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POWDER-DIFFRACTION PATTERNS AND STRUCTURAL MODELS FOR PALYGORSKITE

JIM E. CHISHOLM*
Department of Mineralogy, British Museum (Natural History), Cromwell Road, London SW7 5BD, England

ABSTRACT

Models proposed for the crystal structure of palygorskite are considered and a range of structures identified that have reasonable cation coordination, cation–oxygen distances and O–O nonbonded distances. Powder-diffraction patterns are calculated for these structures and compared with observed patterns. Structural models with a mixture of triple and single chains can be ruled out, as their calculated powder-patterns are completely unlike those observed. The calculated powder-patterns make it possible to identify reflections that are characteristic of the orthorhombic (*Pbmn*) and monoclinic (*C2/m*) double-chain structures proposed for palygorskite. Most palygorskite specimens appear to contain both forms, but there are one or two that are pure or nearly pure monoclinic palygorskite. The differences between powder patterns of different palygorskite specimens are explained by a) variations in the proportions of orthorhombic and monoclinic forms, and b) the sensitivity of certain parts of the powder pattern to the exact value of β for the monoclinic form, which seems to vary within the range 106–108°.

Keywords: palygorskite, attapulgite, X-ray powder diffraction, crystal structure.

SOMMAIRE

Ce travail porte sur l'évaluation des modèles de la structure cristalline de la palygorskite, et des différentes structures qui possèdent une coordinence cationique raisonable et des distances réalistes entre cation et oxygène, et entre atomes d'oxygène non liés. Les spectres de diffraction X obtenus sur poudre ont été calculés pour ces structures, et comparés avec les spectres observés. Les modèles structuraux qui impliquent un mélange de chaînes simples et triples peuvent être éliminés, parce que leur spectre de diffraction ne ressemble aucunement à ceux qui sont observés. Les spectres calculés permettent l'identification de réflexions caractéristiques des structures orthorhombique (*Pbmn*) et monoclinique (*C2/m*) à chaînes doubles qui ont été proposées pour la palygorskite. La plupart des échantillons contiennent les deux formes, mais dans un ou deux cas, seule la forme monoclinique semble être présente. Les différences entre échantillons s'expliquent par a) des variations en proportion des deux formes, et b) la sensibilité de certaines régions du spectre à la valeur exacte de β, qui semble varier entre 106 et 108°.

(Traduit par la Rédaction)

Mots-clés: palygorskite, attapulgite, diffraction X sur poudres, structure cristalline.

INTRODUCTION

An experimental X-ray powder-diffraction study has recently been carried out on a wide range of specimens variously described as palygorskite, attapulgite and pilolite (Chisholm 1990). Attention was drawn to the variability of the powder patterns and inhomogeneity of some specimens. The variations in powder pattern did not appear to arise from experimental technique, which gave reproducible results for a given sample. Although preferred orientation undoubtedly occurs, the variations seem to be independent of this effect. Differences in particle size, particle morphology and structural disorder contribute to the differences in the powder patterns, but are not sufficient to account for the larger variations observed. Generally, the powder patterns show reflections with approximately similar *d*-values but variable intensities, suggesting that palygorskite may be a mixture of two phases.

In the experimental study, it was not possible to derive unit cells and space groups for palygorskite with any certainty. In most cases, the observed data could be fitted satisfactorily and indexed (though with different indices) by more than one (and often by all three) of the unit cells proposed by Christ *et al.* (1969), *i.e.*, orthorhombic, monoclinic with β oblique, and monoclinic with α oblique.

To resolve these difficulties requires a reliable basis for indexing the observed reflections and for identifying the reflections from each phase if there is more than one. As a possible approach, idealized structural models for palygorskite were explored to see if calculated powder-diffraction patterns might

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*Present address: Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, 403 Edgeware Road, London NW2 6LN, England.

provide such a basis for the indexing of reflections and for their assignment to a phase with a particular type of structure.

A similar approach was adopted by Drits & Sokolova (1971) in their study of elongate fibers of palygorskite from the Dzhezdy manganese deposit, Kazakh SSR (now Kazakhstan), from which an X-ray rotation photograph could be obtained. Observed intensities on the zero and first levels (*hk*0 and *hk*1) were found to be in poor agreement with the structural model of Gard & Follett (1968) based on a mixture of triple and single chains. Good agreement was obtained with the double-chain model of Bradley (1940) in space group *C*2/*m*. A monoclinic cell was required to index the reflections, and the double-chain model of Preisinger (1963) in space group *Pbmn* proved untenable. The Bradley structural model was therefore established for this specimen, but other structural models were considered possible in principle. Application and extension of this approach seemed a promising way to explain the observed variations in the powder patterns of palygorskite by relating them to calculated patterns for idealized structural models.

STRUCTURAL MODELS FOR PALYGORSKITE

Since the original X-ray-diffraction study by Bradley (1940), various monoclinic and orthorhombic cells and space groups have been suggested for palygorskite. The structural models and the crystal chemistry of palygorskite have been fully reviewed by Bailey (1980), Jones & Galan (1988) and Chisholm (1990).

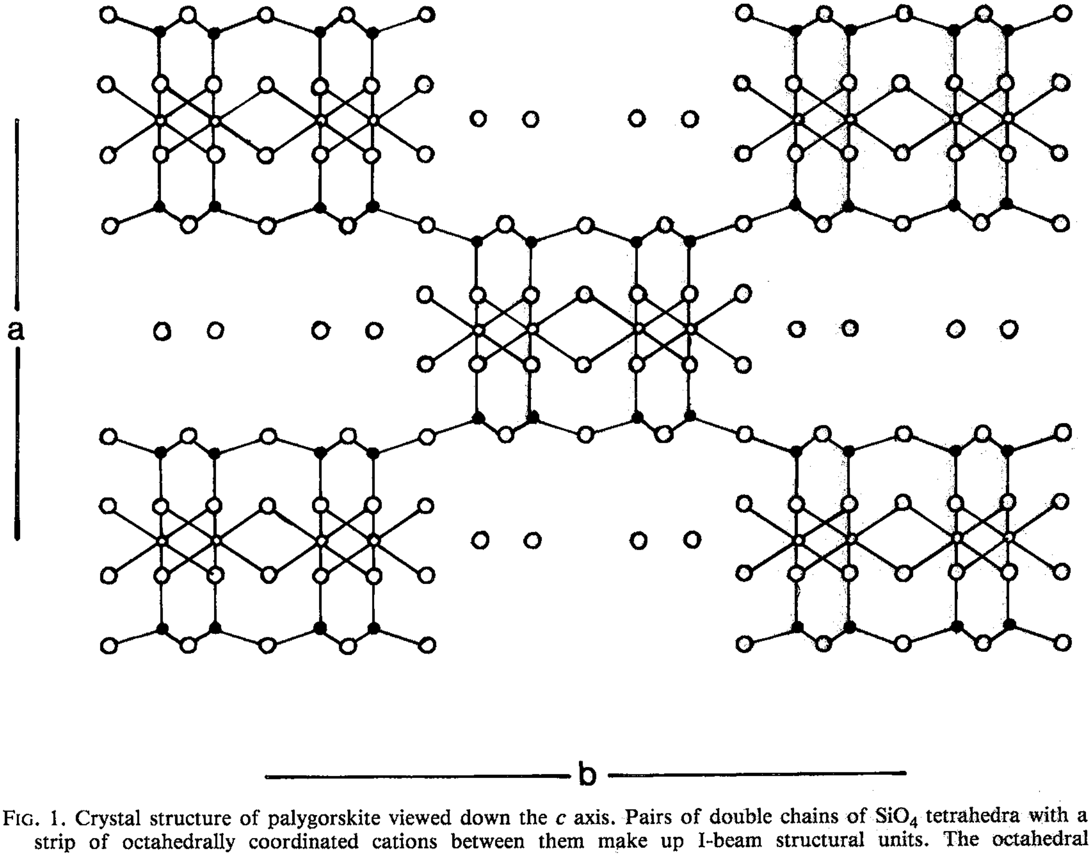

FIG. 1. Crystal structure of palygorskite viewed down the *c* axis. Pairs of double chains of SiO_4 tetrahedra with a strip of octahedrally coordinated cations between them make up I-beam structural units. The octahedral coordination of the cations at the edge of the strip is completed by bonding to two "bound" water molecules; each of the inner cations is linked to two OH groups. Each I-beam shares its corner O atoms with four adjacent I-beams in such a way that the silicate tetrahedra form a corrugated sheet parallel to (100), with the apical oxygen atoms of alternate double chains pointing in opposite directions along the normal to (100). Channels parallel to the *c* axis between the I-beams are occupied by "zeolitic" H_2O molecules. Small open circles: octahedrally coordinated cations (Mg,Al); small filled circles: tetrahedrally coordinated cations (Si,Al); large open circles: O, OH, H_2O.

Two unit-cell settings have been used for palygorskite. The setting with *a* or *a*sinβ $\approx$ 12.8, *b* $\approx$ 17.8 and *c* $\approx$ 5.2 Å was used in the original papers describing crystal structures (Bradley 1940, Preisinger 1963, Drits & Sokolova 1971) and is adopted here to facilitate comparisons. The alternative setting used in the reviews by Bailey (1980) and Jones & Galan (1988) has the *a* and *c* axes interchanged; to convert to this unit cell, the *x* and *z* atomic coordinates have to be interchanged, and the space-group symbol changed accordingly.

The structures proposed for palygorskite (Bradley 1940, Preisinger 1963, Drits & Sokolova 1971) contain "I-beam" units, similar to those in the amphiboles. An I-beam consists of a strip of cations in octahedral coordination sandwiched between two double chains (Si_4O_{11}) of silicate tetrahedra (Fig. 1). As the composition of palygorskite corresponds to the structural formula $(Mg,Al)_4(Si,Al)_8O_{20}(OH)_2(H_2O)_4{\bullet}4H_2O$, the octahedral site in the middle of the strip is believed to be vacant, by analogy with the octahedral sheets of dioctahedral layer silicates. Each of the I-beam units shares its corner oxygen atoms with four adjacent I-beams in such a way that the silicate tetrahedra form corrugated sheets in which the apical O atoms of the double chains of tetrahedra point alternately toward +*a* or +*a*sinβ and -*a* or -*a*sinβ. Between the I-beams, there are channels parallel to the *c* axis. These channels contain four molecules of "zeolitic" water, which is lost at relatively low temperatures. The octahedral coordination of the cations at the edge of the strip is completed by bonding to two molecules of "bound" H_2O at each edge of the strip, which are lost at a higher temperature.

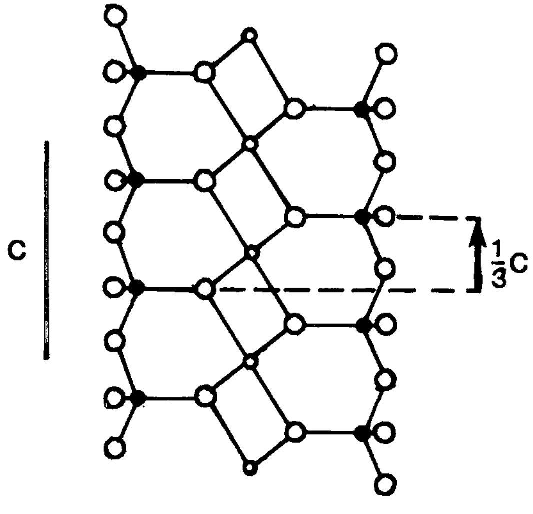

FIG. 2. An I-beam structural unit of palygorskite viewed down the *b* axis. The double chains of silicate tetrahedra on either side of the octahedral strip are displaced along the *c* axis relative to each other. The arrangement shown has regular octahedra and tetrahedra, with ideal relative dimensions. The displacement of the chains of tetrahedra across the strip of octahedra is $\pm c/3$ in the ideal structure, but will deviate from this in real structures. Small open circles: octahedrally coordinated cations (Mg,Al); small filled circles: tetrahedrally coordinated cations (Si,Al); large open circles: O, OH, H_2O.

Figure 2 shows an I-beam viewed down the *b* axis. A key feature of the structure is that the silicate chains on either side of the octahedral strip are displaced relative to each other along the *c* axis. An ideal structure would have regular octahedra and tetrahedra with the correct relative dimensions, and the displacement would then be *c*/3. In fact, the Mg octahedra and Si tetrahedra do not have the ideal dimensions. Some distortion therefore must occur, and the displacement will deviate from the ideal value. The displacement may be in either direction, +*c* or -*c*. In the monoclinic structure, the displacements are all in the same direction (+ + + + + or its twin-related equivalent -----), and the stacking sequence along the normal to (100) is the same as in clinoamphibole and clinopyroxene. In orthorhombic palygorskite, the displacements are alternately along +*c* and -*c*, the sequence +-+-+- being analogous to that in protoamphibole and protopyroxene.

Orthorhombic structural model

Cell dimensions and atomic coordinates for an orthorhombic structure for palygorskite of the type proposed by Preisinger (1963) are given in Table 1. The *x* and *y* coordinates correspond to the projection on (001) of the structural scheme shown in Figure 2 of Preisinger (1963). For the idealized arrangement, the parameter *z* has the value 1/3. The tetrahedral sheets on either side of the octahedral strip are then displaced relative to each other by *c*/3, as they would be in the idealized forms of the analogous amphibole and pyroxene structures. For other values of *z*, the displacement across the octahedral layer is 2*zc* or its equivalent (1-2*z*)*c*.

In the idealized structure with *z* = 1/3 and the cell dimensions quoted, the Mg octahedra are almost regular, with Mg–O distances 2.02 and 2.03 Å. For *z* = 3/8 and a *c*/4 displacement at each octahedral sheet, the octahedra are distorted, and the Mg–O distances are unrealistically long and short (2.23 and 1.94 Å). The same is true but in the opposite sense for *z* = 7/24 and a 5*c*/12 displacement across the octahedral strip (with Mg–O distances 1.86 and 2.13 Å). The range 7/24

TABLE 1. DATA FOR ORTHORHOMBIC STRUCTURAL MODEL FOR PALYGORSKITE

Cell dimensions: a 12.78, b 17.89, c 5.21 A (average of the values for the three orthorhombic unit cells quoted by Christ et al. 1969)
Space group: Pbmn

Atomic coordinates:

Atom	x	y	z
Mg 1	0	0	0
Mg 2	0	1/12	1/2
Mg 3	0	1/6	0
Si 1	5/24	1/12	z+1/2
Si 2	5/24	1/6	z
OH 1	1/12	0	z
O 1	1/12	1/12	z+1/2
O 2	1/12	1/6	z
BW	1/12	1/4	z+1/2
O 3	1/4	0	z+1/2
O 4	1/4	1/4	z
O 5	1/4	1/8	z+1/4
O 6	1/4	1/8	z-1/4
ZW 1	0	1/3	1/2
ZW 2	0	5/12	0

Mg 1 site taken as vacant, corresponding to the structural formula $(Mg,Al)_4Si_8O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$
OH - structural hydroxyl
BW - "bound" H_2O
ZW - "zeolitic" water

Relative displacement of SiO_4 tetrahedral sheets on either side of strips of MgO_6 octahedra is 2zc or the equivalent (1-2z)c.

For idealised structure, z = 1/3 and the relative displacement of the tetrahedral sheets on either side of each octahedral strip is c/3.

$< z <$ 3/8 [$5c/12 >$ displacement at each octahedral sheet $> c/4$] should more than cover any likely departures from the idealized arrangement with z = 1/3 [$c/3$ shift at each octahedral sheet].

Monoclinic structural model

Cell dimensions and atomic coordinates are given in Table 2 for a monoclinic structural model for palygorskite, of the type first proposed by Bradley (1940). In the monoclinic arrangement, the relative displacement of the sheets of tetrahedra on either side of the strip of octahedra determines (or, depending on how one looks at it, is determined by) the angle β.

The idealized arrangement should have a displacement of $c/3$ across each strip of octahedra, as in the idealized forms of the amphibole and pyroxene structures. For cell dimensions [$d(100)$, b, c] similar to those in the orthorhombic model, the idealized monoclinic structure of palygorskite should have a β of 105.20° and an a of 13.24 Å. The octahedral sites are then almost regular, with Mg–O distances in the range 2.02–2.04 Å. As for the orthorhombic case, arrangements with displacements of $c/4$ and $5c/12$ at each sheet of octahedra (β 101.52°, a 13.04 Å and β 108.76°, a 13.50 Å, respectively) probably cover the likely range of departures from the idealized arrangement. Each of these arrangements has highly distorted octahedra (in opposite senses) and unreasonably long and short Mg–O distances.

In both clinopyroxenes and clinoamphiboles, the displacement across the octahedral sheet lies in the range $c/4$ - $c/3$. But the palygorskite with space group $C2/m$ studied by Drits & Sokolova (1971) has a 13.14, b 17.85, c 5.15 Å and β 107°, which implies a displacement of 0.373c at each octahedral sheet. Nevertheless, the unit cell and coordinates quoted by Drits & Sokolova (1971) show that the octahedral sites are nearly regular, with Mg–O distances 2.02, 2.07 and 2.08 Å. Their coordinates, in fact, depart slightly from those expected for the idealized arrangement with a β of 107°.

Christ *et al.* (1969) quoted a monoclinic cell with a 12.78, b 17.864, c 5.24 Å, β 95.78° for a sample of palygorskite from Metaline Falls, Washington. Such a value of β implies a displacement of 0.123c across each octahedral sheet and, in consequence, highly distorted Mg polyhedra. This monoclinic cell therefore appears to be unacceptable, but would be reasonable if it were the $I2/m$ setting of the conventional $C2/m$ cell as Bailey (1980) has

TABLE 2. DATA FOR MONOCLINIC STRUCTURAL MODEL FOR PALYGORSKITE

Cell dimensions: d(100) 12.78, b 17.89, c 5.21 A (corresponding to unit cell adopted for orthorhombic structural model, Table 1)
Space group: C2/m

Atomic coordinates:

Atom	x	y	z
Mg 1	0	0	0
Mg 2	0	1/12	1/2
Mg 3	0	1/6	0
Si 1	5/24	1/12	-(1/24)(acosβ/c)
Si 2	5/24	1/6	1/2 - (1/24)(acosβ/c)
OH 1	1/12	0	1/2 - (1/6)(acosβ/c)
O 1	1/12	1/12	-(1/6)(acosβ/c)
O 2	1/12	1/6	1/2 - (1/6)(acosβ/c)
BW	1/12	1/4	-(1/6)(acosβ/c)
O 3	1/4	0	0
O 4	1/4	1/4	1/2
O 5	1/4	1/8	1/4
O 6	1/4	1/8	3/4
ZW 1	0	1/3	1/2
ZW 2	0	5/12	0

Mg 1 site taken as vacant corresponding to the structural formula $(Mg,Al)_4Si_8O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$
OH - structural hydroxyl
BW - "bound" H_2O
ZW - "zeolitic" water

If sc = relative displacement of tetrahedral sheets on either side of octahedral strips,
relative displacement across unit cell = 2sc
$\tan(180-\beta) = d(100)/2sc$
and $a = d(100)/\sin\beta$

In the idealized structure, s = 1/3, β = 105.20° and a = 13.24 A.

For s = 1/4, β = 101.52° and a = 13.04 A.
For s = 5/12, β = 108.76° and a = 13.50 A.

suggested it may be. In that case, the shift at each octahedral sheet would be 0.377*c*, which is close to that found by Drits & Sokolova (1971). For the same reason, the cell with *a* 12.75, *b* 18.06, *c* 5.22 Å, *β* 95°50′ and space group *P*2/*c* found by Zvyagin *et al.* (1963) also may correspond to the *I*2/*m* setting of the conventional *C*2/*m* cell. Certainly, neither of the cells with $\beta \approx 95.8°$ fits a structure of the kind generally proposed for palygorskite that has reasonable Mg coordination.

Christ *et al.* (1969) also put forward a different type of monoclinic cell, with *α* oblique (for the same *a*, *b* and *c* axes), for their palygorskite from Glasgow, Virginia. It has not proved possible to relate this unit cell to a specific structural model, and it is not considered further here.

Structural model with single and triple chains

To explain the lowering of symmetry from *C*2/*m* to *P*2/*c* reported by Zvyagin *et al.* (1963), Gard & Follett (1968) suggested a monoclinic structure in which alternate I-beam units consist of triple chains and single chains. They also suggested a hypothetical orthorhombic structure with triple and single chains, that would have space group *Pmcm*. Consideration of bond distances for a hypothetical orthorhombic structure of this kind shows that the Mg sites would be highly distorted as the result of the constraints imposed by the *Pmcm* symmetry. A more realistic model with idealized coordination can be obtained by lowering the space-group symmetry to *P*2/*c* with $\beta = 90°$. The latter "orthorhombic analogue" model has been used for the calculation of powder patterns.

Models with triple and single chains are subject to the same requirements for the relative displacement of the chains of tetrahedra across the strips of octahedra as double-chain structures. Only the two idealized forms of triple- and single-chain structures with *c*/3 displacement have been considered: (i) the "monoclinic analogue" of the *C*2/*m* Bradley model with a *β* of 105.20°, and (ii) the "orthorhombic analogue" of the *Pbmn* Preisinger model, having a *β* of 90°.

The idealized positions of zeolitic water between the backs of the triple chains are fairly close to the positions actually found in sepiolite, the triple-chain analogue of palygorskite (Brauner & Preisinger 1956), and are therefore considered reasonable. A change has been made to the position of the zeolitic water between the backs of the single chains. On the projection of Gard & Follett (1968), this water has coordinates $x = 1/12$, $y = 1/2$, which lead to unreasonably short O–O nonbonded contacts to the adjacent zeolitic water and the nearby bound H_2O or OH. Modifying the coordinates to $x = 0$, $y = 25/48$ places the water in a similar position to the middle zeolitic water between the backs of the triple chains and eliminates the short O–O nonbonded distances. The modified coordinates for the zeolitic water between the backs of the single chains have therefore been adopted for the calculation of powder patterns.

CALCULATED POWDER-PATTERNS

All calculations were carried out using a PC and a program written in BASIC by the author. For the various structural models considered, the intensities of powder-diffraction lines were calculated for Cu$K\bar{\alpha}$ radiation and normalized to an intensity of 100 for the strongest line, which is invariably the 110 line, with a *d* of 10.4 Å. Scattering factors for Mg^{2+}, Si^{4+}, O^- were derived from the usual analytical expression and the coefficients of Cromer & Mann (1968). No allowance was made for anomalous scattering. Nor were temperature factors included in the calculation of intensities, since their effect is likely to be less than that of departures from the idealized structural models considered.

Throughout the calculations, the octahedral site at the origin has been assumed vacant on the basis of 4 octahedral cations in the anhydrous formula calculated to 21 oxygen atoms, which seems to be generally accepted (Smith & Norem 1986, Newman & Brown 1987, Weaver & Pollard 1973). This implies some substitution of Al for Mg or Si or

TABLE 3. CALCULATED POWDER-PATTERNS FOR ORTHORHOMBIC STRUCTURAL MODELS FOR PALYGORSKITE

		Displacement at octahedral sheet		
		c/4	c/3	5c/12
hkl	d	I	I	I
110	10.40	100	100	100
020	8.94	2	2	2
200	6.39	5	5	5
130	5.40	4	4	4
111	4.658	1	1	1
021	4.502	4	2	-
040	4.472	13	13	13
121	4.246	11	16	20
310	4.144	3	3	3
131	3.751	1	2	3
221	3.680	12	7	2
240	3.664	3	3	3
231	3.344	2	3	3
311	3.243	1	-	-
400	3.195	15	15	15
321	3.094	7	10	12
331	2.886	6	5	4
251	2.678	5	7	8
421	2.606	2	-	-
002	2.605	2	-	2
440	2.600	6	6	6
061	2.588	7	3	-
102	2.552	8	6	2
161	2.536	8	11	14
112	2.527	-	-	2
351	2.425	7	6	2
202	2.412	3	3	3
212	2.391	6	5	2

Details of the unit cell and structural models are given in Table 1.

TABLE 4. CALCULATED POWDER-PATTERNS FOR MONOCLINIC STRUCTURAL MODELS FOR PALYGORSKITE

	Displacement at octahedral sheet					
	c/4		c/3		5c/12	
	β 101.52°		β 105.20°		β 108.76°	
hkl	d	I	d	I	d	I
110	10.40	100	10.40	100	10.40	100
020	8.94	2	8.94	2	8.94	2
200	6.39	5	6.39	5	6.39	5
130	5.40	4	5.40	4	5.40	4
040	4.472	13	4.472	13	4.472	13
021	4.434	9	4.383	9	4.320	9
$22\bar{1}$					4.164	12
310	4.143	3	4.143	3	4.145	3
$22\bar{1}$	3.980	12	4.074	12		
$13\bar{1}$	3.878	1	3.903	2	3.918	2
240	3.664	3	3.664	3	3.664	3
221	3.378	10	3.281	9		
$33\bar{1}$					3.267	7
400	3.194	15	3.194	15	3.196	15
$33\bar{1}$			3.189	6		
221					3.187	8
$33\bar{1}$	3.112	6				
$42\bar{1}$					3.006	5
$15\bar{1}$					2.947	1
$42\bar{1}$	2.836	3	2.918	3		
331	2.673	3				
$35\bar{1}$					2.638	11
331			2.606	3		
440	2.599	6	2.599	6	2.600	6
$20\bar{2}$					2.599	2
$35\bar{1}$			2.597	10		
$20\bar{2}$			2.581	1		
061	2.575	12	2.565	10		
$35\bar{1}$	2.554	8				
002	2.552	11				
061					2.552	8
331					2.541	3
$26\bar{1}$					2.518	7
002			2.514	7		
$26\bar{1}$			2.498	5		
$31\bar{2}$					2.489	2
$26\bar{1}$	2.476	3				
002					2.466	3
$31\bar{2}$			2.443	3		
112	2.391	4				
$31\bar{2}$	2.391	2				
112			2.332	3		
351	2.294	2				
112					2.270	3

Details of unit cell and structural models are given in Table 2

both, as the results of analyses show. The differences in scattering factor are insufficient to make it worth distinguishing between Al and Si or between Al and Mg.

Calculated powder-patterns are given in Tables 3 and 4 for the orthorhombic and monoclinic structural models whose atomic coordinates and unit cells are given in Tables 1 and 2. Powder patterns were calculated for structural models in which the displacement across each octahedral sheet ranges from *c*/4, *via* the idealized displacement *c*/3, to 5*c*/12, these being considered the probable limits if the cation coordination and bond distances are to be reasonable. Figures 3 and 4 illustrate powder patterns simulated from the calculated ones assuming a Gaussian peak profile with a full width at half maximum (FWHM) equal to 0.3° 2θ; in the observed patterns described by Chisholm (1990), the FWHM varies from 0.2 to 0.6° 2θ, with an average value just over 0.3°.

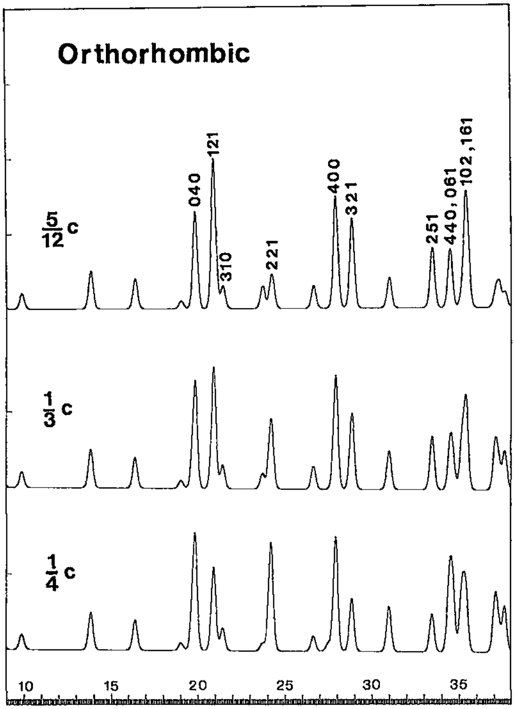

FIG. 3. Calculated powder-patterns for orthorhombic structural models with shifts of 5*c*/12, *c*/3 and *c*/4 at each octahedral sheet. The pattterns were drawn for a 2θ of 9–38° (Cu$K\bar{\alpha}$ radiation) using the calculated intensities and *d*-values from Table 3 and Gaussian peak profiles with a FWHM of 0.3° 2θ. The first reflection at low angle, 110, is omitted, as its intensity is off scale. The reflections occur in the same positions, and the *hk*0 reflections have the same intensities, for all the structural models. The intensities of reflections *hkl* with $l \neq 0$ vary with the shift at the octahedral sheet, this being most obvious for 121, 221, 321, 251, 061 and (102 + 161).

In all the calculated patterns, the strongest line, 110 at 10.4 Å, is six or seven times more intense than any other; this line is not shown in Figures 3 and 4. Apart from the 110 line, the powder patterns of palygorskite are expected to be generally rather weak. The low-angle region consists of *hk*0 reflections, and 400 and 440 are prominent at higher angles. Reflections of the type *hk*0 make up over one-third of the pattern out to 2.5 Å. The intensities of the *hk*0 reflections are the same for both the orthorhombic and monoclinic structural models, the projection down [001] being the same. The *hk*0 intensities also are the same whatever the displacement across the octahedral sheet, which has no effect on the projection of the structure down [001].

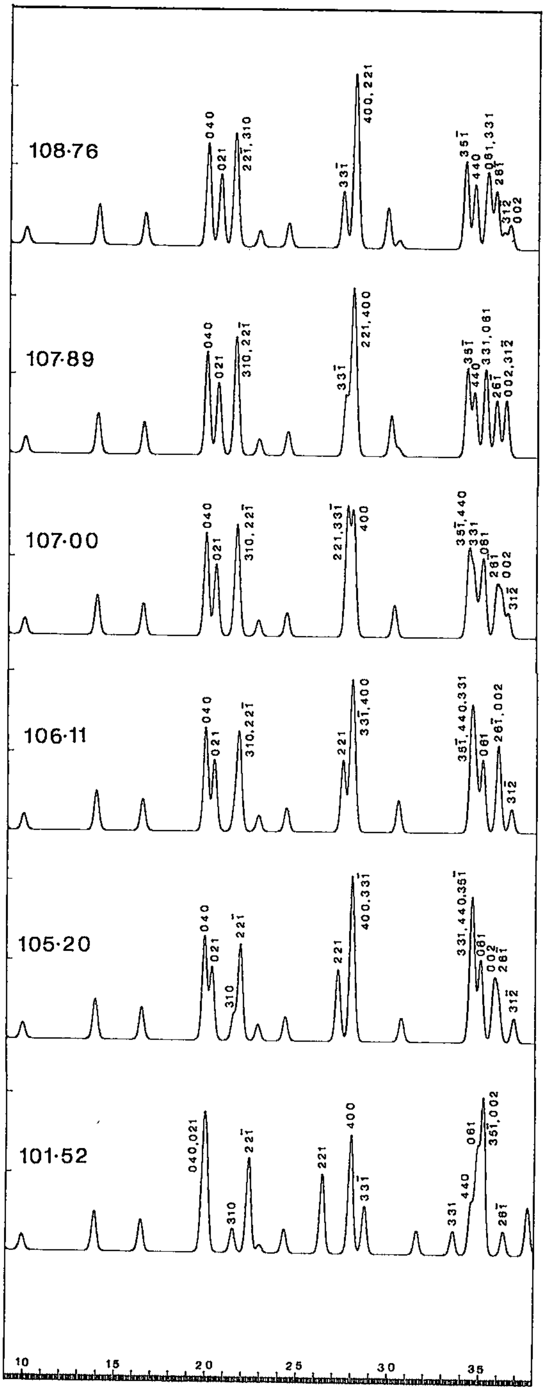

FIG. 4. Calculated powder-patterns for monoclinic structural models with β values of 108.76, 107.89, 107.00, 106.11, 105.20 and 101.52°, corresponding to shifts of $5c/12$, $19c/48$, $3c/8$, $17c/48$, $c/3$ and $c/4$ at each octahedral sheet. The patterns were drawn for the 2θ interval 9–38° (Cu$K\bar{\alpha}$ radiation) using calculated intensities and d-values as in Table 4 and Gaussian peak profiles with a FWHM of 0.3° 2θ. The first reflection at low angle, 110, is omitted, as its intensity is off scale. Differences in the structural model have very little effect on the intensities of the reflections. The d-values for $hk0$ reflections are the same for all models, and these reflections can be used as points of reference. The different β angles give rise to differences in the position of reflections hkl with l ⊙ 0, this being most obvious for 021, $22\bar{1}$, 221, $33\bar{1}$, 331, $35\bar{1}$, 061, 002, $26\bar{1}$, $31\bar{2}$. (Where peaks overlap, the indices are given in order with those for the longest d-value, *i.e.*, lowest 2θ, first).

The d-values for the orthorhombic structural models are all the same for the particular unit-cell adopted (Table 3, Fig. 3). Different displacements across the octahedral sheet are revealed by their effect on the intensity of reflections with l ⊙ 0, this being most marked for 121, 221, 321, 251, 061, 102, 161 (Table 3, Fig. 3).

For the monoclinic structural models, different displacements across the octahedral sheet have little effect on the intensity of reflections with l ⊙ 0 (Table 4) since their effect on the z-coordinates of the atoms is small. But different displacements at the octahedral sheet give rise to changes in β and, for a given $d(100)$, in a, and these in turn change the d-values of reflections with l ⊙ 0. For the range of displacements considered, their influence on d-values is revealed by changes in the proximity of reflections and even by changes in the sequence in which they occur (Table 4, Fig. 4). As examples, note the groups (i) 040, 021, 310 and $22\bar{1}$; (ii) 221, 400 and $33\bar{1}$; (iii) 331, 440, $35\bar{1}$, 061, 002, $26\bar{1}$, and $31\bar{2}$; in each of which the $hk0$ reflections act as markers with the same d-value for all the structural models.

Triple- and single-chain structure models

Powder patterns for structure models of palygorskite with alternate triple and single chains have been calculated but are not tabulated in full. It is sufficient to note that they are strikingly different from those for structures with double chains. The strongest reflections are [d (in Å), (hkl), (I)]: 12.78(100)(100), 10.40(110)(82), 7.33(120)(44) for both the "monoclinic analogue" with a β of 105.20° and the "orthorhombic analogue" with a β of 90°. The monoclinic analogue only has an additional strong line 3.281(221)(44). There are many other differences in the intensities of the reflections compared with the calculated patterns for the double-chain structure models.

COMPARISON WITH OBSERVED POWDER-PATTERNS

Observed powder-patterns from specimens of palygorskite (Bradley 1940, Christ *et al.* 1969, Smith & Norem 1986, Chisholm 1990) do not resemble the calculated powder-patterns for the structural models with triple and single chains of the kind proposed by Gard & Follett (1968). The observed patterns lack the strongest line, having *d* = 12.8 Å, expected for such structural models. The strongest line with *d* = 12.8 Å might just conceivably be mistaken for the intense 110 line of sepiolite (*d* = 12.05 - 12.3 Å, Brindley 1959). Smith & Norem (1986) have reported sepiolite as an impurity in some of their palygorskite specimens, but it has been reliably identified from several lines in the pattern.

The observed powder-patterns show no evidence for the existence of palygorskite with either a monoclinic or an orthorhombic structure of the type proposed by Gard & Follett (1968). This type of structure also was rejected by Drits & Sokolova (1971) since it failed to fit the intensity data in their structure determination. Further comparisons are confined to powder patterns calculated for the monoclinic and orthorhombic double-chain structures of Bradley (1940) and Preisinger (1963).

The powder data of Christ *et al.* (1969) and Chisholm (1990) show that the main differences between the powder patterns of different specimens of palygorskite lie in three "diagnostic regions": 4.0–4.5, 3.05–3.3 and 2.5–2.6 Å. These regions of the observed and calculated patterns are now compared in turn. The monoclinic unit-cell used here differs from those proposed by Christ *et al.* (1969) and, as a result, the indexing here differs from theirs.

The 4.0–4.5 Å regions of observed and calculated patterns are compared in Table 5; calculated patterns are illustrated in Figure 5 and may be compared with observed patterns from a selection of the specimens examined by Chisholm (1990) in Figure 6. The line at 4.24 Å is observed in all but one of the patterns tabulated by Chisholm (1990) and four of the five patterns of Christ *et al.* (1969). This line cannot be explained by the calculated patterns for monoclinic structures, but does match the 121 line on the calculated patterns for orthorhombic structures (Table 5, Fig. 5). It therefore implies the presence of orthorhombic palygorskite. On the other hand, a line at 4.328–4.366 Å is observed on five out of eight patterns tabulated by Chisholm (1990) and in the specimen from Metaline Falls of Christ *et al.* (1969). This line is inconsistent with the calculated patterns for the orthorhombic structure, but fits the 021 line for some monoclinic structures (Table 5, Fig. 5). It must imply the presence of monoclinic palygorskite. The observed *d*-values for this reflection suggest that *β* must lie in the range 106–108° (Table 5).

The 310 line on the calculated patterns for both orthorhombic and monoclinic forms is too weak to account for the observed intensity in the 4.13 Å reflection (Table 5, Fig. 5). Nor will it explain the presence of a doublet on some of the patterns of

TABLE 5. COMPARISON OF 4.0-4.5 Å REGIONS OF OBSERVED AND CALCULATED POWDER-PATTERNS

Observed Patterns

Chisholm (1990) d range	Chisholm (1990) I range	Christ et al. (1969) d range	Christ et al. (1969) I range
4.434-4.457	[100]	4.457-4.481	20-31
4.328-4.366	[0-20]	MF 4.364	4
4.230-4.250	[0-85]	4.240-4.260	0-34
** 4.126,4.156	[65,25]		
4.110-4.129	[40-85]	4.127-4.158	2-17
** 4.110,4.129	[65,45]		

** For two specimens, there appeared to be two lines with the d values and intensities shown.
MF This line was observed only from the specimen from Metaline Falls.

Calculated Patterns

Orthorhombic			Monoclinic (for β values below)						
				105.20		106.11	107.00	107.89	108.76
hkl	d	I	hkl	d	I	d	d	d	d
040	4.472	13 [100]	040	4.472	13 [100]	4.472	4.472	4.472	4.472
			021	4.383	9 [70]	4.368	4.353	4.336	4.320
121	4.246	20 [155]							
			$22\bar{1}$		12 [90]				4.165
310	4.144	3 [25]	310	4.143	3 [25]	4.143	4.143	4.143	4.143
			$22\bar{1}$	4.074	12 [90]	4.098	4.120	4.142	

Intensities in square brackets normalised to I(040) = 100 corresponding to those in Chisholm (1990).

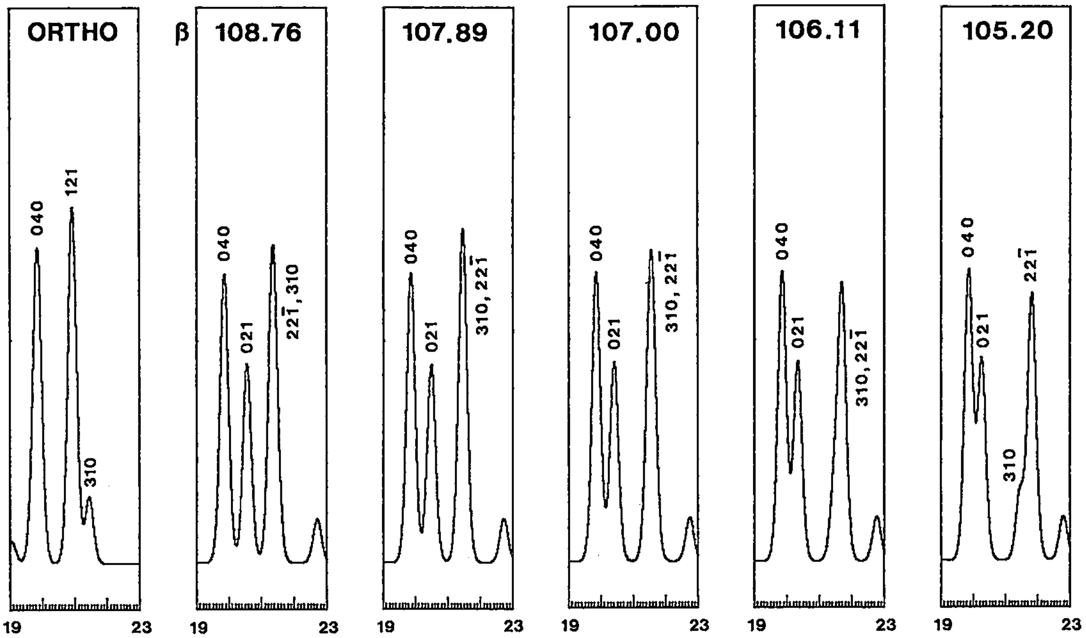

FIG. 5. The 19–23° 2θ range (Cu$K\bar{\alpha}$ radiation), showing the 4.0–4.5 Å diagnostic region, of calculated powder-patterns (Gaussian peak profiles, FWHM = 0.3° 2θ) for idealized orthorhombic palygorskite (with a $c/3$ shift at each octahedral sheet, and for monoclinic palygorskite as in Figure 4. (Where peaks overlap, the indices are given in order with those for the longest d-value, *i.e.*, lowest 2θ, first). The 121 reflection of the orthorhombic form is characteristic of that form; the 021 and strong $22\bar{1}$ reflections are characteristic of the monoclinic form.

Chisholm (1990). A $22\bar{1}$ line from a monoclinic structure will explain the observed intensity if it overlaps or nearly overlaps the 310 line, as it will if β lies in the range 106–108° (Table 5, Fig. 5).

Generally, the observed 021 line for the monoclinic form seems to be rather weaker than would be expected from the calculated patterns (Figs. 5, 6). Atomic coordinates that depart from the idealized values may account for some differences between observed and calculated intensities such as this one. But the intensities in the powder pattern are unlikely to be changed so much as to invalidate the use of the calculated patterns to identify the observed reflections and relate them to the phases present.

The 3.05–3.3 Å regions of observed and calculated patterns are compared in Table 6; the calculated patterns are illustrated in Figure 7 and may be compared with the observed ones in Figure 1 of Chisholm (1990) (in which the direction of increasing 2θ is reversed relative to Figure 7 here). The 321 line (at about 3.09 Å) of orthorhombic palygorskite indicates the presence of that form, as there is no corresponding line in the calculated patterns for monoclinic structures (Table 6, Fig. 7). Neither this 3.09 Å line nor the 4.24 Å line of orthorhombic palygorskite is observed in the pattern of the specimen from Metaline Falls (Christ *et al.* 1969), which must have been almost pure monoclinic palygorskite. Sample 7B of Chisholm (1990) must contain very little orthorhombic palygorskite, as it has only a very weak 3.091 Å line and no 4.24 Å line. Samples 3A and 3B do not show the 3.09 Å line of the orthorhombic form, although the lines at 4.25 and 2.54 Å (see below) are present; this anomaly is unexplained.

Calculated patterns for orthorhombic structures show only a single strong 400 line at 3.195 Å, with no second strong line near 3.22 Å (Table 6, Fig. 7). This second strong line, which is found on all observed powder-patterns, must be attributed to the presence of monoclinic palygorskite; to fit the observed d-values, the angle β must lie in the range 106–108° (Table 6, Fig. 7). The appearance of the lines at about 3.2 Å is sensitive to the angle β. For $\beta \approx 106°$, the $33\bar{1}$ and 400 reflections will overlap, with 221 separated from them on the low-2θ side. The high-angle reflection will be the stronger of the two (Fig. 7). The high angle reflection also will be the stronger of the two for $\beta \approx 108°$, but the positions of the $33\bar{1}$ and 221 reflections are now interchanged: 221 and 400 overlap, with $33\bar{1}$

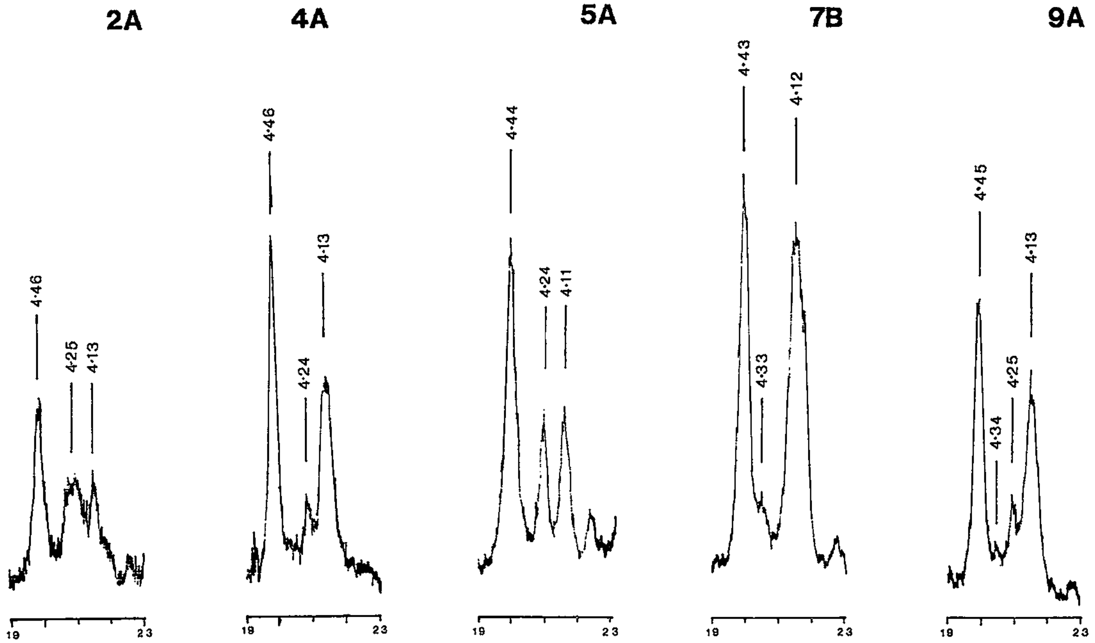

FIG. 6. The 19–23° 2θ range (Cu$K\alpha$ radiation), showing the 4.0–4.5 Å diagnostic region in some observed powder-patterns of palygorskite specimens examined by Chisholm (1990). The patterns were chosen to show the range of variation observed in this region. Details of the numbered specimens are given in Table 1 of Chisholm (1990). The reflection at 4.24–4.25 Å matches the 121 line of the orthorhombic form; that at 4.11–4.13 Å matches the 22$\bar{1}$ of the monoclinic form overlapping the 310 of both forms. The reflection at 4.33–4.34 Å matches 021 of the monoclinic form but is much weaker than predicted (compare Fig. 4). All the specimens shown appear to contain both orthorhombic and monoclinic forms in varying proportions, except for 7B, which seems to contain the monoclinic form only.

separated on the low-angle side (Fig. 7). It is therefore possible to have patterns in which the reflections at about 3.2 Å look similar but actually have different components, with different indices. This ambiguity makes it difficult to find a satisfactory basis for the assignment of indices and therefore for the determination of reliable cell-dimensions for the orthorhombic and monoclinic forms. If $\beta \approx 107°$, the 221 and 33$\bar{1}$ reflections overlap at 3.23 Å and together have an intensity comparable with that of the 400 reflection (Fig. 7). As a result, of the two reflections in the 3.2 Å region, the one at lower 2θ may be stronger for some specimens, and the one at higher 2θ, stronger for others. Departures from the idealized structures may lead to a higher structure-factor for 33$\bar{1}$ or 221 or both, or to a lower structure-factor for 400. It is also unlikely that the orthorhombic and monoclinic forms of palygorskite will have exactly the same cell dimensions. As a result, the 400 reflection of the orthorhombic form may not overlap the 400 of the monoclinic form. Published cell-dimensions for orthorhombic and monoclinic forms (Preisinger 1963, Christ *et al.* 1969, Drits & Sokolova 1971) show sufficient variations to suggest that 400 of the orthorhombic form may overlap 33$\bar{1}$ or 221 of the monoclinic form, and so lead to intensities that differ from those calculated here for exactly related unit-cells. The proximity of d-values for the relevant reflections also means that the appearance of this part of the powder pattern depends on how well those reflections are resolved, *i.e.*, on the breadth of the reflections, which in turn is a function of particle size and morphology and of the degree of structural order.

The variations observed in the 3.05–3.30 Å region are qualitatively consistent, like those in the 4.0–4.5 Å region, with the presence of orthorhombic and monoclinic forms of palygorskite, the latter having a β of approximately 106–108°.

The 2.5–2.6 Å region (33–36° 2θ) of the calculated patterns for orthorhombic and monoclinic structures contains strong reflections and shows differences for the two structures and for different values of β in the monoclinic form (Figs. 3, 4). It is therefore not surprising that different specimens show differences in this region of their powder pattern. Comparing the calculated patterns for orthorhombic and monoclinic palygorskites (Tables 3, 4), a reflection near 2.536 Å can be identified as 161 of the orthorhombic form, of which it must be characteristic since there

TABLE 6. COMPARISON OF THE 3.05–3.3 Å REGIONS OF OBSERVED AND CALCULATED POWDER-PATTERNS

Observed Patterns			
Chisholm (1990)		Christ et al. (1969)	
d range	I range	d range	I range
3.207–3.240	[25–270]	3.223–3.250	14–34
3.154–3.207	[80–175]	3.170–3.206	12–23
3.073–3.112	[5–35]	3.087–3.104	11–23

Calculated Patterns

Orthorhombic			Monoclinic (with β values below)														
			105.20			106.11			107.00			107.89			108.76		
hkl	d	I	hkl	d	I	hkl	d	I	hkl	d	I	hkl	d	I	hkl	d	I
311	3.243	<1[<10]	221	3.281	9[70]	221	3.257	9[70]	221	3.233	9[70]	33$\bar{1}$	3.248	7[55]	33$\bar{1}$	3.267	7[55]
									33$\bar{1}$	3.228	7[55]						
						33$\bar{1}$	3.209	6[45]				221	3.210	9[70]			
400	3.194	15[115]	400	3.194	15[115]	400	3.194	15[115]	400	3.194	15[115]	400	3.194	15[115]	400	3.196	15[115]
			33$\bar{1}$	3.189	6[45]										221	3.187	8[60]
321	3.094	10[75]															

Intensities given in square brackets are normalised to I(040) = 100 corresponding to those in Chisholm (1990).

is no corresponding reflection in the calculated patterns of monoclinic palygorskite. A reflection near 2.50–2.51 Å must be characteristic of the monoclinic form, being 26$\bar{1}$, possibly overlapped by 002 of that form (with β in the range 106–108°) and having no corresponding reflection in the calculated pattern of the orthorhombic form. On this basis, most of the palygorskite specimens

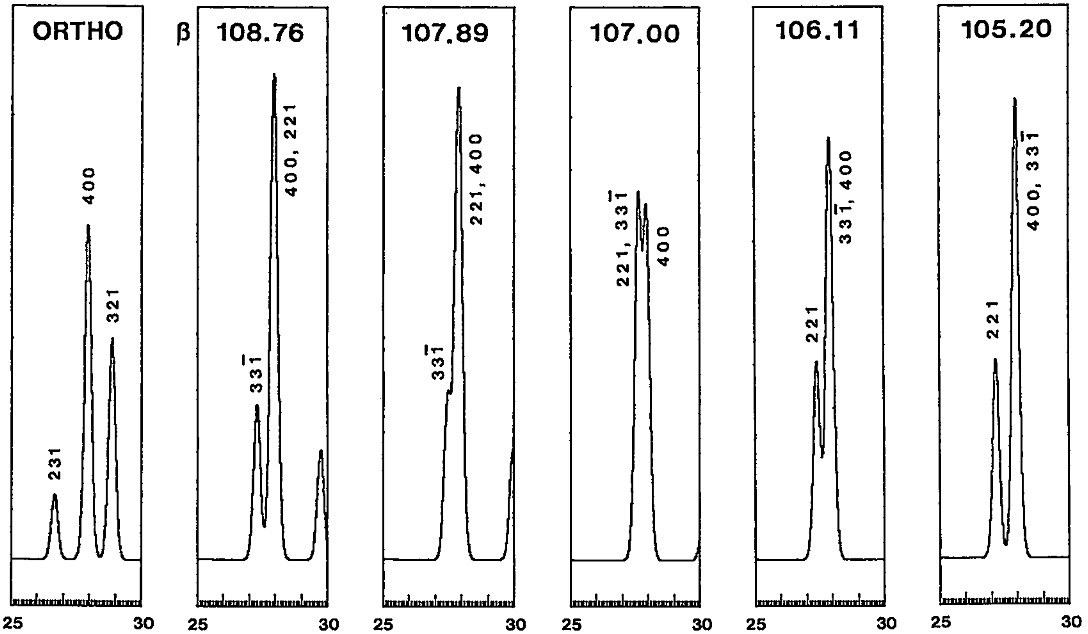

FIG. 7. The 25–30° 2θ range (Cu$K\bar{\alpha}$ radiation), showing the 3.05–3.3 Å diagnostic region, of calculated powder-patterns (Gaussian peak profiles, FWHM = 0.3° 2θ) for idealized orthorhombic palygorskite (with *c*/3 shift at each octahedral sheet) and for monoclinic palygorskite as in Fig. 4. (Where peaks overlap, the indices are given in order with those for the longest *d*-value, *i.e.*, lowest 2θ, first). The 321 line of the orthorhombic form is characteristic of that form. Signs of two lines close together near 400 indicate the presence of the monoclinic form; the exact appearance of this region is sensitive to the value of β in the range 106–108°. Comparison with Fig. 1 of Chisholm (1990) shows that most of the specimens contain both monoclinic and orthorhombic palygorskite except for 7B, which appears to consist of the monoclinic form only.

studied by Chisholm (1990) contain both orthorhombic and monoclinic forms. However, reflections in this region overlap on many patterns, and on some it is hard to identify the component reflections making up the overall profile. Specimen 7 does not show the 121 and 161 lines (expected at 4.246 and 2.536 Å) of the orthorhombic form, and the 321 line of that form at 3.091 Å is weak; this specimen evidently contains only a small proportion of the orthorhombic form. Samples 2A, 2B and 9A of Chisholm (1990) do not show the 161 line of the orthorhombic form, although the 121 and 321 lines are observed; variations in cell dimensions will not account for this anomaly, which remains unexplained and is inconsistent with the interpretation given here. The specimen from Metaline Falls of Christ *et al.* (1969) does not show the 121, 321 or 161 lines of orthorhombic palygorskite and appears to be pure monoclinic palygorskite; there are insufficient non-overlapping reflections with $l \neq 0$ to refine a *C*2/*m* cell with the data for this specimen. The specimen from the same locality studied by Chisholm (1990) is impure. The four other specimens studied by Christ *et al.* (1969) appear to contain both orthorhombic and monoclinic forms.

CONCLUSIONS

Orthorhombic and monoclinic structural models proposed for palygorskite have been considered. For near-octahedral coordination of the cations, the monoclinic form must have a β close to 105.2°, which is not far from the value of 107° found by Drits & Sokolova (1971). Monoclinic cells with smaller values of β proposed by Zvyagin *et al.* (1963) and Christ *et al.* (1969) may represent alternative choices of axes in the monoclinic system, as noted by Bailey (1980).

Structures with a mixture of single and triple chains, of the kind proposed by Gard & Follett (1968), do not occur in any of the palygorskite specimens for which powder data have been published. The observed powder-patterns are completely unlike those expected for structures of this type.

Powder patterns calculated for structures with double chains, the orthorhombic form having space group *Pbmn* (Preisinger 1963) and the monoclinic form *C*2/*m* (Bradley 1940, Drits & Sokoleva 1971), correlate well with the observed powder-patterns. The powder patterns include a high proportion of *hk*0 reflections, which are common to both orthorhombic and monoclinic forms of palygorskite. Nevertheless, each form has some reflections (with $l \neq 0$) not shown by the other, which can be used for discrimination. The following lines indicate the presence of orthorhombic palygorskite (indices in brackets): 4.25 Å (121), 3.09 Å (321), 2.536 Å (161). Lines at 4.36 Å (021) and 2.51 Å (26$\bar{1}$ perhaps overlapped by 002) are attributed to monoclinic palygorskite, though the first may not always be observed. In addition, two lines near 3.20 Å indicate the presence of the monoclinic form, as a single line [3.19 Å (400)] only is expected for the orthorhombic form. [The 231 line at 3.334 Å is not suitable for identification of orthorhombic palygorskite as it is too close to the strongest line of quartz, which is a fairly common impurity.]

Most of the observed powder-patterns described by Chisholm (1990) and given by Christ *et al.* (1969) have lines characteristic of both forms. The variations among different samples of palygorskite can, to a large extent, be accounted for by varying proportions of the two forms. The specimen from Metaline Falls described by Christ *et al.* (1969) seems to be pure monoclinic palygorskite, and sample 7B of Chisholm (1990), from Warren Quarry, Enderby, Leicestershire, is almost pure monoclinic palygorskite. No examples with powder patterns corresponding to pure or nearly pure orthorhombic palygorskite have been encountered.

The observed *d*-values of reflections from the monoclinic form suggest that β lies in the range 106–108°, which agrees well with the 107° of Drits & Sokolova (1971), but is rather higher than the 105.20° expected for the idealized structure. A value of β in the range 106–108° implies a relative displacement of 0.35*c* – 0.40*c* of the chains of tetrahedra on either side of the octahedral sheet, which is a little higher than the ideal value *c*/3. In magnesian clinopyroxenes and clinoamphiboles, the corresponding shift also is close to the ideal *c*/3. But in other monoclinic pyroxenes and amphiboles, the shift lies in the range *c*/4 – *c*/3. In those minerals, the shift and the angle β are related to the size of the *M*2 or *M*4 cations through which adjacent silicate chains are linked (Whittaker 1960a, b). Silicate chains in palygorskite link to form corrugated sheets by sharing oxygen atoms. A different mechanism must operate to control the shift across the octahedral sheet. Precise information on the atomic positions in palygorskite will be required to understand what that mechanism is.

The *d*-values for monoclinic palygorskite depend on β; the sequence in which certain reflections occur is sensitive to variations in β even in the narrow range 106–108°. This can alter the way in which reflections overlap near 3.20 Å on the powder pattern and explains, at least partly, the variations in that region, which are not simply related to the proportion of the monoclinic form. With this additional factor taken into account, only a few anomalies in individual powder-patterns and specimens remain.

All the major variations in powder patterns shown by different specimens of palygorksite can be explained, at least qualitatively, by the presence of orthorhombic and monoclinic forms in varying proportions and by the effect of variations in the β angle of the monoclinic form. The coexistence of two related structures with space groups *Pbmn* and *C2/m* explains how confusion arose when attempts were made to index the powder pattern in terms of a single phase and how different unit-cells and space groups came to be proposed for palygorskite.

It is tempting to consider profile refinement (total pattern fitting) as the next step in the study of the palygorskite structures in greater detail. But the presence of two related phases and the effect of β on the sequence in which reflections occur make it difficult to identify particular reflections and their components and so derive reliable unit-cells for profile refinement. A starting model with unit cells for the orthorhombic and monoclinic forms will have a very large number of parameters and may indeed give convergence but, if so, would the refinement be approaching the true minimum or some other local minimum? To be sure of refinement to the true minimum, independent evidence is required to show that the starting model is correct, particularly in its cell dimensions. Samples of palygorskite in which one of the forms is pure or nearly pure seem to offer the best prospect of successful profile refinement, but such samples appear to be scarce.

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