ZINCIAN ROCKBRIDGEITE*†

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ABSTRACT

Zincian rockbridgeite, (Fe'', Mn'')(Fe'''$_{4-y}$, Zn$_y$)(PO$_4$)$_3$(OH)$_{5-y}$·yH$_2$O, is found in fibrous crusts as an alteration product of triphylite in pegmatite at Maxedo, Portugal. It is orthorhombic with cleavages (100) perfect, and (010) fair. The space group is $B22_12$ (D_2^5); $a_0=13.97$, $b_0=16.88$, and $c_0=5.19$ Å. The color is black. The streak and powder are dark green. H=4 to 4½; G=3.51. Indices of refraction and pleochroism: $\alpha=1.82$ (X=greenish blue), $\beta=1.83$ (Y=greenish to yellow brown), $\gamma=1.88$ (Z=deep blue); biaxial positive; 2V moderate with strong dispersion. Analysis: Na_2O 0.13, K_2O tr., Li_2O 0.01, CaO none, FeO 10.86, MnO 2.11, ZnO 5.20, Fe_2O_3 41.19, Mn_2O_3 none, P_2O_5 33.73, H_2O 6.75; insol. 0.30, total 100.28%.

INTRODUCTION

The mineral here described as zincian rockbridgeite was first encountered during the course of a study of dufrenite-like minerals by one of the authors and a summary notice of the mineral has already been published (Frondel, 1949). Zincian rockbridgeite has been found as a hydrothermal alteration product of triphylite in the pegmatite at Vianua do Castelo, Maxedo, Portugal. The material from Maxedo is associated with reddingite, which forms crystalline masses deposited upon crusts of zincian rockbridgeite, together with quartz and small amounts of granular sphalerite. Similar material from Hagendorf, Bavaria, is associated with phosphoferrite (the iron analogue of reddingite), eosphorite, vivianite, and wolfeite (the iron analogue of triploidite). Members of the frondelite-rockbridgeite series can be differentiated from zincian rockbridgeite on the basis of the intensities of the strongest lines in the powder photograph.

PHYSICAL AND OPTICAL PROPERTIES

Zincian rockbridgeite occurs as crusts and small botryoidal masses with a radial fibrous or thin-bladed structure. The surface of the masses is drusy and composed of subparallel aggregates of minute crystals with rounded and exfoliated terminations. No measurable crystals were found. The color is black, and the streak or fine powder is dark green. The mineral is opaque in large pieces, but crushed grains transmit

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light feebly and have a deep greenish-blue color. The luster of cleavage surfaces is vitreous and brilliant; the luster of the drusy, free surfaces is dull to satiny. The mineral appears to be fresh and unaltered and in this respect differs from dufrenite and members of the frondelite-rockbridgeite series, as ordinarily found. Hardness 4 to $4\frac{1}{2}$. Specific gravity 3.51. There are two cleavage directions parallel to the direction of the fibers; (100) is perfect and (010) fair.

Optically, zincian rockbridgeite is biaxial, positive, with strong dispersion, and 2V medium. The Z vibration direction is perpendicular to the best cleavage. Lath-like cleavage flakes show parallel extinction. The indices of refraction and the absorption colors of the Maxedo material are: $\alpha=1.82$ (X=greenish blue), $\beta=1.83$ (Y=greenish to yellow brown), $\gamma=1.88$ (Z=deep blue). The absorption formula is Z>X>Y.

TABLE 1. CHEMICAL ANALYSES AND RATIOS OF ZINCIAN ROCKBRIDGEITE FROM MAXEDO, PORTUGAL

Analysis		Ratios	Oxygen Equivalent	Metal Equivalent	Atoms per cell		
P_2O_5	33.73	0.2376	1.1880	0.4752	P	12.29	12.29
FeO	10.86	0.1511	0.1511	0.1511	Fe	3.91	4.81 (Fe, Mn, Li, Na)
MnO	2.11	0.0298	0.0298	0.0298	Mn	0.77	
CaO	none						
Li_2O	0.01	0.0003	0.0003	0.0006	Li	0.02	
K_2O	trace						
Na_2O	0.13	0.0021	0.0021	0.0042	Na	0.11	
ZnO	5.20	0.0639	0.0639	0.0639	Zn	1.65	14.99 (Zn, Fe)
Fe_2O_3	41.19	0.2579	0.7737	0.5158	Fe	13.34	
H_2O	6.75	0.3747	0.3747	0.7494	H	19.39	19.39
Insol.	0.30						
Total	100.28	Total O=2.584			O Atoms=66.85		

Lindberg, *analyst.*

Molecular weight by x-ray=2587.2 (G=3.51).

Ideal cell contents of zincian rockbridgeite

$(Fe'', Mn'')_4(Fe'''_{16-x}Zn_x)(PO_4)_{12}(OH)_{20-x}, xH_2O$

Cell contents from analysis

$(Fe'', Mn'')_{4.81}(Fe'''_{13.34}Zn_{1.65})(PO_4)_{12.26}(OH)_{16.23}1.58H_2O$

Formula

$(Fe'', Mn'')(Fe'''_{4-y}, Zn_y)(PO_4)_3(OH)_{5-y}\cdot yH_2O$

CHEMICAL COMPOSITION

An analysis of zincian rockbridgeite from Maxedo, Portugal, is given in Table 1. The mineral is of unusual interest because of the large content of ZnO, 5.20%. The atoms per cell were found by multiplying by the following factors: (1) by 0.01 to convert from a percentage to a fraction scale; and (2) by 2587.2, the molecular weight determined from the *x*-ray cell contents and specific gravity. Because simple ratios were first obtained by grouping zinc with other divalent ions, $Fe''Fe'''_4(PO_4)_4(OH)_4 \cdot H_2O$ was at first thought to be the formula of the mineral. The formula, however, did not satisfy the space-group requirement of a minimum of four equivalent positions per unit cell, there being 6.5 atoms of divalent metals and 13.3 atoms of trivalent metals. Further, *x*-ray study by both single-crystal and powder methods indicates that the mineral is isostructural and equidimensional with frondelite-rockbridgeite and hence should conform to the formula of that series $(Fe'', Mn'')Fe'''_4(PO_4)_3(OH)_5$. H. Neumann (1949) in his discussion of the mineralogy and geochemistry of zinc points out that zinc minerals and ferrous iron-magnesium minerals with a corresponding formula usually have a different crystal structure and that there is a tendency for zinc to show selective replacement for atoms with tetrahedral coordination. If zinc substitutes for ferric iron rather than for ferrous iron, a formula similar to that of rockbridgeite is obtained. The substitution of divalent zinc for trivalent iron apparently is compensated electrostatically by a concomitant conversion of hydroxyl to water. The cell contents for this substitution are shown in Table 1. The formula $(Fe'', Mn'')(Fe'''_{4-y}, Zn_y)(PO_4)_3(OH)_{5-y} \cdot yH_2O$, can be derived from the cell contents by dividing by four, the number of equivalent positions in the unit cell. In this division, x/4 was set equal to y in the formula in order not to have a fraction appear as a variable.

Zincian rockbridgeite was formed by the hydrothermal alteration of triphylite containing admixed sphalerite, from which the zinc was derived. The mineral recalls the occurrence at Hagendorf of phosphophyllite, $Zn_2(Fe'', Mn)(PO_4)_2 \cdot 4H_2O$, which similarly is a secondary mineral found associated with rockbridgeite, phosphosiderite, strengite, fairfieldite, and vivianite, and was derived by the alteration of triphylite admixed with sphalerite. Phosphophyllite was not observed on the present specimens.

Zincian rockbridgeite is easily fusible to a magnetic globule. It is soluble in dilute and concentrated HCl, but insoluble in dilute and concentrated HNO_3 and H_2SO_4. It yields H_2O in a closed tube. A spectrographic analysis by H. R. Harrison, Department of Mineralogy, Harvard University, showed the following elements in amounts less than 0.0X%: Ca, Al, Si, Mg, Be, V, B.

The *x*-ray powder diffraction data suggested that rockbridgeite from Chanteloube, France (U.S.N.M., R5197), may have an intermediate position in the rockbridgeite-zincian rockbridgeite series, and a partial analysis of the material was made (see Lindberg, 1949, p. 543, for optical constants):

insoluble 1.98, P_2O_5 32.80, Fe_2O_3 53.03, Mn_2O_3 none, FeO 0.13, MnO 3.53, ZnO 0.13, H_2O 7.94 (Al_2O_3, CaO, MgO, K_2O, Na_2O not determined), total 99.54%.

X-Ray Data

Single-crystal rotation and Weissenberg photographs were taken using iron radiation and a manganese filter and rotating about the *b* and *c*

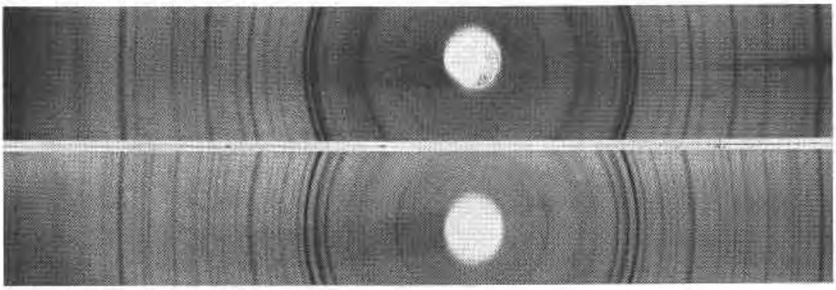

PLATE 1. Powder photographs of zincian rockbridgeite (top) and frondelite (bottom).

axes of fibers of zincian rockbridgeite. C_{2l} symmetry for the 0- and n-level Weissenberg pictures was clearly observed, and the orthorhombic character of the mineral hence confirmed. The lengths of the unit cell edges are $a_0=13.97$, $b_0=16.88$, and $c_0=5.19$ Å; the axial ratio is $a_0:b_0:c_0=0.8276:1:0.3075$. The volume of the unit cell is 1223.9 Å^3. The same space group extinctions noted for frondelite (Lindberg, 1949, p. 546) were observed for zincian rockbridgeite; the space group is $B_{22_12}(D_2^5)$.

In Table 2 are given the intensity and *d* values for corresponding lines of frondelite and zincian rockbridgeite, and the powder photographs are shown in Plate 1. Because of the large number of solutions possible for varying *hkl* for lines of high sin θ, lines with *d* spacings less than 1.5 Å were not solved. The intensity of certain lines, particularly those of low 2θ are quite different and a casual comparison suggests that the minerals are not related. The cell edges and space group, however, are the same as for frondelite, and the substitution of zinc for ferric iron doubtless accounts for different intensities. It is well known that two isomorphous crystals in which atoms of different diffracting powers occupy corresponding sites give diffraction patterns in which corresponding reflections have different intensities.

In the powder photograph of zincian rockbridgeite, (020) and (210) are much weaker than in frondelite. The greatest differences in intensi-

TABLE 2. COMPARISON OF X-RAY DIFFRACTION DATA FOR FRONDELITE AND ZINCIAN ROCKBRIDGEITE

(Iron radiation, manganese filter)
($\lambda=1.9373$)

	Frondelite			Zincian rockbridgeite		
From rotation and Weissenberg photographs		a_0	13.89		13.97	
		b_0	17.01		16.88	
		c_0	5.21		5.19	
Index	I	Observed d	Calculated d	I	Observed d	Calculated d
020	1	8.59	8.51	½	8.40	8.44
200	2	6.90	6.94	3	6.99	6.99
210	1	6.46	6.43	½	6.40	6.45
101	1	4.86	4.88	3	4.84	4.86
111	2	4.69	4.69	1	4.68	4.68
230	1	4.36	4.39	1	4.37	4.38
040	1	4.23	4.25	1	4.20	4.22
131	1	3.68	3.70	1	3.67	3.68
240	4	3.61	3.63	2	3.61	3.61
400	2	3.44	3.46	1	3.47	3.49
301						3.47
410	5	3.38	3.40	2	3.42	3.42
311		3.38	3.39	10	3.33	3.39
420	10	3.20	3.21	9	3.21	3.23
321						3.21
141						3.19
250	3	3.05	3.05	2	3.04	3.04
430	1	2.949	2.960	½	2.968	2.97
331		2.949	2.954	½	2.968	2.95
060	1	2.825	2.835	½	2.812	2.813
151	3	2.779	2.791	1	2.775	2.774
440	1	2.679	2.690	1	2.690	2.690
341	1	2.679	2.685	1	2.690	2.691
002	2	2.597	2.605	2	2.603	2.595
501	3	2.444	2.451			2.460
161			2.452			2.436
202		2.444	2.439			2.432
450			2.432			2.427
351	2	2.415	2.421	3 broad	2.429	2.418
212		2.415	2.414		2.429	2.408
222	1	2.340	2.345	1	2.322	2.338
270	2	2.292	2.294	1	2.279	2.279
610		2.292	2.294			
232	1	2.234	2.224		missing	
460				½	2.185	2.191

TABLE 2. *Continued*

	Frondelite			Zincian rockbridgeite		
From rotation and Weissenberg photographs:		a_0	13.89	13.97		
		b_0	17.01	16.88		
		c_0	5.21	5.19		
Index	*I*	Observed *d*	Calculated *d*	*I*	Observed *d*	Calculated *d*
171	1	2.175	2.175	½	2.160	2.160
080	2	2.121	2.126	½	2.119	2.110
052	2	2.064	2.068	2	2.059	2.057
422	2	2.030	2.024	1	2.032	2.022
252	3	1.979	1.983	2	1.972	1.974
432	2	1.957	1.956		missing	
181			1.949	½	1.937	1.936
062	1	1.913	1.918	½	1.980	1.907
701	3	1.849	1.852	1	1.869	1.863
262			1.849	1	1.845	1.840
480	1	1.808	1.813	½	1.808	1.806
800		missing		1	1.746	1.746
571				1	1.726	1.722
272	1	1.723	1.722	½	1.714	1.713
820	2	1.694	1.700			1.710
0.10.0				½	1.687	1.688
123			1.689			
830				2	1.665	1.667
490	2	1.659	1.661	1	1.651	1.652
840				2	1.615	1.614
323	5	1.598	1.597	2	1.602	1.593
642						1.603
143			1.597			
333	2	1.562	1.563	1	1.561	1.558
153	2	1.537	1.537	1	1.543	1.530

ties occur at values of *d* between 3.7 and 3.2. For frondelite there are two pairs of doublets (3.68, 3.61; 3.44, 3.38) followed by the strongest line at 3.20. In zincian rockbridgeite there are two pairs of doublets (3.67, 3.61; 3.47, 3.42) followed by the two strongest lines at 3.33 and 3.21. The differences in intensity and spacings are tentatively explained thus: in frondelite the line with *d*-spacing 3.38 (observed) corresponds to the (410) and (311) reflections occurring at 3.40 and 3.39 Å (calculated). In zincian rockbridgeite the (410) and (311) reflections are separated and occur at 3.42 (410) (observed and calculated) and 3.33 (311) (observed), 3.39 (calculated). The intensity differences are assumed due in part to isomorphous substitution of zinc. The Weissenberg pictures of both frondelite and zincian rockbridgeite show strong reflections for (311) and (410). There is a greater difference between observed and calculated values for the (311) reflection than was noted for other reflections; the reason for this difference is not readily apparent. It may be noted that the *d*-spacing for this line of intensity 10 is 3.33, not 3.40 as reported by Frondel (1949, p. 538 "Maxedo unknown").

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References

Frondel, Clifford (1949), The dufrenite problem: *Am. Mineral.*, **34**, 513–540.

Lindberg, Marie Louise (1949), Frondelite and the frondelite-rockbridgeite series: *Am. Mineral.* **34**, 541–549.

Neumann, H. (1949), Notes on the mineralogy and geochemistry of zinc: *Mineralog. Mag.* **28**, 575–581.