

X-RAY STUDY OF SHATTUCKITE¹

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ABSTRACT

Shattuckite, from a single crystal *x*-ray study is shown to be rhombic dipyramidal with space group, *Pcab*. The unit cell dimensions resulting from least squares refinement of powder data by digital computer are: $a = 9.881 \pm 0.003$, $b = 19.82 \pm 0.02$, $c = 5.398 \pm 0.003$ Å.

INTRODUCTION

Considerable confusion has existed concerning the possible identity of plancheite and shattuckite. The former was originally described by Lacroix (1908) from Mindouli, the Congo; the latter by Schaller (1919) from the Shattuck Mine, Bisbee, Arizona. Later, Schoep (1930) restudied material from Tantara, the Congo, similar to that described by Lacroix, and concluded that the plancheite of Lacroix and the shattuckite of Schaller were in fact the same mineral. The present paper deals with the characterization of material from the Ajo Mine, Ajo, Arizona which was collected by Berman in 1941 and was labelled "shattuckite." It is specimen #97159 of the Holden Collection of Harvard University.

OCCURRENCE

The shattuckite from Ajo occurs as spherulitic masses composed of small radiating prismatic crystals of deep blue color. Ajoite, as determined by an *x*-ray powder pattern, is intergrown with the shattuckite as are quartz and hematite.

PHYSICAL AND OPTICAL PROPERTIES

Individual shattuckite crystals are one to two millimeters in length. Prominent forms are {100}, {010}, and {110}; shattuckite possesses excellent {010} and {100} cleavages. The optical properties are:

X = b	$\alpha = 1.753 \pm 0.003$	(sodium light, 22° C.)
Y = a	$\beta = 1.782 \pm 0.003$	optic sign (+)
Z = c	$\gamma = 1.815 \pm 0.003$	2V large

The density of a 40–60 mesh hand-picked fraction was determined using the Berman balance and immersing the grains in toluene by means of a small mesh basket. The mean of 10 determinations was 4.01 grams/cc with a standard error of the mean of 0.02 grams/cc.

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X-RAY DATA

Weissenberg zero, first, and second level photographs were taken using filtered copper K_{α} radiation, rotating the crystal about the c -axis. The space group was determined to be $Pcab$. This was verified by zero-level precession photographs of the $(0k0)$ and $h00$ crystallographic planes using molybdenum K_{α} radiation. Preliminary lattice constants, $a = 9.878$, $b = 19.82$, $c = 5.407$ Å, obtained from single crystal photographs, were used to calculate d spacings. This permitted indexing of the powder pattern as shown in Table 1. A set of 14 d spacings with 2θ between 34.73 and 79.82° were used in a least squares analysis of the above powder data. With reference to Table 1, it may be seen that reflections to which more than one set of indices could be assigned have been used. It is assumed that the major contribution to both the position and intensity of any line on the powder pattern is made by the most intense reflection as indicated by the single crystal photographs. The choice of indices, then, has been made by comparing the intensities of appropriate reflections. The least squares analysis was done on an I.B.M. 7094 computer using the program described briefly by Burnham (1962). It should be noted that no systematic correction terms were used. Such treatment yielded the following refinement of the cell parameters:

$$\begin{aligned} a &= 9.881 \pm 0.003 \text{ \AA} \\ b &= 19.82 \pm 0.02 \text{ \AA} \\ c &= 5.398 \pm 0.003 \text{ \AA} \end{aligned}$$

COMPOSITION

After purification by magnetic separation of a -100 mesh sample on the Franz isodynamic separator with hand-picking of the resultant separate, a one gram sample of shattuckite was analyzed. An x -ray powder pattern of this material confirmed the absence of admixed quartz and ajoite. The results obtained are presented in Table 2.

Using the relationship:

$$Z \times \text{g.f.w.} = V\rho N$$

where:

N = Avogadro's number (6.023×10^{23})

V = volume of the unit cell in cc

ρ = measured density in gm/cc

g.f.w. = gram formula weight (*cf.* analysis)

$Z_{\text{calc.}} = 2.00$

Thus the indicated unit cell contents are: $\text{Cu}_{18}\text{Si}_{16}\text{O}_{60}\text{H}_{20}$.

However the symmetry of the space group of shattuckite requires that copper and silicon be present in multiples of 4. The large departure of the

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SHATTUCKITE
(ANALYZED MATERIAL, FILM #26429)

CuK RADIATION, Ni FILTER, CAMERA DIAM. 114.59 MM

I^1	d(obs.)	d(calc.) ²	(hkl.)
4	9.92	9.911	(020)
9	4.96	4.955	(040)
		4.941	(200)
10	4.42	4.430	(140)
		4.422	(220)
<1	4.26	4.274	(121)
2<3	3.65	3.644	(201)
8	3.50	3.499	(240)
1<2	3.42	3.424	(141)
		3.421	(221)
8	3.30	3.304	(060)
2	3.13	3.133	(160)
		3.126	(320)
5	2.94	2.936	(241)
3	2.786	2.784	(311)
7	2.745	2.746	(260)
		2.743	(340)
1<2	2.705	2.699	(002)
		2.705	(321)
2	2.583	2.581	(112) ³
5	2.472	2.478	(080)
		2.470	(400) ³
6	2.400	2.403	(180)
		2.397	(420)
3	2.366	2.370	(042) ³
		2.369	(202)
1	2.334	2.332	(360) ³
2<3	2.297	2.293	(351) ³
<1	2.240	2.236	(271)
		2.246	(401)
1	2.212	2.215	(280)
		2.211	(440) ³
<1	2.186	2.191	(421)
<1	2.137	2.137	(242)
<1	2.089	2.090	(062)
<1	2.043	2.045	(162)
		2.043	(322)
1<2	1.984	1.982	(0.10.0)
		1.980	(380)

¹ Intensities estimated visually with the strongest line assigned an intensity of "10."

² d 's calculated using cell parameters refined by least squares analysis.

³ Reflections used in refinement of cell parameters . . . (760) and (811) were used in addition to those indicated.

TABLE 1—(continued)

I^1	d(obs.)	d(calc.) ²	(hkl.)
3	1.940	1.943	(1.10.0)
		1.938	(520)
1	1.919	1.917	(172) ³
<1	1.857	1.858	(461)
2	1.822	1.825	(082)
		1.822	(402)
		1.824	(521)
4	1.793	1.795	(182) ³
		1.792	(422)
<1	1.765	1.763	(113)
		1.765	(362) ³
<1	1.737	1.734	(391)
		1.738	(541)
1	1.690	1.691	(203) ³
<1	1.662	1.664	(481)
<1	1.646	1.647	(600)
7	1.627	1.629	(1.12.0)
		1.625	(620)
1<2	1.595	1.598	(0.10.2)
		1.596	(462)
4	1.567	1.567	(2.12.0)
<1	1.551	1.550	(532)
		1.552	(571)
<1	1.502	1.501	(173)
1	1.486	1.486	(4.10.1)
		1.485	(581)
1	1.475	1.477	(3.12.0)
2<3	1.436	1.434	(2.11.2)
		1.436	(562) ³
<1	1.416	1.416	(0.14.0)
2<3	1.392	1.392	(622) ³
1	1.372	1.373	(4.12.0)
		1.375	(632)

Cu:Si ratio from 1:1 cannot be accounted for on the assumption that such is due entirely to analytical error. Similar treatment of an analysis by Sun (1961) yields a Cu:Si ratio of 9.20:8.11. Also two of the three original analyses of Schaller (1919) show analogous behavior.

CONCLUSIONS

The author has been unable to resolve the contradiction which exists between the symmetry requirements of the space group and the cell contents as indicated by chemical analysis. If one assumes an amphibole-like structure for shattuckite, *i.e.*, $\text{Cu}_7\text{Si}_8\text{O}_{22}(\text{OH})_2 \cdot 2 \text{Cu}(\text{OH})_2$, with $Z=2$,

then the analytical data are satisfied. However, the symmetry requirements of the space group must still be met. Following this assumption, the material was re-studied optically and additional single crystal photographs were taken. Monoclinic symmetry with the β angle equal to, or very nearly equal to 90° (pseudo-orthorhombic symmetry), could not be demonstrated.

There is, however, evidence that suggests that copper cannot be accommodated in an amphibole or pyroxene type structure. In all low-tem-

TABLE 2. CHEMICAL COMPOSITION OF SHATTUCKITE FROM AJO, ARIZONA
(Analyst: J. Ito)

	Wt. %*	Mol. Quot.	At. Quot. Metals	At. Quot. Ox.	At. %		
CuO	55.2	0.695	0.695	0.695	Cu 15.52	} 15.74 × 0.570 = 8.98	
MgO	0.33	0.008	0.008	0.008	Mg 0.18		
CaO	0.10	0.002	0.002	0.002	Ca 0.04		
Al ₂ O ₃	0.21	0.002	0.004	0.006	Al 0.13		
Fe ₂ O ₃	0.14	(assumed due to admixed hematite)				} 14.09	= 8.03
SiO ₂	37.5	0.625	0.625	1.250	Si 13.96	} 17.60	= 10.04
H ₂ O ⁺	7.1	0.394	0.788	0.394	H 17.60		
					O 52.60		
Total	100.58		2.122	2.355			

Formula: (Cu, Mg, Ca)₉(Al, Si)₈O₃₀H₁₀.

* Spectrographic analysis indicated the presence of trace amounts of Ti, V, Co, Ni, Mo, Mn.

perature compounds copper is never in octahedral coordination with its nearest neighbors. Usually it assumes what is best described as distorted octahedral coordination. Further, copper does not appear to enter the lattice of any of the rock-forming silicates at higher temperature.

In view of what is known then of the crystal chemistry of copper, determination of the structure of shattuckite would be of considerable interest. Additional chemical analyses are also needed.

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REFERENCES

- BURNHAM, C. W. (1962) Lattice constant refinement. *Carnegie Inst. Washington, Yearbook 1961-62*, 132-135.
- LACROIX, A. (1908) Les minéraux accompagnant la diopside de Mindouli (Congo français). *Bull. Soc. Franc. Minéral.* **31**, 247-259.
- SCHALLER, W. T. (1919) Planchéite and shattuckite, copper silicates, are not the same mineral. *Jour. Wash. Acad. Sci.* **9**, 131-134.
- SCHOEP, A. (1930) Nouvelles recherches sur la planchéite et sur la shattuckite. Identité de ces deux minéraux. Remarques sur la bisbeeite et sur la katangite. *Bull. Soc. Franc. Minéral.* **53**, 375-393.
- SUN, M. S. (1961) Differential thermal analysis of shattuckite. *Am. Mineral.* **46**, 67-77

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