THE CRYSTAL STRUCTURE OF PLAZOLITE

ADOLF PABST, *University of California, Berkeley, California.*

Plazolite was described by Foshag[1] from the metamorphosed limestone at Crestmore, Riverside County, California, and as far as the writer is aware has not been reported from other localities. It is found in small colorless dodecahedrons superficially resembling grossularite but with a density of 3.129 and an index of refraction of 1.675. Foshag assigned to plazolite the formula $3CaO \cdot Al_2O_3 \cdot 2(SiO_2, CO_2) \cdot 2H_2O$ and stated that it seems to be most nearly related to sodalite. Winchell[2] suggested that it is closely related to ugrandite garnet.

Through the courtesy of Dr. E. P. Henderson of the United States National Museum the writer obtained a few small crystals of plazolite and a rock fragment from which other minute crystals could be separated. Through the kindness of Mr. W. H. Dore of the Division of Plant Nutrition of the University of California, Berkeley, it was possible to obtain excellent diffraction patterns from crystals and powder of plazolite.

All powder patterns were obtained in a cassette of 8 inch radius with molybdenum radiation screened by zirconium oxide. The cassette radius was checked by a calcite pattern or the film corrected by comparison with a halite pattern on the same film. The effective wave length of the unresolved molybdenum K_α radiation was in all cases taken to be 0.710Å.

In Table 1 are given the measurements of a plazolite powder pattern. From this the length of the edge of the unit cube is found to be 12.14 $\pm$0.01Å, later checked by a rotation pattern.

Using Foshag's value for the density, 3.129, and a ratio of SiO_2 to CO_2 of 8.1, the average from Foshag's analyses, the number of "molecules" in the unit cube is found to be 8.032. Assuming 8 "molecules" in the unit cube the density would be 3.116. Again using the density 3.129 but assuming the composition to be $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which agrees fairly well with Foshag's analysis III, the unit cube would contain 7.966 "molecules." With just 8 of these "molecules" in the unit cube the density would be 3.141.

Since both results show fair agreement of composition, density and lattice constant the CO_2 content will hereafter be disregarded and the formula just given used in all later calculations.

All lines in the powder pattern have $h+k+l=2n$, showing that plazolite has a body-centered lattice and none of the space groups based on

[1] Foshag, W. F., Plazolite, a new mineral: *Am. Mineral.*, vol. **5**, pp. 183–185, 1920.

[2] Winchell, A. N., *Elements of Optical Mineralogy*, part **II**, 3rd edition, page 183, New York, 1933.

such a lattice are excluded by the powder data. Laue patterns taken with unscreened molybdenum radiation, a plate to crystal distance of 5 cms., with the incident ray parallel to [110] and to [001] showed the Laue

TABLE 1. POWDER PATTERN OF PLAZOLITE

2θ	$\sin^2\theta=(h^2+k^2+l^2)q.$	hkl
8.20°	6×0.000853	211
12.54	14×0.000853	321
13.45	16×0.000857	4(100)
15.03	20×0.000855	2(210)
15.73	22×0.000851	332
16.46	24×0.000854	2(211)
17.17	26×0.000857	431
18.44	30×0.000856	521
19.03	32×0.000855	4(110)
20.75	38×0.000853	611, 532
21.29	40×0.000853	2(310)
23.43	48×0.000858	4(111)
24.36	52×0.000856	2(320)
25.32	56×0.000858	2(321)
27.04	64×0.000855	8(100)
30.34	80×0.000856	4(210)
31.13	84×0.000857	2(421)
31.92	88×0.000859	2(332)
33.66	98×0.000855	941, 853
34.71	104×0.000855	2(510, 2(431)
35.75	110×0.000856	10.3.1, 952, 765
36.72	116×0.000855	2(520), 2(432)
37.39	120×0.000856	2(521)
38.57	128×0.000852	8(110)
40.95	144×0.000850	12(100), 4(221)
41.31	146×0.000852	12.1.1, 11.4.3, 981, 974
42.21	152×0.000853	2(611), 2(532)
44.18	164×0.000852	2(621), 2(540), 2(443)
46.18	180×0.000854	2(630), 2(542)

average value of $q=0.000855$.

symmetry O_h. This still leaves T_d^3, T_d^6 O^5, O^8, O_h^9 and O_h^{10} as possible space groups.

With 8 "molecules" in the unit cube it is necessary to accommodate

24 Ca,
16 Al,
16 Si,
96 O } or 96 (O and OH).
and 32 H }

This cell content is somewhat similar to that of garnet for which a structure has been found in the space group O_h^{10} by Menzer.[3]

The plazolite powder pattern closely resembles garnet patterns. For better comparison powder and rotation patterns were prepared from

TABLE 2. COMPARISON OF INTENSITIES IN POWDER PATTERNS OF PLAZOLITE AND GROSSULARITE

Plazolite	*hkl*	Grossularite	
		observed	calculated
w	211	—	0.00
w	321	—	0.07
s	4(100)	s	1.02
vs	2(210)	vs	3.05
vw	332	w	0.26
m	2(211)	m	0.79
m	431	m	0.43
s	521	m	0.53
vw	4(110)	w	0.13
s	611, 532	s	0.79
vw	2(310)	—	0.00
w-m	4(111)	m	0.49
s	2(320)	s	1.16
vs	2(321)	vs	
w-m	8(100)	w-m	
—	741	vw	
m	4(210)	m	
w	2(421)	m	
w	2(332)	w	
vw	941, 853	w	
vw	2(510), 2(431)	vw	
vw	10.3.1, 952, 765	vw	
w	2(520), 2(432)	m	
w	2(521)	w	
w	8(110)	w	
vw	12(100), 4(221)	w	

vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

grossularite, the garnet nearest to plazolite in composition. The grossularite used was analyzed material from near Georgetown,[4] California. The lattice constant determined from 24 lines on an excellent film corrected with halite is 11.85 ± 0.01Å, close to the value, 11.840 ± 0.003Å,

[3] Menzer, G. Die Kristallstruktur der Granate, *Zeits. Krist.*, vol. **69**, pp. 300–396, 1928.

[4] Pabst, A., Vesuvianite from Georgetown, California: *Am. Mineral.*, vol. **21**, pp. 1–10, 1936.

given by Menzer. The density was redetermined by suspension in a solution of thallium formate to be 3.55, whereas the density calculated from the lattice constant is 3.60.

Table 2 shows the similarity of the plazolite and grossularite powder patterns and the good agreement of the observed intensities of the grossularite lines with the intensities recalculated from the structure found by Menzer. The calculations were made by the usual formula, $I_{hkl}=j\cdot F^2\cdot(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$, using James and Brindley's values for the scattering powers of the ions. This gives an even better agreement of observed and calculated intensities than Menzer's method of calculation in which he assumed the scattering power to be proportional to the squares of the atomic numbers.

The two films show a close similarity. The most conspicuous differences are the appearance of the weak lines 211 and 321 in plazolite, the decrease of intensity of 332 and the increase of intensity of 611 and 532 in the plazolite pattern. The differences are also discernible in the photometer curves of the powder patterns, kindly prepared by Professor F. A. Jenkins of the Physics Department, shown in Fig. 1.

Rotation patterns of both plazolite and grossularite were prepared using unscreened molybdenum radiation, a planar film and a film to crystal distance of 5 cms. For the plazolite patterns it was necessary to use a crystal only 0.2 mm. on edge but even this was finally adjusted and both patterns showed a great number of spots that could be indexed with certainty. From Table 3 it may be seen that the differences in the two rotation patterns are essentially the same as those found by comparison of the powder patterns.

The structure of grossularite found by Menzer has 8 "molecules" in the unit cube. The lattice is body-centered and the space group is O_h^{10}. From this it seems that the structure of plazolite must be much like that of grossularite.

The atomic positions for grossularite given by Menzer are:—

16 Al in 16(a) 000;
24 Ca in 24(c) $\frac{1}{4}\,\frac{1}{8}0$;
24 Si in 24(d) $\frac{1}{4}\,\frac{3}{8}0$;
96 O in 96(h) xyz,

where x, y and z are 0.04, 0.055 and 0.64. From one film Menzer obtained the values, 0.035, 0.055 and 0.65, for x, y and z.

In the unit cube of plazolite it is necessary to accommodate

16 Al,
24 Ca,
16 Si
and 96 O and OH.

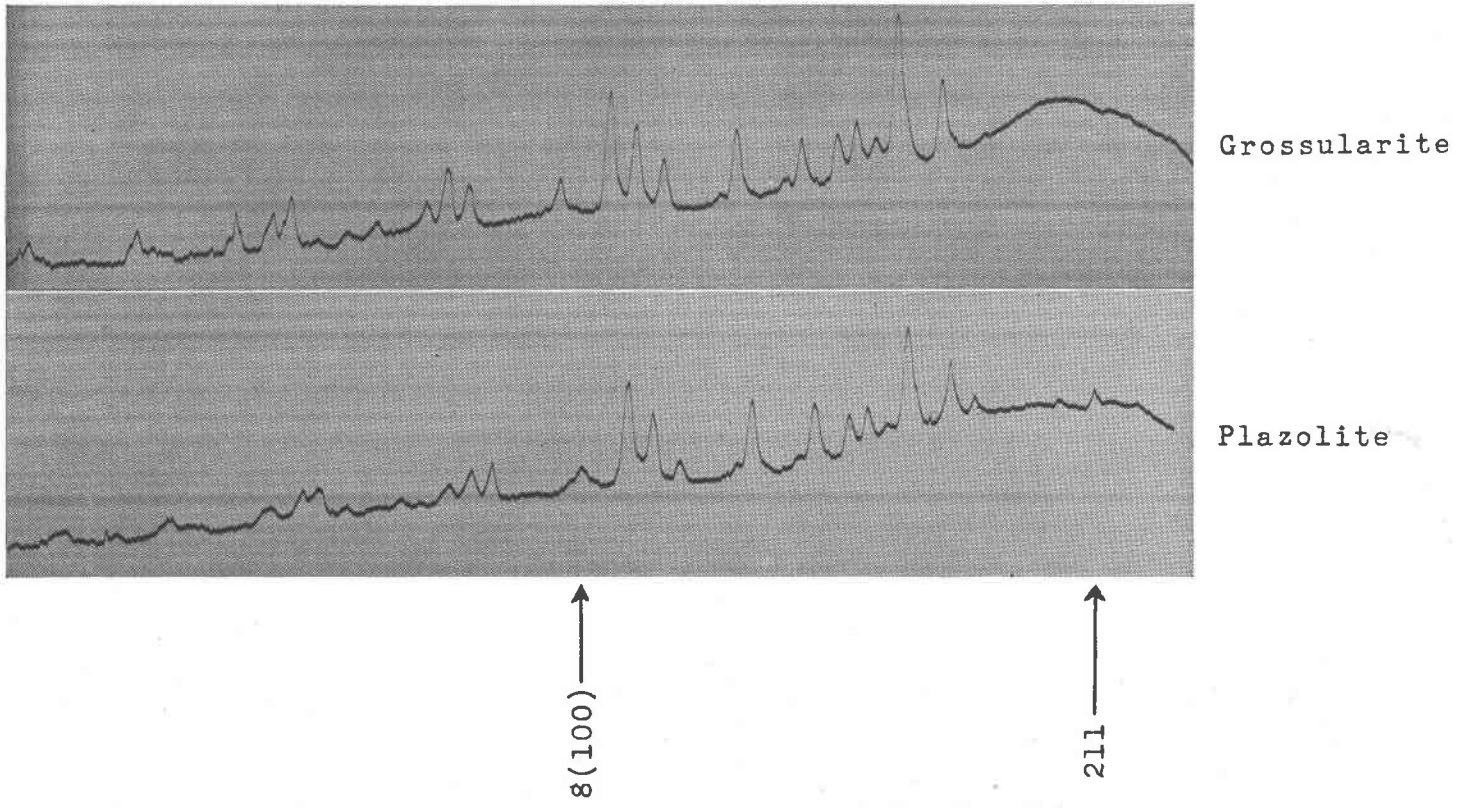

FIG. 1. Photometer curves of powder patterns of plazolite and grossularite.

TABLE 3. COMPARISON OF ROTATION PATTERNS OF PLAZOLITE AND GROSSULARITE

Layer Line																	
Zero	400	420	440	620	640	800	840	10.4.0	880	12.0.0	12.6.0	14.4.0					
P	s	vs	vw	w	s	s	m	w	w								
G	s	vs	vw	vw	s	m	m	w	w	vw	vw	vw					
First	211	321	431	521	611												
P	w	vw	w	m	s												
G		?	w	w	m												
Second	112	312	042	422	512	532	642	842	10.4.2	12.2.2	12.8.2						
P	vw	w	vs	m	m	w	s	w	w	vw							
G			s	m	w	vw	m	m	w	w	w						
Third	213	323	413	523													
P		w	m	m													
G		w	w	w													
Fourth	024	224	314	044	444	064	264	084	284	664	864	10.0.4	10.2.4	10.6.4	12.4.4	10.8.4	10.10.4
P	vs	m	m	vw	m	m	s	w	w	vw		w	vw	vw		vw	
G	vs	m	m	vw	s	m	s	w	m	w		w	w		vw	vw	vw
Fifth	215	325	525														
P	s	m	w														
G	m	w															
Sixth	116	026	046	246	516	646	846	10.4.6	12.0.6	12.6.6							
P	s		s	s	vw	w	vw	vw									
G	s	w	s	s		m	m	vw	vw	vw							
Eighth	048	248	468	088	488	10.4.8	888										
P	m	m	w	m	vw												
G	m	m	w	m	vw	vw	vw										
Tenth	0.4.10	2.4.10	4.6.10	4.8.10													
P	w	w	vw														
G	w	m	vw	vw													

The space group O_h^{10} has two 16-fold positions with the symmetry C_{3i} and D_3 respectively, which would not allow the placing of Si in either of these positions if it is to be at the center of an SiO_4 tetrahedron. Since this rules out 16-fold positions for Si in this space group the only remaining possibility is that the Si ions are either in a shared or in a partly vacant set of positions.

TABLE 4. COMPARISON OF CALCULATED AND OBSERVED INTENSITIES IN A POWDER PATTERN OF PLAZOLITE

hkl		Calculated intensities			Observed intensities
	x	0.04	0.035	0.035	
	y	0.055	0.055	0.04	
	z	0.64	0.65	0.65	
211		0.03	0.30	0.11	w
2(110)		0.11	0.00	0.03	—
321		0.26	0.17	0.12	w
4(100)			0.81	1.22	s
2(210)			2.20	2.69	vs
332			0.27	0.09	vw
2(211)			0.60	0.38	m
431				0.50	m
521				0.70	s
4(110)				0.10	vw
532, 611				0.50, 0.57	s
2(310)				0.10	vw
541, 631				0.00	—
4(111)				0.54	m
543				0.07	—
2(320)				0.78	s
633, 255,* 217				0.02, 0.05, 0.00	—
2(321)				1.48	vs
651, 732†				0.07, 0.00	—
8(100)				0.51	m

* Not discernible on powder pattern, but 255 appears in fifth layer line of rotation pattern.

† This line not measured on powder pattern though discernible on photometer curve and 516 appears in rotation pattern.

The simplest assumption that suggests itself is that the arrangement of ions in plazolite is similar to that found by Menzer for grossularite but with only 16 Si distributed at random in 24(d).

Calculation of the intensities of lines in the powder pattern showed fair agreement but did not fully account for the differences in the plazolite and grossularite patterns. Further trial intensity calculations

were then made with various sets of oxygen parameters, assigning to OH^- the same scattering power as to O^{-2}. Good agreement was obtained with the parameters 0.035, 0.04 and 0.65. Table 4 shows the agreement of calculated intensities of all lines with $h^2+k^2+l^2 \leqq 64$ that may appear in space group O_h^{10} with the observed intensities.

This table also shows a few calculated intensities for plazolite with the two sets of oxygen parameters in grossularite given by Menzer. In each case the calculations were carried only far enough to eliminate a given set of parameters and in this way half a dozen other sets besides those given in the table were eliminated.

TABLE 5. SILICON-OXYGEN DISTANCES IN PLAZOLITE FOR VARIOUS OXYGEN PARAMETERS

Oxygen Parameters	x 0.04	y 0.055	z 0.64	x 0.035	y 0.055	z 0.65	x 0.035	y 0.04	z 0.65
Si-O Distance		1.80Å			1.75Å			1.704Å	

Table 5 shows the distances from O to Si in plazolite with the three sets of parameters considered in Table 4. All three values of the O-Si distance are within the allowable limits but the value 1.704Å, corresponding to the parameters 0.035, 0.04 and 0.65, agrees most closely with the Si-O distance, 1.70 Å, calculated from Goldschmidt's set of ionic radii and gives a further check on the oxygen parameters chosen for plazolite.

SUMMARY

The structure of plazolite is similar to that of grossularite. The lattice constant, 12.14 ± 0.01 Å, is slightly larger than that of grossularite. There are 8 "molecules" in the body centered unit cube.

An atomic arrangement in the space group O_h^{10} has been found for plazolite which satisfactorily accounts for the diffraction data. The arrangement,

16 Al in 16(a) 000;
24 Ca in 24(c) $\frac{1}{4}$ $\frac{1}{8}$ 0;
16 Si in 24(d) $\frac{1}{4}$ $\frac{3}{8}$ 0;
96 O and OH in 96(h), xyz; x 0.035
y 0.04
z 0.65,

may be described as a defective garnet structure in which the Si is distributed at random over two thirds of a 24-fold position and O^{-2} and OH^- share a 96-fold position in the ratio two to one.