

## Cianciulliite, a new magnesium manganese zinc hydroxide from Franklin, New Jersey

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### ABSTRACT

Cianciulliite,  $\text{Mn}(\text{Mg}, \text{Mn})_2\text{Zn}_2(\text{OH})_{10} \cdot 2\text{--}4\text{H}_2\text{O}$ , is a new species from Franklin, New Jersey. It is monoclinic,  $C2/m$ , with  $a = 15.47(2)$ ,  $b = 6.369(6)$ ,  $c = 5.576(6)$  Å,  $\beta = 101.29(9)^\circ$ ,  $Z = 2$ , and  $D_{\text{calc}} = 2.87$  g/cm<sup>3</sup>. It is dark reddish brown, occurs in flattened crystals, shows perfect cleavage on {100}, and has highly contrasting, form-selective lusters, pearly to dull on {100} and vitreous on other forms.

### INTRODUCTION

As part of a detailed study of a number of assemblages with cahnite from Franklin, New Jersey, a brown mineral with lathlike crystals was found; it appeared to be unique and new to science. Our detailed examination has supported that original hypothesis, and the description of this new mineral is given here. We have named this species *cianciulliite* in honor of John Cianciulli of Sussex, New Jersey, in recognition of the substantial assistance he has provided to scientists studying the minerals of Franklin and Sterling Hill and to the Franklin Mineral Museum.

The mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. The holotype specimen is deposited in the Smithsonian Institution under catalog no. M03074, and crystals of the holotype specimen are in the Canadian Museum of Nature under catalog no. CMN 56469.

### DESCRIPTION

Cianciulliite occurs as lustrous, euhedral crystals up to 0.6 mm in length (Fig. 1), but most are considerably smaller. Many of the crystal faces appear to be curved to varying degrees. Cianciulliite crystals, tabular on {100}, are so darkly colored and highly reflective that they appear opaque in all but one direction, normal to the perfect {100} cleavage. The cleavage has a markedly different appearance from the other surfaces; the effect is striking and is the most diagnostic feature of this mineral. The luster of this pinacoid is dull to pearly and noticeably distinct; incipient cleavages are copiously developed and give this pinacoid the appearance of a mica cleavage. The luster of freshly broken surfaces and other crystal faces of cianciulliite is adamantine to vitreous. The density was not determined because there are abundant incipient cleavages; the calculated value is 2.87 g/cm<sup>3</sup> (for 4H<sub>2</sub>O

per unit cell). The flexibility of cianciulliite is comparable to that of clinocllore. The hardness could not be measured, but the mineral is very soft; we estimate it at 2 (Mohs). There is no discernible UV fluorescence.

Only the thinnest fragments of cianciulliite transmit light. Cianciulliite is dark reddish brown, but the exterior of crystals appears opaque dark brown. Because the mineral is very dark red-brown color in transmitted light, the Becke line is difficult to observe. One crystal sufficed to make two grain mounts; no pleochroism was observed, and the indices of refraction are between 1.76 and 1.92. Because we had an exceedingly small amount of material available, only the reflected-light optical properties were determined in detail.

### OPTICAL PROPERTIES IN REFLECTED LIGHT

A crystal cluster was mounted in cold-setting epoxy resin and polished using the procedure outlined in Criddle et al. (1983). An excellent polish could not be obtained because of the mineral's tendency for plucking and pitting along its micalike cleavage. Cianciulliite is very weakly anisotropic, and this, combined with its dominant very fine lamellar structure, meant that areas that would extinguish uniformly between crossed polars could not be found.

In plane-polarized light, cianciulliite is gray, very weakly bireflectant, and not observably pleochroic. When immersed in oil ( $n_D = 1.515$ ), it becomes a slightly darker and bluer gray. It possesses orange-red internal reflections that are evident even in plane-polarized light.

Reflectance measurements were made in air on two areas of the polished section, carefully chosen to exclude internal reflections, using the equipment and procedures described by Criddle et al. (1983) but relative to a silicon carbide reflectance standard (Zeiss no. 472). During measurement, the areas were oriented for measurement at

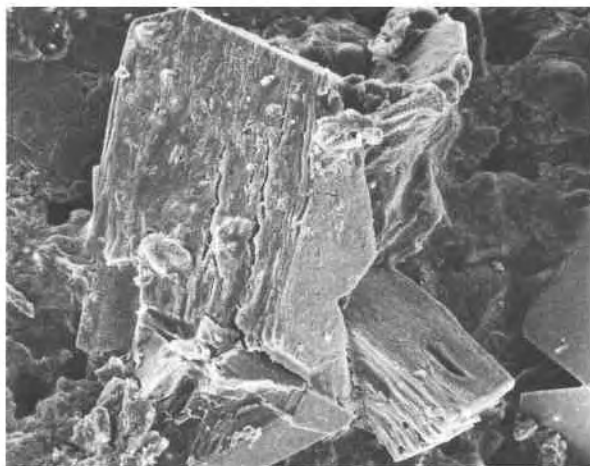


Fig. 1. Typical cianciulliite crystals from Franklin, New Jersey. The abundant incipient cleavage is very obvious. Field of view is 0.3 mm in maximum dimension.

orthogonal positions corresponding to photometric maxima and minima at 550 nm. (Extinction positions could not be determined for the reasons stated above.) Given the imperfection of the polished surfaces, the results (Table 1) should be regarded as approximate. However, refractive indices calculated from the reflectances using the Fresnel relationship at 589 nm of 1.79–1.80 are in keeping with those obtained in transmitted light.

#### CHEMICAL COMPOSITION

Cianciulliite was chemically analyzed using an ARL-SEMQ electron microprobe, a 15 kV acceleration voltage, a 0.025  $\mu$ A sample current, and a 30  $\mu$ m beam spot for the final analysis after checking for homogeneity with a small beam spot. The standards used were manganite (Mn), synthetic ZnO (Zn), and hornblende (Mg). A wavelength-dispersive scan did not reveal the presence of other elements with  $Z > 10$ . There is insufficient material for the determination of H<sub>2</sub>O by any available chemical analytical procedure.

Cianciulliite is markedly unstable under the electron beam. After first checking for homogeneity with a small beam spot, cianciulliite was analyzed using a 30  $\mu$ m beam spot and employing careful migration of the sample. The analyst (P.J.D.) has successfully used this method to analyze numerous other highly hydrated or unstable minerals, some of which have H<sub>2</sub>O contents similar to that of cianciulliite. The analysis under these optimum conditions yielded MgO 9.2, MnO 27.8, ZnO 31.1, H<sub>2</sub>O (31.9), total = 100 wt%. This analysis is presented here as the best obtainable, but as we note below, it is inaccurate.

Crystal structure analysis of cianciulliite (Grice and Dunn, 1991) indicated that the H<sub>2</sub>O content, inferred above by difference, is possibly incorrect, on the high side by a factor of 2. Repolishing, recoating with C, and ad-

TABLE 1. Reflectance values and color values for cianciulliite

nm	Area 1		Area 2	
	$R_1$	$R_2$	$R_1$	$R_2$
400	9.52	9.72	9.67	9.78
420	9.13	9.30	9.13	9.28
440	8.85	8.97	8.85	9.00
460	8.65	8.74	8.67	8.74
480	8.44	8.56	8.46	8.57
500	8.34	8.44	8.32	8.40
520	8.23	8.35	8.24	8.31
540	8.09	8.25	8.16	8.23
560	8.06	8.21	8.07	8.16
580	8.01	8.20	8.01	8.06
600	7.98	8.18	8.01	8.06
620	7.96	8.18	8.05	8.10
640	7.98	8.18	8.08	8.11
660	7.98	8.18	8.07	8.13
680	7.93	8.15	8.03	8.09
700	7.90	8.14	7.99	8.06
Color values (illuminant C)				
$x$	0.303	0.304	0.304	0.303
$y$	0.307	0.308	0.307	0.307
Y%	8.1	8.3	8.1	8.2
$\lambda_d$	472	469	471	471
$P_s$ %	3.7	3.3	3.5	3.8

ditional analyses of the sample, using both the original best-choice standards and additional standards, did not improve the analytical results. The use of a relatively small, 5- $\mu$ m beam appears to have volatilized much of the H<sub>2</sub>O content of cianciulliite, yielding results with greatly enhanced oxide weight percents and a commensurately lower H<sub>2</sub>O content. Metal ratios were unaffected.

Thus, the instability of cianciulliite, resulting from very loosely bound H<sub>2</sub>O molecules (Grice and Dunn, 1991), has precluded an accurate analysis by microbeam methods, and the extreme paucity of material precludes the use of other methods. Accordingly, we have recalculated separately the microprobe analysis given above to sum to 100 wt% with two and with four H<sub>2</sub>O molecules per five octahedral cations, as indicated by the structure determination (Grice and Dunn, 1991). The analysis with 2H<sub>2</sub>O yields MnO 29.7, MgO 9.86, ZnO 33.36, H<sub>2</sub>O 27.08, total = 100 wt%, and the analysis with 4H<sub>2</sub>O yields MnO 27.56, MgO 9.15, ZnO 30.97, H<sub>2</sub>O 32.32, total = 100 wt%. These yield the chemical formula Mn(Mg,Mn)<sub>2</sub>Zn<sub>2</sub>(OH)<sub>10</sub>·2–4H<sub>2</sub>O, with cation site assignments from the crystal structure determination.

#### X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show cianciulliite to be monoclinic with possible space groups  $C2/m$ ,  $Cm$ , and  $C2$ . The crystal structure determination (Grice and Dunn, 1991) establishes the centrosymmetric space group  $C2/m$  as the correct one. Unit-cell parameters were refined from X-ray powder diffraction data obtained with a Gandolfi camera with diameter of 114.6 mm and FeK $\alpha$  radiation (Table 2). The refined unit-cell parameters are  $a = 15.47(2)$ ,  $b = 6.369(6)$ ,  $c = 5.576(6)$  Å, and  $\beta = 101.29^\circ$ , with  $V = 538.8(6)$  Å<sup>3</sup> and  $Z = 2$ .

TABLE 2. X-ray powder diffraction data for cianciulliite

$l_{\text{obs}}$	$d_{\text{meas}}$ (Å)	$D_{\text{calc}}$ * (Å)	$hkl$
10	7.61	7.59	200
1	5.88	5.87	110
2	5.47	5.47	001
<1	4.95	4.92	201
2	4.17	4.16	$\bar{1}11$
1	4.07	4.07	201
5	3.96	3.96	310
<1	3.80	3.79	400
		3.47	$\bar{3}11$
3	3.45		
		3.44	401
1	3.187	3.185	020
4	2.997	2.997	311
<1	2.938	2.936	220
2	2.865	2.865	401
		2.752	021
6	2.745		
		2.749	202
3	2.673	2.673	221
2	2.645	2.643	511
1	2.558	2.554	$\bar{1}12$
<1	2.526	2.529	600
<1	2.509	2.509	221
<1	2.486	2.488	601
		2.458	402
<1	2.459		
		2.439	420
1	2.429	2.431	312
		2.425	202
<1	2.292	2.292	511
<1	2.134	2.133	512
<1	2.104	2.104	312
<1	2.084	2.081	222
		1.981	131
<1	1.980		
		1.980	620
1	1.960	1.961	621
		1.958	330
<1	1.947	1.946	422
1	1.895	1.897	800
1	1.808		
1	1.777		
1	1.740		
<1	1.725		
<1	1.629		
2	1.606		
<1	1.594	1.592	040
<1	1.582	1.583	023
<1	1.557		
<1	1.549		
<1	1.511		
2	1.494	1.494	821
1	1.453		

\* Calculated from cell parameters refined from powder-diffraction data:  $a = 15.47(2)$ ,  $b = 6.369(6)$ ,  $c = 5.576(6)$  Å,  $\beta = 101.29(9)^\circ$ .

### OCCURRENCE

Cianciulliite is found on just one museum specimen from the Franklin mine, Franklin, Sussex County, New Jersey. Nothing is known of the geologic occurrence; the specimen is a micromount and is generally representative

of material found in secondary veins at Franklin. The matrix is an orange, fine-grained mixture of willemite and zincite that have replaced coarse crystals of some other, unknown species. The surface of this composite matrix is coated, irregularly and sparsely, with minute, thin films of black material resembling manganese oxides. The principal minerals present as late crystallizing phases are abundant, colorless disphenoids of cahnite and very sparse cianciulliite crystals, both randomly distributed on the matrix. Cianciulliite is a very rare mineral.

### DISCUSSION

Most Mn at Franklin and Sterling Hill is present as  $\text{Mn}^{2+}$  in the primary ore minerals, carbonates, and the very numerous associated silicates. Divalent Mn occurs secondarily in many anionic groups, particularly in silicates and in over 20 manganese arsenate minerals. Manganosite,  $\text{MnO}$ , is of restricted occurrence at Franklin but was locally abundant.

Pyrochroite, which is common locally in veins, and cianciulliite, the rare mineral described here, are the only two secondary, divalent-manganese hydroxide species found at Franklin or Sterling Hill. The secondary manganese oxide minerals that have Mn in higher oxidation states are generally found in specific localities. With the significant exception of hetaerolite,  $\text{ZnMn}_2^{3+}\text{O}_4$ , which occurs at both ore bodies, secondary trivalent manganese oxides (e.g., feiknechtite, groutite, hausmannite, manganite) are very rare and known principally from the Franklin deposit. Secondary, hydrated, quadrivalent manganese oxides (aurorite, birnessite, chalcophanite, todorokite, and woodruffite) are moderately abundant at Sterling Hill but are mostly restricted to an anomalous and extensively oxidized saprolite zone, the "mud-zone." None of these minerals is present in economically significant amounts at these deposits.

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