

VEATCHITE: CRYSTAL STRUCTURE AND CORRELATIONS WITH *p*-VEATCHITE¹

JOAN R. CLARK AND C. L. CHRIST, *U. S. Geological Survey, Washington, D. C. 20242, and Menlo Park, California 94025, U.S.A.*

ABSTRACT

Crystal-structure analysis of veatchite reveals that its correct chemical formula is $4\text{SrO} \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, in good agreement with a 1950 analysis by Switzer and Brannock. Veatchite is monoclinic, *Aa*, $a = 20.860 \pm 0.005$, $b = 11.738 \pm 0.003$, $c = 6.652 \pm 0.002$ Å, $\beta = 92.10 \pm 0.03^\circ$, cell volume = 1627.67 ± 0.05 Å³, $Z = 4 \{ \text{Sr}_2 [\text{B}_3\text{O}_8(\text{OH})]_2 \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O} \}$, density (g/cm³) 2.664 calc., 2.66 obs. The two crystallographically distinct Sr cations were located from a three-dimensional Patterson synthesis, and the other atoms were found from study of electron-density maps calculated using phases determined by the Sr cations. The structure contains two crystallographically distinct $[\text{B}_3\text{O}_8(\text{OH})]^{2-}$ polyanions; each polyanion (I and II) links to its own *A* face-centered equivalents to form two infinite sheets which have spaces available for the respective Sr cations, each coordinated by six polyanion oxygen atoms. The Sr-O coordination is completed for Sr(1) to a total of ten (ave. Sr-O, 2.68 Å) by a water molecule and three oxygen atoms from the polyanion II sheet. Sr(2) has elevenfold coordination (ave. Sr-O, 2.75 Å), completed by two hydroxyl ions of the $\text{B}(\text{OH})_3$ group and three oxygen atoms from the polyanion I sheet. The edge-sharing of the oxygen polyhedra around the Sr cations links the two polyanion sheets tightly together into the basic building block of the structure. The blocks are held together by six distinct hydrogen bonds; a seventh hydrogen bond also occurs that is considered within the polyanion II sheet as defined including the $\text{B}(\text{OH})_3$ groups. The structures of veatchite and the almost identical *p*-veatchite, solved independently by Gandymov, Rumanova, and Belov, have similar building blocks and differ chiefly in the packing of the blocks. In veatchite adjacent blocks are arranged by the *a*-glide operation, whereas in *p*-veatchite they are arranged by the 2₁ symmetry operation. These two structures provide the first examples in hydrated borates of isolated $\text{B}(\text{OH})_3$ groups existing in the presence of larger borate polyanions.

INTRODUCTION

Veatchite has been an ill-starred mineral from the time of its initial recognition at the old colemanite mine, Lang, Los Angeles County, California (Switzer, 1938) to the present solution of its structure. Some of the vicissitudes that have occurred during its known history are summarized briefly here.

Although it is actually a strontium borate with varying but only minor amounts of calcium, it was originally described as a calcium borate (Switzer, 1938). This error was corrected by Switzer and Brannock (1950), following comment by the late Waldemar T. Schaller, U. S. Geological Survey. The new chemical analyses, summarized in our Table 1, gave experimental results that reduce to very nearly the theoretical values for the oxide form of the correct chemical formula obtained from

¹ Studies of borate minerals (XVI). Publication authorized by the Director, U. S. Geological Survey.

Table 1. Chemical Data Compared for Veatchite and *p*-Veatchite^{a/}

Oxide	Weight %		
	Veatchite ^{b/} California Switzer and Brannock (1950)	<i>p</i> -Veatchite U. S. S. R. Kondrat'eva (1964)	Theoretical for $4\text{SrO} \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$
SrO	30.0	32.4	31.73
CaO	1.6	—	—
B ₂ O ₃	58.5	58.0	58.62
H ₂ O (+)	9.6	9.6	9.66
Σ	100.0	100.0	100.01

^{a/} Among the data available in the literature, we consider these the best.

^{b/} From Table 1, column 6 of reference; average of three analyses, corrected for insolubles and calculated to 100%.

the structural analysis, $4\text{SrO} \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$. However, Switzer and Brannock apparently did not consider this formula, proposing instead either $3(\text{Sr}, \text{Ca})\text{O} \cdot 8\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. These two latter possibilities became a subject of controversy in later publications (Clark *et al.*, 1959; Clark and Mrose, 1960; Jäger and Lehmann, 1963; Clark, 1964a; Lehmann and Kessler, 1968). The correct formula was suggested by Kondrat'eva (1964) following analysis of *p*-veatchite crystals, but she later abandoned this formula in favor of $3\text{SrO} \cdot 8\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Kondrat'eva, 1966).

The mineral *p*-veatchite (or primitive veatchite) was first described by Braitsch (1959) from an occurrence in the Stassfurt Potash Zone, Reyershausen, Germany. Its composition, optical properties, and density lie within the range of values reported to that date for veatchite (Switzer, 1938; Murdoch, 1939; Switzer and Brannock, 1950; Kramer and Allen, 1956; Clark *et al.*, 1959) but the two minerals are crystallographically distinct. Veatchite was described by Clark *et al.* (1959) as having space-group symmetry either *Aa* or *A2/a*, the latter being con-

sidered more likely.¹ The crystals were platy on {100} and the *a*-axis was 20.81 Å. The mineral *p*-veatchite, however, was found by Braitsch (1959) to have space-group symmetry $P2_1$ or $P2_1/m$, and the crystals were tabular on {010} with a *b*-axis of 20.70 Å. Braitsch (1959) gave the Reyershausen mineral the name *p*-veatchite so that the prefix *p* would designate the primitive cell, in contrast to the *A* face-centered cell of veatchite.²

Careful comparison of both minerals by Clark and Mrose (1960) confirmed the previous results, and Beevers and Stewart (1960), on the basis of single-crystal studies, reported that the "veatchite" described by Stewart *et al.* (1954) from an occurrence in the Permian evaporites of Yorkshire, England, was actually *p*-veatchite. In 1960 *p*-veatchite was also found in saline strata in Russia (Kondrat'eva, 1964). On the basis of statistical evaluation of intensity data, Ashirov and Gandymov (1966) assigned the mineral to space group $P2_1$. To the present date, veatchite has been reported only from the California borate region, and a satisfactory answer to the question of whether *p*-veatchite also occurs in California is not available. Because of the close correspondence of the two minerals in so many respects, only appropriate X-ray precession patterns of single crystals identify the minerals unambiguously. In the absence of such evidence, the conclusion of Murdoch and Webb (1964), also given by Pemberton (1968), that both species exist at Lang must be considered unjustified. On the other hand, the suggestion by Clark *et al.* (1969) that ". . . *p*-veatchite has been found only in marine evaporites and veatchite in continental saline environment" may not be justified either. The question remains open, pending further investigation.

In 1968 the structure of *p*-veatchite was solved by Gandymov *et al.*, and a preliminary note on the veatchite structure also appeared (Clark and Christ, 1968). The structural formulas of both minerals are the same, $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O}$. In the remainder of this paper we present our solution of the veatchite structure and compare veatchite with *p*-veatchite in various respects.

EXPERIMENTAL DATA

Chemical and Crystallographic Data. The best available analysis for veatchite seems to be the one given by Switzer and Brannock (1950), and the best one for *p*-veatchite, that reported by Kondrat'eva (1964).

¹ The cell constants given by Switzer (1938) are wrong.

² The prefix *p* was initially misinterpreted by J. R. Clark to mean "*para*" and, following correspondence at that time (Clark to J. Murdoch, written communication, 1961), the name "paraveatchite" has been used by Murdoch and Webb (1964) and Pemberton (1968). However, the correct name is either *p*-veatchite or primitive veatchite.

These analytical data are compared in Table 1 with the theoretical values for $4\text{SrO} \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$; the agreement is excellent and confirms the formula assigned by the structural determination.

Our selection from among the available crystallographic data for both minerals is given in Table 2. It is impossible to ascertain how closely the cell constants may agree for the two minerals, because the errors assigned to the values for *p*-veatchite are rather large, and the substitution of small amounts of Ca for Sr (Table 1) may vary from one crystal to another. The agreement between observed densities and the density calculated using the correct formula is now satisfactory. The crystal used

Table 2. Crystallographic Data Compared for Veatchite and *p*-Veatchite, $\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})]_2 \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O}$

	Veatchite California This study ^{a/}	<i>p</i> -Veatchite U. S. S. R. Gandymov <u>et al.</u> al. (1968)	Transformed values ^{b/}
<u>a</u> (Å)	20.860±0.005	6.70±0.02	11.69
<u>b</u> (Å)	11.738±0.003	20.80±0.05	20.80
<u>c</u> (Å)	6.652±0.002	6.60±0.02	6.60
β (°)	92.10±0.03	119.25	89.75
Volume (Å ³)	1627.67±0.05	802.5	1605.
Z	4	2	4
Space group	<u>Aa</u>	<u>P2</u> ₁	<u>B2</u> ₁
Density, g/cm ³ , calc.	2.664	2.65	
obs.	2.66 ^{c/}	2.685 ^{d/}	

^{a/} Cell constants obtained from least-squares refinement of powder data (Clark et al., 1959), using a computer program by Evans et al. (1963).

^{b/} Transformation: 201/010/001 (Braitsch, 1959).

^{c/} Clark et al. (1959), average value for normal material.

^{d/} Kondrat'eva (1964).

in the structural study was supplied by R. C. Erd, U. S. Geological Survey, from a sample collected at the Four Corners area, Kramer district, San Bernardino County, California. Our crystal was platy on {100} with a rhombic shape given by the {011} forms and was about $0.6 \times 0.3 \times 0.08$ mm.

After the acentric space group Aa had been discovered and confirmed by the successful structural determination, powdered veatchite crystals were examined by the harmonic oscillator method (Kurtz and Perry, 1968) and were found to exhibit a "definite second harmonic response consistent with that expected for an acentric structure" (S. K. Kurtz and K. Nassau, written communication to M. E. Mrose, 1968). Earlier tests made on single crystals with a Giebe-Scheibe apparatus had shown no response, possibly because the available crystals were so small.

Data Collection, Processing and Refinement Procedures. The Picker automatic diffractometer with a scintillation counter was used for collection of about 2600 reflections with Nb-filtered Mo X-radiation set at a take-off angle of 3° . The 2θ -scan method was used, the scan range being calculated following the equation for $\text{MoK}\alpha$ radiation given by Alexander and Smith (1964), with constants adjusted slightly to increase the scan range. Background counts of 20 seconds duration were made for each reflection at the beginning and end points of the scan range. The crystal was mounted with c^* parallel to the ϕ -axis and the 122 reflection was monitored as a standard after each 30 measurements. A number of reflections with related indices hkl , $h\bar{k}l$, $\bar{h}kl$, and $\bar{h}\bar{k}l$ were checked, but no significant differences among such groups were observed.

Computer programs, written by C. T. Prewitt, SUNY, Stony Brook, and modified by D. E. Appleman, U. S. Geological Survey, for the IBM 360/65, were used to obtain the diffractometer settings and to reduce the raw data, including corrections for the total background count, absorption ($\mu = 69.4 \text{ cm}^{-1}$), and Lorentz and polarization factors (program ACACA). No corrections were made for extinction, either primary or secondary; the data appeared to be unaffected by primary extinction. Reflections for which $|F_o|$ was less than three times the standard deviation in $|F_o|$ as determined by the counting statistics numbered 364. These data were coded as "less-thans" and omitted from the refinements, which initially used about 2300 reflections. During the refinements, it was discovered that the small reciprocal spacing of a^* (about 0.05 \AA^{-1}) together with the use of $\text{MoK}\alpha$ radiation had produced overlap in scan range between some adjacent reflections, adversely affecting about 200 reflections. These were then removed from refinement, so the final data set contains about 2100 nonequivalent reflections.

Computer programs for X-Ray 67, *Program System for X-Ray Crystallography*, by J. M. Stewart, University of Maryland, adapted for the IBM 360/65 by D. E. Appleman, U. S. Geological Survey, were used for calculation of Fourier maps, of bond distances and angles, and for some least-squares refinements. Scattering factors for neutral boron and oxygen atoms were taken from MacGillavry and Rieck (1962) and for ionized Sr^{2+} , from Cromer and Waber (1965). The initial residual $R = \Sigma | |F_o| - |F_c| | / \Sigma |F_o|$ was 0.32 for structure factors calculated using coordinates for the two Sr cations only. After coordinates for all atoms were assigned, and the origin fixed as described under Structure Determination, five cycles of least-squares refinement of positional parameters were completed with reflections weighted according to the counter statistics. The residual dropped to 0.17.

When refinement of individual, isotropic temperature factors was attempted, sizeable negative temperature factors occurred for about half the atoms and investigation then revealed the systematic errors in the data due to the scan overlap. After the majority of affected reflections were identified and removed from the data set, two more cycles of refinement for positional parameters, and one cycle including the individual isotropic temperature factors were completed, still using the weighting scheme based on counter statistics. A number of the temperature factors still became negative, so a cycle of refinement with unit weighting of all reflections was tried. This cycle produced positive temperature factors for all atoms except two boron atoms for which B became about -0.1 \AA^2 , and the residual dropped to 0.126 for the 2100 data. However, a number of the bond distances calculated from these parameters were obviously outside the expected range which is now well established for hydrated borate structures (e.g., Zachariassen, 1963; Clark *et al.*, 1964; Konnert *et al.*, 1970). In order to obtain a final, consistent set of parameters, four more cycles of least-squares refinement and final bond distances and angles were calculated using programs written by L. W. Finger, Geophysical Laboratory, Washington, D. C. Anomalous dispersion corrections were included, unit weights were used, and the scattering factors for neutral atoms were taken from the tables given by Doyle and Turner (1968).

The final R is 0.113 for the 2100 reflections. The temperature factor of one boron atom, B(7), remained negative (-0.8 \AA^2), but all the other atoms have positive temperature factors, and the bond distances and angles are reasonably acceptable. The atomic parameters thus obtained are given in Table 3. The observed and calculated structure factors, including those omitted from refinement, are compared in Table 4.¹ The R value is somewhat higher than those usually obtained for diffractometer data, and the standard errors in atomic coordinates and hence for bond lengths and angles remain relatively large. There is little doubt that the results are still affected by the presence of systematic errors in the data. First, the scan overlap problems may have affected more reflections than those identified and removed from the refinement. Second, the use of Mo X-radiation for a mineral containing Sr produces fluorescent radiation for which the intensities cannot be satisfactorily corrected. Third, the platy habit of the crystal precludes application of accurate absorption corrections. All these factors undoubtedly affected the degree of the refinement.

STRUCTURE DETERMINATION

Due to a number of false starts caused in part by assumption of the centrosymmetric space group and in part by the unknown formula, the structure determination went on intermittently over a period of about ten years, an initial Patterson projection on (001) having been obtained in 1958. The difficulties were first ascribed to poor data, and then to lack of enough data, so that in 1964 about 1000 reflections were read visually from a combination of precession and Weissenberg films. The three-dimensional Patterson map thus obtained was correctly interpreted as exhibiting vectors resulting from the presence of two crystallographically distinct Sr atoms in the acentric space group Aa , rather than vectors associated with the eight equivalent Sr atoms produced from one crystallographically unique Sr in centrosymmetric $A2/a$. However, at that point in time a change in computer facilities was occurring, so no further maps could be obtained immediately.

After some delay, new data were collected as described under Experimental Data, a new Patterson map was checked, positions were assigned to the two distinct Sr atoms, and

¹ To obtain a copy of Table 4, order NAPS Document #01607 from National Auxiliary Publications Service, c/o CCM Information Corporation, 866 Third Avenue, New York, N. Y. 10022, remitting in advance \$3.00 for microfiche or \$5.00 for photocopies, payable to CCMIC-NAPS.

Table 3. Atomic Parameters for Veatchite Compared With p-Veatchite

Atom ^{c/}	Veatchite Present study ^{a/}				p-Veatchite Rumanova and Gandymov (1971) Converted for comparison ^{b/}						Original	
	$\bar{B}(\text{\AA}^2)$	\bar{x}	\bar{y}	\bar{z}	\bar{x}_v	\bar{y}_v	\bar{z}_v	\bar{x}_{pv}	\bar{y}_{pv}	\bar{z}_{pv}		
Sr(1)	0.73	0.1124	0.0359	0.5256	0.1130	0.0365	0.5160	0.073	0.	0.020 ₅		
Sr(2)	0.62	0.	0.1881	0.	0.0002	0.1895	0.0000	0.379	-0.1128	0.689 ₅		
Polyanion I												
B(1)	0.9	0.128	0.331	0.724	0.129	0.336	0.705	0.672	0.016	0.131		
B(2)	0.4	0.154	0.485	0.485	0.149 ₅	0.481	0.465	0.962	0.036 ₅	0.516		
B(3)	0.8	0.130	0.288	0.365	0.134	0.292	0.358	0.985	0.021	0.435		
B(4)	0.5	0.147	0.695	0.514	0.152	0.697	0.499	1.394	0.039	0.698		
H(5)	1.8	0.256	0.595	0.500	0.252	0.595	0.512	1.190	0.139	0.583		
O(1)-1	0.3	0.122	0.297	0.919	0.123	0.300	0.900	0.599	0.010	-0.100		
O(1)-4		0.122	0.797	0.419	0.123	0.800	0.400	1.599	0.010	0.900		
O(2)	0.2	0.125	0.443	0.678	0.127	0.453	0.666	0.906	0.014	0.287		
O(3)	0.7	0.130	0.252	0.569	0.136	0.257	0.557	0.514	0.023	0.200		
O(4)	0.2	0.135	0.400	0.322	0.134	0.402	0.302	0.805	0.121	0.600		
O(5)	1.6	0.220	0.493	0.506	0.222	0.491	0.475	0.982	0.109	0.516		
O(6)	0.2	0.120	0.594	0.424	0.121	0.593	0.394	1.186	0.008	0.699		
O(7)-3	0.4	0.127	0.201	0.233	0.129 ₅	0.200	0.217	0.400	0.016 ₅	0.483		
O(7)-4	0.4	0.127	0.701	0.733	0.129 ₅	0.700	0.717	1.400	0.016 ₅	0.483		
O(8)	1.6	0.220	0.699	0.505	0.219 ₅	0.696	0.470	1.393	0.106 ₅	0.727		
OH(9)	3.0	0.318	0.592	0.507	0.318 ₅	0.590	0.486	1.180	0.205 ₅	0.604		
Polyanion II												
B(6)	0.2	-0.007	0.393	0.308	-0.020	0.390	0.312	0.779	-0.133	0.578		
B(7)	-0.8	-0.026	0.239	0.536	-0.033	0.244	0.552	0.489	-0.146	0.193		
B(8)	0.7	-0.013	0.436	0.663	-0.013	0.433	0.659	0.866	-0.126	0.274		
B(9)	0.4	-0.033	0.024	0.504	-0.025 ₅	0.028	0.518	0.057	-0.138 ₅	0.011		
B(10)	0.1	-0.135	0.126	0.514	-0.131	0.124	0.541	0.248	-0.244	0.083		
O(10)-6	0.6	0.003	0.424	0.110	0.002	0.426	0.117	0.852	-0.111	0.809		
O(10)-9		0.003	-0.076	0.610	0.002	-0.074	0.617	-0.148	-0.111	-0.191		
O(11)	0.4	-0.007	0.281	0.345	-0.006 ₅	0.272	0.350	0.545	-0.119 ₅	0.422		
O(12)	1.0	-0.013	0.472	0.459	-0.010 ₅	0.468	0.460	0.937	-0.123 ₅	0.509		
O(13)	0.8	-0.015	0.323	0.700	-0.016	0.323	0.714	0.646	-0.129	0.109		
O(14)	0.6	-0.104	0.226	0.519	-0.101	0.229	0.536	0.458	-0.214	0.193		
O(15)	0.6	-0.002	0.131	0.594	-0.002	0.132	0.622	0.265	-0.115	0.010		
O(16)-8	0.9	-0.006	0.522	0.801	-0.007	0.526	0.800	1.051	-0.120	0.226		
O(16)-9		-0.006	0.022	0.301	-0.007	0.026	0.300	0.051	-0.120	0.226		
O(17)	0.9	-0.096	0.022	0.513	-0.095	0.025	0.541	0.050	-0.208	-0.016		
OH(18)	2.0	-0.198	0.115	0.504	-0.196 ₅	0.118	0.512	0.235	-0.309 ₅	0.105		
B(OH) ₃ group												
B(11)	1.9	-0.159	0.209	0.011	-0.153	0.206	0.033	0.412	-0.266	0.673		
OH(19)	2.5	-0.219	0.210	0.003	-0.219	0.214	0.032	0.428	-0.332	0.682		
OH(20)	1.8	-0.113	0.296	0.015	-0.117	0.305	0.045	0.610	-0.230	0.760		
OH(21)	1.9	-0.123	0.107	0.005	-0.122	0.104	0.006	0.207	-0.235	0.597		
Water molecule												
H ₂ O(22)	2.4	0.229	0.071	0.532	0.228	0.070	0.514	0.141	0.115	0.056		

^a One standard deviation as follows: Sr, $\bar{y} \pm 0.0002$, $\bar{B} \pm 0.03 \text{\AA}^2$; Sr(1), $\bar{x} \pm 0.0002$, $\bar{z} \pm 0.0004$; Sr(2) \bar{x} , \bar{z} fixed at zero to determine origin of Aa; boron atoms, $\bar{x} \pm 0.002$, $\bar{y} \pm 0.003$, $\bar{z} \pm 0.005$, $\bar{B} \pm 0.5 \text{\AA}^2$; oxygen atoms, $\bar{x} \pm 0.001$, $\bar{y} \pm 0.002$, $\bar{z} \pm 0.004$, $\bar{B} \pm 0.3 \text{\AA}^2$ except for OH(9), $\pm 0.5 \text{\AA}^2$ and OH(19), $\text{H}_2\text{O}(22) \pm 0.4 \text{\AA}^2$.

^b Converted as follows: all atoms, $\bar{x}_v = \bar{y}_{pv} + 0.113$, $\bar{y}_v = 0.5 \bar{x}_{pv}$, $\bar{z}_v = 0.5 \bar{x}_{pv} - \bar{z}_{pv} + 0.5$

^c The notation O(1)-1 designates oxygen atom O(1) linked to boron atom B(1), etc.; these are the linkages that form the sheets.

a three-dimensional electron-density map was calculated using these phases. After several weeks of struggle with successive maps and a ball-and-stick model board, it was discovered that the option selected for calculating the electron-density function had not been correctly programmed, and spurious, yet apparently plausible, maps were being produced. When this situation was recognized and a correctly calculated map was obtained, the structure was solved relatively rapidly. One $[\text{B}_3\text{O}_8(\text{OH})]^{2-}$ sheet was first discovered, then the second sheet and the water molecule. The $\text{B}(\text{OH})_3$ group was the last structural unit to be recognized. Space group Aa has no special positions and only one general fourfold position. The

x and z coordinates of one Sr atom were each set at zero to fix the origin, leaving a total number of 103 positional parameters to be determined and refined, *i.e.*, y of one Sr and x , y , z for the second Sr and each of the 22 oxygen and 11 boron atoms that were discovered to be present in the structure.

A few weeks after our solution of the structure, our colleague, M. Fleischer, brought us a copy of the paper by Gandymov *et al.* (1968) who had found the same structural formula for *p*-veatchite in space group $P2_1$. In this paper we follow the numbering system used by them for the *p*-veatchite in order to facilitate comparison of the two structures. When the present paper was nearly complete, Rumanova and Gandymov (1971) published the results of least-squares and Fourier refinements of about 1100 hkl data for the *p*-veatchite. With an overall, isotropic B of 1.6 \AA^2 , the residual was reduced to 0.152. With individual temperature factors (not given), it became 0.142. Although the authors give no estimate of errors, their refinement does allow meaningful comparison of some of the structural details. In a subsequent paper Rumanova *et al.* (1971) compared the *p*-veatchite and veatchite structures, using data for veatchite from the preliminary report by Clark and Christ (1968). The comparison is in general agreement with the results of this study.

DESCRIPTION OF STRUCTURE

The structure is illustrated in the stereoscopic-pair view of Figure 1, in which the various portions of the structure can be picked out. There are two crystallographically distinct $[\text{B}_6\text{O}_8(\text{OH})]^{2-}$ sheets, each associated with a crystallographically distinct Sr^{2+} cation that fits neatly into spaces left by the polyanion network. These two sheets, designated for the respective polyanions I and II, are illustrated in Figure 2; a schematic view of polyanion I without the associated Sr^{2+} , shown in Figure 3, permits easy identification of the linkages. At the present time similar polyanion sheets having different cations are known in two other structures: gowerite, $\text{CaB}_6\text{O}_8(\text{OH}) \cdot \text{B}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, recently solved by J. A. Konnert, U. S. Geological Survey (oral communication, 1970), and synthetic $\text{K}_2\text{B}_6\text{O}_8(\text{OH}) \cdot 2\text{H}_2\text{O}$ (Marezio, 1969). A comparison of these structures

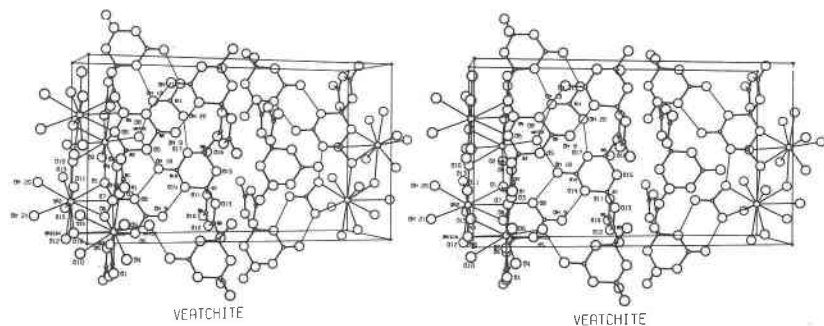
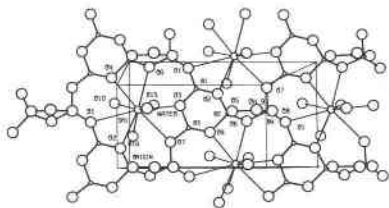
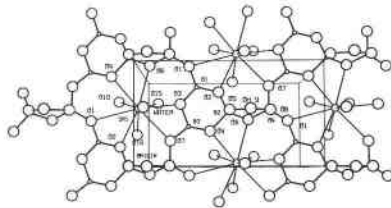


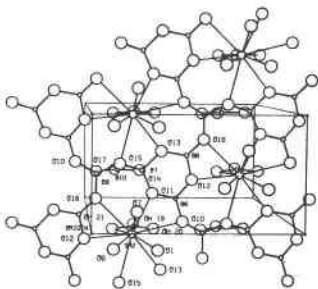
FIG. 1. Stereoscopic-pair view of selected portions of the veatchite structure, showing the polyanion sheets, the Sr-O coordination, and the hydrogen bonds. Atom labelled WATER is $\text{H}_2\text{O}(22)$. Origin is marked, $+a$ horizontal, $+b$ vertical, $+c$ towards viewer.



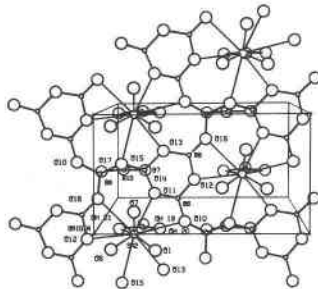
VEATCHITE POLYANION I SHEET



VEATCHITE POLYANION I SHEET

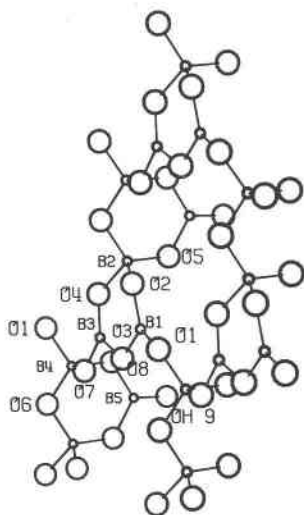


VEATCHITE POLYANION II SHEET

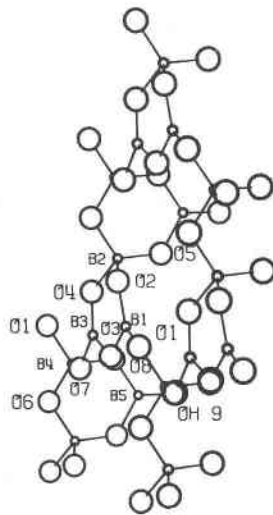


VEATCHITE POLYANION II SHEET

FIG. 2. Stereoscopic-pair view of the polyanion sheets in veatchite; origin marked, $+b$ horizontal, $+c$ vertical, $+a$ towards viewer. (a) Polyanion I sheet with Sr(1) coordination including H₂O(22) labelled WATER. (b) Polyanion II sheet with Sr(2) coordination and the B(OH)₃ group.



VEATCHITE POLYANION I



VEATCHITE POLYANION I

FIG. 3. Stereoscopic-pair schematic view of [B₃O₈(OH)]²⁻ polyanion I, illustrating the linkages in detail.

will be made in a forthcoming paper on gowerite (Konnert *et al.*, in preparation).

In veatchite the two sheets, oriented parallel to (100), are held tightly together by cross-sheet Sr-O bonding that creates sheets of edge-sharing Sr-O polyhedra, as shown in Figure 4. The water molecule coordinates Sr(1) and is located on the periphery of the sheet involving polyanion I. Two of the three hydroxyl ions of the $B(OH)_3$ group coordinate Sr(2) and the group is thus located on the periphery of the sheet involving polyanion II (Fig. 2). We define this entire double-sheet as-

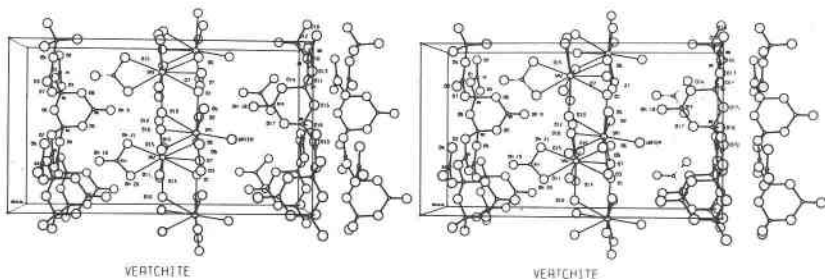


FIG. 4. Stereoscopic-pair view illustrating the Sr-O coordination in veatchite. From the labelled origin, $+a$ is horizontal, $+b$ vertical, and $+c$ towards the viewer. Polyanion sheets are shown at the cell edges but are omitted in the center. Selected portions only are shown; atom labelled WATER is $H_2O(22)$.

semblage as the basic building block of the structure, and the atomic coordinates given in Table 3 are for one such block. Packing occurs so that hydrogen bonds alone hold the blocks together, thus accounting for the observed habit, platy on (100), and the perfect (100) cleavage. Both veatchite and *p*-veatchite contain the same building blocks, as the conversion of atomic coordinates (Table 3) demonstrates. The difference between the two structures is chiefly in the packing arrangement, a point that is illustrated in a later section. For convenience of discussion, the building blocks will be considered as follows: the $[B_5O_8(OH)]^{2-}$ sheets, the Sr-O coordination, and the $B(OH)_3$ groups. The hydrogen-bonding scheme will then be examined, including the charge-balance considerations, and finally the packing and the distinction between veatchite and *p*-veatchite.

The $[B_5O_8(OH)]^{2-}$ Polyanions I and II. Each polyanion has a central BO_4 tetrahedron, from which two six-membered alternating boron-oxygen rings go off in planes approximately perpendicular to one another (82° in polyanion I, 79° in polyanion II). One of these rings is completed

Table 5. Some Bond Distances in the $[B_5O_6(OH)]^{2-}$ Polyanions of Veatchite

Atom number				Distance ^{a/} B-O (Å)		Atom number				Distance ^{a/} B-O (Å)	
Polyanion				Polyanion		Polyanion				Polyanion	
I	II	I	II	I	II	I	II	I	II	I	II
B(2)	B(7)	O(2)	O(13)	1.52	1.49	B(4)	B(9)	O(7)	O(15)	1.53	1.53
		O(4)	O(14)	1.52	1.64			O(8)	O(17)	1.54	1.31
		O(5)	O(15)	1.38	1.40			O(6)	O(16)	1.42	1.48
		O(6)	O(11)	<u>1.50</u>	<u>1.43</u>			O(1)	O(10)	<u>1.45</u>	<u>1.55</u>
		average		<u>1.48</u>	<u>1.49</u>			average		<u>1.48</u>	<u>1.47</u>
B(1)	B(6)	O(1)	O(10)	1.37	1.39	B(3)	B(8)	O(3)	O(12)	1.42	1.42
		O(2)	O(11)	1.36	1.34			O(4)	O(13)	1.35	1.36
		O(3)	O(12)	<u>1.39</u>	<u>1.37</u>			O(7)	O(16)	<u>1.35</u>	<u>1.37</u>
		average		<u>1.37</u>	<u>1.37</u>			average		<u>1.37</u>	<u>1.38</u>
B(5)	B(10)	O(5)	O(14)	1.43	1.34					B-B (Å)	
		O(8)	O(17)	1.43	1.46	B(2)	B(7)	B(4)	B(9)	2.47	2.54
		OH(9)	OH(18)	<u>1.28</u>	<u>1.32</u>	B(2)	B(7)	B(1)	B(6)	2.48	2.40
		average		<u>1.38</u>	<u>1.37</u>			B(3)	B(8)	2.49	2.48
								B(5)	B(10)	2.50	2.63
						B(4)	B(9)	B(1)	B(6)	2.53	2.58
								B(3)	B(8)	2.61	2.54
								B(5)	B(10)	2.57	2.44
						B(1)	B(6)	B(3)	B(8)	<u>2.44</u>	<u>2.42</u>
								average		<u>2.51</u>	<u>2.50</u>

^{a/} One standard deviation, B-O ± 0.03 Å, B-B ± 0.04 Å. Average O-O distances: triangles, 2.38 Å; tetrahedra, 2.41 Å.

with two BO_3 triangles, and the other, with a BO_4 tetrahedron plus a $BO_2(OH)$ triangle. The linkage is illustrated for polyanion I in Figure 3. The polyanion resembles the $[B_5O_6(OH)_4]^{1-}$ polyanion found by Zachariassen (1937) in the structure of potassium pentaborate tetrahydrate. The $[B_5O_6(OH)_4]^{1-}$ polyanion also has a central BO_4 tetrahedron, but the two six-membered rings in it are completed by linking $BO_2(OH)$ triangles.

The relevant bond distances in the two polyanions are given in Table 5; the average distances are in good agreement with those found in numerous borate structures: average B-O, tetrahedral 1.48 Å, triangular 1.37 Å, average B-B 2.50 Å. Detailed comparison with the corresponding distances in *p*-veatchite is not made because the standard deviations in both cases are so large. However, the agreement between the two is satisfactory.

The O-B-O angles in veatchite range from 103° to 117° ($\pm 2^\circ$) in the tetrahedra, with an overall average of 109.3° , and from 113° to 127° ($\pm 2^\circ$) in the triangles, with an average 120° overall. The B-O-B angles in the rings average 121° , with a range of 115° to 127° ($\pm 2^\circ$). Each triangular boron atom lies exactly in the plane of its three associated oxygen atoms within the limits of error.¹ However, there does appear to

¹ For *p*-veatchite, see footnote of Table 6.

be some deviation of the boron atoms from the plane defined by the ring oxygen atoms, and such deviations may well be real, caused by the necessities of the polyanion linkages. The distances of atoms from the various planes are given in Table 6 in comparison with the related distances in *p*-veatchite. The triangles having the hydroxyl ions are bent from the ring planes appreciably more than are the other triangles.

Sr-O Coordination (Table 7, Fig. 4). The Sr(1) is associated with polyanion I and is coordinated by six oxygen atoms of this polyanion plus three from neighboring polyanion II and the lone water molecule, the average Sr-O distance being 2.68 Å for the tenfold coordination. Sr(2) is associated with polyanion II and is coordinated by six oxygen atoms of this polyanion plus three from neighboring polyanion I and two hydroxyl ions of the B(OH)₃ group, the average Sr-O distance being 2.75 Å for the elevenfold coordination. In each polyanion oxygen atoms that are comparable in character coordinate the associated Sr, or, in other words, these polyanions have available a space into which a cation of appropriate size fits nicely. The average Sr-O distance for these six oxygen atoms only is 2.69 Å for both polyanions in veatchite, but in *p*-veatchite the corresponding average values are somewhat smaller, 2.65 Å (I) and 2.64 Å (II).

In a recent review paper on ionic radii, Shannon and Prewitt (1969) give references for Sr coordinated by six, seven, eight, ten, and twelve oxygen atoms. Veatchite and *p*-veatchite thus apparently provide the first examples of Sr with elevenfold coordination. The other structures in which tenfold coordination has been reported are: strontioiginorite, SrCaB₁₄O₂₀(OH)₆·5H₂O, with average Sr-O distance 2.680 Å (Konnert *et al.*, 1970); tunellite, SrB₆O₉(OH)₂·3H₂O, with average Sr-O distance 2.736 Å (Clark, 1964b); Sr(MnO₄)₂·3H₂O, with average Sr-O distance 2.677 ± 0.074 Å (Ferrari *et al.*, 1966); and Sr₃(PO₄)₂ with average Sr-O distance 2.67 Å (Zachariasen, 1948).

The polyhedra of the crystallographically distinct pair of Sr cations share an O(7)–O(16) edge, and further linkages are provided by sharing with adjacent polyhedra the O(1)–O(10) and O(6)–O(15) edges. A tightly held polyhedral sheet is thus built up between the two crystallographically distinct polyanion sheets. We consider the B(OH)₃ groups and the water molecules as part of the construction by virtue of their coordination to the Sr cations. The closest Sr-Sr approach is 4.39 Å in veatchite and 4.35 Å in *p*-veatchite.

There appears to be a slight but real difference between veatchite (V) and *p*-veatchite (pV) in the coordination polyhedra. The coordinating oxygen atoms are the same and most of the Sr-O distances are the same

Table 6. Distances of Other Atoms from Planes of Polyanion Oxygen Atoms, and Angles Between Planes Compared for Veatchite and \bar{p} -Veatchite

	Distances (Å) from planes and angles between planes ^{a/}											
	Polyanion I						Polyanion II					
	Ring 1		Ring 2		Ring 1		Ring 2		Ring 1		Ring 2	
Ring oxygen atoms	Atom	V	pV	Atom	V	pV	Atom	V	pV	Atom	V	pV
	O(2), O(3), O(4)	0(5), O(6), O(8)	0(11), O(12), O(13)	0(14), O(15), O(17)								
Associated atoms	B(1)	0.1	0.0	B(2)	0.2	-0.3	B(6)	0.0	-0.3	B(7)	-0.3	0.3
	B(2)	0.5	0.4	B(4)	0.4	-0.5	B(7)	-0.3	-0.4	B(9)	-0.4	0.5
	B(3)	-0.1	-0.1	B(5)	-0.2	-0.1	B(8)	0.1	0.0	B(10)	0.2	-0.2
	O(1)	0.0	-0.1	O(1)	0.0	0.0	O(10)	0.2	0.1	O(10)	0.2	0.1
	O(7)	-0.3	-0.3	O(7)	2.0	-2.0	O(16)	0.3	0.3	O(16)	-1.8	2.0
				OH(9)	-0.5	0.4				OH(18)	0.4	-0.4
Angle between planes 1, 2		82°	79°					81°	79°			
Oxygen atoms of triangle	O(1), O(2), O(3)			O(5), O(8), OH(9)			O(10), O(11), O(12)			O(14), O(17), OH(18)		
Angle of triangle to ring plane		1.1°	3.9°		14.4°	11.4°		4.7°	2.1°		12.1°	10.7°
Oxygen atoms of triangle	O(3), O(4), O(7)						O(12), O(13), O(16)					
Angle of triangle to ring plane		7.3°	7.7°					8.6°	7.2°			

^{a/} Atoms at X, Y, Z of Table 3. Veatchite (V), this study; \bar{p} -veatchite (pV), Rumanova and Gandymov (1971), planes and angles calculated during this study from data in reference. The boron atoms of the triangles are in the plane of the associated oxygen atoms except for the following ones in \bar{p} -veatchite: B(5), -0.2 Å; B(6), -0.3 Å; B(10), -0.1 Å.

Table 7. Bond Distances for Strontium
to Oxygen Atoms in Veatchite

Polyanion	Oxygen atom	Coordinates of oxygen atom			Sr(1)-O distance ^{a/} (Å)
		<u>x</u>	<u>y</u>	<u>z</u>	
I	O(1)	0.122	-0.203	0.419	2.90
	O(3)	0.130	0.252	0.569	2.57
	O(4)	0.135	-0.100	0.822	2.57
	O(6)	0.120	0.094	0.924	2.74
	O(2)	0.125	-0.057	0.178	2.58
	O(7)	0.127	0.201	0.233	<u>2.77</u>
		average of 6			<u>2.69</u>
II	O(10)	0.003	-0.076	0.610	2.71
	O(15)	-0.002	0.131	0.594	2.69
	O(16)	-0.006	0.022	0.301	2.85
	H ₂ O(22)	0.229	0.071	0.532	<u>2.47</u>
		average of 10			<u>2.68</u>
					Sr(2)-O distance ^{a/} (Å)
II	O(10)	0.003	0.424	0.110	2.86
	O(11)	-0.007	0.281	0.345	2.55
	O(12)	-0.013	-0.028	-0.041	2.56
	O(13)	-0.015	0.323	-0.300	2.56
	O(15)	-0.002	0.131	-0.406	2.78
	O(16)	-0.006	0.022	0.301	<u>2.80</u>
		average of 6			<u>2.69</u>
I	O(1)	0.122	0.297	-0.081	2.91
	O(6)	0.120	0.094	-0.076	2.81
	O(7)	0.127	0.201	0.233	3.03
B(OH) ₃	OH(20)	-0.113	0.296	0.015	2.69
	OH(21)	-0.123	0.107	-0.005	<u>2.73</u>
		average of 11			<u>2.75</u>

^{a/} One standard deviation, ± 0.02 Å, except for H₂O(22), ± 0.03 Å. Coordinates of Sr cations as in Table 3.

within three or four standard deviations. However, the O(6)-O(15) edge that is shared between two Sr cations is longer in veatchite, 3.33 Å compared with 3.16 Å in *p*-veatchite, and the Sr(1)-O(6) distances are, respectively, 2.74 Å (V) compared with 2.59 Å (pV), and Sr(2)-O(15) is 2.78 Å (V), 2.58 Å (pV). This difference in the two structures appears to be real and extends to the B(4)-O(6) values observed, 1.42 Å (V), 1.54 Å (pV), and also to the B(7)-O(15) values, 1.40 Å (V), 1.53 Å (pV). Just as might be expected, the oxygen atoms associated with the longer Sr-O distances have shorter B-O distances, and *vice versa*. This change appears to be in turn related to further adjustments in the boroxol rings containing B(4) and B(7), as follows: B(4)-O(8), 1.54 Å (V) to 1.41 Å (pV); B(2)-O(5), 1.38 Å (V) to 1.51 Å (pV); B(7)-O(14), 1.64 Å (V) to 1.43 Å (pV); and B(9)-O(17), 1.31 Å (V) to 1.45 Å (pV). These changes can be best envisioned by examination of Figures 2 and 4.

The B(OH)₃ Groups. Polymerized boric-acid side chains are known to attach to larger borate polyanions. A [BO(OH)₂]¹⁻ triangle occurs on the polyanion of kaliborite, HKMg₂B₁₂O₁₆(OH)₁₀·4H₂O (Corazza and Sabelli, 1966), and a linked pair of triangles, [B₂O₂(OH)₃]¹⁻, attaches to the polyanion of strontioiginorite, SrCaB₁₄O₂₀(OH)₆·5H₂O (Konnert *et al.*, 1970). The presence of isolated B(OH)₃ groups, as in veatchite and *p*-veatchite (and gowerite, *op. cit.*), is therefore reasonable even though unexpected. In the B(OH)₃ group the average B-OH distance is 1.36 Å, and the average OH-B-OH angle, 120°. However, the individual B-OH distances vary as follows: OH(19), 1.25 Å, OH(20), 1.40 Å, OH(21), 1.42 Å (one standard deviation ± 0.04 Å), and the individual angles, as follows: OH(20)-B(11)-OH(21) 105°, OH(20)-B(11)-OH(19) 132°, OH(21)-B(11)-OH(19) 123° (one s. d. ± 3°). If real the distortions are those that would occur as a result of sharing the OH(20)-OH(21) edge with the Sr(2) polyhedron. In orthoboric acid (sassolite, Zachariasen, 1954) the borate triangles are quite regular, however, and the B(OH)₃ group in *p*-veatchite also is. In view of the limits of error the reality of the distortion in the veatchite B(OH)₃ group cannot be confirmed at present. The boron atom B(11) is exactly in the plane of the three hydroxyl ions within the limits of error. In veatchite the three triangles having hydroxyl ions are aligned parallel and within 2° of the same plane (Figs. 1, 5). There is a larger departure, about 7°, in *p*-veatchite although the alignment is similar.

Water Molecule H₂O(22) and Hydrogen Bonds (Table 8, Fig. 1). The water molecule is closely held to Sr(1) by the shortest observed Sr-O distance in both veatchite (Table 7) and *p*-veatchite (2.42 Å). The two hydrogen

Table 8. Hydrogen Bonds and Water Molecule

Environment in Veatchite (see Fig. 1)

Donor atom	Acceptor atom	Coordinates of acceptor atom			Distance ^{a/} (Å)
		\bar{x}	\bar{y}	\bar{z}	
H ₂ O(22)	OH(18)	0.302	-0.115	0.504	2.67
H ₂ O(22)	OH(19)	0.281	0.290	0.503	2.80
OH(9)	O(14)	0.396	0.774	0.519	2.69
OH(18)	O(8)	-0.280	0.301	0.505	2.76
OH(19)	O(5)	-0.280	0.007	0.006	2.70
OH(20)	O(17)	-0.096	0.522	0.013	2.67
OH(21)	OH(9)	-0.182	-0.092	0.007	2.64
Atoms					Angle
OH(18)-H ₂ O(22)-OH(19)					122°
OH(18)-H ₂ O(22)-Sr(1)					115°
OH(19)-H ₂ O(22)-Sr(1)					122°

^{a/} One standard deviation, distances ± 0.04 Å, angles $\pm 1^\circ$. Coordinates of donor atoms as in Table 3.

bonds the water molecule forms to hydroxyl ions OH(18) and OH(19) in a neighboring building block are important in holding the blocks together. The distances and angles involved are normal for a water molecule with this environment (Table 8), and are similar in veatchite and *p*-veatchite.

All the hydroxyl ions participate in hydrogen bonding and the donors can be unambiguously identified by chemical considerations. In determining the hydrogen-bonding scheme, edges of the oxygen polyhedra around strontium cations have been avoided. Our independent assignment agrees exactly with that arrived at by Rumanova and Gandymov (1971) for *p*-veatchite. No attempt was made to locate hydrogen atoms in veatchite by electron-density methods, due to the presence of the Sr cations and the relatively poor refinement.

Of the seven hydrogen bonds, six link together adjacent building blocks as defined. Only one, OH(20) to O(17), occurs entirely within the sheet of polyanion II as defined (Fig. 1; for *p*-veatchite, Fig. 3 of Rumanova and Gandymov, 1971). All the hydrogen bonds are of normal lengths; the range in veatchite is from 2.64 to 2.80 Å (± 0.04 Å).

Charge Balance Considerations. Satisfactory totals ranging from 1.85 to 2.20 valence units (v.u.) are found for each oxygen atom on the basis of

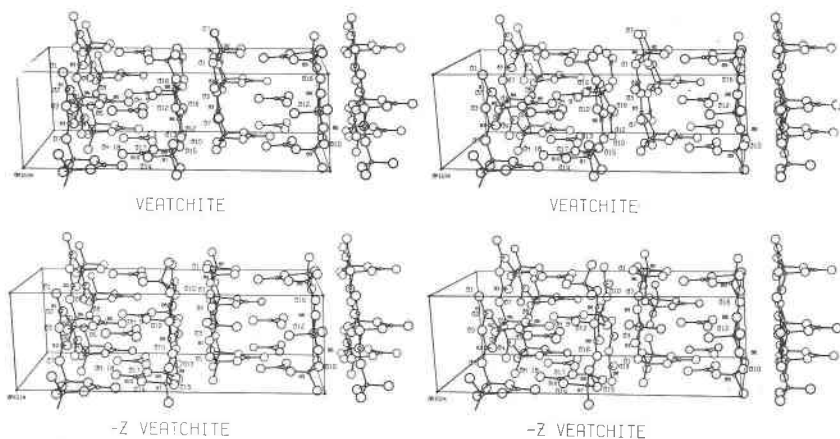


FIG. 5. Stereoscopic-pair views showing the packing possibilities; selected atoms, with Sr cations omitted. From the labelled origin, $+a$ is horizontal, $+c$ vertical, and $+b$ into the paper. (a) Veatchite with the correct Aa translations. The basic building block is on the right and a portion also on the left. Note the sequence along c of O(1)-O(3)-O(7) which remains the same at the left and in the center, and O(10)-O(12)-O(16), marked on the right and in the center. (b) Veatchite with the translation $\frac{1}{2}+x, \bar{y}, \bar{z}$ applied. Same basic building block as in (a), but note changes in center of cell, where the sequence is now reversed from that shown in (a).

a simple ionic model (Pauling, 1929) as follows. A strength of 1.00 v.u. is given to the oxygen atoms in triangular coordination with boron, and 0.75 v.u., to those in tetrahedral coordination. Strengths of 2/10 and 2/11 v.u. are assigned each oxygen atom coordinating the respective strontium cations. A strength of 0.90 v.u. is assigned each hydrogen-bond donor and 0.10 v.u., to each acceptor. The errors in bond distances are such that use of the bond strength *vs.* distance curves developed by Zachariasen (1963) does not improve the sums. With either model the sums for O(1), O(12), and O(16) are at the high end of the range and the sums for O(13), O(14), and O(15) are at the low end of the range.

Packing of Veatchite and p-Veatchite. Because the basic building blocks are so nearly alike in these two structures, and even the hydrogen-bond network between adjacent blocks is the same, the differences are obviously slight. In Figure 5a a stereoscopic-pair view of veatchite is given minus the Sr cations which are not necessary for the present discussion. The view is along b , with a horizontal and c vertical. On the right the basic building block can be seen with coordinates as given in Table 3 (except $x+1$) and the polyanion I portion is repeated at the left. In the center of the cell is the block related by the a -glide translation: $1/2+x,$

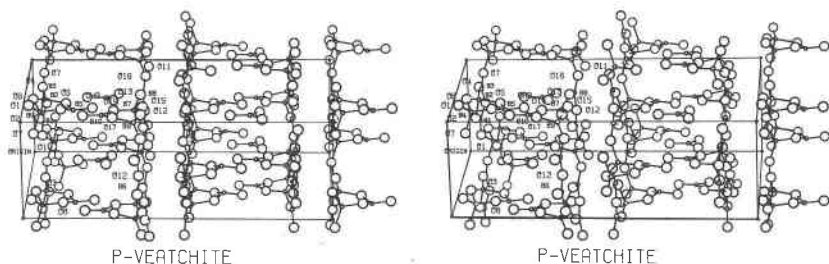


FIG. 6. Stereoscopic-pair view of selected portions of the *p*-veatchite structure from data of Gandymov *et al.* (1968). From the labelled origin, $+b$ is horizontal, $+c$ vertical, and $+a$ towards the viewer. The basic building block like the one in veatchite is located at the center of the cell. The sequence reversal for polyanion I can be noted on the left.

\bar{y} , z . Study of the array shows that because z remains the same everywhere, the sequence along c of O(1)-O(3)-O(7) and O(16)-O(12)-O(10), for example, is the same in the center as it is in the basic group. If, however, an operation of $1/2+x, \bar{y}, \bar{z}$ is applied (invalid for Aa), the sequences for the central group reverse to O(7)-O(3)-O(1) and O(10)-O(12)-O(16), as illustrated in Figure 5b labelled $-z$ veatchite. This structure is that of *p*-veatchite which has space group $P2_1$; the long axis becomes b and the 2_1 symmetry axis relates the central building block to those on the ends. A view of *p*-veatchite plotted with the actual *p*-veatchite cell and coordinates given by Gandymov *et al.* (1968) is shown in Figure 6. Due to the shift in origin (see coordinate transformation, Table 3), the basic building block chosen in veatchite is here located at the center. Although not all atoms are labelled, the symmetry change due to the 2_1 operation is apparent and is emphasized by the various locations of the B(5) atom (coordinates prior to the refined values).

The reason this slight change does not affect the nature of the structure may be because of the similarity of so many atoms in the polyanion. For example, O(1) and O(7) in polyanion I, and O(10) and O(16) in polyanion II, each coordinate two Sr cations and link a triangular and a tetrahedral boron. As a result the polyanion sheets can be reflected or rotated without major changes as long as the relative orientation of the groups with the hydroxyl ions remains the same. Nevertheless a finite, although small, energy difference must exist for otherwise there would not be crystals of both kinds; in fact, it is really more surprising that the two kinds do actually occur.

There is some evidence indicating that the a -glide packing is not regularly maintained in veatchite. Some crystals exhibit diffuse streaking along a^* , indicating possible packing errors along (100) planes. It is rea-

sonable to suppose that *p*-veatchite-type packing does occur, perhaps occasionally, perhaps semi-regularly, as mistakes in the veatchite structure. The *p*-veatchite crystals that we have examined, however, do not exhibit any diffuse streaking, so the packing array is apparently ordered by the 2_1 operation without any mistakes occurring. Thus it appears that it may be more difficult to achieve a perfect *a*-glide packing arrangement.

CHEMICAL CONSIDERATIONS

Both structural formulas that were proposed, one for veatchite (Christ, 1960) and one for *p*-veatchite (Kondrat'eva, 1966) were based on incorrect, although different, oxide formulas, and so were necessarily wrong. However, the observed polyanion sheets $[B_5O_8(OH)]^{2-}$ are in accord with the rules formulated by Christ (1960). The crystal-structure studies since 1960 show that in addition to these rules, a fifth one must be added (Clark, 1971), as follows: the boric acid group, $B(OH)_3$, may exist in isolated form in the presence of more complex polyanions, or such insular groups may themselves polymerize, attaching as side chains to the complex polyanions. The chemical conditions that govern the crystallization of these various borate minerals are still not understood, much less what is responsible for such subtle differences as those between veatchite and *p*-veatchite.

ACKNOWLEDGMENTS

This study has been continuing over so many years that all our indebtedness cannot be covered here, but we express our appreciation to all who have assisted, including a number of scientists in Germany, Great Britain, and Italy. Special mention is due to colleagues at the U. S. Geological Survey: Richard C. Erd, who supplied crystals, references, and constant encouragement; M. Fleischer, who translated Russian articles and kept us informed about the relevant literature; Daniel E. Appleman, who provided indispensable help with the perpetual computer problems; and Judith A. Konert, who checked drawings and manuscript. Drs. K. Nassau and S. K. Kurtz, Bell Telephone Laboratories, carried out the harmonic oscillator tests and gave permission to quote the results. All the drawings were produced with ORTEP (Johnson, 1965), and we are grateful to Dr. Carroll K. Johnson, Oak Ridge National Laboratories, for this program, without which it would have been most difficult to illustrate adequately this complex structure.

REFERENCES

- ALEXANDER, LEROY E., AND GORDON S. SMITH (1964) Single-crystal diffractometry: The improvement of accuracy in intensity measurements. *Acta Crystallogr.* **17**, 1195-1201.
- ASHIROV, A., AND O. GANDYMOV (1966) On the symmetry of *p*-veatchite [in Russian]. *Izvest. Akad. Nauk Tur. SSR, Ser. Fiz.-Tekh. Khim. Geol. Nauk* **1966**, 123-124.
- BEEVERS, C. A., AND F. H. STEWART (1960) *p*-Veatchite from Yorkshire. *Mineral. Mag.* **32**, 500-501.

- BRAITSCH, OTTO (1959) Über *p*-Veatchit, eine neue Veatchit-Varietät aus dem Zechstein-salz. *Beitr. Mineral. Petrogr.* **6**, 352–356.
- CHRIST, C. L. (1960) Crystal chemistry and systematic classification of hydrated borate minerals. *Amer. Mineral.* **45**, 334–340.
- CLARK, JOAN R. (1964a) Comment about the formula of veatchite. *Z. Anorg. Allgem. Chem.* **331**, 348–349.
- (1964b) The crystal structure of tunellite, $\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. *Amer. Mineral.* **49**, 1549–1568.
- (1971) Crystal chemistry of borates [abstr.]. *Amer. Chem. Soc., Div. Water, Air, Waste Chem. Symposium*, Washington, D. C.
- , AND C. L. CHRIST (1968) Crystal structure of veatchite. *Naturwissenschaften* **55**, 648.
- , AND MARY E. MROSE (1960) Veatchite and *p*-veatchite. *Amer. Mineral.* **45**, 1221–1229.
- , DANIEL E. APPLEMAN, AND C. L. CHRIST (1964) Crystal chemistry and structure refinement of five hydrated calcium borates. *J. Inorg. Nucl. Chem.* **26**, 73–95.
- CLARK, JOAN R., JUDITH A. KONNERT, AND C. L. CHRIST (1969) Crystal structures and origin of two borate minerals, veatchite and fabianite [abstr.]. *Geol. Soc. Amer., Abstr. with Programs for 1969*, Part 7, p. 35.
- , MARY E. MROSE, A. PERLOFF, AND G. BURLEY (1959) Studies of borate minerals (VI): Investigation of veatchite. *Amer. Mineral.* **44**, 1141–1149.
- CORAZZA, EGIZIO, AND CESARE SABELLI (1966) The crystal structure of kaliborite. *Accad. Naz. Lincei, Rend. Cl. Sci. Fis., Mat. Nat.* **41**, 527–552.
- CROMER, DON T., AND J. T. WABER (1965) Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18**, 104–109.
- DOYLE, P. A., AND P. S. TURNER (1968) Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Crystallogr.* **A24**, 390–397.
- EVANS, HOWARD T., JR., DANIEL E. APPLEMAN, AND DAVID S. HANDWERKER (1963) The least-squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method [abstr. E-10]. *Amer. Crystallogr. Assoc., Program Abstr., Cambridge, Mass.*, p. 42.
- FERRARI, A., A. BRAIBANTI, G. BIGLIARDI, AND A. M. MANOTTI LANFREDI (1966) The crystal structure of strontium permanganate trihydrate. *Acta Crystallogr.* **21**, 681–685.
- GANDYMOV, O., I. M. RUMANOVA, AND N. V. BELOV (1968) Crystal structure of *p*-veatchite $4\text{SrO} \cdot 11\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O} = \text{Sr}_4\text{B}_{22}\text{O}_{34} \cdot 7\text{H}_2\text{O} = 2\text{Sr}_2[\text{B}_5\text{O}_8(\text{OH})_2] \cdot \text{B}(\text{OH})_3 \cdot \text{H}_2\text{O}$ [in Russian]. *Dokl. Akad. Nauk SSSR* **180**, 1216–1219.
- JÄGER, H., AND H.-A. LEHMANN (1963) Synthese und Formel des Veatchits $\text{Sr}_3\text{B}_{16}\text{O}_{27} \cdot 5\text{H}_2\text{O}$. *Z. Anorg. Allgem. Chem.* **323**, 286–291.
- JOHNSON, CARROLL K. (1965) ORTEP: A FORTRAN thermal-ellipsoid plot program for crystal structure illustrations. *Nat. Tech. Info. Service ORNL* **3794**, Revised.
- KONDRAT'eva, V. V. (1964) X-ray study of *p*-veatchite from halogen rocks [in Russian]. *Rentgenogr. Mineral'n. Syr'ya Vses. Nauchn.-Issled. Inst., Akad. Nauk SSSR* **4**, 19–24
- (1966) Formula of *p*-veatchite [in Russian]. *Rentgenogr. Mineral'n. Syr'ya, Vses. Nauchn.-Issled. Inst. Mineral'n. Syr'ya, Akad. Nauk SSSR* **1966**, 66–68.
- KONNERT, JUDITH A., JOAN R. CLARK, AND C. L. CHRIST (1970) Crystal structure of strontoginorite, $\text{SrCaB}_{14}\text{O}_{20}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$. *Amer. Mineral.* **55**, 1191–1931.
- KRAMER, HENRY, AND ROBERT D. ALLEN (1956) A restudy of bakerite, priceite, and veatchite. *Amer. Mineral.* **41**, 689–700.
- KURTZ, STEWART K., AND T. T. PERRY (1968) A powder technique for the evaluation of nonlinear optical materials. *J. Appl. Phys.* **39**, 3798–3813.

- LEHMANN, H.-A., AND G. KESSLER (1968) Bildung von Veatchit und Strontium-Colemanit. *Z. Anorg. Allgem. Chem.* **360**, 267-276.
- MACGILLAVRY, C. H., AND G. D. RIECK, Editors (1962) *International Tables for X-Ray Crystallography*, Vol. 3. The Kynoch Press, Birmingham, England.
- MAREZIO, M. (1969) The crystal structure of $K_2[B_5O_8(OH)] \cdot 2H_2O$. *Acta Crystallogr.* **B25**, 1787-1795.
- MURDOCH, JOSEPH (1939) Crystallography of veatchite. *Amer. Mineral.* **24**, 130-135.
- , AND ROBERT W. WEBB (1964) Minerals of Calif. for 1958 through 1961. *Suppl. 2 to Bull. 173, Calif. Div. Mines Geol.*, p. 16.
- PAULING, LINUS (1929) The principles determining the structure of complex ionic crystals. *J. Amer. Chem. Soc.* **51**, 956-975.
- PEMBERTON, H. EARL (1968) The minerals of the Sterling Borax Mine, Los Angeles County, Calif. *The Mineral Explorer (Mineral. Res. Soc. Calif., Bull.)* **3**, 5-7.
- RUMANOVA, I. M., AND O. GANDYMOV (1971) Crystal structure of the natural strontium borate, *p*-veatchite, $Sr_2[B_5O_8(OH)]_2 \cdot B(OH)_3 \cdot H_2O$ [in Russian]. *Kristallografiya* **16**, 99-106 [Transl. *Sov. Phys. Crystallogr.* **16**, 75-81.]
- , ———, AND N. V. BELOV (1971) The crystal structure of veatchite and its relationship to the structure of *p*-veatchite [in Russian]. *Kristallografiya* **16**, 286-291. [Transl. *Sov. Phys. Crystallogr.* **16**.]
- SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925-946.
- STEWART, F. H., R. A. CHALMERS, AND R. PHILLIPS (1954) Veatchite from the Permian evaporites of Yorkshire. *Mineral. Mag.* **30**, 389-392.
- SWITZER, GEORGE (1938) Veatchite, a new calcium borate from Lang, California. *Amer. Mineral.* **23**, 409-411.
- , AND W. W. BRANNOCK (1950) Composition of veatchite. *Amer. Mineral.* **35**, 90-92.
- ZACHARIASEN, W. H. (1937) The crystal structure of potassium acid dihydronium pentaborate $KH_2(H_3O)_2B_5O_{10}$, potassium pentaborate tetrahydrate. *Z. Kristallogr.* **98**, 266-274.
- (1948) The crystal structure of the normal orthophosphates of barium and strontium. *Acta Crystallogr.* **1**, 263-265.
- (1954) The precise structure of orthoboric acid. *Acta Crystallogr.* **7**, 305-310.
- (1963) The crystal structure of monoclinic metaboric acid. *Acta Crystallogr.* **16**, 385-392.

Manuscript received, June 21, 1971; accepted for publication, August 4, 1971.