

## PALYGORSKITE: NEW X-RAY DATA<sup>1</sup>

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### ABSTRACT

Analysis of X-ray diffraction powder data for five palygorskite samples shows that three of the samples are orthorhombic and two are monoclinic. Retaining the same cell setting for all palygorskites, in one of the monoclinic samples the unique axis is *b*, and in the other, is *a*. Unit-cell parameters are in agreement with the values given in the literature. For both the monoclinic and the orthorhombic minerals systematic extinctions in *hkl* reflections lead to a primitive cell with an *n*-glide on (001), consistent with the projected structure of Bradley (1940). Data in the literature are in general agreement with the symmetry results of the present study.

### INTRODUCTION

Recently, palygorskite<sup>4</sup> has been shown to be an appreciable constituent of the clay fraction of certain continental-shelf and deep-sea sediments (Heezen *et al.*, 1965; Hathaway and Schlee, 1966). These descriptions add to an already broad variety of modes of occurrence of palygorskite. Heystek and Schmidt (1953) have shown that in the Springbok Flats, Transvaal, palygorskite is presently forming from montmorillonite. Descriptions of palygorskite in lagoonal or lacustrine environments are numerous (*e.g.*, see Caillère and Rouaix, 1958). Palygorskite of probable hydrothermal origin in the Shetland Islands has been described by Stephen (1954). The palygorskite from Sapillo Creek, New Mexico, reported in the present study, occurs with large (up to 1 in. in largest dimension) calcite crystals as hydrothermal veins in a volcanic conglomerate.

In spite of the geochemical importance of palygorskite, its *x*-ray crystallography and structure have remained uncertain. Bradley (1940), working with material from Attapulgius, Georgia, prepared "fiber diagram" powder patterns from aggregated flakes. These patterns yielded *hk0* reflections from which Bradley deduced an approximate structure, as projected on (001). The chain structure found by Bradley (1940) is the generally accepted structure today. Bradley (1940) concluded that palygorskite is monoclinic, space group *C2/m*, with  $a\sin\beta = 12.9 \text{ \AA}$ ,

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

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<sup>4</sup> The names palygorskite and attapulgiite are mineralogically synonymous, although there is a tendency to refer to the fine-grained material found in lagoonal, lacustrine, or soil environments as attapulgiite. The name palygorskite has precedence.

$b = 18 \text{ \AA}$ , and  $c = 5.2 \text{ \AA}$  ( $\beta$  not determined; two-fold monoclinic axis taken along  $b$ ). In the following discussion, the unit-cell setting chosen by Bradley will be used.

Other investigators, working with material from various localities, have concluded that their particular palygorskites were orthorhombic, except Zvyagin *et al.* (1963) who found palygorskite (locality not given) to be monoclinic,  $P2/c$ . There is general agreement about the values of the cell edges, within the limits of precision obtained in various studies, but disagreement as to the symmetry of palygorskite. Whether the symmetry of palygorskite varies with the chemical composition is not known.

In this paper, we present new X-ray powder data for five palygorskite samples, and the unit-cell parameters and symmetries derived from these data. Our results are compared with those of previous investigators, and, where necessary, the previous work is reinterpreted in light of our findings.

#### SAMPLE DESCRIPTIONS

The palygorskite sample designated Sapillo, N. M., No. 21, was collected from massive, white calcite-bearing vein material in the Bates Meerschaum Mine, located near Sapillo Creek, Grant County, New Mexico. A second sample, designated Glasgow, Va., was collected from the Shady Formation, Lone Jack Quarry, Rockbridge County, near Glasgow, Virginia. This sample contains finely-divided calcite. A third sample was collected by M. G. Dings, U.S. Geological Survey (field no. 55MD67) from near Metaline Falls, Stevens County, Washington. The Metaline sample contains abundant finely-divided quartz and pyrite. A fourth sample from Zaachila, Oaxaca, Mexico, consisted of a palygorskite-based pigment found in a tomb. For comparison, a fifth sample from the classical locality, Attapulgis, Georgia, was obtained from Ward's Natural Science Establishment. It contains abundant finely-divided quartz and minor montmorillonite.

#### EXPERIMENTAL

It proved impossible to separate the impurities from the palygorskite samples, except that calcite was removed by hand-picking from the Sapillo material. A portion of each sample was ground by hand in a mullite mortar, and the ground material tapped into the rear of an aluminum sample holder, through a small sieve (200 mesh), in order to minimize preferred orientation. Two diffraction patterns were made of each sample, using two different diffractometers, with Ni-filtered Cu radiation at 40 KV and 20 ma. Other instrumental constants were:  $1^\circ$  divergence slit,  $1^\circ$  scatter slit, 0.006 in. receiving slit; scanning speed,  $1/2^\circ 2\theta$  per minute; chart scale,  $1^\circ 2\theta$  per inch; scale factor either 4, 8, or 16; time constant, 4 seconds. No internal standard was used because of masking effects; however diffraction patterns of standard silicon, at the same instrumental settings, were run before and after each palygorskite run, in order to calibrate the patterns. Diffraction peaks were measured to the nearest  $0.01^\circ 2\theta$  and converted to d-spacings using  $\lambda = 1.54178 \text{ \AA}$  ( $\text{CuK}_\alpha$ ).

Other diffraction patterns were made of each sample using a scanning speed of  $2^\circ 2\theta$  per minute, with the same instrumental settings as described above, except that a scale factor of 32, a time constant of 2 seconds and an X-ray tube current of 40 ma. were used. Three of the resulting patterns are reproduced in Figure 1. The illustrated patterns have considerably less detail than the patterns from which the measurements were made.

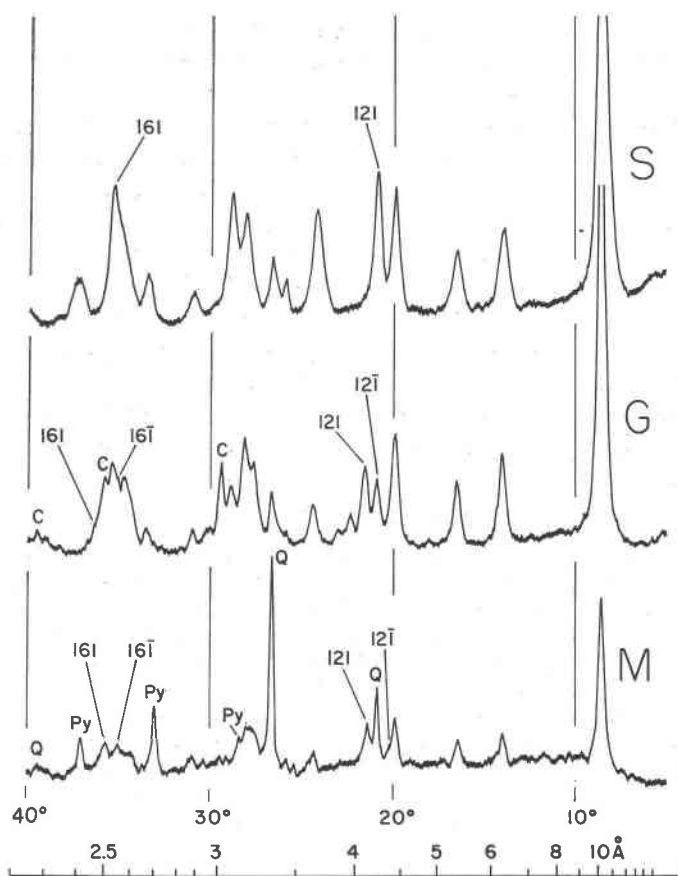


FIG. 1. Diffractometer tracings for the palygorskite samples, Sapillo, N. M., No. 21 (S); Glasgow, Va. (G); and Metaline, Wash. (M); scanning speed  $2^\circ 2\theta$  per minute. Indicated is the splitting of the 121 and 161 peaks of the orthorhombic Sapillo palygorskite into the 121 and  $12\bar{1}$ , and 161 and  $16\bar{1}$  peaks of the monoclinic Glasgow and Metaline palygorskites. Peaks due to impurities are denoted as C (calcite), Py (pyrite), and Q (quartz).

### RESULTS AND DISCUSSION

The X-ray powder data for the five samples studied are shown in Table 1, and the computer-refined cell parameters derived from these data in Table 2. The refinements were made by using the computer program of Evans, *et al.* (1963). For the samples Sapillo, N. M., No. 21, Zaachila, Mexico, and Attapulcus, Ga. the spacings can be indexed readily on the basis of orthorhombic symmetry. However, it was apparent by inspection that the patterns for the Glasgow, Va. and Metaline, Wash. samples contain extra peaks that cannot be reconciled with orthorhombic

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TABLE I. X-RAY POWDER DATA FOR PALYGORSKITE

Sapillo, N. M., No. 21			Zaachila, Mexico			Attapulguas, Ga.			Glasgow, Va.			Metaline, Wash.		
<i>hkl</i>	<i>d</i> (calc.) Å	<i>d</i> (obs.) Å	<i>hkl</i>	<i>d</i> (calc.) Å	<i>d</i> (obs.) Å	<i>hkl</i>	<i>d</i> (calc.) Å	<i>d</i> (obs.) Å	<i>hkl</i>	<i>d</i> (calc.) Å	<i>d</i> (obs.) Å	<i>hkl</i>	<i>d</i> (calc.) Å	<i>d</i> (obs.) Å
110	10.37	10.44	100	10.40	10.42	100	10.34	10.54	110	10.34	10.35	110	10.35	10.35
200	6.362	6.36	13	200	6.390	6.38	15	200	6.411	6.42	10	200	6.357	6.36
130	5.395	5.395	9	130	5.403	5.385	15	130	5.416	5.418	7	130	5.384	5.382
040	4.468	4.466	20	040	4.471	4.464	31	040	4.481	4.479	23	040	4.457	4.459
121	4.260	4.262	22	121	4.240	4.262	34	121	4.244	4.258	15	121	4.364	4.364
310	4.127	s 4.129	2	310	4.144	4.146	6	310	4.158	s 4.137	10	121	4.132	4.137
				201	4.033	s 4.004	3					201	3.985	3.988
				131	3.760	sh	14							
				221	3.686	3.679	15	131	3.751	sh		240	3.650	3.649
								221	3.682	3.681	7			
								240	3.673	sh		150	3.433	s 3.441
				150	3.441	s 3.440	2	150	3.453	b 3.444	5	150	3.433	s 3.441
				231	3.347	3.348	7	231	3.340	3.347	47	231	3.229	Q
				311	3.243	sh		311	3.241	3.250	34	311	3.228	3.228
												321	3.228	
				400	3.181	3.179	12	400	3.195	3.191	23	400	3.179	3.179
				321	3.094	3.096	16	321	3.092	3.104	23			
				331	2.885	2.889	4	241	2.995	2.992	3			
				411	2.689	sh		411	2.691	2.698	6			
				251	2.679	2.679	8	251	2.679	2.681	sh			
								251	2.676	2.680	9			
				421	2.602	sh						341	2.615	2.609
				012	2.593	sh		421	2.604	2.610		421	2.596	2.606
				440	2.591			440	2.600	2.607	b 2.601	10		
				061	2.590			061	2.590	2.590		440	2.584	2.585
				102	2.567	2.567	12					421	2.566	sh
								012	2.548	2.548	13b	161	2.563	sh
								161	2.535	2.539		012	2.550	sh
												061	2.530	2.536
												102	2.511	2.507
												112	2.500	sh
												161	2.506	2.506
												102	2.505	2.505
												202	2.502	2.502

Plus many additional lines, mostly weak and broad, for all samples; s = peak poorly resolved because of low ratio of peak intensity to background; sh = peak present, but as shoulder on adjacent, more intense peak; b = broad; Q = peak due to quartz present.

TABLE 2. X-RAY CRYSTALLOGRAPHIC DATA<sup>a</sup> FOR PALYGORSKITE

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Monoclinic angle	<i>V</i> (Å <sup>3</sup> )	Symmetry	Space Group or Diffraction Aspect
Sapillo, N.M. No. 21 This paper	12.725 ± 0.009	17.872 ± 0.017	5.242 ± 0.004	—	1192 ± 1	Orthorhombic	<i>P</i> * <i>n</i> *
Zaachila, Mex. This paper	12.781 ± 0.011	17.885 ± 0.014	5.199 ± 0.006	—	1188	Orthorhombic	<i>P</i> * <i>n</i> *
Attapulugus, Ga. This paper	12.823 ± 0.024	17.925 ± 0.030	5.199 ± 0.033	—	1195 ± 7	Orthorhombic	<i>P</i> * <i>n</i> *
Glasgow, Va. This paper	12.681 ± 0.003	17.864 ± 0.009	5.127 ± 0.003	$\alpha$ 92°14' ± 3'	1160.6 ± 0.7	Monoclinic	<i>Pn</i> <sup>e</sup>
Metaline, Wash. This paper	12.78 <sup>b</sup>	17.83	5.24	$\beta$ 95°46'	1188	Monoclinic	<i>Pn</i> <sup>e</sup>
Brazil Huggins <i>et al.</i> (1962)	12.690 <sup>e</sup>	17.857	5.207	—		Monoclinic <sup>d</sup>	<i>Pn</i> <sup>e</sup>
Attapulugus, Ga. Bradley (1940)	12.9 <sup>c</sup> (= <i>a</i> sin $\beta$ )	18.	5.2	$\beta$ not determined		Monoclinic	<i>C2/m</i>
Palygorskaya USSR Preisinger (1963)	12.65 <sup>e</sup>	17.9	5.26	—		Orthorhombic	<i>Pbmn</i>
Unknown locality Zvyagin <i>et al.</i> (1963)	12.75 <sup>e</sup>	18.06	5.22	$\beta$ 95°50'		Monoclinic	<i>P2/c</i>

<sup>a</sup> The unit-cell parameters and diffraction aspects for the first five samples listed, are based on the powder data given in Table 1. The values of the unit-cell parameters, and their associated standard errors were determined by computer, using the program of Evans *et al.* (1963).

<sup>b</sup> The data were not sufficient to yield computer-calculated standard errors.

<sup>c</sup> No errors reported.

<sup>d</sup> Authors indexed powder pattern on the assumption of orthorhombic symmetry; however, reexamination of their data indicates monoclinic symmetry.

<sup>e</sup> Symbols used to denote primitive monoclinic cell with *n*-glide on (001); there is no conventional notation for these elements with the cell setting used here.

symmetry. As shown in Figure 1, a significant difference between the orthorhombic Sapillo, N. M. palygorskite and the Glasgow, Va. palygorskite occurs near 20° 2 $\theta$ , where the 121 peak of the Sapillo sample is split into two peaks in the pattern of the Glasgow sample. There are also two corresponding peaks, in the same 2 $\theta$  region, in the pattern of the Metaline sample. Moreover, in both cases, the sum of the relative intensities of the split peaks is approximately equal to the relative intensity of the 121 peak in the orthorhombic Sapillo sample. These features suggest that the

Glasgow and Metaline palygorskites are monoclinic, with the split peaks representing the 121 and  $\bar{1}21$  reflections. Other peak-splitting of this kind occurs, as indicated in Figure 1. By indexing the split peaks on the basis of their single-peak orthorhombic counterparts, it was possible to obtain approximate values of the monoclinic angles of the two samples, and approximate cell edges. These approximate values were used in the least-squares program of Evans *et al.* (1963) to generate refined cell parameters, and calculated  $d$  based upon these parameters. The results show that the patterns of the Glasgow and Metaline samples can, indeed, be satisfactorily indexed on the basis of monoclinic symmetry, as indicated by comparison of  $d(\text{calc})$  and  $d(\text{obs})$  values in Table 1.

The very interesting result emerges from this analysis of the Glasgow and Metaline samples, that for the Metaline palygorskite the unique monoclinic axis is the  $b$ -axis, whereas for the Glasgow palygorskite, the monoclinic axis is the  $a$ -axis (retaining the same cell-setting for all five palygorskites). Thus, the monoclinic angle is designated as  $\alpha$  for the Glasgow sample, and as  $\beta$  for the Metaline sample in Table 2.

The reported work on palygorskite of other investigators was examined. The unit-cell parameters, and space-groups (if reported) given by others are listed in Table 2, along with the results of the present study. In addition, we studied the X-ray powder data published by Bradley (1940), and Huggins *et al.* (1962), in light of our own findings.

As pointed out in the foregoing, Bradley (1940) reported only  $hk0$  data. To the limited extent of his data, his results are in agreement with ours and with those of Huggins *et al.* (1962). All of our patterns, orthorhombic or monoclinic, show the same  $hk0$  reflections, and these are the same  $k$  reflections reported in the three other studies listed. Observed  $d$  and relative intensities reported by Huggins *et al.* (1962) for a Brazil palygorskite correspond very closely to those of the Glasgow palygorskite. These latter investigators indexed their observed reflections on the basis of an orthorhombic cell, but the same arguments that induced us to assign monoclinic symmetry to the Glasgow palygorskite suggest that the Brazil palygorskite also possesses monoclinic symmetry.

In the present study, a sufficient number of general  $hkl$  reflections were recorded to make feasible a search for systematic extinctions. From Table 1, it can be seen that for all five samples the only general class of extinctions occurs for the  $hk0$  reflections, which are present only for  $h+k=2n$ . The published powder data of Huggins *et al.* (1962) show this same result. For both monoclinic and orthorhombic cells, the observed extinctions are consistent with a primitive cell, with an  $n$ -glide on (001). The structure for palygorskite proposed by Bradley (1940) was based only upon  $hk0$  data, and therefore is necessarily a structure projected

upon (001). Bradley (1940) assigned the space group  $C2/m$  as being consistent with his structure. However, *in projection* upon (001),  $C$ -centering and an  $n$ -glide on (001) are the same, so that the more modern powder data are consistent with the structure of Bradley, but rule out a face-centered cell.

Preisinger (1963) assigned the orthorhombic space group  $Pbmn$  to palygorskite, but gave no data to support this assignment. The space groups  $Pbmn$  and  $C2/m$  give the same projection upon (001), yielding the plane group  $cm$ . Thus, all of the results quoted above are consistent with the projected structure of Bradley (1940). The monoclinic space group  $P2/c$  found by Zvyagin *et al.* (1963) is not consistent with any of the other findings.

In summary, we conclude that palygorskite occurs in structurally closely-related monoclinic and orthorhombic forms. We would guess that these variations in symmetry reflect variations in chemical composition, but no correlated data are available to test this hypothesis. The projected structure of Bradley (1940) is consistent with all the data available (except that of Zvyagin *et al.*, 1963), but even an approximate three-dimensional structure has not yet been found.

Note added in proof: Since submission of this paper a reference has appeared in which it is suggested that palygorskite occurs in both orthorhombic and monoclinic forms, and some speculations concerning possible structures are listed:

GARD, J. A. AND E. A. C<sup>1</sup>FELLETT (1968) A structural scheme for palygorskite. *Clay Minerals* **7**, 367-369.

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*Manuscript received, July 22, 1968; accepted for publication, September 3, 1968.*