Canadian Mineralogist
Vol. 28, pp. 329-339 (1990)

AN X-RAY POWDER-DIFFRACTION STUDY OF PALYGORSKITE

JIM E. CHISHOLM

Department of Mineralogy, British Museum (Natural History), Cromwell Road, London SW7 5BD, England

ABSTRACT

Thirteen specimens of palygorskite, "attapulgite" and "pilolite" have been examined by X-ray powder diffraction. Many specimens are impure. The powder-diffraction patterns show a greater variation than has been described in previous studies on fewer specimens. The powder patterns show maxima with essentially the same *d*-values but differing intensities. Such variations suggest the presence of two (or more?) phases with similar or related unit-cells in palygorskite; in different specimens and even in samples of the same specimen, the proportions of the two phases seem to vary, as also does the degree of structural order. Although the experimental observations of Christ *et al.* (1969) are confirmed, the greater variability of the patterns raises doubts over their indexing in terms of an orthorhombic and two monoclinic cells (with β and α oblique). Unit-cell refinements show that other unit cells also may fit the observed powder patterns. Some of the unit cells and symmetries proposed for palygorskite are not as well established as appeared from previous results.

Keywords: clay minerals, palygorskite, "attapulgite", "pilolite", X-ray diffraction, unit-cell refinement.

SOMMAIRE

Treize échantillons de palygorskite, "attapulgite" et "pilolite" ont été étudiés par diffraction X (méthode des poudres). Plusieurs échantillons contiennent des impuretés. Les spectres de diffraction témoignent d'une plus grande variabilité que révélée dans les études antérieures, sur une plus petite collection. Les maxima possèdent essentiellement les mêmes valeurs de *d*, mais les intensités sont différentes. De telles variations font penser qu'il s'agit de deux mailles (ou plus?) pour le cas de la palygorskite; dans les différents spécimens, et même dans différents échantillons d'un seul spécimen, la proportion des deux mailles semble varier, ainsi que le degré d'organisation structurale. Quoique les résultats expérimentaux de Christ *et al.* (1969) sont confirmés, la grande variabilité des spectres soulève des doutes à propos de leur indexation en termes d'une maille orthorhombique et de deux mailles monocliniques (avec β et α obliques). Les affinements de la maille élémentaire montrent que d'autres mailles pourraient expliquer les spectres de poudres observés. Parmi les mailles et les symétries proposées pour la palygorskite, certaines options semblent moins bien établies que dans les études antérieures.

(Traduit par la Rédaction)

Mots-clés: argiles, palygorskite, "attapulgite", "pilolite", diffraction X, affinement des paramètres réticulaires.

INTRODUCTION

The electron-microprobe data of Smith & Norem (1986) have effectively established the chemical formula of palygorskite, but confusion remains over its unit cell, symmetry and crystal structure, as is apparent from the recent review by Jones & Galan (1988). Nor is it clear how specimens described as palygorskite, "attapulgite" and "pilolite" differ and whether or not they represent distinct mineral species. In an attempt to resolve some of this confusion, a range of specimens, referred to here as palygorskite, has been examined using X-ray powder diffraction, and the results related to the possible unit-cells and structural models.

Two unit-cell settings have been used for palygorskite. One of these is based on the view of palygorskite as a layer silicate and takes the corrugated silicate layers parallel to (001), so that $a \simeq 5.2$, $b \simeq 17.8$ and c or $c\sin\beta \simeq 12.8$ Å. The second places more stress on the chains of SiO_4 tetrahedra and MgO_6 octahedra making up the layers and takes [001] as the chain direction, giving a or $a\sin\beta \simeq 12.8$, $b \simeq 17.8$ and $c \simeq 5.2$ Å. The latter has generally been adopted for indexing powder-diffraction data and is used in the present paper.

The essential features of the unit cell and crystal structure were elucidated by Bradley (1940) in the first X-ray-diffraction study on "attapulgite" from Attapulgus. Bradley proposed a structural scheme for the (001) projection in which I-beams (as they are now called) of the amphibole type are linked by sharing the edge O atoms of the silicate double chains with adjacent I-beams [see Fig. 1.35 of Bailey (1980) or Fig. 1 of Jones & Galan (1988), in both of which a full description of the crystal structure is given]. The outermost octahedral cations of each I-beam are each linked to two "bound" or "coordinated" water molecules, and the channels between the backs of the I-beams contain four "zeolitic" water molecules. Bradley concluded that the unit cell is monoclinic, with $a\sin\beta$ 12.9, b 18, c 5.2 Å, and probable space-group $C2/m$. The preponderance of $hk0$ maxima in the powder pattern led Bradley to concentrate on the (001) projection; β was not determined (c was derived from X-ray fiber-texture patterns).

Comparison of palygorskite from Palygorskaja with sepiolite (Brauner & Preisinger 1956) led

TABLE 1. BM REGISTERED NUMBERS, DESCRIPTIONS, LOCALITIES AND PHASES IDENTIFIED BY X-RAY POWDER DIFFRACTION

1. BM 53853. Pilolite, fine platy masses, white to dirty brown.
Cabrach, Aberdeenshire.
Samples A and B: Palygorskite + quartz

2. BM 1905,280. Pilolite, two thin ragged leaves (10 x 4 cm) and on matrix.
Bardon Hill, Leicestershire.
Sample A: Palygorskite + calcite + ?plagioclase feldspar + chlorite + ?trace of gysum
Sample B: Palygorskite + calcite + quartz + ?plagioclase feldspar + chlorite + ?trace of gypsum

3. BM 1958,484. Palygorskite, several masses with celadonite.
Berestovetz, Volyn, Ukraine.
Samples A and B: Palygorskite + chlorite + 10 Å clay + ?plagioclase feldspar

4. BM 1960,545. Palygorskite, leathery masses.
Gustavus, Alexander archipelago, Alaska.
Samples A and B: Palygorskite

5. BM 1962,448. Palygorskite, white to buff fibrous masses on matrix.
Lone Jack Quarry, Glasgow, Rockbridge Co., Virginia.
Samples A and B: Palygorskite + calcite

6. BM 1940,73. Palygorskite (= attapulgite), greyish white mass.
Attapulgus, Decatur Co., Georgia, USA.
Samples A and B: Palygorskite + quartz

7. BM 1955,101. Palygorskite, thin sheet.
Warren quarry, Enderby, Leicestershire.
Samples A and B: Palygorskite

8. BM 96149. Pilolite, dirty white broken felty leaf.
Idria, Venezia Guilia, Italy.
Samples A and B: Palygorskite + dolomite + quartz

9. BM 60017a. Pilolite, white leathery.
Seaton, Devon.
Sample A: Palygorskite
Sample B: Palygorskite + trace of calcite

10. BM 1936,367. Palygorskite (pilolite deleted), thin leathery.
Tolpetherwin quarry, South Petherwin, Cornwall.
Sample A: Palygorskite + feldspar (probably potash feldspar) + chlorite
Sample B: Palygorskite + quartz + chlorite

11. BM 1947,194. Palygorskite (= attapulgite), white, powdered.
Quincy, Gadsden Co., Florida.
Samples A and B: Palygorskite + quartz

12. BM 60020. Pilolite, white to pale-yellow and brown cavernous platy mass, with calcite.
Portsoy, Banffshire.
Sample A: Sepiolite + calcite

13. BM 1967,6. Palygorskite, white leathery mass invested with calcite crystals.
Pend Oreille mine, Metaline Falls, Pend Oreille Co. [in error - should be Stevens Co.], Washington.
Sample A: Calcite + pyrite + quartz + palygorskite
Sample B: Calcite + quartz + palygorskite + ?trace pyrite
Sample C: Calcite + quartz + palygorskite + pyrite

Preisinger (1963) to propose an orthorhombic cell (*a* 12.65, *b* 17.9, *c* 5.26 Å) having the same (001) projection as Bradley's and space group *Pbmn*.

A review of chemical compositions by Drits & Aleksandrova (1966) demonstrated that on average four out of five octahedral cation sites are occupied. The deficiency most probably involves vacant octahedral sites in the middle of the I-beams, by analogy with the corresponding sites in dioctahedral micas. The recent electron-microprobe data of Smith & Norem (1986) have established an anhydrous structural formula that may be simplified to $M_4\square Si_8O_{21}$.

Partial indexing of texture electron-diffraction patterns by Zvyagin *et al.* (1963) gave a monoclinic cell with *a* 12.75, *b* 18.06, *c* 5.22 Å, β 95°50′. Reflections violating the *C*2/*m* reflection conditions were observed, and the space group *P*2/*c* was suggested, which might correspond to a lowering of symmetry from Bradley's model. To account for the loss of *C*-face centering, Gard & Follett (1968) proposed a structural scheme with I-beams three chains wide and one chain wide alternating along the *b* axis. They also described a hypothetical orthorhombic version of this arrangement, with space group *Pmcm*.

Drits & Sokolova (1971) showed that the observed X-ray fiber diffraction intensities of palygorksite from the Dzhezdy manganese deposit in Kazakh SSR fit those calculated for a structural model in *C*2/*m* (*a* 13.14, *b* 17.85, *c* 5.15 Å, β 107°), with coordinates close to those of Bradley's and $(Mg,Al)_{3.86}Si_8O_{19.4}(OH)_{2.6}(H_2O)_4$ as structural formula.

In the most detailed and complete X-ray powder-diffraction study to date, Christ *et al.* (1969) distinguished three types of palygorskite, one having a *Pbmn* orthorhombic cell similar to Preisinger's, and two monoclinic cells. One of the monoclinic cells has *a* 12.78, *b* 17.83, *c* 5.24 Å, β 95.78°, and the other, *a* 12.681, *b* 17.864, *c* 5.127 Å, α 92.23°. Both monoclinic cells are said to be primitive and to have an *n*-glide plane parallel to (001), *i.e.*, to obey the reflection condition (*h* + *k*) even for *hk*0.

EXPERIMENTAL

The specimens studied, all from the British Museum (Natural History) collection, are listed and described in Table 1.

Powder diffractometry

Specimens were prepared for diffractometry by grinding under acetone and spreading the powder into a thin smear mount using two or three drops of acetone. A silicon single-crystal substrate was used to reduce the background diffuse scattering. The observed diffracted intensities will of course be affected by preferred orientation of the elongate particles of palygorskite. By lightly regrinding and preparing a new smear mount, it was established that the technique gave reproducible results. The SEM photographs of Smith & Norem (1986) and others of some specimens studied here do not show marked differences in morphology that might lead to differing degrees of preferred orientation. Preferred-orientation effects are, therefore, considered unlikely to account for major differences in powder pattern among specimens.

All the specimens in Table 1 were examined using a Philips PW1050 diffractometer with CuKα radiation (graphite monochromator in the diffracted beam), a 0.1-mm receiving slit and 1° divergence and antiscatter slits. In the earlier stages of the investigation, continuous scans were carried out at ¼° 2θ per min., not to improve resolution, which is limited by the specimen broadening, but to try to reduce fluctuations and obtain a smoother trace. The distinction between monoclinic or orthorhombic cells might depend on detecting splitting or asymmetry of the peak profiles. Since the key to the problem of palygorskite seemed to lie in the nature of the unit cell and symmetry rather than in the exact values of the lattice repeats, an internal standard was not used. In the later stages of the investigation, after computer control and a data-processing system had been acquired, step scans were carried out using 5-s counts at intervals of 0.02° 2θ, the emphasis again being on improving signal-to-noise ratio rather than obtaining high angular precision.

Powder photography

For X-ray powder photography, a small amount of powder was mixed with gum and made into a small sphere, which was then mounted on a glass fiber. Photographs were taken using a Philips camera (11.46 cm diameter) and CuKα radiation. The powder photographs in some instances showed a weak reflection not detected by diffractometry which might be either an 002 reflection from a trace of 10 Å clay or a weak 003 from a trace of chlorite.

Microdensitometer traces from powder photographs were found to be similar to the diffractometer results. The intensities of reflections in a group are in the same order for both methods, but the actual measured values may not agree exactly. Debye–Scherrer photography and diffractometry are both subject to preferred-orientation effects, but these are likely to differ in the two methods. Diffractometry uses reflection geometry, and the powder is deposited onto a flat substrate, whereas Debye–Scherrer photography uses transmission geometry, and the preparation offers less chance for particles to settle in a particular orientation. For a given sample, diffractometry and Debye–Scherrer photography yield similar powder patterns despite the different degrees of preferred orientation expected for the two techniques. The same variations between samples are found using both methods and are therefore unlikely to be the result of preferred-orientation effects.

POWDER-DIFFRACTION RESULTS

Impurities

The phases identified by X-ray powder diffraction for each of the specimens are given in Table 1 in order of abundance, based on X-ray intensities. The present study shows that samples of palygorskite are commonly impure; the impurities encountered in this study generally are much the same as those found by Smith & Norem (1986) and Christ *et al.* (1969). The clay impurities, principally chlorite and 10 Å clay, were identified on the basis of their 00*l* spacings. The non-clay impurities were usually recognized by the much narrower peak profiles of their reflections compared with the broader peaks of palygorskite. Because the line profiles were used for recognition, it is possible some non-clay impurities with broader peaks have been missed or taken for palygorskite reflections.

Comparison with other powder-diffraction patterns of palygorskite

The most authoritative and significant powder-diffraction data are those of Christ *et al.* (1969), who distinguished an orthorhombic and two monoclinic forms of palygorskite. As well as tabulating the data, they illustrated the features on which they based their distinctions. The relevant reflections lie in two diagnostic regions, 4.0-4.5 Å and 2.5-2.6 Å. Christ *et al.* attributed the differences to splitting of the 121 and 161 reflections of the orthorhombic form into pairs 121 and 12$\bar{1}$, 161 and 16$\bar{1}$, for the two monoclinic forms.

Specimens 5, 6 and 13 studied here are from the same localities as specimens examined by Christ *et al.* (1969). The present study gave essentially the same *d*-values and relative intensities in the diagnostic regions, confirming the results of Christ *et al.* (1969) and establishing a basis for comparison.

The match is, however, not quite perfect. In the powder patterns of the Metaline Falls palygorskite (specimen 13), the peak at ~4.25 Å looks like a sharp quartz peak overlying a palygorskite one and appears too intense in relation to the main quartz maximum to be accounted for by quartz alone. In the Metaline Falls material, there appears to be a contribution to the 4.25 Å peak from palygorskite; that additional line raises a doubt over the assignment of the indices 12$\bar{1}$ and 121 to the 4.36 and 4.13 Å lines and hence the validity of the monoclinic cell (with β oblique) based on that indexing.

For the purposes of this study, a further "diagnostic region" at about 3.05–3.3 Å also was examined in detail since major differences involving strong reflections occur in this area also. Comparisons with the results of Christ *et al.* show the same

TABLE 2. EXAMPLES OF THE MAJOR VARIATIONS IN POWDER-DIFFRACTION PATTERNS OF PALYGORSKITE

Specimen number 4		4		5		5		6		7		9		9	
Sample letter A		B		A		B		B		B		A		B	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
4.457	100	4.435	100	4.444	100	4.444	100	4.443	100	4.434	100	4.448	100	4.440	100
4.366	15	4.328	15							4.332	20	4.344	20	4.341	10
4.238	20	4.230	25	4.238	50	4.242	40	4.250	85NQ			4.248	35	4.234	30
		4.126	65			4.156	25								
4.129	70B			4.110	55			4.133	65	4.117	85B	4.129	75	4.122	40
		4.110	65			4.118	45								
3.214	80sh	3.207	55	3.216	45	3.236	270	3.241	130	3.218	95sh	3.216	75	3.230	25
3.164	175	3.154	110	3.159	85	3.162	100	3.207	80sh	3.175	120	3.167	110	3.165	105
3.089	30	3.073	15	3.078	35	3.079	35	3.112	35sh	3.091	15	3.098	15	3.085	5
2.602	45	2.601	35	2.600	30	2.606	35	2.607	55	2.606	60	2.607	35	2.604	15
2.579	80	2.572	55	2.573	55	2.578	65			2.592	65	2.570	50	2.578	50
		2.565	50												
		2.550	45							2.550	60	2.551	45	2.551	30
2.536	60	2.540	45	2.530	60	2.536	60	2.530	80B					2.530	35
2.505	70	2.500	55	2.496	45C	2.500	30C			2.502	85	2.506	55	2.504	30
				2.480	15sh	2.476	10sh								

C - intensity may be affected by calcite impurity

NQ - intensity probably not affected by quartz impurity as line is not sharp

The major variations occur in the regions 4.0-4.5 A, 3.05-3.3 A and 2.5-2.6 A.

Intensities are taken as peak heights as the maxima are broad and there are many instances of overlap. Intensities are normalised to I=100 for the 040 reflection at about 4.45 A, chosen as a recognizable and apparently invariant feature of all diffraction patterns. B denotes a broad reflection, sh a reflection occurring as a shoulder on a more intense maximum.

reflections in both studies and the same relative intensities for specimens 6 and 13. But two different samples from specimen 5 gave different relative intensities for the 3.22 and 3.16 Å lines, approximately in the ratios 1:2 and 2:1. Because there are no other major differences in the pattern, it seems improbable that differing degrees of preferred orientation should affect only two reflections. The variation in relative intensity is taken as evidence of some kind of inhomogeneity in the specimen of palygorskite from Glasgow, Virginia.

Examination of specimens from the same localities as those studied by Christ *et al.* confirms the essential features of their observations, but there are doubts over the validity of their indexing for the Metaline Falls material (monoclinic with β oblique) and over the homogeneity of the Glasgow, Virginia specimen (monoclinic with α oblique).

Variations in the powder patterns and the heterogeneity of palygorskite

More specimens of palygorskite, "attapulgite" and "pilolite" have been examined in the present study than in that of Christ *et al.* (1969). In general, two samples have been taken from each specimen to evaluate the degree of inhomogeneity. As might perhaps have been expected, the wider-ranging study has revealed a greater variability in the X-ray powder-diffraction patterns than so far reported.

The principal variations occur in three "diagnostic regions" covering the ranges 4.0–4.5 Å, 3.05–3.3 Å and 2.5–2.6 Å, which include strong reflections and show the largest and most easily recognized differences. The differences in the patterns are not confined to these regions. The 4.0–4.5 and 2.5–2.6 Å regions include the reflections used to distinguish orthorhombic and monoclinic forms by Christ *et al.* (1969).

Although most attention will be given here to the differences in powder pattern shown by different specimens of palygorskite, the patterns are unmistakably similar. There would have been no difficulty in identifying the specimens as palygorskite of some kind without prior knowledge.

As it has not proved possible to give a full interpretation of all the variations, little purpose would be served in tabulating all of them. Some representative examples are given in Table 2, and the main differences are now described before discussing their significance. In the 4.0–4.5 Å region, the relative intensity of the reflections at about 4.25 and 4.13 Å varies widely (after allowance has been made for the contribution from any quartz impurity at 4.25 Å), the first being the stronger in some cases and weaker in others, and in one case (specimen 7) unobserved. The weak maximum or shoulder at about 4.35 Å may or may not be observed. The maximum at about 4.13 Å is broad on many patterns, and on some appears to consist of two maxima close together.

In the 3.1–3.3 Å region, there are two strong max-

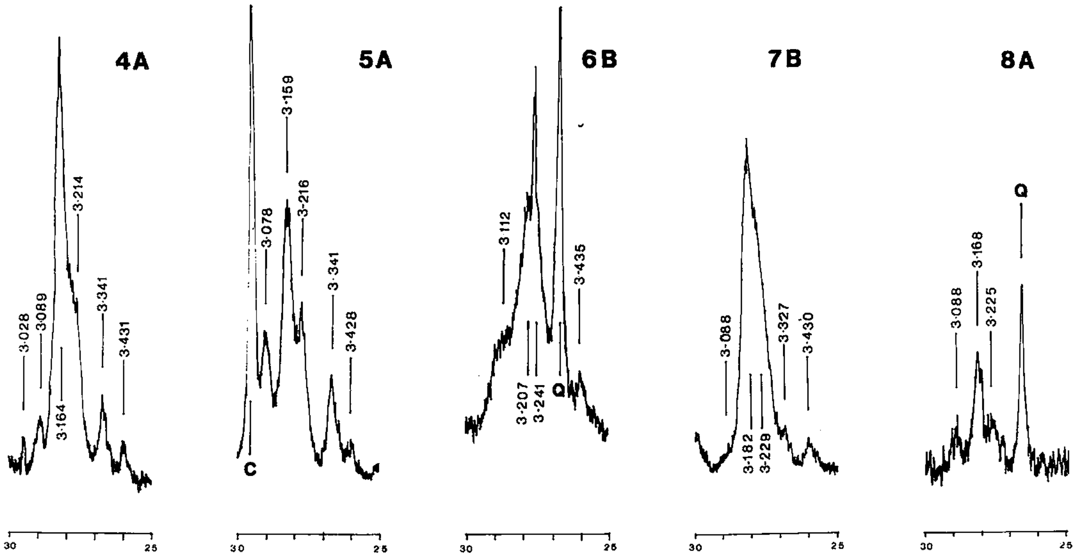

FIG. 1. Diffraction maxima in the 2θ range 25–30° (Cu$K\alpha$) showing the variations in the intensity, peak profiles and resolution in the diagnostic region 3.05–3.3 Å for specimens 4A, 5A, 6B, 7B, 8A. Values of d are marked; Q denotes reflection from quartz, and C one from calcite.

ima at about 3.22 and 3.17 Å: the first is the stronger on some patterns, and the second on others (Table 2). The appearance of the two maxima also varies: in some specimens the weaker maximum appears as a shoulder on the side of the stronger, whereas in others the two peaks are clearly separate (Fig. 1). This difference depends on the peak positions, width and separation, *i.e.*, on the exact cell-dimensions, the degree of structural order, the particle size and shape. The intensity of the reflection at about 3.09 Å also is variable.

In the 2.5-2.6 Å region, the patterns differ in the number and position of peaks that can be recognized and their relative intensity, in which the cell dimensions, degree of order and particle morphology again play a part.

Overall, the palygorskite powder patterns show lines with similar d-values but different intensities, the sort of behavior that would be expected if palygorskite were a mixture in which the proportions of the components vary between and within specimens. But what might palygorskite be a mixture of? Might there be some impurity present?

Initially it was thought that a plausible impurity might be alkali feldspar, which has strong lines in the diagnostic regions of the powder pattern. (The plagioclase feldspars have one of their strong lines at about 4.04 Å, which is too short to explain the variations in the 4.0-4.5 Å region. The tentative identification of plagioclase feldspar in specimen 3 is based mainly on this line.) Feldspar has definitely been found only in specimen 10, sample (A), for which the feldspar peaks are distinctly sharper than those of palygorskite. Whereas it is difficult to establish the complete absence of alkali feldspar from X-ray data alone, such an impurity will not account in detail for the observed variations in the powder patterns of palygorskite. For example, pattern 7 of Table 1 has no line at about 4.24 Å; feldspar must, therefore, account for all the intensity in this line observed in the other patterns. This implies a high proportion of feldspar in some samples, so high, in fact, that other feldspar lines outside the diagnostic regions should be observed. They are not. In addition, an alkali feldspar impurity would have to be virtually ubiquitous in palygorskite to explain the variability in the powder patterns. Yet feldspar was not found in any of the specimens examined in the SEM and analytical study of Smith & Norem (1986). In addition, their average composition for palygorskite, which contains more Ca than Na and K, is not consistent with the presence of more than a small amount of alkali feldspar.

No other mineral has been identified which, if admixed, would account for the observed variations in the powder patterns.

Particle size, particle morphology and peak profiles

It is necessary to consider how far the variations in the powder patterns of palygorskite may result from differences in the peak profiles, particularly since peak heights are used as a measure of intensity. The main factors likely to affect the breadth

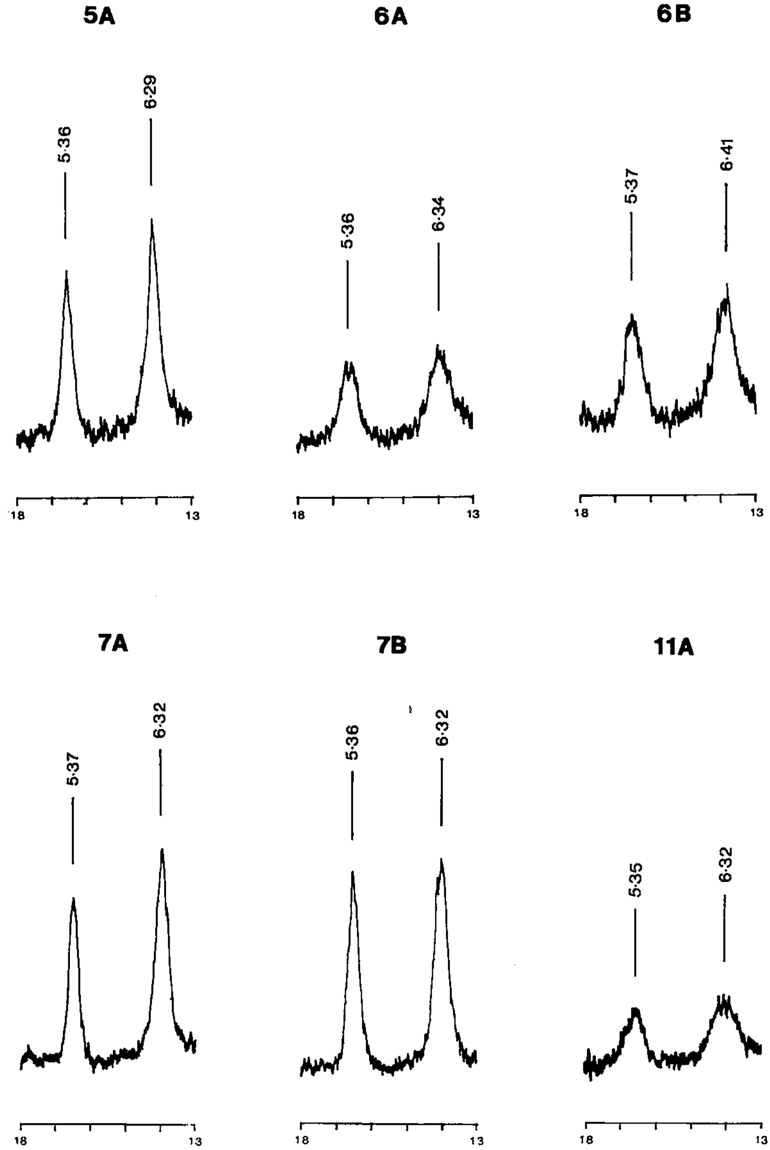

FIG. 2. Diffraction maxima in the 2θ range 13-18° (Cu$K\alpha$), showing the variations in the breadth and profile of the 200 and 130 reflections, with *d*-values about 6.35 and 5.35 Å. There are no other reflections with different indices in the vicinity. The fibrous habit of the particles should cause *hk*0 reflections, such as 200 and 130, to be broadened more than others. The variations in peak profile thus indicate the extent of variations in particle size, particle morphology and structural disorder and their maximum effect on peak width.

and asymmetry of peak profiles are particle size, particle morphology and structural disorder.

Diffraction peaks from specimens consisting of small spherical particles are broadened; the smaller the particles, the greater the broadening. The full width at half maximum of a peak is proportional to $\lambda/\cos\theta$, *i.e.*, the breadth of the reflections varies monotonically with 2θ. Within a small range of 2θ such as over the diagnostic regions, the reflections will, to a first approximation, be broadened equally. Their relative peak-heights then approximate their relative integrated intensities. Normalization of intensities relative to one particular peak, as has been done here, largely, but not entirely eliminates the effect of broadening due to particle size so long as the assumption that the particles are spherical holds.

The small particles of palygorskite are not spherical, but distinctly fibrous, as in the SEM images of Smith & Norem (1986), with the *c* axis as fiber axis. The distribution of intensity around each reciprocal lattice point will, therefore, not be spherical but will take the form of a disc in the a^*–b^* plane. Because of the way the reflecting sphere intersects these discs, reflections are broadened to different extents depending on their indices. The broadening will be greatest for *hk*0 reflections, 00*l* peaks will have the sharpest profiles, and *hkl* reflections will have intermediate widths. Because different peaks are affected differently, variations in particle morphology could, in principle, lead to differences of the kind described among the powder patterns of palygorskite.

Since there are no other reflections with different indices in the vicinity, the peak widths of the 200 and 130 maxima at about 6.35 and 5.35 Å can be used as a convenient guide to the effect of variations in particle morphology. The breadth of these reflections does indeed vary, and some appear asymmetrical, but their relative peak-heights do not show large variations (Fig. 2). In contrast, the variations in the diagnostic regions (Table 2, Fig. 1) are generally much larger than those in the 200 and 130 reflections. Distinct shoulders are recognizable on peaks from some samples. Furthermore, the variations in Figure 1 do not always correlate with the breadth of the 200 and 130 reflections, *e.g.*, specimen 7B has a broad asymmetrical peak at about 3.2 Å (Fig. 1), but sharp 200 and 130 peaks (Fig. 2). Variations in the particle size and morphology of palygorskite may have an effect on the powder patterns, but it does not appear to be large enough, or in some cases of the right kind, to account for the observed differences among patterns.

Line broadening and structural disorder

Structural disorder may also lead to broadening of reflections. In general, which reflections are broadened and to what extent depends on the nature as well as the degree of disorder. Several types of disorder are possible:

(a) The *C*2/*m* and *Pbmn* structural models proposed differ in the stacking sequence along *a*sin*β* (Bailey 1980). The chains of tetrahedra on either side of a layer of octahedra are displaced relative to each other in the *c* direction, the displacements being in the same direction in the monoclinic form (+ + + + + + + + +), and alternately in opposite directions (+ − + − + − + − + −) in the orthorhombic form (analogous to clinopyroxene and protopyroxene). Disorder in this stacking sequence would cause reflections with $l \neq 0$ to be broad, but *hk*0 reflections would be unaffected. However, *hk*0 reflections in the observed patterns do show variations in breadth (Fig. 2); therefore, other factors must have more effect in producing variations in line width than this type of structural disorder.

(b) Evidence for a random intergrowth of double chains of palygorskite and triple chains of sepiolite has been given by Martin Vivaldi & Linares Gonzalez (1962). The Gard & Follett (1968) model for the palygorskite structure, with single and triple chains, suggests that other types of chain-width disorder may be possible. Martin Vivaldi & Robertson (1971) illustrated 45-Å *b*-axis lattice fringes on electron micrographs that correspond to quintuple chains and mentioned evidence for other fringe spacings in multiples of 9 Å. Such chain-width errors are analogous to those in the pyriboles (Veblen 1981, Zoltai 1981) but are not restricted to the (010) plane, as the diagram of Martin Vivaldi & Linares Gonzalez (1962) shows. As in the case of the pyriboles, a structural displacement of $\pm \frac{1}{4}b + \frac{1}{2}c$ in terms of the palygorskite cell is associated with each chain-width error (by analogy with the amphiboles; Chisholm 1975). For random errors, reflections with $k + 2l \neq 4n$ will be diffuse. The powder pattern of palygorskite does not have sufficient reliably indexed, well-resolved reflections to test this condition, but the 040 reflection (at about 4.46 Å) is usually sharper than the others, as would be expected, and faults of this kind would explain diffuse *hk*0 reflections. But if such faults occur, they are not sufficiently numerous nor all of the same type to cause the shift of the 110 maximum away from the 10.3 Å of palygorskite toward the 12 Å of sepiolite observed by Martin Vivaldi & Linares Gonzalez (1962). Therefore, it seems unlikely that disorder of this kind is sufficiently widespread, or differences in it sufficiently large, to explain the large variations in the diagnostic regions of the powder patterns.

(c) When palygorskite is dehydrated sufficiently for the structural water to be lost, a structural change occurs in which the symmetry is lowered and alternate I-beams are rotated in opposite senses about the *c* axis, with the result that the layers of tetrahedra are folded [see Fig. 4 of Preisinger (1963) and Fig. 5 of VanScoyoc *et al.* (1979)]. Such a change requires a temperature of at least 210°C (Hayashi *et al.* 1969) and the loss of 50–65% of the bound water (VanScoyoc *et al.* 1979); it is accompanied by a shift in the 110 peak to a *d* of 8.6–9.2 Å, a loss of intensity and broadening. This shift has not been observed in natural samples of palygorskite at ordinary temperatures, and large-scale dehydration is unlikely. Some limited local disordered rotation of I-beams may contribute to the broadening of reflections, but it is unlikely to be sufficient to account for the observed variations in the diagnostic regions of powder patterns of palygorksite.

Palygorskite phases

The variations in the powder patterns of palygorskite specimens are not the result of impurities, nor can they be fully accounted for by variations in peak width related to particle size, morphology or structural disorder. The diagnostic regions of the powder patterns each appear to consist of a series of lines that have approximately similar *d*-values in all the patterns, but different relative intensities. (It is assumed that weak lines may become undetectable on some patterns.) The variations in relative intensity suggest that two phases (or possibly more) are present and that their proportions vary in different samples.

The complete patterns are generally similar, sufficiently so for the specimens to be identified as palygorskite. So, if there are two phases, as there seem to be, both must have the essential features of the palygorskite structure and a unit cell with dimensions close to a or $a\sin\beta \simeq 12.8$, $b \simeq 17.8$, $c \simeq 5.2$ Å. The similarity of the *d*-values for lines in the diagnostic regions also suggests that the two phases have similar or related unit-cells. But the *d*-values do not match exactly, and there are differences in the separation of peaks, *e.g.*, the peak at $\simeq 4.12$ Å is split into two in samples 4B and 5B (Table 1). The unit cells of the two phases are evidently not the same in all samples, nor are they exactly related.

The nature of the two phases cannot be inferred from the powder data alone. The most likely possibilities are:

(i) an orthorhombic form (perhaps with space group *Pbmn*; Preisinger 1963) and a monoclinic one (perhaps with space group *C2/m*; Bradley 1940, Drits & Sokolova 1971);

(ii) two different monoclinic forms, perhaps those proposed by Christ *et al.* (1969);

(iii) a form with double chains of tetrahedra linked into sheets (Bradley 1940, Preisinger 1963, Drits & Sokolova 1971) and one with alternate triple and single chains along the *b* axis (Gard & Follett 1968), and,

(iv) a hydrated form and a partially dehydrated form of the kind shown in Figure 4 of Preisinger (1963), though such a partly dehydrated form is unlikely for the same reasons as the structural defects related to it.

INTERPRETATION AND DERIVATION OF UNIT CELLS

Christ *et al.* (1969) noted strong reflections at about 4.25 and 2.54 Å on three of their powder patterns and indexed these reflections as 121 and 161 in terms of an orthorhombic cell. Their two other patterns each showed pairs of reflections whose combined intensity was approximately the same as that of the corresponding single peaks identified as 121 as 161 of the orthorhombic cell. These pairs were interpreted as resulting from a lowering of symmetry to monoclinic. The pairs were indexed as $121-12\bar{1}$ and $161-16\bar{1}$ and used to derive and refine the corresponding monoclinic cells, one of which had β as the oblique angle and the other α.

With the available data, the above interpretation is a reasonable one. But the present study, covering a wider range of specimens, reveals much greater variations in the powder patterns, many of which do not fit the simple intensity relationship for single reflections splitting into two as the symmetry is lowered from orthorhombic to monoclinic. The interpretation advanced by Christ *et al.* must now be regarded as tentative, and the unit cell and symmetry of palygorskite seem as problematical as ever.

To see whether any conclusions could be drawn concerning the unit cell and symmetry, unit-cell refinements were carried out on a selection of specimens (4, 5, 6, 7, 8, 9 and 13) using data from Debye–Scherrer photographs. No correction was made for film shrinkage, as this is known to be negligible for the film and processing used. The precision of the Debye–Scherrer method is lower than that of diffractometry, but it turns out in practice that the precision is limited by the specimen (breadth of lines and signal–to–noise ratio) rather than the experimental technique. Three refinements were carried out using the powder photograph measurements for each specimen and indices based on each of the tabulated powder-patterns of Christ *et al.* for an orthorhombic cell, a monoclinic one with β oblique and a monoclinic one with α oblique.

In order to assess the validity of the three cells, we require a measure of how well the calculated 2θ values fit the observed ones. Such a measure is provided by the standard deviation of a single observation, $\sigma(2\theta)$, defined by

$$\sigma^2(2\theta) = \Sigma_{\text{all } m}\,[(2\theta)_{\text{obs}} - (2\theta)_{\text{calc}}]^2/(m - n)$$

where m represents the number of observations, and n, the number of parameters. This gives a measure of the fit between observed and calculated values that is independent of both the number of observations and the number of parameters. Thus it can be used to compare monoclinic and orthorhombic unit-cells. The lower this standard deviation, the better is the fit.

To use this fit parameter properly, one needs to relate it to the likely experimental precision and to appreciate one of its limitations. A cell that gives a fit significantly worse than the experimental precision may be rejected as incorrect. But it is possible that a wrong cell and wrong indexing may, nevertheless, give a mathematical fit consistent with the experimental precision. So a good fit does not necessarily prove that a particular cell is correct.

An indication of the expected precision was obtained from unit-cell refinements on four specimens of sepiolite, which gave standard deviations of a single observation $\sigma(2\theta)$ in the range 0.05–0.1° 2θ. As sepiolite is structurally related to palygorskite and commonly similar in habit, it is reasonable to expect values of $\sigma(2\theta)$ in the same range for cell refinements on palygorskite specimens.

Inspection of the standard deviations in Table 3 shows that for some specimens, all the unit cells give a reasonable fit between observed and calculated 2θ values. We may, however, reject the orthorhombic cell for specimen 5 and perhaps specimen 13 also, whereas the β-oblique monoclinic cell may be rejected for specimen 11. Otherwise, no definite conclusion can be reached in assigning a particular unit-cell to any of the palygorskite specimens in Table 3; the unit-cell dimensions obtained in the refinements are, therefore, not given, as they may not be meaningful.

An attempt was made to assess the validity of the proposed unit-cells by looking for reflections that could not be satisfactorily indexed. But the number of unindexed reflections did not provide a basis for distinguishing unit cells. The number of unindexed reflections is usually small and, more significantly, reflections may be unindexed for reasons other than an incorrect unit-cell. An observation may happen to be inaccurate and lie outside the 95% confidence interval used for indexing. In other cases, two reflections close together may be measured as one, which will fail to index satisfactorily whatever unit cell is chosen. Finally, it has already been noted that palygorskite specimens are impure; it is possible that a weak reflection may arise from some unidentified impurity and not from palygorskite itself.

The results of Christ *et al.* were re-examined in a similar way, trying all three unit-cells and indexing schemes for each of their specimens. The standard deviations of a single observation obtained are shown in Table 4. With the exception of their Attapulgus specimen, the unit cell that gives the best fit is in each case the one adopted by Christ *et al.* (1969). However, other cells also give a reasonable fit between observed and calculated 2θ values. The monoclinic cell with α oblique can be rejected for their Zaachila specimen, as perhaps might those with β oblique for the Glasgow, Virginia and Sapillo specimens, though with rather less confidence. Beyond that, no reliable conclusion can be drawn.

Thus neither the experimental results of the present study nor the re-examination of their data contradict the conclusions of Christ *et al*; indeed they show that. those conclusions fit the observations. But those conclusions are not positively established as correct either, since other unit cells also fit the observations reasonably well, bearing in mind the experimental precision. So the old uncertainties over the unit cell and symmetry of palygorskite remain, the powder pattern being consistent with some kind of monoclinic or orthorhombic cell with a or $a\sin\beta \simeq$ 12.8 Å, b 17.8 Å, $c \simeq$ 5.2 Å and in the monoclinic case either β or α oblique (the latter close to 90°).

Being consistent with more than one type of unit cell, the results of the cell refinements fit the earlier conclusion that palygorskite may consist of two forms whose proportions vary among specimens.

TABLE 3. LEAST-SQUARES FIT FOR POSSIBLE UNIT CELLS OF PALYGORSKITE AS MEASURED BY THE STANDARD DEVIATION OF A SINGLE OBSERVATION, σ(2θ)

Specimen number (in Table 1)		σ(2θ)	
	Orthorhombic	Monoclinic ß oblique	Monoclinic a oblique
4	0.089	0.076	0.076
5	0.122	0.070	0.070
6	0.076	0.066	0.036
7	0.120	0.062	0.066
8	0.047	0.071*	0.050
9	0.066	0.048	0.044
11	0.081	0.125	0.080
13 (sample 1)	0.108	0.074	0.028
13 (sample 2)	0.060	0.027	0.040

* least-squares fit for the cell of Christ et al. (1969); there is only one observed reflection with l ≠ 0 which is insufficient to define c and ß.

TABLE 4. LEAST-SQUARES FIT FOR POSSIBLE PALYGORSKITE UNIT-CELLS USING THE DATA OF CHRIST ET AL. (1969)

Locality		σ(2θ)	
	Orthorhombic	Monoclinic ß oblique	Monoclinic a oblique
Sapillo, N.M.	0.028	0.058	0.042
Zaachila, Mexico	0.035	0.044	0.081
Attapulgus, Ga.	0.054	0.062	0.041
Glasgow, Va.	0.052	0.063*	0.025
Metaline, Wash.	0.038	0.021	0.029

Fit measured using the standard deviation of a single observation σ(2θ) as in Table 3.

* least-squares fit for the cell quoted by Christ et al. (1969); there is only one observed reflection with l ≠ 0, which is insufficient to define c and ß.

SUMMARY AND CONCLUSIONS

(1) X-ray powder diffraction shows that most specimens of palygorskite are impure, as was also found by Smith & Norem (1986) in their SEM-EPMA study. Calcite, quartz, dolomite and chlorite seem to be the most common impurities.

(2) A greater range of variation in the X-ray powder patterns has been found in this study than in previous ones, in which fewer specimens were examined. This greater variation casts doubt on the criteria used to distinguish the orthorhombic and the two monoclinic varieties (with β and α oblique, respectively) defined by Christ *et al.* (1969).

(3) The effects of particle size, particle morphology and structural disorder do not appear to be large enough to explain the observed variations in the powder patterns of palygorskite.

(4) The variations in the powder patterns suggest that palygorskite consist of two (or more?) phases, present in varying proportions. The two phases appear to have similar or related unit-cells and are probably different variants of the palygorskite structure-type.

(5) Least-squares refinement of unit-cell dimensions does not provide a basis for deciding which of the possible unit-cells is the correct one for a given specimen. A reasonable fit consistent with the precision of the experimental technique can be obtained for more than one cell. A fit for more than one cell would be expected if the specimens contained two phases with related unit-cells.

The problem of the correct unit-cell and symmetry for palygorskite remains unresolved and perhaps more uncertain than was previously considered, especially as the evidence suggests there is more than one phase present. Resolution of the problem will require a reliable basis for the indexing of reflections and for assignment of reflections to a particular phase.

Attempts to obtain useful electron-diffraction patterns failed as palygorskite rapidly underwent beam damage and gave patterns of poor quality with strong low-angle scattering and signs of disorder. Rautureau *et al.* (1979) were successful in obtaining a few crystals of a palygorksite that gave electron-diffraction patterns and structure images. They were able to confirm the structural scheme with I-beams two chains wide and to relate their patterns to previously proposed values for a or $a\sin\beta$, b and c, but were unable to determine β or the symmetry.

Work is in progress on the calculation of powder-diffraction patterns for the various structural models that have been or can be devised for palygorskite. These calculated patterns may provide some basis for the indexing of observed reflections and for deciding what the structures of the palygorskite phases present are.

The status of palygorskite, "attapulgite" and "pilolite", *i.e.*, whether they are the same species or distinct ones, has long been an open question. The two "attapulgite" samples (6 and 11) examined in the present study do not contain the sepiolite, illite and clay impurities that were found by Smith & Norem (1986), even though they are from the same localities. But both have broad reflections and appear to be highly disordered. Perhaps the most that can be said is that "attapulgite" seems to be very variable in character and purity. The same appears to be true of "pilolite"; certainly no obvious features distinguishing "attapulgite" and "pilolite" from palygorksite have emerged.

The present study suggests that there is probably more than one species present in palygorskite, but those species seldom occur in isolation, and their proportions may vary. The species probably have similar or related unit-cells and structures.

ACKNOWLEDGEMENTS

I am grateful to the two reviewers for their critical comments and for helping me to appreciate the importance of peak profiles and the factors affecting them.

REFERENCES

BAILEY, S.W. (1980): Structures of layer silicates. *In* Crystal Structures of Clay Minerals and their X-Ray Identification (G.W. Brindley & G. Brown, eds.). *Mineral. Soc., Mon.* **5**, 1-123.

BRADLEY, W.F. (1940): The structural scheme of attapulgite. *Am. Mineral.* **25**, 405-410.

BRAUNER, K. & PREISINGER, A. (1956): Struktur und Entstehung des Sepioliths. *Tschermaks Mineral. Petrogr. Mitt.* **6**, 120-140.

CHISHOLM, J.E. (1975): Crystallographic shear in silicate structures. *In* Surface and Defect Properties of Solids (M.W. Roberts & J.M. Thomas, eds.). *Chem. Soc., Specialist Periodical Rep.* **4**, 126-151.

CHRIST, C.L., HATHAWAY, J.C., HOSTETLER, P.B. & SHEPARD, A.O. (1969): Palygorskite: new X-ray data. *Am. Mineral.* **54**, 198-205.

DRITS, V.A. & ALEKSANDROVA, V.A. (1966): The crystallochemical nature of palygorskites. *Zap. Vses. Mineral. Obshchestva* **95**, 551-560.

______ & SOKOLOVA, G.V. (1971): Structure of palygorskite. *Sov. Phys. Crystallogr.* **16**, 183-185.

GARD, J.A. & FOLLETT, E.A.C. (1968): A structural scheme for palygorskite. *Clay Minerals* **7**, 367-370.

HAYASHI, H., OTSUKA, R. & IMAI, N. (1969): Infrared study of sepiolite and palygorskite on heating. *Am. Mineral.* **54**, 1613-1624.

JONES, B.F. & GALAN, E. (1988): Sepiolite and palygorskite. *In* Hydrous Phyllosilicates (exclusive of micas) (S.W. Bailey, ed.). *Rev. Mineral.* **19**, 631-674.

MARTIN VIVALDI, J.L. & LINARES GONZALEZ, J. (1962): A random intergrowth of sepiolite and attapulgite. *Clays Clay Minerals* **9**, 592-602.

______ & ROBERTSON, R.H.S. (1971): Palygorskite and sepiolite (the hormites). *In* The Electron-Optical Investigation of Clays (J.A. Gard, ed.). *Mineral. Soc., Mon.* **3**, 255-275.

PREISINGER, A. (1963): Sepiolite and related compounds: its stability and application. *Clays Clay Minerals* **10**, 365-371.

RAUTUREAU, M., CLINARD, C., MIFSUD, A. & CAILLÈRE, S. (1979): Étude morphologique de la palygorskite par microscopie électronique. *C.R. 104^e Congr. Nat. Socs. sav.* **III**, 199-212.

SMITH, D.G.W. & NOREM, D. (1986): The electron-microprobe analysis of palygorskite. *Can. Mineral.* **24**, 499-511 and 791.

VANSCOYOC, G.E., SERNA, C.J. & AHLRICHS, J.L. (1979): Structural changes in palygorskite during dehydration and dehydroxylation. *Am. Mineral.* **64**, 215-223.

VEBLEN, D.R. (1981): Non-classical pyriboles and polysomatic reactions in biopyriboles. *In* Amphiboles and Other Hydrous Pyriboles - Mineralogy (D.R. Veblen, ed.). *Rev. Mineral.* **9A**, 189-236.

ZOLTAI, T. (1981): Amphibole asbestos mineralogy. *In* Amphiboles and Other Hydrous Pyriboles - Mineralogy (D.R. Veblen, ed.). *Rev. Mineral.* **9A**, 237-278.

ZVYAGIN, B.B., MISHCHENKO, K.S. & SHITOV, V.A. (1963): Electron diffraction data on the structures of sepiolite and palygorskite. *Sov. Phys. Crystallogr.* **8**, 148-153.

Received July 24, 1989, revised manuscript accepted February 28, 1990.