

PAPAGOITE, A NEW COPPER-BEARING MINERAL  
FROM AJO, ARIZONA\*C. OSBORNE HUTTON, *Stanford University, Stanford, California,*  
AND ANGELINA C. VLISIDIS, *U. S. Geological Survey,*  
*Washington, D. C.*

## ABSTRACT

Papagoite, a rare hydrous copper calcium aluminum silicate, has been recognized, together with ajoite, as a strictly local occurrence, in metasomatically altered rocks at Ajo, Pima County, Arizona. The mineral forms more or less equidimensional crystals, less than 1 mm. in length, that are slightly flattened parallel to {001} with faces in the zone [010] well developed. The forms  $c\{001\}$ ,  $g\{401\}$ , and  $m\{110\}$  are dominant in most cases, with  $d\{102\}$ ,  $e\{101\}$ ,  $f\{201\}$ ,  $h\{601\}$ , and  $a\{100\}$  usually less prominent. Goniometric measurements lead to an axial ratio of 1.109:1:0.415, with  $\beta=100^\circ30'$ . A distinct cleavage parallel to (100) was noted in thin sections but it was not evident in crystals or fragments thereof. Papagoite is monoclinic prismatic, space group  $Cm$ ,  $C2$ , or  $C2/m$ , with  $a=12.91 \text{ \AA}$ ,  $b=11.48$ ,  $c=4.69$ , all values  $\pm 0.01 \text{ \AA}$ ;  $\beta=100^\circ38'$ ;  $a:b:c=1.124:1:0.408$ . A powder pattern is recorded and it has been indexed up to  $2\theta \sim 65^\circ$ ; the  $d$ -spacings and intensities of the five strongest lines are: 2.874  $\text{\AA}$  (10), 4.29 (9), 2.204 (9), 2.795 (8), and 3.44 (8).

The mineral has a cerulean blue color in hand specimen and is distinctly pleochroic. Biaxial, negative;  $\alpha=1.607$ ,  $\beta=1.641$ ,  $\gamma=1.672$ ,  $\gamma-\alpha=0.065$ ;  $2V=78^\circ$ ; dispersion faint,  $r>v$ ; X=very pale glaucous green to colorless, Y=cendre blue, Z=Venice green;  $Z>Y>K$ ;  $X \wedge c=44^\circ$  or  $X \wedge a=35^\circ$ , both in the acute angle, and  $Z=b$ . Y is very nearly normal to the form  $f\{201\}$ . Specific gravity=3.25 (meas. and calc.).

A complete chemical analysis is reported, and dehydration and ammonia-exchange experiments indicate strongly that hydrogen is present as (OH) and not as  $H_2O$  molecules. Calculation of cell contents indicates that a small amount of silicon in the [Si-O] tetrahedra may be replaced by  $[H_4]$ , and accordingly the following formula is proposed for papagoite:  $Ca_4(Cu, Mn, Fe)_{4.02}(Al, Mg, Ti)_4[Si(H_4)Al]_8O_{24}(OH)_{12.18}$ . This may be simplified to:  $4\{CaCuAl[SiO_3]_2(OH)_3\}$ .

The mineral has been named for the Indian tribe that once inhabited the region in which the mining center of Ajo, Arizona, is situated.

## OCCURRENCE

The papagoite-bearing specimens were found at Ajo, Arizona, in an isolated pocket 150 ft. below ground-level at the 1750 level in an area that has now been entirely removed. The nearest high-grade sulfide ore now lies 50 ft. below and 1000 ft. east of the papagoite locality.

The mineral, together with minor amounts of fibrous radiating aggregates of later-formed ajoite (Schaller and Vlisidis, 1958), form narrow veinlets (Fig. 1) and veneers on slip-surfaces in an altered rock that consists chiefly of interlocking anhedral quartz and dusty albite ( $Ab_{97-98}$ ). Associated with this assemblage are lesser amounts of sericite, epidote, and calcite, and minor quantities of apatite that is weakly dichroic,

\* Publication authorized by the Director, U. S. Geological Survey.

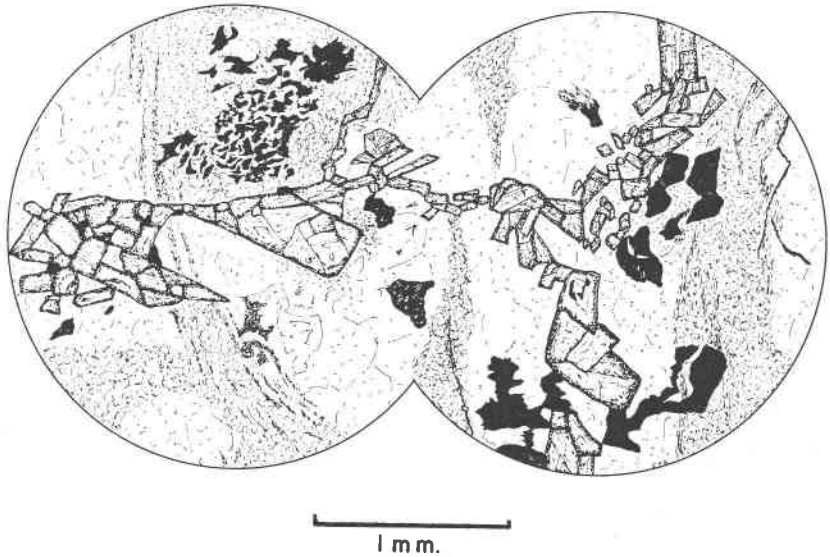


FIG. 1. Veinlets of papagoite in an assemblage of clear quartz and dusty albite; the black areas are manganese and iron oxides and hydroxides. The small patch of fibrous material near the center of the drawing is ajoite. Ajo, Arizona.

stumpy crystals of rutile, sphene, slightly metamict zircon, tiny well-formed, sharply pyramidal crystals of anatase, alunite, and patches of brown manganese and iron hydroxides; rare tenorite may also be present in these brown areas. Sulfides were not detected in the material examined. Clearly the specimens are the product of metasomatism but, since no relicts of the original unaltered material remain, one is unable to say if the specimens have been derived from the monzonite<sup>1</sup> itself.

The mineral described herein has been named papagoite<sup>2</sup> after the Indian tribe that inhabited the area in which the active mining center of Ajo is situated.

#### PHYSICAL PROPERTIES

In hand specimen, the color of papagoite is very close to Ridgway's cerulean blue (Ridgway's Plate 8, 45. BG-B), and in thin section, or in crushed particles with a thickness of about 0.03–0.04 mm., a strong pleochroism is evident. The following optical data have been determined:  $\alpha = 1.607, \pm 0.001, \beta = 1.641, \gamma = 1.672, \gamma - \alpha = 0.065$ ; X = colorless to very

<sup>1</sup> For comprehensive studies of the geology of Ajo, Arizona, in particular, and the region in general, the reader is referred to the work of J. Gilluly (1937 A, 1937 B, 1946).

<sup>2</sup> PĀPĀGŌAIT (Royal Geographic Society (R.G.S. II) System); pāpāgōite (American usage).

pale greenish-blue (pale glaucous green, Ridgway's Plate 33, 39". B-G, f), Y = blue (cendre blue, Ridgway's Plate 8, 43. G-B, b), Z = deep greenish blue (Venice green, Ridgway's Plate 7, 41. BB-G, b).  $Z > Y > X$ .  $2V = 78^\circ \pm 1^\circ$ , and negative optic sign. Dispersion is exceedingly faint with  $r > v$ . The extinction angle  $X \wedge c = 44^\circ$ , or  $X \wedge a = 35^\circ$ , both in the acute angle, whereas  $Y \wedge c = 46^\circ$ . Y to the perpendicular to (001) is approximately  $36^\circ$ .  $Z = b$  (Fig. 2).

If crystals that exhibit prominent development of the form {201} are oriented in mounting media with (201) parallel to the microslide, slightly

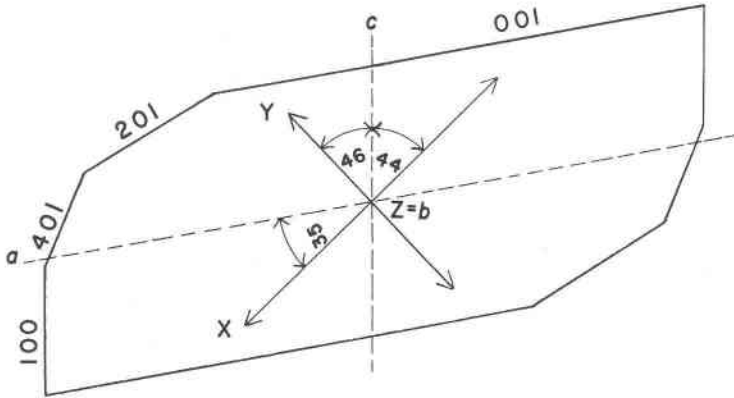


Fig. 2. Optical orientation of papagoite from Ajo, Arizona. The plane of the drawing is perpendicular to the  $b$ -crystallographic axis [=Z].

off-centered optic normal interference figures are observed. The refractive index  $\gamma$  and a value very close to  $\alpha$  may be measured when a crystal is oriented in this fashion, whereas for crystals lying on the dominant face in the zone [010], viz., (001), the appropriate vibration directions have the refractive indices  $\alpha' = 1.615$  and  $\gamma = 1.672$ . This is the most usual aspect assumed by crystal fragments in immersion media if the appropriate face in the zone [010] has not been destroyed during removal of crystals from matrix. If crystal fragments should lie on (401), then the refractive indices are equivalent to  $\gamma$  and a value almost equal to  $\alpha$ .

The mineral has a hardness of about  $5-5\frac{1}{2}$ , that is, it may be scratched by adularia but not by apatite, and the specific gravity at  $19^\circ$  C. of the analyzed material was determined to be 3.25 by centrifuging the powder in bromoform—diiodomethane mixtures. During separation of papagoite from the matrix the specific gravity of any one fraction did not vary from 3.25 by more than 0.005. A distinct cleavage parallel to (100) is evident, but this is to be seen only in sections of papagoite that have

been carefully oriented and cut parallel to a plane perpendicular, or nearly so, to the vertical crystallographic axis.

#### CRYSTALLOGRAPHY

Only partially complete crystals were available to the writers and these were found in occasional vugs in quartz veinlets; none exceeded 0.75 mm. in length. Although they were detached from the walls of the host with care no complete euhedra were found.

Crystals tend to be slightly elongated parallel to the  $b$ -axis, the dominant zone axis, and somewhat flattened parallel to  $\{001\}$ . All faces in the

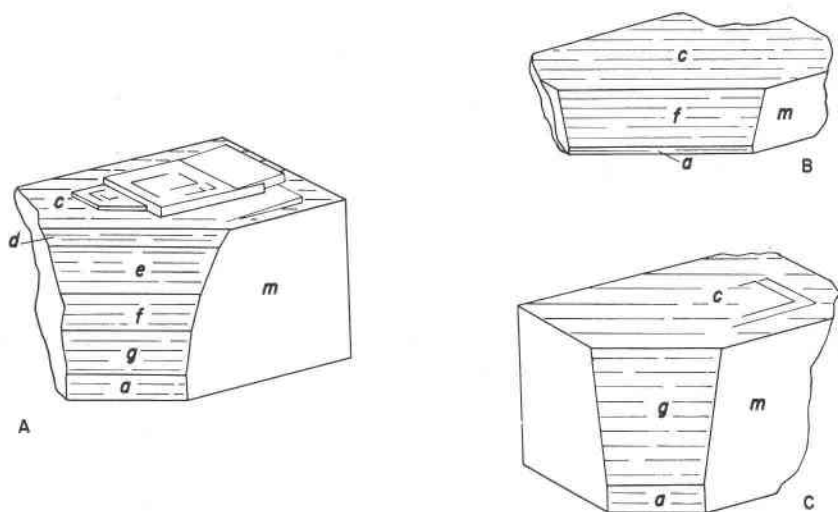


FIG. 3. Typical crystals of papagoite from Ajo, Arizona.

zone  $[010]$  are strongly striated parallel to the zone axis. Goniometric measurements yielded data that lacked desirable preciseness on account of oscillatory combination of faces, but more so because of the presence of satellites and accessories that may depart as much as  $4^\circ$  from the orientation of the planes which support them (Fig. 3A, C). Only one general habit was found, and in most of the crystals observed  $c\{001\}$ ,  $g\{401\}$ , and  $m\{110\}$  are dominant (Fig. 3C). Other faces in the zone  $[010]$  are  $d\{102\}$ ,  $e\{101\}$ ,  $f\{201\}$ ,  $h\{601\}$ , and  $a\{100\}$ . The dominance of  $c\{001\}$  and  $d\{102\}$ , or sometimes  $f\{201\}$ , and a marked suppression of  $a\{100\}$  leads to crystals that are tabular in form (cf. Fig. 3B). Faces of the form  $m\{110\}$  are, for the most part, devoid of satellites and striations and consequently they yield good reflections. The satellites are clearly

TABLE 1. INTERFACIAL ANGLES FOR PAPAGOITE

	Meas. angles	No. of meas. made	Calc. angles*
100 $\wedge$ 110	47°30'	5	47°50'
001 $\wedge$ 102	10°	4	9°50'
102 $\wedge$ 101	9°	4	8°40'
101 $\wedge$ 201	13°30'	4	13°40'
201 $\wedge$ 401	16°	4	16°10'
401 $\wedge$ 601	8°30'	2	8°25'
601 $\wedge$ 100	22°30'	2	22°35'
110 $\wedge$ 110	84°	5	84°15'
110 $\wedge$ 001	83°	5	82°55'

\* Since the unit cell dimensions from *x*-ray data are considered to have an accuracy of one part in 1,000, the calculated angles in this column are given to the nearest 5'. This argument applies to the angles listed in Table 2 also.

the result of crystal growth, since no indications of etch phenomena are apparent. Pyramidal faces appear to be absent from the nine crystals that were available for study.

Goniometric measurements, which are considered to have an accuracy that is no better than  $\pm 30'$ , are given in Table 1, where these data may be compared to the interfacial angles that have been derived by calculation from cell dimensions yielded by single-crystal *x*-ray work. The values listed for the measured angles are, in each case, averages of several measurements.

The data secured by goniometric measurement lead to an interaxial ratio of  $a:b:c=1.109:1:0.415$  with  $\beta=100^\circ 30'$ , compared to the data derived from *x*-ray measurements, *viz.*,  $a:b:c=1.1245:1:0.4085$ ,

TABLE 2. STANDARD ANGLE TABLE FOR PAPAGOITE

Monoclinic prismatic.  $a:b:c=1.1245:1:0.4085$ ;  $\beta=100^\circ 38'$ ;  $p_0:q_0:r_0=0.3632:0.4015:1$ ;  $r_2:p_2:q_2=2.4906:0.9046:1$ ;  $\mu=79^\circ 20'$ ;  $p_0'=0.3695$ ,  $q_0'=0.4085$ ,  $x_0'=0.1877$ .

	$\phi$	$\rho$	$\phi_2$	$\rho_2=B$	C	A
<i>c</i> 001	90°00'	10°40'	79°20'	90°00'	0°00'	79°20'
<i>a</i> 100	90°00'	90°00'	0 00	90 00	79 20	0 00
<i>m</i> 110	42 10	90 00	0 00	42 10	82 55	47 50
<i>e</i> 101	90 00	29 10	60 50	90 00	18 30	60 50
<i>f</i> 201	90 00	42 50	47 10	90 00	32 10	47 10
<i>g</i> 401	90 00	59 00	31 00	90 00	48 25	31 00
<i>h</i> 601	90 00	67 25	22 35	90 00	56 50	22 35
<i>d</i> 102	90 00	20 25	69 35	90 00	9 50	69 35

$\beta = 100^{\circ}38'$ . On the basis of the latter, the standard angles, linear, axial, and polar ratios, etc., have been calculated and presented in Table 2.

#### X-RAY STUDY

Considerable difficulty arose when attempts were made to orient crystal fragments for single-crystal study because of the development of satellites or accessories on each crystal. Even fragments that measured about 0.1 mm. in diameter yielded x-ray diffraction patterns that one would expect to find for polycrystalline material. In the simplest case, it was possible to orient the fragment so that straight, parallel layer lines yielded by the host were dominant, but, at the same time, were considerably obscured by reflections due to satellites whose orientations differed from that of the host by as much as  $4^{\circ}$  in some instances. This situation was most serious for rotations about the  $a$  and  $b$  axes, since the reciprocal spacings perpendicular to these directions are relatively small, with the result that layer lines are crowded. After considerable experimentation it was found that crystal fragments with diameters considerably less than 0.1 mm. were necessary if clean, single-crystal patterns were to be secured, and this situation made handling and orientation difficult.

Using Ni-filtered copper radiation, and a camera of 57.29 mm. diameter, single-crystal rotation photographs were obtained for rotation about three axes, and Weissenberg films for each layer were also obtained. Zero-layer photographs, calibrated with quartz, gave the following cell dimensions:  $a = 12.91 \text{ \AA}$ ,  $b = 11.48$ ,  $c = 4.69$ , all values  $\pm 0.01 \text{ \AA}$ ;  $\beta = 100^{\circ}38' \pm 6'$ . This leads to the ratio  $a:b:c = 1.1245:1:0.4085$ . A study of the Weissenberg films indicates the following extinctions:  $hkl$  with  $h+k$  odd; hence a  $C$  lattice. With the morphology of the crystals taken into account, this leads to three possible space-groups:  $Cm$ ,  $C2/m$ , or  $C2$ . No tests for centrosymmetry have been made.

The powder pattern for papagoite (Table 3) has been indexed up to approximately  $2\theta = 65^{\circ}$ , on the basis of the cell dimensions obtained by single-crystal study. Reflections at angles greater than  $2\theta = 65^{\circ}$  tend to be weak and often are quite diffuse; furthermore, owing to numerous coincidences, indexing of the high-angle reflections is unsatisfactory.

#### CHEMICAL COMPOSITION

Crystal fragments of papagoite must be heated in a closed tube to a dull red heat before any indication of decomposition is observed; when this does occur the mineral breaks down without decrepitation and water is evolved. A drab brown powder remains and since the temperature of decomposition is high, fusion with the glass of the tube results.

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR PAPAGOITE, AJO, ARIZONA  
 Analyzed material; film No. 717.  $Cu_{k\alpha}$  (Ni filter),  $K\alpha=1.5418 \text{ \AA}$ . Camera  
 diameter=114.59 mm., cut-off at ca. 18.5  $\text{\AA}$ . Spacings corrected for  
 film shrinkage. Simplified formula:  $4\{Ca, Cu, Al [SiO_3]_2(OH)_3\}$ .  
 $a=12.91 \text{ \AA}$ ,  $b=11.48$ ,  $c=4.69$ ,  $\beta=100^\circ 38'$ ;  $Cm$ ,  $C2/m$ , or  $C2$ .

I <sup>1</sup>	d (meas.)	d (calc.) <sup>2</sup>	hkl	I <sup>1</sup>	d (meas.)	d (calc.) <sup>2</sup>	hkl
7	6.33	6.36	200	<1	1.935	1.934	422
		5.74	020			1.9295	222
7	4.61	4.61	001	6	1.912	1.913	060
9	4.29	4.28	$\bar{1}11$			1.908	332
		4.255	220			1.905	132
1	4.12	4.11	$\bar{2}01$	5	1.864	1.864	$\bar{5}12$
1	3.95	3.96	310	<1	1.846	1.848	441
7	3.85	3.85	111			1.819	531
1	3.67	3.67	130			1.800	601
		3.59	021	3	1.798	1.798	$\bar{2}42$
8	3.44	3.44	201			1.797	042
1	3.34	3.34	$\bar{2}21$			1.791	710
6	3.30	3.30	$\bar{3}11$			1.767	061
<1 D	3.17	3.17	400			1.726	$\bar{6}02$
2	2.95	2.95	221			1.720	402
		2.945	$\bar{1}31$	4	1.719	1.719	621
10	2.874	2.872	$\bar{4}01$	4	1.702	1.703	550
		2.870	040			1.693	$\bar{5}32$
1	2.833	2.836	330			1.690	332
8	2.795	2.796	131	<1	1.680	1.680	$\bar{6}41$
		2.780	311			1.669	$\bar{4}42$
		2.777	420	7	1.667	1.667	242
2	2.616	2.616	240			1.652	$\bar{6}22$
2	2.565	2.570	$\bar{4}21$			1.648	422
		2.563	$\bar{3}31$			1.638	730
2	2.477	2.479	510	{ 2	1.638	1.632	731
3	2.437	2.436	041	{ 2	1.633	1.632	731
1	2.409	2.413	401	3 B	1.591	1.587	800
4	2.368	2.367	$\bar{5}11$			1.561	$\bar{2}03$
		2.352	$\bar{2}41$	1	1.560	1.559	712
		2.307	$\bar{2}02$			1.554	512
		2.305	002	1	1.545	1.546	$\bar{1}13$
{ 2 B	2.299	2.297	$\bar{1}12$			1.537	003
{ 3 B	2.292	2.293	331	<1	1.534	1.535	821
		2.225	421			1.529	820
9	2.204	2.204	241			1.525	641
		2.159	112	4	1.524	1.524	$\bar{3}13$

<sup>1</sup> Intensities were estimated visually.

<sup>2</sup>  $d_{hkl}$  calculated for all reflections observed on Weissenberg films down to 1.428  $\text{\AA}$ .

B: Broad line.

D: Diffuse line.

TABLE 3 (Continued)

I <sup>1</sup>	d (meas.)	d (calc.) <sup>2</sup>	hkl	I <sup>1</sup>	d (meas.)	d (calc.) <sup>2</sup>	hkl
2	2.140	2.141	222	<1	1.498	1.496	403
		2.139	022	1	1.483	1.484	023
1	2.130	2.130	440			1.479	642
		2.116	530, 600	2	1.475	1.475	442
<1	2.073	2.073	801			1.472	062
1	2.052	2.053	402			1.468	731
		2.048	202			1.455	732
		2.045	531	1	1.450	1.451	532
<1	2.034	2.035	511			1.447	423
		2.030	441			1.445	133
<1	1.999	1.999	132	2	1.437	1.437	802
1	1.983	1.984	620			1.435	080, 203
		1.950	621			1.433	602
				1	1.4305	1.428	333

I	d (meas.)	I	d (meas.)
<1	1.416	2	1.162
<1	1.403	<1 D	1.146
2	1.393	1 B	1.133
{1	1.376	1	1.1195
{2	1.372	1	1.102
2	1.356	1	1.084
1 D	1.323	2	1.063
1	1.293	1	1.0495
2	1.284	1	1.023
1	1.275	1	1.013
<1	1.240	1	.972
2	1.229	<1	.959
2 D	1.219	<1	.9525
<1	1.195	<1	.944
<1 D	1.172	<1	.925
1	1.168	<1	.838
		<1	.790

Finely crushed papagoite dissolves very slowly in boiling concentrated HCl, and after 24 hours treatment with a hot constant-boiling mixture of HCl, only partial solution has occurred with concomitant separation of a flocculent form of silica.

Several crystals were immersed in ammonium hydroxide (sp. gr. approx. 0.89 at 21° C.) in a tube, and the appearance of the mineral par-



ticles was observed from time to time. Absolutely no change was observed at the end of 72 hours. The same crystals were then placed in a tube and about 20 ml. of liquid ammonia added; the tube was then immersed in a mixture of acetone and dry ice in a Dewar flask. After 24 hours some liquid ammonia was still present but the tube was caked with ammonium carbonate crystals. On recovery, the color of the papagoite crystals was found to be completely unchanged. Accordingly, in neither experiment had a significant amount of ammonia-exchange taken place.

A 0.42-gm. sample of pure papagoite was heated to temperatures up to 800° C., and at intervals of approximately 50°–75° C., the weight of water evolved was recorded. Virtually no water was given off until a temperature of 500° C. was attained. Between that temperature and 750° C. almost all of the water was freed from the mineral. No indication of any discontinuity was found in the dehydration curve (Fig. 4).

For the determination of the extent of physical changes in papagoite during heat-treatment, x-ray powder patterns were obtained for samples

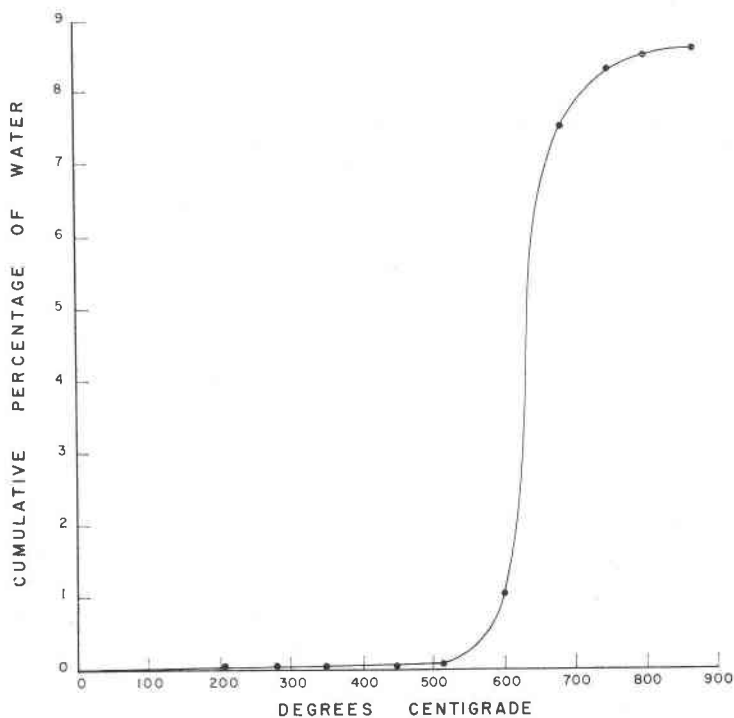


FIG. 4. Dehydration curve for papagoite. Temperatures of 700° and 800° C. are  $\pm 50^\circ$  C.

TABLE 4. ANALYSIS OF PAPAGOITE AND CALCULATED CELL CONTENTS  
Analyst: Angelina C. Vlisidis

	Wt. per cent	Ionic radii	Cations		
SiO <sub>2</sub>	33.60	0.41	Si	7.48	7.48
				(H <sub>1</sub> )	.30
					.22
Al <sub>2</sub> O <sub>3</sub>	15.78	0.50	Al	4.14	3.92
MgO	0.09	0.65	Mg	.03	.03
TiO <sub>2</sub>	0.26	0.68	Ti	.05	.05
FeO	0.27	0.75	Fe	.05	.05
MnO	0.10	0.80	Mn	.02	.02
CuO	23.53	0.83	Cu	3.95	3.95
CaO	17.02	0.99	Ca	4.06	4.06
H <sub>2</sub> O+	9.01	—	H	13.38	(To Si) 1.20
H <sub>2</sub> O-	0.04				12.18 12.18
	99.70				
Si:				7.48	
Σ Al, Mg, Ti, Fe, Mn, Cu, Ca:				12.30	
Oxygen:				36.07	
Hydrogen:				13.38	
Cell weight:				2220.25 × 10 <sup>-24</sup> gms.	
Factor:				1337.26	

heated in air at temperatures of 460° and 720° C. The material heated at the lower temperature yielded a pattern that is identical with that of the untreated mineral. On the other hand, papagoite heated at 720° C. for 2½ hours yields a complex powder pattern in which lines due to tenorite are dominant, but many additional, but less intense lines, not due to the copper oxide, are present. The strongest lines of these correspond in a general way to those reported for the artificial orthorhombic silicate of aluminum and calcium (Davis and Tuttle, 1952, p. 110), a compound that might be expected with these conditions. Accordingly, the absence of ammonia-exchange phenomena, and the x-ray data yielded by heat-treated material would seem to suggest that in papagoite hydrogen is present entirely as hydroxyl and not as molecular water.

A complete chemical analysis of papagoite is reported in Table 4. A 2-gm. sample for the analytical work was obtained by first handpicking a crude concentrate of papagoite from a specimen that had been crushed to pass through a 16-mesh screen (Tyler Series). This concentrate was then

hand-crushed to pass through bolting silk of approximately 0.06 mm. mesh, and the resulting material was repeatedly centrifuged until a pure fraction was secured.

The cell contents have been calculated from the weight per cent of each oxide on the basis of the relationship  $P_m/100M \times W/1.6603$ , where the oxide is expressed as  $P_mO_n$ ,  $M$  = molecular weight of the oxide, and  $W$  = cell weight. It will be noted that the numbers of Al, Cu, and Ca ions are extremely close to the figure of 4 in each case, oxygen to 36, but the figures for Si and H are irrational. In attempting to write a formula it should be remembered that dehydration data and failure to prepare ammonia-exchange products suggest very strongly that water molecules are absent, and instead, hydrogen is present as hydroxyl. One of the difficulties that arises, however, is the means of accommodating all of the hydrogen ions. If all of the hydrogen is present as (OH) ions, the Si-O ratio that appears to be most probable is 1:3, that is,  $[\text{SiO}_3]_n$ . The Si-O arrangement found in the phyllosilicates, *viz.*,  $[\text{Si}_4\text{O}_{10}]$ , appears to be a possible linkage if large amounts of the Al are considered to be in four-coordinated positions. Under these circumstances, a rather unsatisfactory formula may be developed but it should be noted that the physical properties of the mineral do not seem to support the belief that papagoite has a sheet structure; caution must be observed, however, in this respect, since datolite contains infinite sheets (Ito and Mori, 1953, p. 30; Christ, 1959, p. 176), even though the external physical properties of that mineral do not suggest it.

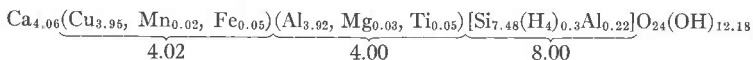
On the basis of an Si-O ratio of 1:3 one may write a simple formula, except that one finds a deficiency of Si and an overabundance of H ions. This leads one to envisage the different ways in which hydrogen, unaccompanied by extra oxygen, may be accommodated in silicates. These possibilities may be summarized as follows:

1. Replacement of oxygens in the Si-O tetrahedra by (OH) so that  $(\text{SiO}_3\text{OH})$  groups are formed as in the mineral afwillite,  $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (Megaw, 1952, p. 477-491).
2.  $[\text{OH}]_4$  may replace  $[\text{SiO}_4]$  as in hydrogrossular (Hutton, 1943), zircon, thorumgummit (Fron del, 1953), viséite (McConnell, 1952), etc., and it may partially replace  $[\text{SiO}_4]$  groups that link together to form the  $\text{Si}_{16}\text{O}_{44}$  arrangement in amphiboles (Zussman, 1955, p. 301-308; Nicholls and Zussman, 1955, p. 717-722; Hutton, 1956, p. 231-232).

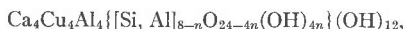
Now, so far as papagoite is concerned, replacement of some of the oxygens of the Si-O tetrahedra in the  $[\text{SiO}_3]$  groups by [OH], in a manner similar to that which has been shown to be the case for afwillite, is unsatisfactory since there are insufficient cations of suitable ionic radius to bring the Z group to the supposed figure of 8, and, at the same time, pro-

vide a suitable electrostatic balance elsewhere in the arrangement. With the second alternative arrangement, however, a good measure of agreement is obtained if 1.20 hydrogens and 0.22 aluminum are considered to replace silicon in order to bring the  $Z$  group to the figure of 8; at the same time this leaves approximately 12 hydrogens to form hydroxyl and 24 oxygens for the  $[\text{SiO}_3]_n$  groups. Upon this understanding, the suggested distribution of ions is given in Table 4.

On the basis of the figures in the last two columns in Table 4 the empirical cell contents may be expressed as follows:



The formula may be expressed more generally as follows:



or under the assumption that the silicon positions may be, under other circumstances, fully occupied by silicon, the formula for papagoite may be written as follows:



#### ACKNOWLEDGMENTS

The authors wish to thank Mr. Scott J. Williams of Scottsdale, Arizona, for the material that formed the basis of this study, and to acknowledge his perspicacity in recognizing that the mineral was of an unusual character. Furthermore, we are indebted for helpful discussion of several points, to Dr. Waldemar T. Schaller, Dr. Michael Fleischer, and Professor Adolf Pabst, and to Dr. Frederick G. Tickell for assistance in the laboratory.

#### REFERENCES

- CHRIST, C. L. (1959), Garrelsite and the datolite structure group: *Am. Mineral.*, **44**, 176-177.
- DAVIS, G. L., AND TUTTLE, O. F. (1952), Two new crystalline phases of the anorthite composition,  $\text{CaO-Al}_2\text{O}_3\text{-2SiO}_2$ : *Am. Jour. Sci., Bowen Volume*, 107-114.
- FRONDEL, C. (1953), Hydroxyl substitution in thorite and zircon: *Am. Mineral.*, **38**, 1007-1018.
- GILLULY, J. (1937A), Geology and ore deposits of the Ajo Quadrangle, Arizona: *Ariz. Bur. Mines, Geol. Ser. No. 9*, Bull. No. **141**, 1-83.
- (1937B), Physiography of the Ajo region, Arizona: *Geol. Soc. America Bull.*, **48**, 323-348.
- (1946), The Ajo mining district, Arizona: *U. S. Geol. Survey, Prof. Paper* **209**, 1-112; and supplement.
- HUTTON, C. O. (1943), Hydrogrossular, a new mineral of the garnet-hydrogarnet series: *Royal Soc. New Zealand, Trans.*, **73**, 3, 174-180.
- (1956), The composition of an actinolite: *Acta Cryst.*, **9**, 231-232.

- ITO, T., AND MORI, H. (1953), The crystal structure of datolite: *Acta Cryst.*, **6**, 24-32.
- McCONNELL, D. (1952), Viséite, a zeolite with the analcime structure and containing linked  $\text{SiO}_4$ ,  $\text{PO}_4$ , and  $\text{H}_2\text{O}_4$  groups: *Am. Mineral.*, **37**, 609-617.
- MEGAW, HELEN D. (1952), The structure of afwillite,  $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$ : *Acta Cryst.*, **5**, 477-491.
- NICHOLLS, G. D., AND ZUSSMAN, J. (1955), The structural formula of a hydrous amphibole: *Mineral. Mag.*, **30**, 230, 717-722.
- RIDGWAY, R. (1912), Color standards and color nomenclature, R. Ridgway, Washington, D.C.
- SCHALLER, W. T., AND VLISIDIS, ANGELINA C. (1958), Ajoite, a new hydrous aluminum copper silicate: *Am. Mineral.*, **43**, 1107-1111.
- ZUSSMAN, J. (1955), The crystal structure of actinolite: *Acta Cryst.*, **8**, 301-308.

*Manuscript received August 10, 1959.*