

STUDIES OF BORATE MINERALS (VI): INVESTIGATION OF VEATCHITE

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ABSTRACT

Veatchite is a hydrated strontium borate originally described by Switzer (1938). In the present study x -ray precession patterns have been correlated with crystal habit and indices of refraction to yield the following data: monoclinic, space group $A2/a-C_{2h}^6$ (or less likely, $Aa-C_s^4$), $a = 20.81 \pm 0.04$, $b = 11.74 \pm 0.03$, $c = 6.637 \pm 0.02$ Å, $\beta = 92^\circ 02' \pm 05'$, $V = 1620$ Å³; dominant forms $\{100\}$, $\{111\}$, $\{h11\}$ with $h = 2, 3, 4$; cleavage perfect parallel to (100) and (011); optical orientation $Z = b$, $X = c$, $Y \wedge a = -2^\circ$. Previous chemical analyses considered together with the present crystallographic data show that the correct formula is $SrO \cdot 3B_2O_3 \cdot 2H_2O$, one of two possibilities proposed by Switzer and Brannock (1950). For eight $[SrO \cdot 3B_2O_3 \cdot 2H_2O]$ per cell, the calculated density is 2.86 g.cm.⁻³; an observed density of 2.78 ± 0.03 g.cm.⁻³ was obtained on the Berman balance for a 2.4 mg. sample of excellent single crystals. X -ray powder pattern data are given with calculated interplanar spacings for $d \geq 2.300$ Å.

INTRODUCTION

Veatchite from Lang, Los Angeles County, California, was originally described by Switzer (1938) as a hydrous calcium borate. Subsequent chemical analyses (Switzer and Brannock, 1950) showed that veatchite was actually a strontium borate, and two chemical formulas were proposed, either $3(Sr, Ca)O \cdot 8B_2O_3 \cdot 5H_2O$ or $SrO \cdot 3B_2O_3 \cdot 2H_2O$. The second formula, according to Stewart, Chalmers, and Phillips (1954), agrees well with a chemical analysis of veatchite from the Permian evaporites of Yorkshire, England. On the other hand, the first formula was said by Kramer and Allen (1956) to fit their chemical analysis of material from Los Angeles County, California.

X -ray data taken from rotation and Weissenberg patterns were reported by Switzer (1938). His data are listed in Table 1, column 1; the crystals were identified as monoclinic, and perfect cleavage was found parallel to (010), a secondary cleavage, parallel to (001). Optically veatchite was described as biaxial positive, with indices of refraction (for Na light): $\alpha = 1.551$, $\beta = 1.553$, $\gamma = 1.621$ (all ± 0.002), and with $Y = b$, $Z \wedge c = -38^\circ$. Euhedral veatchite crystals were examined by Murdoch (1939), who corrected β to $121^\circ 02'$ but retained $\{010\}$ as the dominant form. Indices of refraction found by Murdoch (1939) were "in essential agreement" with those measured by Switzer (1938) and were also confirmed by Stewart *et al.* (1954), who revised the angle $Z \wedge c$ to -30° . Specific gravity measurements were reported as follows: 2.69, by suspension in bromoform (Switzer, 1938); 2.58 ± 0.01 , by suspension

in Clerici solution (Murdoch, 1939); 2.6, by suspension in bromoform-benzene mixtures (Stewart *et al.*, 1954).

Further examination of veatchite crystals was suggested by C. L. Christ, U. S. Geological Survey, who pointed out that *x*-ray precession techniques could be used to determine more accurate cell constants and to find the possible space groups. The proposed chemical formulas could then be checked by comparison of observed and calculated densities considered together with the space group requirements. Such an investigation was undertaken first at the U. S. National Bureau of Standards under the direction of Dr. S. Block, and later at the U. S. Geological

TABLE 1. CRYSTALLOGRAPHIC DATA FOR VEATCHITE

Symmetry: monoclinic

	Switzer (1938)	Present Study
<i>a</i>	6.72 kX	20.81 ± 0.04 Å
<i>b</i>	41.26	11.74 ± 0.03
<i>c</i>	41.20	6.63 ₇ ± 0.02
β	67° (from morphology)†	92°02' ± 05'
Space Group	not determined	$A2/a - C_{2h}^6$ (or less likely, $Aa - C_3^4$)
Volume		1620 Å ³
Cell Contents	16[(3SrO·8B ₂ O ₃ ·5H ₂ O) or 44[(SrO·3B ₂ O ₃ ·2H ₂ O)]††	8[SrO·3B ₂ O ₃ ·2H ₂ O]
Density (calc.)	2.586, 2.590 g.cm. ⁻³	2.85 ₆ g.cm. ⁻³
(obs.)	2.69	2.78 ± 0.03

† Murdoch (1939) corrected β to 121°02'.

†† Switzer and Brannock (1950) proposed these formulas and calculated the corresponding densities.

Survey under the direction of C. L. Christ. Density measurements and *x*-ray single-crystal studies were carried out at both laboratories; other data given here were found during study at the U. S. Geological Survey.

EXPERIMENTAL TECHNIQUES

All crystals of veatchite used in this study originated in drill core no. 5, Four Corners area, Kramer district, San Bernardino County, California, and were supplied to us by Richard C. Erd, U. S. Geological Survey. Single-crystal *x*-ray studies were made on quartz-calibrated precession cameras with both Mo/Zr and Cu/Ni radiations (λ MoK α = 0.7107 Å; λ CuK α = 1.5418 Å). Film measurements were corrected for both horizontal and vertical film shrinkage. A 114.59 mm. diameter powder camera was used with Cu/Ni radiation to obtain the powder film

and the measurements from this pattern were corrected for film shrinkage. Indices of refraction were examined only to establish agreement with those previously reported; optical orientation was checked for several crystals by matching to an appropriate index oil a crystallographic direction previously identified from precession x -ray work. Density determinations were carried out at the National Bureau of Standards (NBS) using the bromoform suspension method and at the U. S. Geological Survey (USGS) using the Berman balance with toluene as the immersion liquid, the sample weights ranging from 2 to 15 mg. Because there was insufficient material for a chemical analysis, a semi-quantitative spectrographic analysis was made on a sample of about 15 mg.

X-RAY DATA AND MORPHOLOGY FOR VEATCHITE CRYSTALS

Examination of x -ray precession photographs failed to reveal any distances as large as those of about 40 Å which had been reported by Switzer (1938). Instead the cell constants given in Table 1, column 2, were found. Systematic diffraction extinctions occur for all hkl reflections when $k+l=2n+1$ and for all $h0l$ reflections when $h=2n+1$ (and $l=2n+1$). Possible space groups are therefore non-centrosymmetric $Aa-C_2^4$ and centrosymmetric $A2/a-C_{2h}^0$. Piezoelectric tests of the crystals were made on an apparatus of the Giebe-Scheibe type with negative results. Study of the morphology yields no evidence for assuming departure from centrosymmetry. Although the non-centrosymmetric space group cannot be definitely ruled out, available evidence favors the centrosymmetric $A2/a$.

The Four Corners veatchite crystals used in the present study have the platy habit described by Murdoch (1939) and illustrated in his Figs. 1 and 2. According to the present x -ray data, the monoclinic symmetry axis (taken as b) lies in the plane of the plate, and not normal to it. Therefore, if the convention $c < a$ is followed, the correct indices for the plate form are $\{100\}$ and the perfect cleavage is parallel to (100) and not to (010) as assumed in all previous work. In the present cell elongation of the plates is in the [011] direction and the secondary cleavage is parallel to (011). The optical orientation now is $Z=b$, $X=c$, $Y \wedge a = -2^\circ$.

Numerous veatchite crystals were measured on an optical goniometer by Murdoch (1939), who indexed observed forms according to the description of the cell by Switzer (1938). It was not found possible to derive a matrix which would transform Murdoch's indices to the indices based on the cell chosen from the present study; it is believed that Murdoch's indexing may be inconsistent. The angular measurements made by Murdoch are shown on the stereogram section of Fig. 1a with

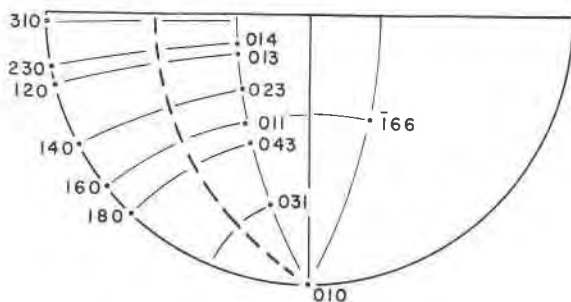


FIG. 1a. (above) Stereogram plotted from angular measurements by Murdoch (1939); indices originally assigned by him. Dashed line marks position of correct mirror plane.

his indices; the correct mirror plane and the faces related by the mirror symmetry are marked. Fig. 1*b* shows the same data after appropriate transformation; the faces are now indexed for the present cell. Both sets of indices are compared in Table 2 and the simplification of indices in the present cell is of interest.

X-ray powder data for veatchite have previously been given by Stewart *et al.* (1954) for the Yorkshire material, and by Kramer and Allen (1956) from a diffractometer pattern on material from Los Angeles County, California. Both sets of observed data are given in Table 3, columns 1 and 2. Observed interplanar spacings found on a pattern taken of the Four Corners veatchite are given in Table 3, column 3, and are generally in good agreement with the earlier findings. Interplanar spacings were calculated from the x-ray cell constants down to values of 1.5 Å on the USGS Datatron computer with a program developed by D. E. Appleman. Table 3, column 4, lists all calculated spacings for $d \geq 2.300$ Å. Because measurements from the pattern of the present study are

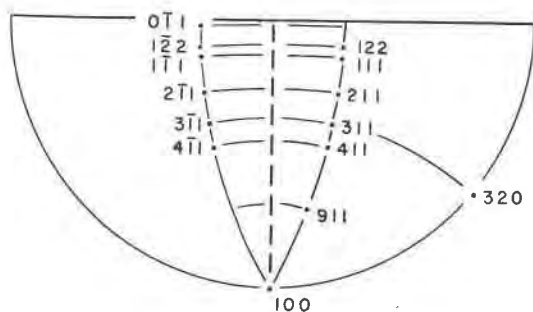


FIG. 1*b*. (below) Stereogram from Murdoch's measurements after transformation; indices are those for the present cell. Dashed line marks the mirror plane.

corrected for film shrinkage, they approach the calculated values more closely than do the earlier measurements.

CHEMICAL FORMULA AND DENSITY OF VEATCHITE

Spectrographic analysis of Four Corners veatchite is in accord with the previous chemical analyses (Switzer and Brannock, 1950; Stewart *et al.*, 1954; Kramer and Allen, 1956), all of which agree well with one another. The correct chemical formula must therefore satisfy these analyses and in addition must meet the crystallographic requirements that follow from the *x*-ray data. First, an integral number *Z* of formula units in the cell of volume 1620 Å³ must lead to a calculated density in

TABLE 2. OBSERVED FORMS ON VEATCHITE CRYSTALS
(Original angular measurements by Murdoch, 1939)

Indices $\{hkl\}$ of Observed Forms	
Assigned by Murdoch (1939) (see Fig. 1a)	Present Study (see Fig. 1b)
010	100†
310	0 $\bar{1}$ 1†
013, 120	111, 1 $\bar{1}$ 1†
023, 140	211, 2 $\bar{1}$ 1
011, 160	311, 3 $\bar{1}$ 1
043, 180	411, 4 $\bar{1}$ 1
014, 230	122, 1 $\bar{2}$ 2
031	911 (?)
$\bar{1}$ 66	320
not observed	010†

† Forms observed on Four Corners veatchite crystals in present study.

reasonable accord with the observed density. A count can then be made of the total number of each kind of atom present in the cell. Since space groups *Aa* and *A2/a* contain only positions of fourfold and eightfold multiplicity, a second crystallographic requirement is that in one cell each kind of atom be present in number as some integral multiple of four. Finally, the postulated total number of atoms per cell must fit into the available 1620 Å³ volume. Christ (1953) pointed out that in the colemanite series of minerals the calculated volume per oxygen atom ranges from 17.6 Å³ in colemanite, CaB₃O₄(OH)₃·H₂O, to 20.5 Å³ in inyoite, CaB₃O₃(OH)₅·4H₂O. Values toward the lower end of this range are to be expected for the volume per oxygen atom in veatchite because it is a lower hydrate.

The first formula proposed by Switzer and Brannock (1950) is

TABLE 3. X-RAY POWDER DATA FOR VEATCHITE, $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Monoclinic $A2/a$: $a = 20.81 \pm 0.04$, $b = 11.74 \pm 0.03$, $c = 6.637 \pm 0.02$ Å; $\beta = 92^\circ 02' \pm 05'$

Measured						Calculated†	
Stewart, Chalmers and Phillips (1954) ^a		Kramer and Allen (1956) ^b		Present Study ^c		Present Study	
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
vs ¹	10.3	10 1 1	10.53 8.27 ^d 6.94 ^e	100 1	10.5 8.29 ^d	10.40	200
m	5.65	1	5.63	6	5.64	5.870 5.775 5.649 5.609 5.521 5.199	020 011 120 111 111 400
m	5.13	3	5.22	6	5.12	{ 5.115 5.112 4.985	211 220 211
w	4.47	1	4.20	2 2	4.51 4.37	{ 4.505 4.480 4.372	311 320 311
m	3.88 ^f	1 1	3.93 3.69	4 3	3.92 3.81	{ 3.924 3.892 3.807	411 420 411
w	3.48	10	3.47	20	3.47	3.466 3.425 3.394 3.370	600 511 520 031
				3	3.37	{ 3.336 3.328 3.318	131 511 131
vs ²	3.33	2	3.32	35	3.32	{ 3.316 3.223 3.192	002 231 202
w	3.20			3	3.22	3.190 3.128 3.053	231 202 331
wb	2.99			3b 2	3.00 2.936	{ 3.013 3.010 2.985	011 331 620
						{ 2.935 2.933 2.906	040 611 140
m	2.87	3	2.88	9	2.865	2.887 2.872 2.851 2.848	022 122 431 122

† All calculated spacings listed for $d_{hkl} \geq 2.300$ Å.^a "Order of intensities: vs¹, vs², s³, m, w, vw, vvw; b indicates broad line. 9 cm. camera cut off at 10.8 kX. Cu-K α radiation ($\lambda = 1.5374$ kX)." No shrinkage correction; kX units converted to Angstrom units by present authors.^b X-ray diffractometer data, Cu/Ni radiation.^c Corrected for film shrinkage; b=broad, d=diffuse. Radiation: Cu/Ni, $\lambda\text{CuK}\alpha = 1.5418$ Å. Lower limit of 2θ measurable: approximately 7° (13 Å).^d (200), FeK α radiation.^e Not veatchite.^f The value of 4.00 kX given in the original listing should have been 3.87 kX (private communication, R. Phillips, 1958).

TABLE 3. (Continued)

Measured						Calculated†	
Stewart, Chalmers and Phillips (1954) ^a	Kramer and Allen (1956) ^b		Present Study ^c		Present Study		
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
						2.841	402
						2.825	240
						2.806	431
						2.804	222
						2.761	222
						2.753	402
vw	2.77	1	2.79	1	2.798	2.703	340
						2.695	322
vw	2.70	1	2.76	1	2.763	2.675	711
						2.651	720
						2.642	531
						2.637	322
						2.610	711
						2.600	800
s^3	2.60	10	2.61	25	2.600	2.596	531
						2.558	422
						2.556	440
vw	2.53			1	2.564	2.492	422
				1	2.495	2.439	602
						2.438	631
						2.406	522
						2.398	540, 811
m	2.39	1	2.40	6	2.398	2.395	631
						2.377	820
						2.356	602
						2.344	811
						2.339	522
				2	2.245		
m	2.20	1	2.21	3	2.204		
		1	2.17	2	2.171		
w	2.151	1	2.16	2	2.155		
				2	2.115		
m	2.082	9	2.08	6	2.079		
				4	2.045		
m	2.037						
				4	2.029		
vw	1.996						
				3d	1.958		
m	1.936	1	1.924	3	1.925		
				2	1.876		
vw	1.863			2	1.854		
vvw	1.836	1	1.833	2	1.828		
vw	1.801			4	1.784		
wb	1.761	2	1.735	1	1.730		
				1	1.700		
vvw	1.676			1	1.680		
vvw	1.653			3	1.660		
plus additional lines							
all vw or vvw			all with $I \leq 2$				

$3\text{SrO} \cdot 8\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. A minimum of four formula units per cell is needed if the number of Sr atoms is to satisfy the second crystallographic requirement. However, the calculated density for four such formula units is

3.9 g.cm.⁻³, compared to observed values ranging from 2.6 to 2.7 g.cm.⁻³. Furthermore, four of these formula units contain 128 oxygen atoms so that a maximum volume of 13 Å³ is available to each oxygen atom in the cell. Clearly this chemical formula is unsatisfactory. On the other hand, the second formula proposed by Switzer and Brannock (1950) is SrO·3B₂O₃·2H₂O, which, for Z=8, gives a calculated density of 2.86 g.cm.⁻³. Each of the 96 oxygen atoms in the cell has available 16.9 Å³, a value that compares closely to the 17.6 Å³ per oxygen atom in colemanite (Christ, 1953). The formula, SrO·3B₂O₃·2H₂O, therefore satisfies both chemical and crystallographic requirements.

Calculated and observed densities do not agree as well as usually expected, and calculations show that substitution of Ca for some Sr in the formula does not satisfactorily explain the small discrepancy. In the present study an average observed density of 2.66 g.cm.⁻³ was found when normal material was used. However, an average observed value of 2.78 ± 0.03 g.cm.⁻³ was obtained from measurements on the Berman balance for a 2.4 mg. sample of excellent single crystals. Unfortunately larger samples of comparable quality crystals were not available. Veatchite crystals are generally composed of stacked cleavage plates, probably containing entrapped air. When such crystals are immersed in liquid, the cleavage plates have a tendency to flake apart and some even float on the liquid surface, presumably held there by surface tension. These factors account for the low observed values and the variable range of density readings which are obtained when average material is used in the density determinations.

ACKNOWLEDGMENTS

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