FERROLAUEITE, a New Mineral From Monmouth County, New Jersey

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Abstract

Ferrolaueite, end-member $Fe^{2+}(H_2O)_4Fe_2^{3+}(H_2O)_2\ (OH)_2(PO_4)_2\cdot 2H_2O$, is a new member of the laueite structure type. It occurs as a minor constituent with ferrostrunzite, beraunite, cacoxenite and glauconite in marl banks along My Creek near New Egypt, Monmouth County, New Jersey.

Crystals to 200μm, light brown to orange-brown blades, hardness 3, cleavage good {100} and {010}, specific gravity 2.515. The optical characters are $\alpha = 1.610$, $\beta = 1.665$, $\gamma = 1.692$, 2V = 68°, pleochroism X = brown, Y = yellow, Z = light brown. X-ray characters are **a** = 5.34, **b** = 10.63, **c** = 7.21 Å, $\alpha = 107.35$, $\beta = 111.26$, $\gamma = 71.27°$, three strongest X-ray lines are 6.56/10/001, 3.28/10/002, 9.87Å/9/010. Crystal forms are b{010}, M{1$\bar{1}$0}, c{001}, a{100} and m{110}.

It is likely that ferro- and ferri-analogues of the related stewartite and pseudolaueite will be found in a similar environment.

INTRODUCTION

Each investigator played a specific role in this study. Therefore, initials of the investigator's name (such as C.G.S. for Curt G. Segeler) will be used when needed.

Publication of the occurrence of ferrostrunzite in the Cretaceous sediments at Mullica Hill, N. J. by Peacor et al. (1983) suggested that the three hypothetical phases related to ferrostrunzite, e.g., "ferrolaueite", "ferrostewartite" and "ferropseudolaueite", might exist and occur elsewhere in similar New Jersey sedimentary deposits where there was an absence of Mn. Indeed, these related Mn^{2+}-bearing minerals are principally known from granitic pegmatites. The hypothetical phases would have predominant Fe^{2+} in lieu of Mn^{2+} found in the established species laueite, stewartite and pseudolaueite. Since Fe^{2+} ion oxidizes much more easily than Mn^{2+}, we would even expect "ferri-" analogues. Indeed, Peacor et al. (1987) described the new mineral ferristrunzite from Blaton, Belgium.

F. L. had already noted a number of occurrences of "strunzite" in marl in Monmouth and Burlington Counties, in usually fine specimens near Marlton and as abundant material at Mullica Hill. Tests by C. G. S. showed that Mn was absent and that ferrous iron was abundant. The specimens were deemed to be ferrostrunzite.

Searching along the banks of My Creek not far from New Egypt, Monmouth County, F. L. found ferrostrunzite intergrown with crystals of appearance and color resembling laueite, a mineral that had not previously been reported from New Jersey. Optical and qualitative chemical tests by C. G. S. suggested the likelihood that the mineral was the ferrous iron analogue of laueite. The refractive indices and density were somewhat higher than those obtained from laueites found at the Palermo Quarry, North Groton, N. H. Electron probe, Mössbauer resonance and vapor pressure analyses; and single crystal and powder X-ray investigation have now confirmed that the mineral is indeed the ferrous iron analogue of laueite, or **ferrolaueite** named according to its novel chemical composition and its isomorphism to the laueite structure type. As yet, beyond strunzite and laueite, the ferrous iron analogues of the other related phases have not been found.

The ferrolaueite garnered for investigation appeared as euhedral crystals and formed the basis of the entire study. The new mineral is nowhere common and appears to occur in restricted environments. The limited amount available forced us to use several rather specialized techniques. The name received approval from the International Commission on New Minerals and New Mineral Names (International Mineralogical Association). The holotype is preserved in the collection of the University of Chicago, and co-types have been sent to the U. S. National Museum (Smithsonian Institution).

OCCURRENCE (F. L.)

Ferrolaueite was found at two locations embedded in marl along creek banks in the area whose coordinates are 74°32.6′ West Longitude and 40°5.5′ North Latitude. The first location is 2000 feet north of the bridge that crosses My Creek along the Monmouth-Burlington County border road near New Egypt. At that point a small brook crosses the road through a culvert. The ferrolaueite was found in the marl banks along the brook some 20 to 50 feet east of the road. It is intergrown with ferrostrunzite, and appears to be the later mineral of the two. Vivianite, beraunite and cacoxenite (kakoxen) were found with the ferrolaueite but their paragenetic sequence was uncertain. Specimens have been found, however, with vivianite (a Fe^{2+} mineral) replacing the beraunite (a Fe^{2+}-Fe^{3+} mineral). This suggests that redox reactions became more reducing with time.

The second locality was about 3000 feet along My Creek east of the road bridge and on the south bank just past a small side stream entering from the north. The ferrolaueite was not found throughout the marl but only made a sporadic appearance in narrow bands, even down below the water level. At this locality the crystals are free-standing and are not intergrown with ferrostrunzite. Here, the marl is black to greenish in color. Glauconite-1M, K(Fe, $Al)_2^{3+}[AlSi_3O_{10}](OH)_2$, occurs throughout as bluish-green small balls up to 1 mm in diameter. It was identified by X-ray powder diffraction and compared well with JCPDS 9-439 (Bayliss, 1986). This dioctahedral mica was not investigated further.

Both sites are on posted private property and permission from the owners is essential for collecting purposes. Access to the sites is possible only by wading in the creeks.

DIAGNOSTIC CHARACTERS

a. Physical Properties. Ferrolaueite occurs as sporadic crystals and crystal bunches in marl. The crystals range from 50 μm to 200 μm in maximum dimension. Rosettes of several crystals, with individual blades striated $\{100\}\|[001]$ are typical. The crystals are light brown to orange-brown, translucent to transparent, vitreous luster and palest yellow streak. Crystals easily dehydrate, especially under a microscope lamp, and become ivory-colored. It is suspected that only water which is hydrogen-bonded and not ligated to a metal is lost. Weak but discernible powder lines indicating a slightly collapsed cell were obtained.

Ferrolaueite is not stimulated by short- or long-wave UV radiation. The hardness of crystals is 3, tenacity brittle, cleavage good $\|\{100\}$ and $\{010\}$; and fair $\|\{001\}$. Fracture is uneven, parting none. The specific gravity, determined by suspension in heavy liquids, ranges 2.514–2.519, mean 2.515(2). The density determined from the mean formula and unit cell parameters (*vide infra*) is 2.506(2) g cm^{-3}, the estimated standard deviations in parenthesis.

b. Optical Properties (C. G. S.). The optical characters of ferrolaueite were determined by oil immersion spindle stage. The mineral is biaxial (–), $\alpha = 1.610(3)$, $\beta = 1.665(3)$, $\gamma = 1.692(3)$, 2V(obs) = 68(2)° and 2V(calc) = 68(3)° in white light with a blue filter. Errors in parenthesis are combined estimates of deviations in the oils, and of several independent readings of immersed crystals.

The dispersion is $r > v$ moderate, orientation Z:c = 50° and Z:a = 66°. The pleochroism is X = brown, Y = yellow, Z = light brown. The absorption was not determined.

c. Chemical Analyses (M.D.D. and I.M.S.) Chemical analysis was the most difficult part of the ferrolaueite study. But little bulk material was available, and the laueite structure type is complex. Knowledge of the structure type is of tantamount importance. The laueite structure was analyzed by Moore (1965), back at the time when very few mineral phosphate structures were known. With $R = 0.12$, the structure results admitted refinement of 13 atoms in the asymmetric unit. Bond distances were good to ±0.03 Å, and gave clear evidence for assigning atomic species. Three distinct transition metal cation sites were available: $M(1) = Mn^{2+}$, $M(2) = Fe^{3+}$ and $M(3) = Fe^{3+}$. The cell contents are:

$$1[Mn^{2+}(H_2O)_4Fe_2^{3+}(H_2O)_2\ (OH)_2(PO_4)_2.2H_2O].$$

The formula is expressed to portray as best possible the ligands which are associated with the appropriate cations. All three unique larger cations are octahedrally coordinated by ligands. The M(1) corresponds to Mn^{2+} of the $[Mn^{2+}(H_2O)_4(O_p)_2$, O_p = phosphate oxygen] octahedron, M(2) to the $[Fe^{3+}(OH)_2(O_p)_4]$ octahedron, and M(3) to the $[Fe^{3+}(H_2O)_2(OH)_2(O_p)_2]$ octahedron. The M(1) octahedron does not link to another octahedron, but M(2) and M(3) link to form corner-sharing octahedral chains through bridging $(OH)^-$ ligands. Thus, there exist two charged octahedral cations, Mn^{2+} and Fe^{3+}, and three distinct octahedra, each with a unique ligand environment.

Mössbauer resonance was the method of choice to allocate atom species and charges in ferrolaueite. A good review applied to mineralogy can be read in Dyar (1984). In our study, Table 1 outlines the observed results on ferrolaueite. Four

57_{Fe} Mössbauer doublets (peaks) must be explained among the three Fe-bearing unique octahedral sites. We interpreted Table 1 as follows: M(1)-Fe^{2+} 21(2)% + Fe^{3+}13(2)%; M(2)-Fe^{3+}30(2)%; M(3)-Fe^{3+}33(2)%. The Fe^{2+}:Fe total ratio is 0.21(2) and fixes the Fe valences for ferrolaueite.

CAMECA electron microprobe, using synthetic $Ca_2P_2O_7$ and maganoan hortonolite (FeO 44.15%) standards and wavelength dispersive detector (15 kV, 20 nA, 20 μm beam spot) on 10 points from three grains, provided the elemental contents with atomic number greater than fluorine.

Water content was determined by cryopump and vapor pressure measurement on 340(10) μg crystals. The losses were 80°C 0.6%, 200°C 23.4%, 500°C 10.5%, total 34.5%. The errors at each pass are uncertain. We thank Prof. A. T. Anderson for this determination, the procedure announced by Harris (1981). Chemical analyses for ferrolaueite appear in Table 2.

Astute readers will note that the Mössbauer peak sum is low. This is believed to be 3(2)% Fe^{2+} contaminant (peaks 2–7) from some associated ferrostrunzite.

d. X-ray Crystallography (P.B.M.). Establishing the crystallographic characters for ferrolaueite was not a simple problem, either. Preliminary Buerger precession photographs (MoK_α radiation) confirmed the earlier derived reciprocal lattice of the structure type. Gandolfi mount powder photographs (FeK_α radiation) were then obtained from crushed pure single crystals. It was hoped that least-squares refinement of the **d**-spacings would yield cell parameters of reasonable precision.

Unfortunately, most of the Miller indices in the International Centre for Diffraction Data (JCPDS) file (Bayliss, 1986), a standard reference for diffraction data, appear to be incorrect. The file for laueite, JCPDS 14-246, could not be reconciled with our data. Triclinic crystals are difficult to index, because no extinction criteria exist and many d-spacings with different Miller indices may overlap. Fortunately, the complete $F(hk\ell)_{obs}$ - $F(hk\ell)_{calc}$ data were preserved from the single crystal structure study of Moore (1965). It was simply a matter of matching d-spacing with intensities from the visually estimated powder data for related ferrolaueite. Table 3 gives the powder data for ferrolaueite.

With the d-spacings and new Miller indices at hand, the initial unit cell for the precession photographs was refined, including six variable parameters (**a**, **b**, **c**, α, β, γ) and the first 28 observed powder data which were corrected for absorption. Combining the pertinent diagnostic characters:

a	5.34(1)
b	10.63(1)
c	7.21(1) Å
α	107.35(8)
β	111.26(8)
γ	71.27(8)°
V	353.2(7) Å^3

Cell formula: $1[(Fe^{2+}_{1-x}Fe^{3+}_{x})\ (H_2O_{4-x}OH_x)Fe^{3+}_2\ (H_2O)_2(OH)_2(PO_4)_2\cdot\ 2H_2O]$

Since the Fe valences were fixed to Fe^{2+}:Fe(total) = 0.21(2) by Mössbauer resonance, x = 0.6 or $(Fe^{2+}_{0.6}\ Fe^{3+}_{0.4})\ (H_2O_{3.6}OH_{0.4})\ Fe^{3+}_2(H_2O)_2(OH)_2(PO_4)_2\cdot 2H_2O$.

This formula indicates a **ferrian ferrolaueite**. Its calculated density is D(calc) = 2.506(2) g cm^{-3}, that for the hypothetical ferrous end-member, $Fe^{2+}(H_2O)_4Fe^{3+}_2(H_2O)_2\ (OH)_2(PO_4)_2\cdot 2H_2O$ is D(calc) = 2.517 g cm^{-3}. These values compare favorably with D(obs) = 2.515. The hypothetical "ferrilaueite" ($Fe^{3+} > Fe^{2+}$ in M(1)) almost certainly exists: a simple test for Fe^{3+}/Fe^{2+} or Fe^{2+}/Fe_{total} ratio in other My Creek occurrences would be helpful.

The good cleavage ‖{010} expresses the sheet-like character of the structure. This plane includes the $[Fe^{3+}_2(H_2O)_2(OH)_2(PO_4)_2]^{2-}$ corner-linked system of octahedra and tetrahedra (Moore, 1975).

Ferrolaueite crystals resemble the type laueite and paravauxite (Palache et al., 1951). The forms and frequency from observations on one dozen crystals are: b{010}(10), M{1$\bar{1}$0}(6), c{001}(5), a{100}(3), m{110}(1). A SEM photo of ferrolaueite crystals in parallel growth surrounded by and having attached ferrostrunzite appears in Figure 1. It demonstrates the likelihood of ferrostrunzite contaminant in ferrolaueite studies.

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Table legends

Table 1. Ferrolaueite ^{57}Fe Mössbauer results

Table 2. Ferrolaueite chemical analyses

Table 3. Ferrolaueite X-ray powder diffraction data

Figure legends

Figure 1. Ferrolaueite blades in parallel growth. The acicular crystals on and around ferrolaueite are ferrostrunzite. The bar on the left is 200 μm.

Table 1. FERROLAUEITE ^{57}Fe Mössbauer results

Peaks	**δ**	**σ**	**Δ**	**σ**	**% area**
1–8	1.26	0.006	3.13	0.009	21 ± 2%
2–7	1.32	0.137	1.72	0.025	3 ± 2%
3–6	0.40	0.005	1.29	0.005	30 ± 2%
4–5	0.41	0.005	0.66	0.002	46 ± 2%

Note: Four doublets are listed, δ = isomer shift, σ = standard deviation, Δ = quadrupole splitting. See Dyar (1984) for explanation. Peak 4–5 is broad.

Table 2. FERROLAUEITE chemical analyses

	1	2	3
FeO	6.9 (0.5)	7.1	13.4
Fe_2O_3	30.8 (2.2)	31.5	29.8
P_2O_5	26.2 (2.5)	26.9	26.5
H_2O	34.5	34.5	30.3
Total	98.4%	100.0%	100.0%

Note: 1. The Fe^{2+}:Fe ratio from Mössbauer resonance and electron probe is 0.21(2). H_2O by cryopump and vapor pressure measurement. The results are weight per cent oxides. Low total due to cracks? This result gives $H_{20.6}Fe^{2+}_{0.52}Fe^{3+}_{2.09}P_{2.00}O_{18.96}$ for P = 2 and

D(cal) = 2.506 g cm^{-3}. The CAMECA probe range was Fe 24.7–28.5% and P = 10.6–12.8%. The mean is Fe 26.9, P 11.4%. These were the only elements detected above 0.2 wt % which were greater than fluorine. Estimated errors in parenthesis.

2. FeO, Fe_2O_3 and P_2O_5 × 1.0263 to give total 100.0% assuming cracks.

3. For ideal $Fe^{2+}(H_2O)_4\ Fe^{3+}_2(H_2O)_2(OH)_2(PO_4)_2 \cdot 2H_2O$.

Determined water probably high. For $H_{18}Fe^{2+}Fe^{3+}_2\ P_2O_{18}$, this gives D(cal) = 2.517 g cm^{-3}.

Table 3. FERROLAUEITE X-ray powder diffraction data

I/I_0	d(obs)	d(calc)	hkℓ	I/I_0	d(obs)	d(calc)	hkℓ
9	9.87	9.85	0 1 0	4	2.19	2.19	$1\bar{2}2$
10	6.56	6.56	0 0 1	3	2.13	2.13	1 2 2
3	6.08	6.08	$0\bar{1}1$ *	3	2.09	2.09	2 1 1
8b	4.90	4.93	0 2 0 *	1	2.03	2.03	$\bar{2}\bar{3}3$
1	4.23	4.24	$\bar{1}\bar{2}1$ *	3	2.01	2.01	$\bar{1}40$
6	3.97	3.99	$\bar{1}10$ *	2b	1.998	1.994	$\bar{2}20$
5	3.92	3.94	1 2 0 *	1	1.903	0.904	1 3 2
2	3.66	3.68	$\bar{1}11$ *	1	1.874	1.872	$0\bar{5}2$
3	3.42	3.42	$\bar{1}\bar{1}2$ *	3	1.843	1.840	$\bar{2}22$
10	3.28	3.28	0 0 2 *	4	1.805		
2	3.19	3.19	$\bar{1}02$ *	1	1.760		
5	3.10	3.11	$\bar{1}20$	1	1.744		
5	2.86	2.87	$\bar{1}21$ *	1	1.714		
3b	2.73	2.72	0 3 1 *	4	1.679		
4	2.61	2.61	$\bar{1}\bar{4}1$ *	4	1.670		
1	2.53	2.53	$\bar{2}01$ *	4	1.652		
4b	2.47	2.46	0 4 0	5	1.641		
5	2.40	2.40	1 0 2	3	1.611		
3b	2.32	2.32	$\bar{1}22$	4	1.594		

Note: Miller indices were assigned based on single crystal **F(hkℓ)** observed intensities. Those indices at variance with JCPDS 14-246 are starred. JCPDS indices stopped at **d** = 2.50 Å. Our X-ray data were corrected for absorption. The film was corrected for minor shrinkage.

Fig. 1

Top

Fig 1 - Large crystal of Ferrolaueite with small acicular crystals of ferrostrunzite

232X
6KV WD:12MM
S:00000 P:00001
200UM

e 17 Ferrolaueite, large crystal with smaller acicular Ferrostrunzite

fig #2

Fig #3 Ferrostrunzite