, except those reported here. Franklinfurnaceite dissolves slowly in 1:1 HCl. A determination of the oxidation state of Fe, using microchemical tests (Kraus et al., 1959), showed  $\text{Fe}^{3+}$  to be present. The valence state of Mn was determined in part through the cation-polyhedra geometries and interatomic distances, as revealed by the crystal-structure determination referred to below. One site (of rank two) has the characteristic octahedral geometry reflecting a Jahn-Teller distortion indicative of  $\text{Mn}^{3+}$ . In addition, the association with hetaerolite,  $\text{ZnMn}_3^{2+}\text{O}_4$ , and the uncommon and intense pleochroism are consistent with the presence of  $\text{Mn}^{3+}$ . Other polyhedral geometries and M-O distances are consistent with  $\text{Mn}^{2+}$ . Water was determined by thermogravimetry using a Mettler TA-1 Thermoanalyzer and simultaneous evolved-gas analysis using an Inficon IQ200 quadrupole mass spectrometer. For this analysis, 6 mg of franklinfurnaceite were separated from fine-grained admixed phases by repeated centrifuging in Clerici density columns. Purity was

TABLE 1. Microprobe analyses of franklinfurnaceite

Sample no.:	JEM 1093	R19144	C6309
$\text{SiO}_2$	14.5	14.6	15.0
$\text{Al}_2\text{O}_3$	0.8	1.3	0.4
$\text{Fe}_2\text{O}_3$	9.4	8.6	9.3
MgO	3.6	4.3	0.6
CaO	14.3	13.7	12.6
ZnO	22.7	23.6	24.1
MnO	17.0	17.3	19.0
$\text{Mn}_2\text{O}_3$	9.5	9.6	10.6
$\text{H}_2\text{O}$	n.d.	n.d.	8.4
Total			100.0

Note: Precision of data is  $\pm 3\%$  of the amount present for major elements. F absent or present only as traces. Oxidation state of Mn calculated by crystal-structure refinement.

confirmed by X-ray powder diffraction of the separate; in addition, the (001) interplanar spacing was found to be unchanged by the separation process. The sample was heated at  $10^\circ\text{C}/\text{min}$  in vacuum. A single water loss of 8.4 wt% occurred between 300 and  $630^\circ\text{C}$ , with a maximum rate of loss at  $515^\circ\text{C}$ . Thus, the mineral lacks significant adsorbed and interlayer water. Although franklinfurnaceite has chemical dissimilarities to known chlorites, a similar single-step decomposition in this temperature range has been observed for cookeite ( $510^\circ\text{C}$ ), chamosite ( $523^\circ\text{C}$ ), and sudoite ( $<500^\circ\text{C}$ ) (Smykatz-Kloss, 1974).

The resultant analyses are presented in Table 1. The analysis of the type specimen (no. C6309), calculated on the basis of 36 oxygens, gives the empirical formula  $\text{Ca}_{3.75}\text{Fe}_{1.94}^{3+}\text{Al}_{0.13}\text{Mg}_{0.25}\text{Mn}_{2.47}^{2+}\text{Mn}_{3.24}^{3+}\text{Zn}_{4.94}\text{Si}_{4.17}(\text{OH})_{15.57}\text{O}_{20.43}$ . The structural formula, for sample JEM-1093, with the cations separated onto their respective 2- and 4-fold equi-points, is  $\text{Ca}_4(\text{Fe}_{1.53}^{3+}\text{Al}_{0.47})(\text{Mn}_{1.07}^{2+}\text{Mg}_{0.57}\text{Zn}_{0.36})\text{Mn}_2^{3+}(\text{Mn}_{1.94}^{2+}\text{Mg}_{0.06})(\text{Mn}_{1.07}^{2+}\text{Mg}_{0.57}\text{Zn}_{0.36})\text{Zn}_4\text{Si}_4\text{O}_{20}(\text{OH})_{16}$ . This may be idealized as  $\text{Ca}_2\text{Fe}^{3+}\text{Mn}^{3+}\text{Mn}_3^{2+}\text{Zn}_2\text{Si}_2\text{O}_{10}(\text{OH})_8$  with  $Z = 2$  and four Zn and four Si in tetrahedral coordination. The structure contains  $\text{Zn}_4\text{Si}_4\text{O}_{20}$  sheets analogous to the aluminosilicate sheets in phyllosilicates. Since the Zn is tetrahedrally coordinated, franklinfurnaceite is properly termed a zincosilicate.

#### CRYSTALLOGRAPHY

Weissenberg and precession photographs showed that franklinfurnaceite is monoclinic with space group  $C2/m$ ,  $C2$ , or  $Cm$ , with lattice parameters  $a = 5.483(7)$ ,  $b = 9.39(3)$ ,  $c = 14.51(1)$   $\text{\AA}$ ,  $\beta = 97.04(8)^\circ$ , and  $V = 741(2)$   $\text{\AA}^3$ . These parameters were obtained by least-squares refinement of powder-diffraction data (Table 2) that were obtained with a 114.6-mm-diameter Gandolfi camera, a polycrystalline sample,  $\text{FeK}\alpha$  (Mn-filtered) radiation, and NBS Si as an internal standard. The powder pattern is similar to those of minerals of the chlorite group (e.g., Bailey, 1980) only in the lines having large interplanar spacings. The crystal-structure analysis showed  $C2$  to be the correct space group.

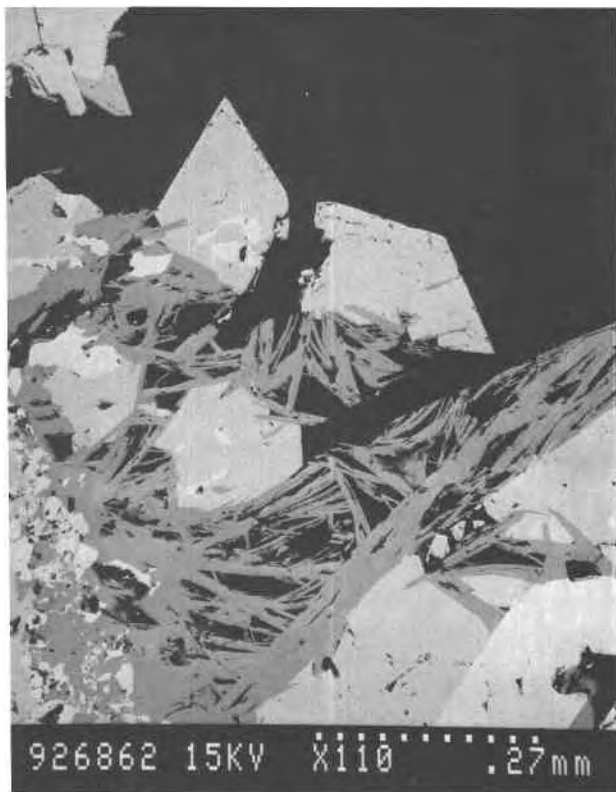


Fig. 2. Backscattered-electron image of a thin section. Franklinfurnaceite is dark gray, hodgkinsonite is medium gray, hetaerolite is light gray, and open space is black. The dotted line represents 0.27 mm.

The lattice parameters are similar to those of one-layer chlorite and, together with a general similarity of some aspects of the composition and physical properties (e.g., a perfect {001} cleavage), imply that franklinfurnaceite and chlorite-group minerals are closely related. However, the 22 cations per unit cell exceed the value for even trioctahedral chlorites (20), suggesting that there is not a one-to-one relation in structure. Three-dimensional single-crystal intensity data were therefore measured in order to determine the structure of franklinfurnaceite. The structure, which has been refined to a residual of 0.035 for all reflections, is indeed isotypic with that of chlorite, but with a total of 22 cations. Its principal features are (1) 6-membered rings of alternating  $\text{ZnO}_4$  and  $\text{SiO}_4$  tetrahedra in the tetrahedral sheets of the talc-like layer, (2)  $\text{Mn}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $(\text{Mn}^{2+}, \text{Mg}, \text{Zn})$  ordered in three sites in the trioctahedral sheet of the talc-like layer, (3)  $(\text{Fe}^{3+}, \text{Al})$  and  $(\text{Mn}^{2+}, \text{Mg}, \text{Zn})$  ordered in two sites in the dioctahedral gibbsite-like interlayer and, (4) Ca in octahedrally coordinated sites between the talc-like and gibbsite-like layers. The franklinfurnaceite structure is the first verification by crystal-structure analysis of the hypothesis put forth by Belov (1950) that Ca might enter the chlorite structure in octahedral sites between the talc-like layer and brucite-like interlayer, if it were paired with octahedral-cation

TABLE 2. X-ray powder-diffraction data for franklinfurnaceite

$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$d_{\text{obs}}$	
50	14.4	14.4	001	5	1.917
10	7.2	7.2	002	2	1.817
30	4.71	4.70	020	1	1.779
		4.71	110	20	1.747
1	4.35	4.34	111	40	1.692
1	4.15	4.15	112	2	1.677
5	3.76	3.76	112	10	1.645
40	3.60	3.60	004	20	1.596
10	3.55	3.56	113	40	1.577
50	3.35	3.36	023	10	1.568
40	3.20	3.20	113	2	1.485
30	3.018	3.019	114	30	1.462
20	2.873	2.879	005	10	1.445
80**	2.707	2.713	130	5	1.380
		2.697	131	5	1.358
70**	2.602	2.615	201	2	1.344
		2.592	132	1	1.307
1	2.499	2.502	203	2	1.297
2	2.454	2.455	025		
		2.448	202		
2	2.430	2.427	133		
5	2.352	2.354	220		
		2.348	115		
		2.348	040		
100	2.305	2.311	204		
		2.311	222		
		2.302	133		
5	2.239	2.236	116		
		2.234	134		
2	2.212	2.208	223		
5	2.169	2.170	222		
10	2.112	2.111	205		
10	2.072	2.074	224		
10	2.037	2.038	135		

\* Intensities visually estimated.

\*\* Very broad.

vacancies in the latter. Details of the franklinfurnaceite structure will be reported in a subsequent paper.

## OCCURRENCE

Franklinfurnaceite occurs in the Franklin mine, Franklin, Sussex County, New Jersey. It has not been found at the nearby and genetically related deposit at Sterling Hill. The mineral was first discovered in the collections of the Smithsonian Institution; subsequently, other similar specimens have been found in private collections. It remains a very rare mineral.

Franklinfurnaceite occurs in an uncommon assemblage of vuggy intergrowths with five other minerals, all of which contain tetrahedrally coordinated zinc. These are willemite,  $\text{Zn}_2\text{SiO}_4$ , clinohedrite,  $\text{CaZnSiO}_3(\text{OH})_2$ , hodgkinsonite,  $\text{MnZn}_2\text{SiO}_4(\text{OH})_2$ , hetaerolite,  $\text{ZnMn}_3^+\text{O}_4$ , and franklinite,  $\text{ZnFe}_2^+\text{O}_4$ . It is evident from its occurrence in interstices and as free-growing crystals in vugs that franklinfurnaceite is the last mineral to form. Figure 2 illustrates the typical assemblage texture of hodgkinsonite crystals and franklinfurnaceite in a vug. The franklinfurnaceite occurs as a complex intergrowth of flat plates, which appear to be prismatic in cross section. Willemite occurs as subhedral masses and euhedral crystals entirely enclosed

within massive hodgkinsonite. Hetaerolite commonly occurs as small, angular, brecciated grains (Fig. 2) as does some hodgkinsonite, but euhedral crystals of both coat vug surfaces, implying fracturing and production of these vugs during crystallization of hetaerolite, hodgkinsonite, and willemite. Franklinfurnaceite crystallized late in the sequence, but intergrowths of it and other minerals imply overlap in the growth of these minerals. Barite and rhodonite were also observed as irregular grains, approximately 1 mm in diameter, associated with hodgkinsonite.

#### ACKNOWLEDGMENTS

This study was supported, in part, by a grant from Mrs. E. Hadley Stuart, Jr.; P.J.D. thanks the trustees of the Franklin Mineral Museum for their continued assistance and the curator, John L. Baum, for his valuable advice and counsel. We are grateful for reviews by A. C. Roberts, D. L. Bish, and J. A. Speer that led to improvements in the text.

#### REFERENCES

- Belov, N.V. (1950) Ocherki strukturnoy mineralogii. Mineralogicheskiy Sbornik Lvovskogo Geologicheskogo Obshchestva, 4, 21-34.
- Bailey, S.W. (1980) Structures of layer silicates. In G.W. Brindly and G. Brown, Eds., Crystal structures of clay minerals and their X-ray identification, p. 1-124. Mineralogical Society, London.
- Kraus, E.H., Hunt, W.F., and Ramsdell, L.S. (1959) Mineralogy, an introduction to the study of minerals and crystals. McGraw-Hill, New York.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, 19, 441-450.
- Smykatz-Kloss, W. (1974) Differential thermal analysis, p. 122-128. Springer-Verlag, New York.

MANUSCRIPT RECEIVED NOVEMBER 21, 1986

MANUSCRIPT ACCEPTED APRIL 3, 1987