CHILDRENITE-EOSPHORITE SERIES*

CORNELIUS S. HURLBUT, JR., Harvard University, Cambridge, Massachusetts

Abstract

An optical study of the childrenite-eosphorite series shows twinning in all well-crystallized members indicating monoclinic symmetry. In singly terminated crystals twinning is on {100}; in doubly terminated crystals twinning is on both {100} and {001}. The dimensions of the pseudo-orthorhombic unit cell as determined on crystals from Newry, Maine are: $\alpha_0=10.45$ Å, $b_0=13.49$ Å, $c_0=6.93$ Å, $\beta=90^{\circ}00'$. A re-examination of material from old localities and study of crystals from three new localities shows a fairly uniform increase in refractive index and specific gravity with increase in FeO. The optical properties of zoned crystals indicate a complete isomorphous series between the iron and manganese endmembers. The optical orientation and dispersion for eosphorite is: $Z/c=3^{\circ}-8^{\circ}$, r<v; for high iron childrenite, $Y/c=6^{\circ}-8^{\circ}$, r>v. Extrapolating from measured values of specific gravity, G=3.20 for the iron end-member, G=3.05 for the manganese end-

INTRODUCTION

Eosphorite was first described by Brush and Dana (1878) from Branchville, Connecticut. They pointed out the crystallographic similarity of their new mineral to childrenite and showed that the formulas of the two were identical with the exception of the dominant divalent metal which was manganese in eosphorite and iron in childrenite. Later Drugman (1914) extended the knowledge of this isomorphous series by crystallographic measurements and chemical analyses of childrenite from the Crinnis mine, Cornwall, and of eosphorite from Poland, Maine. Other analyses of eosphorite are given by Landes (1925) and Palache and Shannon (1928), and of childrenite by Otto (1935).

During the optical examination of crystals of eosphorite in a recently acquired specimen from Newry, Maine, the writer noticed the presence of twinning. An examination of specimens from other localities showed this phenomenon to be found in all well-crystallized material. Since twinning in eosophorite has not been previously reported, a reexamination of the whole group was felt to be desirable.

Eosphorite from three new localities, Red Hill and Black Mountain, both in Rumford, Maine, and North Groton, New Hampshire, was available for study.

Because of Professor Larsen's outstanding contributions to the knowledge of the optical properties of minerals, it seems fitting to include this optical study in a volume dedicated to him. Moreover, it was he in the various capacities of teacher, employer, colleague and friend who influenced the writer to undertake a career in mineralogy.

^{*} Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 317.

Eosphorite

The name eosphorite was given by Brush and Dana (1878) to the ironpoor analogue of childrenite. The mineral described by them contained 7.22% FeO (average of three analyses). The formula for the manganese end-member of the isomorphous series can be written MnAl(PO₄) (OH)₂.H₂O. Eosphorite was described as orthorhombic with crystallographic measurements and axial ratios closely resembling those of childrenite, FeAl (PO₄) (OH)₂.H₂O.

Newry, Maine. Eosphorite from Newry was described by Palache and Shannon (1928). During 1949 several specimens of the mineral were found there which proved to be very similar to the original. The smallest crystals (about 0.1 mm. long) are a light brown but with increasing size they become darker and the largest (4 mm. long) are black. The habit of most of the crystals is the same with a nearly square cross section formed by the pinacoids $a\{100\}$ and $b\{010\}$ as shown in Fig. 1. However, a few of the smaller crystals are flattened on $\{010\}$ (Fig. 2). All are terminated by $s\{121\}$.



Eosphorite. Newry, Maine.

Optical examination of these smaller more transparent crystals showed, when lying on $\{010\}$, a difference in the extinction positions of the two halves of the crystal. In all cases the line dividing the two parts was sharp and the extinction angle varied from 6° to 8°. There seems to be no other interpretation but that the crystals are twinned by reflection on $\{100\}$ and that they are monoclinic rather than orthorhombic. Figure 3 is a photomicrograph of such a twin and Fig. 4 shows the optical orientation of the two individuals.

It will be noted in Fig. 3 that in addition to the line marking the twin boundary, there are zone lines parallel to the apex of the crystal. From the indices of refraction it is apparent that these lines represent changes in the composition from the base to the top. The following optical properties were obtained on a crystal one millimeter long:

Optical Propertie	5 OF	EOSPHORITE,	NEWRY, MAINE
-------------------	------	-------------	--------------

Orientation	Base of crystal $n(Na)^*$	Tip of crystal $n(Na)$	
X = b	1.638	1.639	Opt.—
Y	1.660	1.664	$2V = 50^{\circ}$
$Z \wedge c = 6^{\circ} - 8^{\circ}$	1.667	1.671	r < v, strong

From the curves given in Fig. 11, these variations in refractive indices would indicate that the base of the crystal contains approximately 10%



FIG. 3. Photomicrograph of eosphorite lying on {010} showing twinning.



FIG. 4. Optical orientation of twinned individuals shown in Fig. 3.

FeO and the tip approximately 13% FeO. However, the FeO content in the crystals as a whole is 10.10 (average of three determinations) indicating that the iron-rich portion is small.

Shannon, in his analysis of eosphorite from Newry, reported 3.74% FeO. Two new iron determinations^{**} made on the original material of Palache and Shannon (1928) gave 9.56% and 10.28% FeO. The FeO in the new material was found to be 10.45%. Since the optical and other physical properties of the two specimens are identical, it would appear that the original analysis is in error.

Because the Newry eosphorite crystals are rough and striated, goniometric measurements were unsatisfactory and did not lead to the determination of axial ratios. The measurements, however, were sufficiently

* The indices of refraction as given throughout were determined by the immersion method using sodium light and are correct to ± 0.001 .

** All the new chemical analyses reported here were made by F. A. Gonyer, Harvard University.

good to determine that the only forms present are $a\{100\}$, $b\{010\}$, and $s\{121\}$. The pseudoorthorhombic symmetry is produced by the repetition of $\{121\}$ at the back of the crystal by twinning.

Rotation photographs and zero, first and second layer line Weissenberg x-ray photographs were taken about both [010] and [001], using a single individual. Additional Weissenberg photographs were taken using a twin. The corresponding photographs of the twin and single crystal were identical showing that the crystallographic angle β is 90° and that the twinning brings about no nonparallelism in the lattice. In Table 1 are given the dimensions of the unit cell and the axial ratios for the established pseudo-orthorhombic position, which it seems wise to retain. The corresponding values for childrenite determined by Barnes (1949) are also given.

 TABLE 1. DIMENSION OF THE UNIT CELL AND AXIAL RATIOS OF

 EOSOPHORITE AND CHILDRENITE

Unit Cell Dimensions

	Eosphorite (Newry)	Childrenite (Tavistock)
	$a_0 = 10.45 \text{ Å}$	$a_0 = 10.38$ Å
	$b_0 = 13.49 \text{ Å}$	$b_0 = 13.36$ Å
	$c_0 = 6.93 \text{ Å}$	$c_0 = 6.911 \text{ Å}$
	A	xial Ratios
Morphology:	a:b:c=0.7745:	$1:0.5139^*$ $a:b:c=0.7780:1:0.5258$
Unit Cell:	$a_0:b_0:c_0=0.7745:$	$a_0:b_0:c_0=0.7766:1:0.5173$

* Morphological ratios from the unpublished manuscript of the 7th edition of Dana's System of Mineralogy.

The extinctions observed on the Weissenberg photographs of eosphorite are the same as those reported for childrenite by Barnes (1949), who determined the space group as *Bba2*. It seems impossible to reconcile these extinction criteria with the optical properties. However, inasmuch as the optical evidence for monoclinic symmetry is strong, the lower symmetry is here assumed to be correct and the mineral monoclinic.

The specific gravity of eosphorite from Newry was given by Palache and Shannon as 3.069. Several new determinations using the large black crystals gave various values ranging from 3.06 to 3.08. However, the specific gravity of the smaller transparent crystals was determined as 3.10 by suspension in methylene iodide. Since these crystals lack the cracks and slight alteration present in the larger ones, the higher value is assumed to be more nearly correct. Using the cell dimension for eosphorite given above, the calculated specific gravity is 3.112.

Buckfield, Maine. Eosphorite from Buckfield was described by Landes (1925); his original material was available for study. The eosphorite is in long yellow prismatic crystals as shown in Fig. 5. The chemical analysis made by Vassar (Landes, 1925) shows 1.38% FeO, the lowest percentage

of iron reported in any eosphorite. The indices of refraction are also the lowest and probably are very near those of the iron free end member. The specific gravity is 3.10. The crystals are all twinned by reflection on $\{100\}$ and each of the individuals shows an extinction angle against the twin plane of 5°-6°. Most of the crystals are zoned in much the same way as those from Newry and Red Hill with the material with higher refractive index at the tips. The major portion of each crystal has nearly constant refractive indices, those given by Landes.

Optical Properties of Eosphorite, Buckfield, Maine

Orientation	Bulk of crystals $n(Na)$	Tips of crystals $n(Na)$	Opt.—
X = b	1.629	1.637	$2V = 45^{\circ} - 50^{\circ}$
Y	1.650	1.661	r < v
$Z \wedge c = 5^{\circ} - 6^{\circ}$	1.658	1.668	

Hebron, Maine. The first description from an American locality of the childrenite-eosphorite series was given by Brush (1863) for the material from Hebron. Because its physical, pyrognostic and crystallographic properties were similar to the earlier described childrenite, it was called childrenite. Cooke (1863) described the crystallography and oriented the crystals with the b axis vertical. Larsen (1921) determined the optical properties and, because of the relatively low indices of refraction, concluded the mineral was eosphorite.



FIG. 5. Eosphorite. Buckfield, Maine.

FIG. 6. Eosphorite. Hebron, Maine.

The writer obtained from the National Museum the same specimen from Hebron (U.S. National Museum specimen #82429) used by Larsen. The crystals are uniform in size, about 2 mm. wide and 4 mm. long. They are flattened on $\{010\}$ with other forms $a\{100\}$, $m\{110\}$, $s\{121\}$, $q\{232\}$ (Fig. 6). Although Brush and Dana (1878) show a figure of a doubly terminated crystal from Hebron, all those seen were attached at one end. The crystals are partially altered and manganese oxide coatings along cracks give them a black color and render them nearly opaque. The crystals are probably twinned, but because it is impossible to transmit light through a complete crystal, no twinning was observed. The alteration also made it impossible to tell whether there is zoning. However, the variation within a single crystal of the indices of refraction, as given below, indicates zoning. Only the tips of the crystals give the higher indices.

OPTICAL PROPERTIES OF EOSPHORITE, HEBRON, MAINE

Orientation	n(Na)	
X = b	1.631-1.635	Opt.—
Y	1.657-1.665	$2V = \sim 50^{\circ}$
Z	1.663-1.671	r < v

A chemical determination gives 4.52% FeO. The specific gravity is 3.08 but may be low because of the altered nature of the crystals.

Poland, Maine. Drugman (1914) gives two analyses of eosphorite from Poland. An average of the two gives 5.15% FeO, 26.03% MnO. By the method of minimum deviation he determined nX = 1.642, nZ = 1.669.

A few isolated and broken crystals of eosphorite on specimens of other iron-manganese phosphates from Poland, Maine are all that are at present available in the Harvard collection. An optical study of these gave the following results: nX = 1.638, nY = 1.657, nZ = 1.665; X = b, $Z \land c = 3^{\circ}$, $2V = 45^{\circ}$, r < v. It is difficult to reconcile these refractive indices with Drugman's, for his method of determination should have been at least as accurate as that used by the writer. The specific gravity is 3.09.

Branchville, Conn. In their description of the minerals from Branchville, Brush and Dana (1878) give a crystal drawing of eosphorite. It is of a singly terminated crystal with the forms: $a\{100\}$, $b\{010\}$, $m\{110\}$, $n\{120\}$, $p\{111\}$, $s\{121\}$, $q\{232\}$. No crystals were available in the present study, for the only Branchville eosphorite in the Harvard collection is a rough radial aggregate. Consequently, the presence of twinning could not be determined.

Two chemical analyses by Penfield and one by Wells (Brush and Dana, 1878) give an average of 7.22% FeO and 23.15% MnO. Constant refractive indices indicate that the material is uniform and the optical properties determined by Larsen (1921) were verified. However, the specific gravity of 3.09, obtained both by suspension in heavy liquid and with the Berman balance, is at variance with G=3.134 given by Brush and Dana.

Black Mountain, Rumford, Maine. Eosphorite from Black Mountain found in cavities in feldspar is in excellent prismatic crystals ranging in length from 0.10 to 20.0 mm. The larger crystals are a reddish brown, the smaller are pale yellow. Thus in color there is a close resemblance to the crystals from Red Hill three miles away. The habit of the crystals from the two localities is somewhat similar, with the Black Mountain crystals showing the forms $a\{100\}$, $b\{010\}$, $m\{110\}$ and $s\{121\}$ (Fig. 7). In addition to the well crystallized material, a pale pink to colorless cosphorite also occurs at Black Mountain in coarse radial aggregates.

The indices of refraction of the crystals show a considerable range from base to tip indicating a compositional variation along the *c* axis. Several long crystals were broken and the specific gravity taken of the ends. For the base G=3.104; for the tip G=3.121. These values probably do not represent the true density of either extreme end, for the pieces used were not of uniform composition as shown by the refractive indices. For the coarse radial eosphorite G=3.10. Optically it appears to be very uniform, and a chemical analysis of it is given beyond.

Optical Properties of Eosphorite, Black Mountain, Maine

	Cry	stals	Coarse	
Orientation	Base	Tip	Aggregate	
	n(Na)	n(Na)	n(Na)	
X = b	1.638	1.642	1.640	Opt. $(-)$
Y	1.660	1.674	1.660	$2V = 50^{\circ}$
$Z \wedge c = 6^{\circ}$	1.667	1.680	1.667	r < v

Analysis 1 below is of the radial eosphorite from Black Mountain. For comparison are given analyses of eosphorite from Buckfield, Maine (2) and of childrenite from St. Austell, Cornwall, England (3).

	1	2	3
P_2O_5	30.91	29.89	29.92
SiO_2		.90	
Al_2O_3	23.90	22.37	21.43
FeO	11.37	1.38	28.56
MnO	18.41	29.94	3.11
CaO			0.65
Na ₂ O	2000		0.37
H_2O	15.26	15.34	15.80
F		trace	
Total	99.85	99.82	99.84

CHEMICAL ANALYSES OF EOSPHORITE AND CHILDRENITE

1. Black Mountain, Rumford, Maine. F. A. Gonyer, analyst.

2. Buckfield, Maine. H. Vassar, analyst (Landes, 1925).

3. St. Austell, Cornwall, England. (H. Otto, 1935).

North Groton, New Hampshire. In the spring of 1949 eosphorite was discovered at the Palermo mine, North Groton, associated with other

iron-manganese phosphates. The best specimen from this locality was found by Mr. Charles Weeks and was loaned to the writer for study. The crystals are transparent, of a light brown color and very similar in habit to those from Newry (Fig. 2), flattened on {010}.



FIG. 7. Eosphorite. Black Mountain, Rumford, Maine.

FIG. 8. Childrenite. Tavistock, Devonshire, England.

The Palermo eosphorite crystals show extreme compositional variation from the base to the tip as indicated by the refractive indices. All the crystals show twinning by reflection on $\{100\}$ with an extinction angle angle against c of 8°. It was impossible to segregate separate portions of the crystals for iron determinations or for specific gravity measurements. For the crystals as a whole there is 12.15% FeO and G = 3.12.

Optical Properties of Eosphorite, North Groton, New Hampshire

	Base of crystals	Tip of crystals		
Orientation	n(Na)	n(Na)		
X = b	1.641	1.653	colorless	Opt. –
Y	1.665	1.673	colorless	
$Z \wedge c = 8^{\circ}$	1.669	1.683	brown	r < v
	$2V = 35^{\circ}$	$2V = 50^{\circ}$		

Red Hill, Rumford, Maine. The Red Hill eosphorite is in cavities in feldspar associated with amythestine quartz. It is reddish brown in color. There are two generations of crystals; the earlier are the larger with a maximum length of about 1 cm. The later crystals which vary in length from 0.1 to 1.0 mm. are arranged in radial groups and as subparallel overgrowths on the earlier crystals. The habit of both generations of crystals is the same and similar to crystals from Black Mountain (Fig. 7) with the forms $a\{100\}$, $m\{110\}$, and $s\{121\}$ and on some crystals $b\{010\}$ poorly developed.

CHILDRENITE—EOSPHORITE SERIES

The indices of refraction, as given below, indicate that the earlier deposition, as in the zoned crystals at Newry and elsewhere, is lower in iron. Moreover, the specific gravity, which for the earlier crystals is 3.14 and for the later crystals 3.15, indicates a like compositional difference. In the larger crystals there is 14.62% FeO and 13.86% MnO. Because of insufficient material chemical determinations were not made on the smaller crystals but the curves in Fig. 11 would indicate about 20% FeO.

Optical Properties of Eosphorite from Red Hill, Rumford, Maine

Early	/ large crystals	Late	small crystals
Orientation	n(Na)	Orientation	n(Na)
$\mathbf{X} = b$	1.640 colorless	X = b	1.644 colorless
Y	1.664 yellow	Y	1.673 pale yellow
$Z \wedge c = 4^{\circ}$	1.670 light brown	$Z \wedge c = 2^{\circ}$	1.679 yellow
	For both crystals: Opt.	$-, 2V = 45^{\circ}, r < v, s$	trong.

CHILDRENITE

Of the specimens available for study only those from England have a sufficiently high excess of FeO over MnO to be called childrenite. The average of four childrenite analyses by Drugman (1915) from the Crinnis mine near St. Austell, Cornwall gives 28.30% FeO, 3.35% MnO. Otto (1935) in an analysis of material from the same locality gives 28.56% FeO, 3.11% MnO. The other major occurrence is in the George and Charlotte mine near Tavistock, Devonshire. Three analyses of childrenite from Tavistock are available; Rammelsberg (1852), Church (1873), Penfield (1880). No indices of refraction are given for the first two, but Otto (1936) gives indices which he implies are for the childrenite analyzed by Penfield. The writer checked these indices and on the same material Gonyer determined 26.40% FeO. Penfield's analysis gives 26.54% FeO and 4.87% MnO.

Crystals from the two English localities, unlike crystals of eosphorite, are doubly terminated. Figure 8 illustrated a common habit at Tavistock and Fig. 9 at St. Austell. It was hoped that these doubly terminated crystals would show some morphological evidence of twinning that is lacking in the singly terminated eosphorite. However, as illustrated in the figures, the crystals appear to have perfect orthorhombic symmetry.

When a crystal is cut or broken so that it will lie parallel to $\{010\}$, it shows twinning under polarized light. Moreover, in addition to twinning by reflection on $\{100\}$ as in eosphorite, it is also twinned by reflection on $\{001\}$. Between crossed nicols a $\{010\}$ plate shows a fourling (Fig. 10) made up of two individuals.

It is not surprising that this twinning has not been noted previously

since the {010} form is lacking or is poorly developed and it is only with difficulty that a crystal can be oriented in such a way as to permit the twinning to be observed.

The optical properties of childrenite can be summarized as follows:

	OPTICAL PROPERT	IES OF CHILDRENITE	
	Tavistock	St. Austell	
Orientation	n(Na)	n(Na)	
X = b	1.643	1.643-1.646	Opt. –
$Y \land c = 8^{\circ}$	1.678	1.676-1.681	$2V = 50^{\circ}$
Z	1.684	1.681-1.687	r > v, strong

Childrenite differs from eosphorite not only in having higher indices of refraction but also in dispersion and in optical orientation. In all eosphorite the dispersion is r < v; in childrenite r > v, strong. In eosphorite Z makes a small extinction angle with c; in childrenite Y makes the



FIG. 9. Childrenite. St. Austell, Cornwall, England.

FIG. 10. Childrenite lying on (010) showing optical orientation in fourling.

corresponding extinction angle with c. Although most of the crystals examined from St. Austell gave an 8° extinction angle, some portions of zoned crystals show an extinction angle as low as 1°. This low angle is on that portion with the lower refractive indices.

The specific gravity of childrenite has been given as high as 3.24. However, several determinations gave consistant results as follows: Tavistock G = 3.18, St. Austell G = 3.19. The calculated value of Barnes (1949) for childrenite is G = 3.186.

Other Occurrences. Gordon (1944) describes childrenite from Llallagua,

802

Bolivia, and gives a chemical analysis showing 21.69% FeO and 4.21% MnO. However, his indices of refraction, nX = 1.652, nY = 1.660, nZ = 1.678, give the mineral a *positive* optical sign which is at variance with the sign as determined on all other members of the series. His specific gravity of 3.05 is also low for such a high iron member.

Mason (1942) reported the presence of eosphorite in a specimen from Hühnerkobel, Bavaria. Since he gives no chemical analysis and the material was not available for an iron determination, his data are not listed in Table 2. The indices of refraction, nX = 1.642, nY = 1.663, nZ = 1.669, fit the curves in Fig. 11 reasonably well and correspond to an eosphorite with about 12% FeO. The specific gravity is given as 3.07.

Locality	% FeO	% MnO	nX	nY	nΖ	2V	Orienta- tion X=b	Dis- persion	G
1. Buckfield, Maine	1.38	29.94	1,629	1.650	1.658	45°	$Z \wedge c = 5^{\circ}$	r < v	3.10
2. Hebron, Maine	4.52		1.631	1.657	1.663	50°		r < v	3.08
3. Poland, Maine	5.15	26.03	1.638	1.657	1.665	45°	$Z = c = 3^{\circ}$	r < v	3.09
4. Branchville, Conn.	7.22	23.15	1.633	1.656	1,664	51°		r < v	3.09
5. Newry, Maine	10.10		1.638	1.660	1.667	50°	$Z = c = 6^{\circ}$	r < v	3.10
6. Black Mt., Rumford,				G (1947	0.000		G Å (0		
Maine	10.26		1.640	1.660	1.667	50°	$Z \land c = 6^{\circ}$	r <v< td=""><td>3.11</td></v<>	3.11
 North Groton, N. H. Red Hill, Rumford, 	12.15		1,641	1.665	1.669	35°	$Z \land c = 8^{\circ}$	r <v< td=""><td>3.12</td></v<>	3.12
Maine 9. Tavistock, Devonshire,	14.62	13.86	1.640	1.664	1.670	45°	$Z \land c = 4^{\circ}$	r <v< td=""><td>3.14</td></v<>	3.14
England 10. St. Austell, Cornwall,	26.54	4.87	1,643	1.678	1,684	50°	Y∕\c=6°	r>v	3.18
England	28.56	3.11	1.646	1.681	1.687	50°	Y∕\c=8°	r>v	3.1

TABLE 2. SUMMARY OF OPTICAL DATA EOSPHORITE-CHILDRENITE SERIES

The curves of Fig. 11 made from the data summarized in Table 2 show a rather uniform increase in refractive index with increase in FeO. The birefringence also increases slightly with FeO. No analysis, with the exception of Gordon's, shows percentage of FeO between 14.62% and 26.56%. For this reason one might suspect that the series is one of limited isomorphism. However, the refractive indices of the zoned eosphorite crystals argue against this. If the higher sets of indices of these zoned crystals were plotted on the curves, they would fall within the gap, indicating that a portion of certain crystals have this intermediate composition. Both the high and low index parts of the zoned crystals have the same optical orientation and dispersion. Only in the high iron childrenite from England is there a change in the optical orientation and a reversal in dispersion.

C. S. HURLBUT, JR.



FIG. 11. Variation of indices of refraction and specific gravity with composition in childrenite-eosphorite series.

With only one marked exception, the specific gravity shows a regular increase with increase of FeO. Extrapolating from the curve, for the pure iron end-member G=3.20, for the pure manganese end-member G=3.05.

804

References

BARNES, W. (1949), Am. Mineral., 34, 12-18.

BRUSH, G. J., AND DANA, J. D. (1878), Am. Jour. Sci., Series 3, 16, 33-45.

CHURCH, A. H. (1873), Jour. Chem. Soc., 26.

COOKE, J. P. (1863), Am. Jour. Sci., 36, 258.

DRUGMAN, JULIEN (1915), Mineral. Mag., 17, 193-201.

GORDON, S. G. (1944), Proc. Acad. Nat. Sci. Phila., 96.

LANDES, K. K. (1925), Am. Mineral., 10, 384-386.

LARSEN, E. S. (1921), Bull. U. S. Geol. Survey, 679.

OTTO, VON HELMUT (1936), Mineralogische Mitt., 47, 89-140.

PALACHE, C., AND SHANNON, E. V. (1928): Am. Mineral., 13, 392-396.

PENFIELD, S. L. (1880), Am. Jour. Sci., 19, 315-316.

RAMMELSBERG, C. F. (1852): Ann. Phys. Chem., 85, 435.