## VEATCHITE AND p-VEATCHITE\*

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## ABSTRACT

Comprehensive single-crystal x-ray precession studies on type material of two strontium borate hydrates, veatchite (Switzer, 1938; Switzer and Brannock, 1950; Clark et al., 1959) and p-veatchite (Braitsch, 1959), show that despite striking similarities the two minerals can be distinguished by single-crystal x-ray diffraction patterns. Both minerals are monoclinic: veatchite A2/a (or Aa), a=20.81, b=11.74,  $c=6.62_6$  Å (all  $\pm 0.3\%$ ),  $\beta=92^{\circ}07'\pm05'$  perfect cleavage parallel to dominant plate form  $\{100\}$ , optical orientation Z=b, X=c,  $Y \land a=2^{\circ}$ ; p-veatchite  $P2_1/m$  (or  $P2_1$ ),  $a=6.72_9$ , b=20.70,  $c=6.58_1$  Å (all  $\pm 0.3\%$ ),  $\beta=119^{\circ}40'\pm05'$ , perfect cleavage parallel to dominant plate form  $\{010\}$ , optical orientation Y=b, X=c,  $Z \land a=29^{\circ}40'$ . Indexed x-ray powder data, presented for both minerals, are inadequate for positive identification. Assumption of the chemical formula,  $SrO \cdot 3B_2O_3 \cdot 2H_2O$ , for each mineral yields the following comparison of calculated and observed densities (g. cm.  $^{-3}$ ): veatchite  $2.85_7$  calc. (8 formula units per cell),  $2.78\pm0.03$  obs. (Clark et al., 1959); p-veatchite  $2.90_7$  calc. (4 formula units per cell), 2.60-2.65 obs. (Braitsch, 1959). Dimorphism is possible but not established by present evidence.

A new mineral p-veatchite, (Sr, Ca)O·3B<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O, has been described by Braitsch (1959) from an occurrence in Revershausen, near Göttingen, Germany. Noted by Braitsch were numerous striking similarities of pveatchite to veatchite, SrO·3B<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O (Switzer, 1938; Switzer and Brannock, 1950; Clark et al., 1958, 1959). Chemical, spectrographic, and x-ray fluorescence analyses, as well as indices of refraction, measured density values, crystal habit and crystal class, and x-ray powder patterns, all are the same within limits of observational errors for the two minerals. The only distinction between them was found in the single-crystal x-ray study, which revealed a change in direction of the unique monoclinic symmetry axis in p-veatchite compared with veatchite, together with variations outside the limits of error for values of the observed cell constants. Such a close relationship between two different substances is sufficiently unusual to raise doubts concerning the validity of the descriptions. However, the relationship has been fully confirmed by the present authors, who give briefly here the results of concurrent singlecrystal and powder x-ray examinations.

Crystals from the following localities were studied: veatchite from drill core no. 5, Four Corners area, Kramer district, San Bernardino County, California, supplied by R. C. Erd, U. S. Geological Survey, and described previously by Clark *et al.* (1958, 1959); veatchite taken from the type specimen, USNM 105697, Lang, Los Angeles County, California

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(Switzer, 1938; Switzer and Brannock, 1950); p-veatchite from type material, USNM 113264, Revershausen, Germany (Braitsch, 1959). The latter two specimens were made available to us through the courtesy of Dr. George Switzer, U. S. National Museum. Because the p-veatchite specimen consists of only two large crystals, preparation of a powder spindle was not feasible; however, Dr. Otto Braitsch, Mineralogical Institute, University of Göttingen, Germany, kindly permitted our use of the p-veatchite powder spindle prepared at the University of Göttingen from Reyershausen material. We are most grateful to each of these individuals, as well as to several colleagues at the U.S. Geological Survey: D. E. Appleman who suggested that the type veatchite be reexamined and carried out calculations for d-spacings of p-veatchite on a digital computer, E. C. T. Chao who gave valuable suggestions on presentation of the optical data, and C. L. Christ who provided critical guidance and helpful discussion during the course of the study. We are also indebted to Dr. C. A. Beevers, University of Edinburgh, Scotland, for permission to present his unpublished data on Eskdale material, originally described by Stewart, Chalmers, and Phillips (1954).

Single-crystal x-ray studies were carried out on quartz-calibrated precession cameras using Zr-filtered Mo radiation ( $\lambda$ =0.7107 Å) and Ni-filtered Cu radiation ( $\lambda$ =1.5418 Å). Film measurements were corrected for both horizontal and vertical film shrinkage. The crystallographic data found during the present study for veatchite and p-veatchite are given in Table 1. Several crystals were examined from the specimen of type veatchite from Lang, and all give single-crystal x-ray data identical within limits of observational errors with the data found for the Four Corners veatchite by Clark et al. (1959). No p-veatchite crystals were discovered on the Lang specimen, although the possibility of their presence in association with veatchite cannot be definitely ruled out. Comparison of available data for p-veatchite is made in Table 2. The findings of Braitsch (1959) are confirmed not only by the present study but also by Beevers (written communication, October 14, 1959) for Eskdale material, which his study identifies as p-veatchite.

The unit cell of p-veatchite can be chosen so as to be analogous in dimensions to the cell taken for veatchite (Clark et al., 1959), and comparison of these two similar cells is made in Table 1 and throughout the following discussion. Both minerals have a dominant plate form, to which the perfect cleavage is parallel and to which the short reciprocal axis (associated with the  $\sim$ 21 Å direct axis) is normal. In p-veatchite this axis is the monoclinic symmetry axis, its character being demonstrated by the intensity relationships among appropriate hkl reflections and the exactly 90° angles the axis makes with  $a^*$  and  $c^*$ , respectively.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR VEATCHITE AND p-VEATCHITE\*

	Veat	chite p-Veatchite <sup>a</sup>					
	Four Corners <sup>b</sup>	Lange	Reyershausen				
			(1) <sup>d</sup>	(2)			
a	20.81Å	20.81Å	11.69Å	6.729			
b	11.74	11.74	20.70	20.70			
c	6.637	6.626	$6.58_{1}$	6.581			
β	92°02′	92°07′	90°24′	119°40′			
	(All cell lengths $\pm 0.3\%$ ; angles $\pm 05'$ )						
a:b:c	1.773:1:0.565	1.773:1:0.564	0.565:1:0.318	0.325:1:0.318			
Space Group	A2/a (or $Aa$ )	A2/a (or $Aa$ )	е	$P2_1/m$ (or $P2_1$ )			
Volume	1620 ų	1618 Å3	1592 ų	796 ų			
Number of		-					
[SrO·3B <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> O] per unit cell	8	8	8	4			
Density, calc.	2.85 <sub>7</sub> g.cm. <sup>-3</sup>	2.86 <sub>1</sub> g.cm. <sup>-3</sup>	2.90 <sub>7</sub> g	.90 <sub>7</sub> g.cm. <sup>-3</sup>			
obs.	$2.78 \pm 0.03$	2.69f	2.60-2.				

<sup>\*</sup> Data of present study unless otherwise noted.

In veatchite the short reciprocal axis is at a distinct 88° angle to  $c^*$  and the intensity relationships among hkl reflections are not compatible with assignment of twofold symmetry to the short reciprocal axis. Accordingly, the axis normal to the plate must be  $b^*$  in p-veatchite, and, following the convention c < a, it becomes  $a^*$  in veatchite. Direct comparison of precession photographs of the similar reciprocal nets, veatchite h0l with p-veatchite 0kl, and veatchite 0kl with p-veatchite k0l, immediately reveals these distinctive differences. The p-veatchite x-ray cell chosen by Braitsch (1959) can be transformed to the cell that is analogous to veatchite with the matrix 201/010/001 (as noted by Braitsch).

The optic plane in each mineral is parallel to the plate form, and correlation of the optical directions and the x-ray crystallography is shown in Fig. 1a for veatchite and in Fig. 1b for p-veatchite. It is not clear whether the optical orientation given for p-veatchite by Braitsch (1959) is for the

 $<sup>^{\</sup>rm a}$  Values for p-veatchite crystals from type material (USNM 113264).

<sup>&</sup>lt;sup>b</sup> Values taken from Clark et al. (1959).

<sup>&</sup>lt;sup>c</sup> Values for veatchite crystals from type specimen (USNM 105697).

<sup>&</sup>lt;sup>d</sup> Values obtained from (2) using transformation matrix 201/010/001.

 $<sup>^{\</sup>circ}$  B2<sub>1</sub>/m, not a standard setting of Int. Tables (1952).

f Switzer (1938).

g Braitsch (1959).

	Present Study <sup>a</sup>	Braitsch (1959) <sup>b</sup>	Beeverse
a	6.72 <sub>9</sub> ±0.02 Å	6.72 <sub>1</sub> ±0.02 Å	6.74 Å
b	$20.70 \pm 0.04$	$20.81 \pm 0.02$	20.62
c	$6.58_1 \pm 0.02$	$6.64_7 \pm 0.02$	6.60
β	119°40′ ± 05′	$119^{\circ}04' \pm 10'$	119°38′
a:b:c	0.325:1:0.318	0.323:1:0.319d	0.327:1:0.320
Space Group	$P2_{1}/m \text{ (or } P2_{1})$	$P2_1/m$ or $P2_1$	$P2_1/m \text{ (or } P2_1)$
Volume	796 ų	$813 \pm 5 \text{ Å}^3$	797 Å <sup>3d</sup>
Cell Contents	$4[SrO \cdot 3B_2O_3 \cdot 2H_2O]$ ?	4[(Sr, Ca)O·3B <sub>2</sub> O <sub>3</sub> ·	
		2H <sub>2</sub> O]?	
Density (calc.)	2.90 <sub>7</sub> g.cm. <sup>-3</sup>	_	-
(obs.)	-	2.60-2.65	-

Table 2. Comparison of Crystallographic Data for p-Veatchite

cell defined by his x-ray study. The observation  $Z \land c = -30^{\circ}$  (Stewart, Chalmers, and Phillips, 1954) is evidently not correct for the present description of the cell (Table 2, Fig. 1b).

Lang veatchite was described by Switzer (1938) as occurring in vein fibres; an angle of  $-38^{\circ}$  was observed between the Z optical direction and the fibre axis (taken as c), an observation confirmed by Murdoch (1939). In the present study two crystals of fibrous habit from the original Lang specimen of veatchite were examined. On one crystal an angle of approximately 39° was observed between the elongation direction and the Z optical direction. X-ray examination shows that in the present veatchite cell, the elongation direction of this crystal is [042]: the crystal is flattened on {100}. Rotation about [042] would produce a bewildering array of closely spaced reflections, undoubtedly explaining the two approximately 41 Å cell lengths originally reported by Switzer (1938). The second crystal examined from the original specimen in the present study was observed to extinguish parallel and perpendicular to the fibre direction, and x-ray study of this crystal shows that in the present veatchite cell the elongation axis is [001], and the crystal is flattened on {100}.

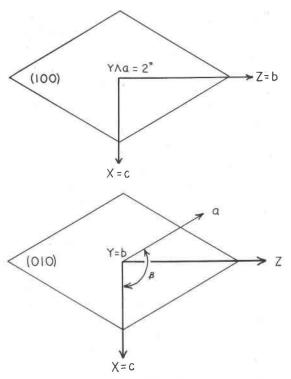
Neither optical nor x-ray evidence for twinning was found during the present study for either mineral. Evidence for some stacking disorder in veatchite occurs in the streaking of reflections along the  $a^*$  direction;

<sup>&</sup>lt;sup>a</sup> Cell constants from precession film measurements; Reyershausen *p*-veatchite (USNM 113264).

<sup>&</sup>lt;sup>b</sup> Cell constants from Weissenberg film measurements; Reyershausen p-veatchite.

<sup>&</sup>lt;sup>o</sup> Values found for crystals from Eskdale no. 2 borehole near Aislaby, north Yorkshire, England (Stewart, Chalmers and Phillips, 1954); written communication from Beevers, October 14, 1959.

<sup>&</sup>lt;sup>d</sup> Values calculated by authors from data of original investigator.



F<sub>1G</sub>. 1a (above). Optic plane (100) of veatchite. Orientation referred to crystal cell with a = 20.81, b = 11.74, c = 6.63,  $\hat{A}$ ,  $\beta = 92^{\circ}02'$ .

b (below). Optic plane (010) of p-veatchite. Orientation referred to crystal cell with a=6.72, b=20.70, c=6.58, Å,  $\beta=119^{\circ}40'$ . Z/ $\alpha=29^{\circ}40'$ .

such streaking is not observed in any direction for the p-veatchite reflections.

X-ray powder patterns for both veatchite and p-veatchite were taken with a 114.59 mm. diameter powder camera using Ni-filtered Cu radiation ( $\lambda = 1.5418$  Å), and the measurements were corrected for film shrinkage. Single-crystal intensities for each hkl reflection were estimated visually from precession films of varying exposure times. These intensities, together with the observed and calculated  $d_{hkl}$  and the intensities of the observed powder lines, are listed in Table 3 for both minerals. As might be expected from the similarity of the minerals, their powder patterns are much alike. Specifically, the observed d-spacings for the first three lines in order of strongest intensities are the same for each. The remainder of the lines have d-spacings so nearly alike that unless powder patterns are prepared and measured with extreme care the minor differ-

Table 3. X-Ray Powder Data for Veatchite and p-Veatchite,  $SrO \cdot 3B_2O_3 \cdot 2H_2O(?)$ 

	Veatchite					p-Veatchite				
Cal	Calculated <sup>a</sup> Measured			Measured			Calculateda			
$hkl$ $d_{hkl}$	Single Crys- tal <sup>b</sup> Powder		c	Powder		Single Crys- tal <sup>b</sup>	Crys-	hkl		
		I	$d_{hkl}$	1	I	$d_{hkl}$	I			
200	10.40	vs	$10.5 \pm 0.1$ $8.29^{d}$	100	100	10.4 ±0.1 8.17d	vs	10.35	020	
020 011	5.870 5.775	abs.	512)		2	6.17	abs. vw abs.	5.847 5.752 5.718	$\frac{100}{101}$	
120 111 111	5.649 5.609 5.521	s m m	$5.64 \pm 0.05$	6	20	$5.64 \pm 0.05$	S	5.627	110 T11	
400 211 220 211	5.199 5.115 5.112 4.985	m m) s) w	5.12 ±0.05	6	10	5.10 ±0.05	m w m s	5.512 5.175 5.091 5.028	011 040 120 121	
311 320	4.505 4.480	m w	4.51 ±0.03	2	5	4.43 ±0.03	vw {vw w	5.005 4.461 4.418 4.403	021 130 131 031	
311 411 420	4.372 3.924 3.892	w s m	$\begin{array}{ccc} 4.37 & \pm 0.03 \\ 3.92 & \pm 0.03 \end{array}$	2 4			( m	3.875	140	
411	3.807		2.04. 1.0.02	2	10	3.85 ±0.03	{m s	3.847 3.837	140 141 041	
600 511 520	3.466 3.425 3.394	vs ms w	$3.81 \pm 0.03$ $3.47 \pm 0.02$	3 20	20	3.46 ±0.02	vs	3.450	060	
031	3.370	s	3.37 ±0.02	3	15	3.38 ±0.02	$\begin{cases} w \\ vs \\ ms \end{cases}$	3.379 3.364 3.360	$\frac{150}{201}$ $\overline{151}$	
T31 511 131 002	3.336 3.328 3.318 3.316	ms m m vs	3.32 ±0.02	35	60	3.31 ±0.02	$\begin{bmatrix} ms \\ vs \\ ms \\ s \\ vs \end{bmatrix}$	3.353 3.344 3.320 3.301 3.290	051 101 211 111 102	

<sup>\*</sup>  $d_{hkl}$  calculated from the following data: veatchite  $a = 20.81 \pm 0.04$ ,  $b = 11.74 \pm 0.03$ ,  $c = 6.63_7 \pm 0.02$  Å,  $\beta = 92^{\circ}02' \pm 05'$ , space group A2/a or Aa; p-veatchite  $a = 6.72_9 \pm 0.02$ ,  $b = 20.70 \pm 0.04$ ,  $c = 6.58_1 \pm 0.02$  Å,  $\beta = 119^{\circ}40' \pm 05'$ , space group  $P2_1/m$  or  $P2_1$ . All calculated spacings listed for  $d \ge 2.800$  Å.

b Single crystal intensities estimated visually from various precession films taken with different exposure times; vs=very strong, s=strong, ms=medium strong, m=medium, w=weak, vw=very weak, abs.=absent.

<sup>d</sup> Fe K $\alpha$  radiation: (200) of veatchite, (020) of p-veatchite.

<sup>\*\* 114.59</sup> mm. diameter camera, Ni-filtered Cu radiation ( $\lambda$ =1.5418 Å). Film measurements corrected for shrinkage; b=broad. Lower limit of  $2\theta$  measurable: approximately 7° (13 Å). Veatchite from Four Corners area, Kramer district, San Bernardino County, California, film no. 13418, spindle no. 10104; type p-veatchite from Reyershausen, near Göttingen, Germany, film no. 14856 (spindle courtesy of Dr. O. Braitsch, University of Göttingen).

Table 3 (Continued)

Veatchite				p-Veatchite					
Caicı	aiculated <sup>a</sup> Measured			Measured			Calculateda		
hkl dhkl	Single Crys- tal <sup>b</sup>	Powder	Powder <sup>c</sup>		Powder		$d_{hkl}$	hkl	
		I	$d_{hkl}$	I	I	$d_{hkl}$	I		
231 202 231 202	3.223 3.192 3.190 3.128	s w m vw	3.22 ±0.02	3	5	3.19 ±0.02	m \s\\s \v	3.250 3.199 3.182 3.136	$     \begin{array}{r}       \hline       112 \\       \hline       221 \\       \hline       121 \\       \hline       122 \\       122 \\       \hline       122 \\   $
331 611 331 620	3.053 3.013 3.010 2.985	ms m ms	3.00 ±0.02	3b	5 5	$\begin{array}{c} 3.02 \pm 0.02 \\ 2.97_1 \pm 0.01 \end{array}$	w s ms vw ms m	3.024 3.009 2.971 2.970 2.959 2.954	231 131 160 132 163 063
040 611	2.935 2.933	s m	$2.93_{6} \pm 0.01$	2				2.923	200
140 022 122 431 122 402 240	2.906 2.887 2.872 2.851 2.848 2.841 2.825	m vw s w s vw s	2.865±0.01	9	15	2.854±0.01	m W W s vs	2.895 2.876 2.859 2.849 2.832 2.820 2.813	$   \begin{array}{c}     21 \\     \hline{20} \\     00 \\     \hline{21} \\     01 \\     \hline{24} \\     22   \end{array} $
$\frac{431}{222}$	2.806 2.804	vw m	2.798 ± 0.01	1	2	2.782	W	2.809	14
			2.763  2.704 2.600 2.564 2.495 2.398 2.245 2.204 2.171 2.155 2.115 2.079 2.045 2.029 plus many add at lines, all I≤4		2 2 30 2 10 10 5 2 10 10 5 10 10 5 10 10	2.746 2.696 2.592 2.517 2.394 2.200 2.161 2.140 2.078 2.033 2.002 1.938 many additionnes, all with			

ences in line positions will not be significant. There are variations in the line intensities between the veatchite and *p*-veatchite patterns, but variations in line intensities among known veatchite patterns have been observed and are attributed to preferred orientation, a hazard that is common with these minerals because of their micaceous cleavage parallel to the common plate form. Therefore, line intensity variation is not considered a reliable means of differentiation.

The powder data for veatchite that are given in Table 3 are taken from Clark et al. (1959) and are from measurements of a film made using a spindle of the Four Corners veatchite. Powder patterns of type veatchite from Lang were also prepared. All the lines found on the Four Corners veatchite patterns are present and identifiable on the Lang patterns, but an additional compound which has eluded all efforts at identification is also present on the Lang patterns, giving rise to additional lines and possible superpositions. Therefore, an indexed pattern of type veatchite has not been presented; the pattern of Four Corners veatchite (Table 3) is considered to represent the best available x-ray powder data for veatchite.

Assignment of the chemical formula SrO·3B<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O to veatchite was made by Clark *et al.* (1959) on the basis of previously reported chemical analyses (Switzer and Brannock, 1950; Stewart, Chalmers and Phillips, 1954), taken together with a confirming spectrographic analysis, observed density determinations, and the x-ray crystallography. Braitsch (1959) gives for p-veatchite the chemical formula (Sr, Ca)O·3B<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O. The calculated density based on 4[SrO·3B<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O] per cell is not as close in value to the observed range of densities (Table 1) as might be expected, and a similar situation exists for veatchite (Clark *et al.*, 1959). Substitution of Ca for Sr in amounts sufficient to lower the calculated density to a value more in accord with the observed densities would require the presence of a much higher percentage of Ca than the relatively small percentages reported to date from the chemical analyses of Switzer and Brannock (1950) and of Stewart, Chalmers and Phillips (1954).

From consideration of the structural principles governing hydrated borate crystals (Christ, 1959, 1960) and the chemical composition of veatchite and p-veatchite, it is possible to make some prediction of the composition and structure of the boron-oxygen polyanions contained in these crystals. The polyanion will probably contain boron-oxygen tetrahedra and triangles, sharing corners, in the ratio 1:2. One such possible arrangement, corresponding to the proposed composition  $SrO \cdot 3B_2O_3 \cdot 2H_2O$ , would consist of infinite chains of composition  $[B_6O_8(OH)_4]_n^{-2n}$ . Another possibility suggested by Christ (1960) is a linkage of the same boron-oxygen elements to form isolated dimers of

composition  $[B_6O_7(OH)_6]^{-2}$ . The presence of such dimers in the crystal structure would require that the chemical formula of veatchite be  $SrO \cdot 3B_2O_3 \cdot 3H_2O$ .

Veatchite and p-veatchite might be polymorphs if the same anion element is present in each but arranged differently about the cation, or if the boron-oxygen triangles and tetrahedra link together differently in each compound. However, the two minerals need not be polymorphs, for even if they contain identical anion elements, the one might have a different water content from the other. Another complication that might occur is the substitution of silicon for some of the tetrahedrally-coordinated boron in one or the other compound. Final determination of the chemical formula or formulas of the two minerals and elucidation of the interesting relationship between them probably will be revealed only after crystal structure analyses have been completed.

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