

## AJOITE, A NEW HYDROUS ALUMINUM COPPER SILICATE\*

W. T. SCHALLER AND ANGELINA C. VLISIDIS, *U. S. Geological  
Survey, Washington 25, D. C.*

### ABSTRACT

Ajoite is a new bluish-green hydrous aluminum copper silicate from Ajo, Pima County, Arizona. It was collected by Harry Berman in 1941 and recognized by him at that time as probably a new mineral. Mostly massive, a few cavities contain platy crystals or laths elongated parallel to  $c$  and flattened parallel to  $\{010\}$ . It is biaxial positive with indices of refraction  $\alpha = 1.565$ ,  $\beta = 1.590$ ,  $\gamma = 1.650$ ,  $+2V = 68^\circ$ ,  $X = b$ ,  $Z \wedge c = 15^\circ$ . The specific gravity is 2.96. The x-ray powder pattern could not be related to that of any other copper silicate. The strongest lines are: 12.4 (100), 3.34 (25), 6.19 (9), 4.12 (9), 3.09 (9). Examination with an x-ray diffractometer showed that neither medmontite nor any montmorillonite group mineral can be present. Chemical analysis yielded the formula  $\text{Al}_2\text{O}_3 \cdot 6\text{CuO} \cdot 10\text{SiO}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ . Ajoite is not related to any of the several impure mixtures of copper silicates and aluminum minerals.

### INTRODUCTION

Specimens of a bluish-green copper aluminum silicate, named ajoite† after the locality Ajo in northwestern Pima County, Arizona, were collected by Harry Berman of Harvard University, in August 1941 together with specimens of dark blue shattuckite. Preliminary examination by him, chiefly optical, indicated that the greenish mineral was probably a new species. It had been planned by Berman and Schaller to collaborate on the study of this new mineral and possibly to extend such a collaborative investigation so as to include all the known copper silicate minerals, a plan nullified by Berman's untimely death in 1944. It is a tribute to Berman's keen perception that his earlier prediction of a new mineral has been borne out.

The two gram sample of massive ajoite prepared for analysis by Berman was further purified by hand-picking the few remaining small spherulites of blue shattuckite enclosed in the greenish ajoite. The resulting purified sample was analyzed by Angelina C. Vlisidis after a pycnometer determination of the specific gravity and a preliminary spectrographic analysis.

Later, the entire collection of these specimens was forwarded by Prof. Clifford Frondel (Harvard University) for completion of the study. A second small sample of massive ajoite was prepared from these samples for the several qualitative tests made, checking the optical determinations, and taking additional x-ray powder-diffraction patterns.

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† Pronounced ah'hō-ite.

## ASSOCIATION

Most of the ajoite is compact massive, resembling some deeper colored chrysoprase in color and specimen structure, and is intimately mixed with dark blue shattuckite and white massive quartz. Occasional small cavities contain aggregates of elongated plates of ajoite, a millimeter and less in length. Other less abundant associated minerals observed are minute pearly scales of sericite, white powdery quartz, pyrite, very pale blue altering shattuckite, limonitic stains, and on one specimen massive conicalcrite. Berman (letter to W. T. Schaller, dated June 12, 1942) also noted the presence of this mineral (he referred to it as "higginsite") perched on the new copper silicate.

As observed in a thin section, the relation between ajoite and shattuckite seems rather indefinite, but, in general, the greenish ajoite appears to have replaced the shattuckite, as noted by Berman. On the other hand, the presence of small seams of shattuckite, grading down in size to isolated minute spherulites, suggests to one of us (W.T.S.) that shattuckite may be forming at the expense of the ajoite and later than it.

## PHYSICAL AND OPTICAL PROPERTIES

In color ajoite approaches very closely Ridgway's Venice green, Plate VII, 41. BB-G, about 75 per cent green and 25 per cent blue.

A letter, dated June 12, 1942, from Berman to Schaller, stated that the light green, lathlike ajoite found replacing the shattuckite is monoclinic, elongated parallel to  $c$  and flattened parallel to  $\{010\}$ . Berman determined the indices of refraction to be  $\alpha=1.565$ ,  $\beta=1.590$ ,  $\gamma=1.650$ , with a birefringence of 0.085. From these indices  $2V$  is calculated to be  $68^\circ$ . Optically positive,  $X=b$ ,  $Z \wedge c=15^\circ$ . These values have been confirmed by Schaller.

The specific gravity of the analyzed sample is 2.96 (pycnometer).

## X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction patterns (films 5759, 12557, and 12559) of the massive analyzed material are identical with those taken of the better crystallized material (films 5757 and 5757A) on which Berman made his optical determinations. The measured powder data listed in Table 1 were obtained from a pattern (film 12559) taken by Mary E. Mrose, U. S. Geological Survey, with a Debye-Scherrer camera (114.59 mm. diameter) using the Straumanis technique, with  $\text{CuK}\alpha$  radiation (Ni filter),  $\lambda=1.5418 \text{ \AA}$ . Film 12557 is reproduced in Fig. 1.

## COMPOSITION

The analysis of the small sample of ajoite first purified by Berman and later by Schaller, guided by prior spectrographic examination,

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR AOJITE FROM AJO, ARIZONA  
 (analyzed material; film 12559)  
 CuK $\alpha$  (Ni filter),  $\lambda=1.5418\text{\AA}$   
 Camera diameter 114.59 mm.; cutoff at 17.7  $\text{\AA}$   
 Corrected for shrinkage (by M. E. Mrose)

I <sup>1</sup>	d(meas.)	I	d(meas.)	I	d(meas.)
100	12.4	1	2.37	1	1.577
4	9.98	3	2.30	1	1.555
9	6.19	3	2.28	2	1.540
1	5.19	3	2.26	1	1.527
1	4.99	1	2.21	1	1.506
3	4.53	1	2.16	1	1.489
3	4.25	1	2.12	2	1.480
9	4.12	1	2.08	2	1.449
1	3.87	1	2.02	1	1.416
1	3.73	1	2.00	1	1.384
4	3.48	1	1.978	1	1.373
2	3.40	1	1.949	2	1.347
25	3.34	1	1.862	1	1.333
9	3.09	1	1.841	1	1.309
5	2.93	3	1.818	1	1.296
6	2.79	1	1.802	1	1.278
3	2.66	1	1.775	1	1.268
2	2.59	1	1.752	1	1.250
3	2.55	2	1.672	1	1.228
4	2.51	1	1.642	1	1.198
6	2.46	1	1.617	1	1.184
1	2.43	1	1.595	1	1.181

Plus many more weak lines

<sup>1</sup> Intensities were obtained by visual comparison with a calibrated intensity strip based on  $\log \sqrt{2}$ .

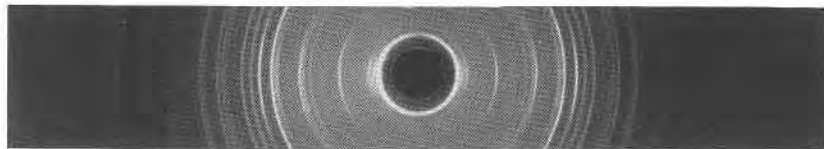
showed that ajoite is a hydrous aluminum copper silicate with the formula  $\text{Al}_2\text{O}_3 \cdot 6\text{CuO} \cdot 10\text{SiO}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ .

The spectrographic analysis by K. J. Murata, U. S. Geological Survey, showed:

- XO Si, Cu
- X Al, As, Ba
- O.X Ca, Fe, Mg, Mn, Ti
- O.OX Na
- O.OOX B
- Not found: P, Pb, V, Sn, Be, Bi, Cr, Ge, Li, Sb, Zr, Zn

The results of the chemical analysis are given in Table 2. The formula derived therefrom is  $\text{Al}_2\text{O}_3 \cdot 6\text{CuO} \cdot 10\text{SiO}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ .

Ajoite is readily decomposed by acids, leaving a coherent white mass

FIG. 1. X-ray powder-diffraction pattern of ajoite. Cu  $K\alpha$ , Ni filter.

of hydrated silica with small unattacked particles of blue shattuckite scattered through it. At room temperature, with 1:1 HCl, decomposition takes place overnight. In 1:1  $\text{NH}_4\text{OH}$  several days are required. When the mineral was treated with  $\text{NH}_4\text{OH}$  at room temperature overnight, no reaction was noticed.

The role of arsenic and barium in the mineral is not definitely known, but the arsenic is considered as due to admixed conicalcrite and the barium to barite as the ratios of BaO (0.0033) and  $\text{SO}_3$  (0.0029) are very close. Based on the determined percentages of  $\text{As}_2\text{O}_5$  and of BaO, 3 per cent of conicalcrite and 0.76 per cent of barite are deducted as impurities. The value given for FeO is for total iron.

TABLE 2. ANALYSIS OF AJOITE

(by A. C. Vlisidis)

Analysis		Deducting conicalcrite and barite	Remainder Ajoite	Ratios		
$\text{SiO}_2$	45.90	—	45.90	0.7642	0.7642	10.10
CuO	33.90	0.92	32.98	.4146	.4494	5.94 $6 \times 0.99$
FeO	.78	—	.78	.0109		
MnO	.10	—	.10	.0014		
MgO	.66	—	.66	.0164		
CaO	.99	.65	.34	.0061	.0736	0.97 $1 \times 0.97$
BaO	.50	.50	—	—		
$\text{Al}_2\text{O}_3$	7.30	—	7.30	.0716		
$\text{TiO}_2$	.16	—	.16	.0020	.4151	5.49 $5\frac{1}{2} \times 1.00$
$\text{As}_2\text{O}_5$	1.33	1.33	—	—		
$\text{SO}_3$	.23	.23	—	—		
$\text{H}_2\text{O}^-$	2.55	—	2.55	.1415		
$\text{H}_2\text{O}^+$	5.03	.10	4.93	.2736		
	99.43	3.73	95.70			
G	2.96					

Determinations of the water content of ajoite were repeated on two other small samples of the material, (1) a second small sample prepared by Berman and (2) a small sample prepared by Schaller. The results obtained are:

	(1)	(2)	Analyzed sample
H <sub>2</sub> O <sup>-</sup>	1.85	1.92	2.55
H <sub>2</sub> O <sup>+</sup>	5.69	6.34	5.03
Total H <sub>2</sub> O	7.54	8.26	7.58

If the values of (2) are substituted for those given in the analysis, then the ratio of the total H<sub>2</sub>O becomes 5.96, very close to 6.

#### RELATIONS TO OTHER COPPER SILICATES

John C. Hathaway of the U. S. Geological Survey examined ajoite with an x-ray diffractometer using both air-dried and ethylene glycol saturated samples and was unable to detect any montmorillonite group mineral. X-ray examination of ajoite heated at 400° C. showed no collapse in the structure. These results demonstrate that neither medmontite, a copper-bearing (20.96 per cent CuO) clay of the montmorillonite group, nor any other montmorillonite group mineral can be present.

Ajoite is not closely related to any of the several described hydrous copper aluminum silicates such as traversoite, a light blue "new variety of chrysocolla" with 21.84 per cent Al<sub>2</sub>O<sub>3</sub> and 32.84 per cent H<sub>2</sub>O, believed to be a mixture of chrysocolla and gibbsite; or pilarite with 16.9 per cent Al<sub>2</sub>O<sub>3</sub> and 21.7 per cent H<sub>2</sub>O, or to similar material from Utah with 10.78 per cent Al<sub>2</sub>O<sub>3</sub> and 25.76 per cent H<sub>2</sub>O, the alumina being ascribed to admixed allophane; or to any of the several probably impure bluish chrysocollas with small amounts of Al<sub>2</sub>O<sub>3</sub>. A mixture of chrysocolla and alunite (or natroalunite) has also been described. Most of these chrysocollas containing appreciable amounts of alumina are probably mixtures of typical chrysocolla (essentially CuO·SiO<sub>2</sub>·2H<sub>2</sub>O) with other copper free minerals. Alumina is commonly present in these mixtures as hydrate, phosphate, sulfate, or silicate. All these mixtures contain much more water than is present in ajoite.

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