

THE FORMULA OF SHATTUCKITE<sup>1</sup>

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## ABSTRACT

New chemical analyses of shattuckite, a basic hydrous copper silicate from Ajo, Arizona, establish the formula as  $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$ .

The formula  $4[\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2]$  fulfills the requirement of the space group symmetry that atoms in the structure be present in multiples of 4.

## INTRODUCTION

The original description of shattuckite, a basic hydrous copper silicate, published by Schaller in 1915, was based on material from Bisbee, Arizona, (Schaller, in Ford, 1915). The formula was given as  $2\text{Cu} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ . Previously, Lacroix (1908*a, b*) had described and named planchéite which is a hydrous copper silicate from the French Congo, with suggested formula  $15\text{CuO} \cdot 12\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ . Zambonini (1918) confused the issue by suggesting that Schaller's shattuckite and Lacroix's planchéite were the same mineral. Schaller (1919) defended the separate identities of the two minerals on the basis of their indices of refraction. The indices of refraction of shattuckite are in the range 1.75 to 1.815, distinctly higher than the values given for the material Lacroix called planchéite.

It appears that Lacroix (1908*a, b*) prepared his samples according to the four different aspects in which it occurred: "(1) in dark blue 'concretions' . . . ; (2) in spherulites of pale blue . . . ; (3) in fibres of clear blue . . . ; (4) in spherulites of fibres." Lacroix states that the chemical analysis was made on material with aspect (1) as it was the most pure. Once the mechanical separation was made, the three aspects appeared the same when examined under the microscope. Reconstructing what must have happened, from work done since on these minerals, we can conclude that Lacroix had two different minerals and that the cut on which the chemical analysis was made should now be considered to have been shattuckite, and the remaining cuts, on which Lacroix did his optical determinations, and from which Zambonini (1918) and Larsen (1921 p. 30-32) received their material, were planchéite. Larsen's indices of refraction for type planchéite in the range of about 1.64 to 1.71 verified those measured by Lacroix and have been obtained repeatedly on different specimens chiefly by Schoep (1930) and other Belgian scientists in their descriptions of planchéite from the Belgian Congo. The Belgian scientists refer to planchéite of the different aspects as *Planchéite Types*.

About 1930, additional shattuckite from Bisbee was procured. Studies

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

of many thin sections and oil immersion mounts of this material, when compared with those of the type material, showed that the type material was so impure that shattuckite must be reexamined and new analyses must be made in order to establish the composition of the mineral.

It was not until the present study,<sup>1</sup> in which the formula for shattuckite is established as  $4[5\text{CuO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}]$  by chemical analyses of material from Ajo, Arizona, that it was noted that Lacroix's formula for aspect (1),  $15\text{CuO} \cdot 12\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ , actually is that of shattuckite plus a little extra water,  $3(5\text{CuO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}) + 2\text{H}_2\text{O}$ . Determination of water by loss on ignition could account for the excess water if reduction of copper was allowed to take place, as suggested by Sun (1961). Further confirmation of the presence of shattuckite in Lacroix's planchéite is given by a recent examination of material on a specimen Lacroix had sent to Dr. Edmond O. Hovey of The American Museum of Natural History (New York). The presence of both minerals in this specimen was confirmed by X-ray identification.

Guillemin and Pierrot (1961), ignoring the differences in optical properties, concluded that shattuckite and planchéite are identical. Their new data on material they refer to as planchéite are evidently for shattuckite, from their X-ray and optical data.

#### OCCURRENCE

Both specimens of shattuckite studied by us were collected at the Ajo mine in Ajo, Arizona, in 1941 by the late Harry Berman of Harvard University. We are indebted to Mary Mrose for obtaining from the National Museum one of these (N.M. 104164) and purifying it for chemical analysis. This is listed as Sample No. 2. The specimen that Newberg (1964) used in his recent study of shattuckite is also from the same specimen lot. The shattuckite occurs as spherulitic masses composed of small radiating prismatic crystals of deep blue color. Quartz, hematite, and ajoite were found randomly disseminated throughout the spherulitic aggregates of shattuckite, making it extremely difficult to prepare a pure sample of the mineral for chemical analysis.

#### CHEMICAL COMPOSITION

After preliminary purification the samples were hand-picked and checked for impurities by microscopic examination. Quartz, ajoite, and hematite were still scattered throughout the hand-picked material used

<sup>1</sup> A preliminary notice of this formula was presented at the meeting of The Mineralogical Society of America at Gatlinburg, Tennessee, July, 1965 [Mary E. Mrose and Angelina C. Vlisidis (1966). Proof of the Formula of Shattuckite. (abstr.) *Amer. Mineral.* 51, 266-267].

TABLE 1. CHEMICAL ANALYSIS OF SHAFTUCKITE FROM AJO MINE, AJO, ARIZONA

Oxides	Sample 1		Sample 2		Theoretical		Ratios	
	Wt. %	Calc. to 100%	Wt. %	Calc. to 100%	Wt. %		Sample 1	Sample 2
SiO <sub>2</sub>	33.18	35.54	36.06	36.68	36.62		0.5918	0.6104
CuO	56.99	61.04	59.39	60.41	60.63		0.7674	0.6104
FeO	0.20	0.22	0.19 <sup>1</sup>	0.19			.0031	.7595
CaO	0.04	0.04	0.01 <sup>1</sup>	0.01			.0007	.0026
MgO	0.13	0.14	0.02 <sup>1</sup>	0.02			.0035	.0002
MnO	0.01	0.01	0.03 <sup>1</sup>	0.03			.0001	.0005
H <sub>2</sub> O <sup>+</sup>	2.81	3.01	2.62	2.66	2.75		.1671	.0004
	93.36	100.00	98.32	100.00	100.00		.1671	.1476
Quartz	5.60		0.58					
Al <sub>2</sub> O <sub>3</sub>	0.29		0.02 <sup>1</sup>					
Fe <sub>2</sub> O <sub>3</sub>	0.85		—					
TiO <sub>2</sub>	0.04		—					
P <sub>2</sub> O <sub>5</sub>	0.06		—					
H <sub>2</sub> O <sup>-</sup>	0.09		—					
	100.29		98.92					
Specific Gravity:								
Measured	4.00		4.08					
Corrected for Quartz	4.11		4.09					
Calculated	4.09		4.09					
Formula	5 CuO·4SiO <sub>2</sub> ·H <sub>2</sub> O or Cu <sub>5</sub> (SiO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub>							

<sup>1</sup> Calculated from the semiquantitative spectrographic analysis by Joseph L. Harris.

TABLE 2. SUMMARY OF CHEMICAL COMPOSITIONS ASSIGNED TO SHATTUCKITE

	Mol	fractions	CuO/SiO <sub>2</sub>	Formula
Schaller (1915)	SiO <sub>2</sub>	0.656	1.04	2CuO·2SiO <sub>2</sub> ·1H <sub>2</sub> O
	CuO	0.684		
	H <sub>2</sub> O	0.328		
Newberg (1964)	SiO <sub>2</sub>	0.625	1.12	9CuO·8SiO <sub>2</sub> ·5H <sub>2</sub> O
	CuO	0.695		
	H <sub>2</sub> O	0.394		
Sun (1961)	SiO <sub>2</sub>	0.597	1.16	3CuO·3SiO <sub>2</sub> ·1H <sub>2</sub> O
	CuO	0.695		
	H <sub>2</sub> O	0.224		
Guillemin and Pierrot (1961) "planchéite" Sample 2	SiO <sub>2</sub>	0.606	1.21	6CuO·5SiO <sub>2</sub> ·1.5-2H <sub>2</sub> O
	CuO	0.735		
	H <sub>2</sub> O	0.206		
Guillemin and Pierrot (1961) "planchéite" Sample 3	SiO <sub>2</sub>	0.597	1.20	
	CuO	0.717		
	H <sub>2</sub> O	0.220		
Vlisidis Sample 1	SiO <sub>2</sub>	0.592	1.30	
	CuO	0.775		
	H <sub>2</sub> O	0.167		
Vlisidis Sample 2	SiO <sub>2</sub>	0.610	1.25	5CuO·4SiO <sub>2</sub> ·1H <sub>2</sub> O
	CuO	0.763		
	H <sub>2</sub> O	0.148		

for the analysis. The quantity of iron oxide present in the shattuckite analyzed is too small to influence the calculated ratios, whether it be considered as FeO or Fe<sub>2</sub>O<sub>3</sub>. Spectropraghic analyses showed less than 0.01% titanium and boron on sample No. 1 and less than 0.03% boron, molybdenum, and vanadium on sample No. 2.

Briefly the method of analysis was as follows: the water content was determined by the Penfield method; copper was determined electrolytically; silica was obtained by dehydration with hydrochloric acid, and the aluminum and iron on the ammonium hydroxide precipitate. Quartz was determined by breaking up the sample with hydrochloric acid, filtering and treating the quartz and silica thus obtained with hot five percent sodium carbonate solution. The insoluble quartz was then filtered, ignited and weighed. The efficacy of the separation was checked by microscopic examination of the residue. Sun's discussion of the reduction of copper to

Cu<sub>2</sub>O in water determined by loss on ignition would thus not be applicable to this analysis.

The results of the chemical analyses are given in Table 1. The formula derived therefrom is 5CuO·4SiO<sub>2</sub>·H<sub>2</sub>O or Cu<sub>5</sub>(SiO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>. The analyses, after being calculated to 100% to allow for the impurities are in good agreement with the theoretical composition. Table 2 compares the new formula for shattuckite with those previously proposed by Schaller, Guillemin and Pierrot, Sun, and Newberg.

The measured specific gravities, after correcting for quartz as an impurity, are 4.11 and 4.09, respectively; the calculated specific gravity is 4.09.

Using the cell dimensions of shattuckite determined by Newberg which are  $a = 9.881 \pm 0.003 \text{ \AA}$ ,  $b = 19.82 \pm 0.02 \text{ \AA}$ ,  $c = 5.398 \pm 0.003 \text{ \AA}$ , and the measured specific gravity of 4.11 of this study,  $Z$  is calculated as 3.99. The cell thus contains four formula weights and should be written as 4[Cu<sub>5</sub>(SiO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>] or Cu<sub>20</sub>Si<sub>16</sub>O<sub>56</sub>H<sub>8</sub>. This formula fulfills the requirements imposed by the space group *Pcab*, as pointed out by Newberg—that all the atoms in the shattuckite structure must be present in multiples of 4. The X-ray powder data are given by Newberg (1964).

The difficulty in preparing a pure sample of shattuckite, uncontaminated by quartz, hematite, and other copper silicates, probably accounts for the erratic formulas obtained by the earlier analysts.

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