Canadian Mineralogist
Vol. 30, pp. 355-365 (1992)

THE NUMBER OF SECTORS IN POLYGONAL SERPENTINE

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

ABSTRACT

In their electron microscope study of polygonal serpentine (Povlen-type chrysotile), Yada & Wei (1987) noted that the number of sectors in a complete polygonal section was restricted to 15 or 30 in the majority of cases. This observation suggests an ideal geometrical model for the growth of equal polygonal sectors. The model depends first on the incorporation of five extra *b*-repeats in the perimeter of each new layer added to the polygonal structure, just as five extra *b*-repeats must be incorporated in the circumference of each new layer added to the cylindrical structure of ordinary chrysotile. Further, this addition of five extra *b*-repeats is accomplished by the addition of whole numbers of extra $Mg(O,OH)_6$ octahedra to the new layer in each sector. These two requirements are met with minimal strain across sector boundaries by polygonal microstructures with 15 or 30 sectors, and so account for the observations of Yada & Wei (1987).

Keywords: serpentine, polygonal serpentine, chrysotile, Povlen-type chrysotile, lizardite.

SOMMAIRE

Dans leur étude de la serpentine polygonale (dite de type Povlen) par microscopie électronique, Yada & Wei (1987) ont découvert que le nombre de secteurs dans une section polygonale complète se limite à 15 or 30 dans la majorité des cas. Ce fait mène à l'hypothèse d'un modèle géométrique idéal pour la croissance de secteurs polygonaux égaux. Le modèle repose d'abord sur l'insertion de cinq périodes supplémentaires le long de *b* dans le périmètre de chaque nouveau feuillet ajouté à la structure polygonale, tout comme cinq périodes supplémentaires doivent être incorporées le long de *b* à la circonférence de chaque nouveau feuillet ajouté à la structure cylindrique du chrysotile ordinaire. De plus, cette addition de cinq périodes *b* s'accomplit par l'addition de nombres entiers d'octaèdres $Mg(O,OH)_6$ supplémentaires au nouveau feuillet dans chaque secteur. Ces deux conditions sont satisfaites avec un minimum de contrainte transversale aux bordures des secteurs des microstructures polygonales avec 15 ou 30 secteurs, expliquant ainsi les observations de Yada & Wei (1987).

(Traduit par la Rédaction)

Mots-clés: serpentine, serpentine polygonale, chrysotile, chrysotile de type Povlen, lizardite.

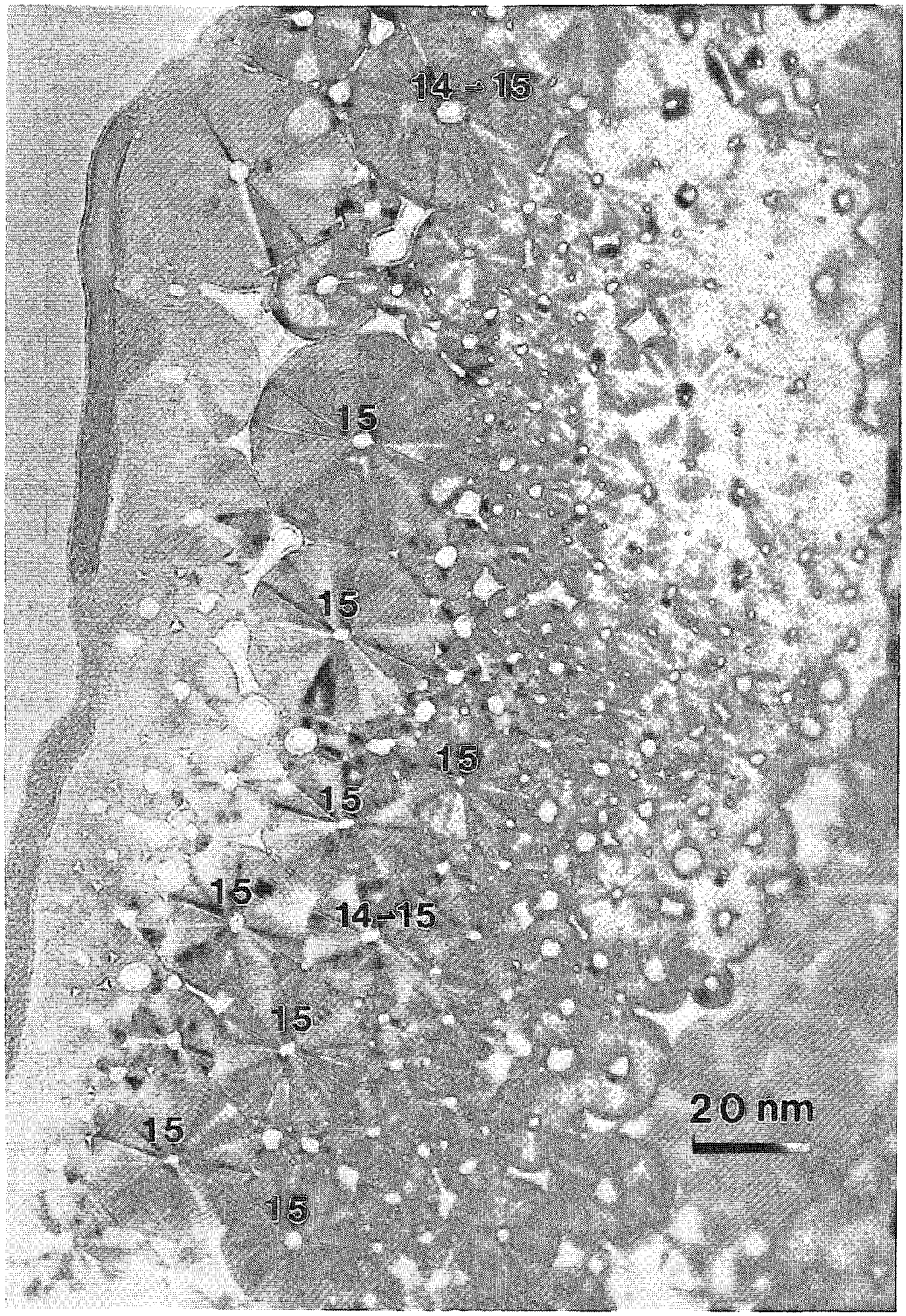
INTRODUCTION

Anomalous X-ray-diffraction and electron-diffraction patterns have been described from poorly aligned splintery and lath-like "chrysotile" (Eckhardt 1956, Zussman *et al.* 1957, Krstanović & Pavlović 1964, 1967). The patterns show a series of sharp *hkl* reflections on *h* odd layer lines instead of the *hk*0 reflections with diffuse tails characteristic of diffraction by cylindrically wrapped layers in chrysotile. Specimens that give the anomalous diffraction patterns are often referred to as "Povlen-type chrysotile" following Krstanović & Pavlović (1964).

A detailed interpretation of the diffraction patterns of Povlen-type chrysotile led Middleton & Whittaker (1976) to conclude that the anomalous features result from a polygonal tubular structure, possibly with a normal cylindrical core. Their interpretation received immediate confirmation from a study of ion-thinned samples of serpentinite by transmission electron microscopy; this study revealed large fibers (with diameters up to 0.1 μm) with a structure of flat layers stacked in sectors to form polygonal prisms, either alone or with a core of cylindrical chrysotile (Cressey & Zussman 1976). More examples of similar and more complex structures with flat layers stacked in sectors have been observed in subsequent TEM studies (Cressey 1979, Wei & Shaoying 1984, Mellini 1986, Yada & Wei 1987, Mitchell & Putnis 1988).

The polygonal microstructure raises a problem of nomenclature. The name *lizardite* is used for the

*Present address: Health & Safety Executive, Occupational Medicine and Hygiene Laboratory, Broad Lane, Sheffield S3 7HQ, England.


14 → 15
15
15
15
15
15
14→15
15
15
15
20 nm

serpentine polymorph with flat layers, *chrysotile* for that with cylindrical or spiral layers, and *antigorite* for that with undulating layers. The stacking sequences are different for the flat layers in lizardite and the curved layers in chrysotile (Wicks & Whittaker 1975). The flat layers in Povlen-type chrysotile suggest that the name *lizardite* should be adopted, but Cressey & Zussman (1976) have described sections with polygonal layers around the outside of a core with cylindrical layers. The intensities of the 20*l* reflections from monoclinic Povlen-type chrysotile indicate a stacking sequence of the kind found for the curved layers in chrysotile-$2M_{cl}$, but those of orthorhombic Povlen-type chrysotile indicate the sequence found for the flat layers of lizardite-$2H_1$. The more general term "polygonal serpentine" was adopted by Cressey & Zussman (1976) and avoids any contradiction.

In their TEM study of a sample of Povlen-type chrysotile, Yada & Wei (1987) found that in most cases, the number of sectors making up a complete polygon section was confined to either 15 or 30. The present paper considers how their finding is related to the crystal structure of serpentine and the cylindrical wrapping of the layers in chrysotile.

Observations of Sectors in Polygonal Serpentine

In their study of Povlen-type chrysotile from the Guangyuanpu asbestos mine, Sichuan Province, China, Yada & Wei (1987) were able to obtain electron micrographs of more than thirty complete polygonal cross-sections. They reported that more than half of these have 15 sectors, almost a quarter have 30, and in the remainder, the number of sectors is "not explicit but close to 15 or 30". Figure 1 (kindly provided by Dr. Yada) shows several examples of polygonal cross-sections with 15 sectors; for some cross-sections, the sectors and their boundaries are not easily recognizable, and the exact number of sectors is uncertain, but close to 15. A polygonal cross-section with 30 sectors is illustrated in Yada & Wei (1987) and Wicks & O'Hanley (1988).

These observations are supported by other published electron micrographs: the polygonal sections in Figures 2 and 7 of Cressey & Zussman (1976) both have 15 sectors. Of the several polygonal sections in Figure 9 of Cressey (1979), two have 15 sectors, and others appear to have 14, 15 or 16. The exact number of sectors is uncertain in some cases because there is little difference in contrast at the boundaries between adjacent sectors. The two polygonal sections in Figure 9 of Mitchell & Putnis (1988) each have approximately 30 sectors.

Although it has not been specifically pointed out, published micrographs of polygonal sections show that the sectors are approximately uniform; the sector angles do not vary very much, although they are not all exactly equal. In the two examples taken from Cressey & Zussman (1976), both with 15 sectors, the sector angles range from 20 to 30° (with a standard deviation of ± 3°) in their Figure 2, and from 18 to 30° (with a standard deviation of ± 3°) in their Figure 7. These measured sector angles lie within approximately two standard deviations of the ideal 24° as expected if the sector angle were a random variable. In another example [Plate 5b of Wei & Shaoying (1984)], also with 15 sectors, the sector angles range from 17.5 to 30.5° with a standard deviation of ± 3.5°. And in the example with 30 sectors illusrated by Yada & Wei (1987), the sector angles range from 8 to 17° with a standard deviation of ± 2.5°.

In attempting to measure the sector angles of complete polygonal sections, it became apparent that the sectors are in some cases only approximately concentric. They do not always have a common center at a single point. Some of the variability in measured "sector" angles may be related to eccentricity. Examples of incomplete polygonal structures [Fig. 3 of Cressey & Zussman (1976) and particularly Fig. 5 of Mellini (1986)] show much greater variations in "sector" angle, probably in part for the same reason.

If the fiber section is not exactly normal to the fiber axis, or if the section is not normal to the electron beam, the sector angles observed will differ from their true values, depending on the direction and amount of the tilt. This too may contribute to the observed variability of the sector angles measured.

Nevertheless, for complete polygonal sections, the sector angles are approximately equal. Uniform sector angles are assumed in the main discussion

FIG. 1. Transmission electron micrograph of polygonal serpentine showing cross-sections of many fibrils. Several fibrils with 15 sectors are visible. In some other fibrils, it is difficult to recognize all the sectors and their boundaries, but the number is close to 15. [Previously unpublished micrograph kindly provided by Dr. Keiji Yada, Research Institute for Scientific Measurements, Tohoku University, Sendai, Japan].

that follows, and possible scope for variations in sector angle is considered later.

Sector Angles, Sector Boundaries and Lateral Addition to Layers Stacked in Sectors

An idealized form of polygonal structure with equal sectors is the simplest to consider. Let n be the number of sectors in such a polygonal structure. For $n = 15$ and $n = 30$, the sector angles are 24° and 12°, respectively. The radial planes bounding the sectors are very close to {061} and {0,12,1}, for which the angles $(0kl):(0\bar{k}l)$ are 23.68° and 11.97° respectively, based on a single-layer cell with a b of 9.2, a c of 7.325 Å, and a β of 93°16′ for chrysotile-$2M_{c1}$ (Whittaker 1956). [In considering the wrapping of layers, it is convenient to use a single-layer subcell with a c of 7.3 Å, although the true unit cells for chrysotile-$2M_{c1}$ and $2Or_{c1}$ contain two layers.] Fifteen sectors bounded by planes {061} or thirty sectors bounded by planes {0,12,1} would make up complete polygons with only minor strain due to misfit across each sector boundary.

The geometry of the polygonal microstructure can be related to the crystal structure and the modifications to it that are required in polygonal serpentine. Take the $n = 15$ case first and consider successive layers of a [100] projection bounded by (061) and (0$\bar{6}$1) (Fig. 2). Going outward from one layer, the next layer must extend an extra $b/6$ on each side of the normal to (001) (Fig. 2). This corresponds to the addition of one extra Mg–O octahedron to the brucite sheet, as there are six Mg atoms across the b repeat. The addition of two Mg–O octahedra, one on each side of the normal to (001), to successive serpentine layers (Fig. 2) gives a sector bounded by radial planes {061}. To maintain stoichiometry, it is necessary to add, on average, one SiO_4 tetrahedron to both sides of the serpentine layer at two out of three successive layers stacked in the sector. Figure 2 shows an example of one of a number of ways in which this might be done.

For the $n = 30$ case, going outward, each layer must extend an extra $b/12$ on each side of the normal to (001). This corresponds to the addition of half an $Mg(O,OH)_6$ octahedron to each side of the brucite sheet. It may mean either that an $Mg(O,OH)_6$ octahedron is added to both sides of every second layer (Fig. 3a), or that one octahedron is added at each successive layer alternately to the left-hand and right-hand edges (Fig. 3b). Random arrangements also will give rational indices for the boundary plane so long as, on average, half an octahedron is added to both sides of each successive layer. For stoichiometry, one SiO_4 tetrahedron must be added to both sides of the layer at one out of three successive layers (Fig. 3). Figures 3a and b each show an example of part of only one of the possible ways in which this might be done.

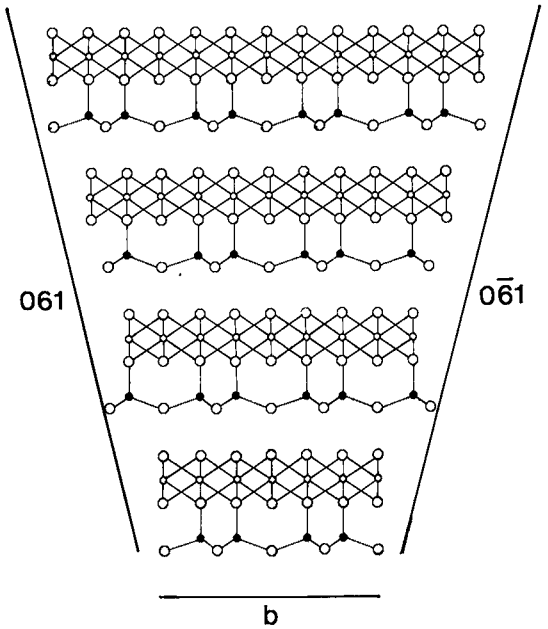


FIG. 2. Serpentine layers in one 24° sector of an idealized polygonal structure with 15 equal sectors in the complete polygon. In each new layer, one $Mg(O,OH)_6$ octahedron is added at each edge of the sector, corresponding to sector boundaries {061}. To maintain the serpentine composition, one SiO_4 tetrahedron also must be added at each edge of the sector at two out of three layers. The diagram shows only one of the possible ways in which this may be done. Small open circles Mg, small filled circles Si, large open circles O,OH.

The possibility that additions of octahedra are random may point to an explanation for variations in sector angle. Random incorporation of extra octahedra at some layers, or the failure to add octahedra, would lead to sector boundaries close to {061} or {0,12,1} but with irrational indices, and thus to sector angles that depart from the ideal values.

In order to minimize strain at the sector boundary, the boundary must be the same crystallographic plane in the two crystals that form the two adjacent sectors, *i.e.*, the boundary plane must be {061} or {0,12,1} in both, otherwise the radial spacings in the two crystals will not match along the boundary plane. But one may imagine a sector bounded on one side by a plane {061} and on the other by a plane {0,12,1}, for example, with a sector angle of 17.82°. Whereas this might explain

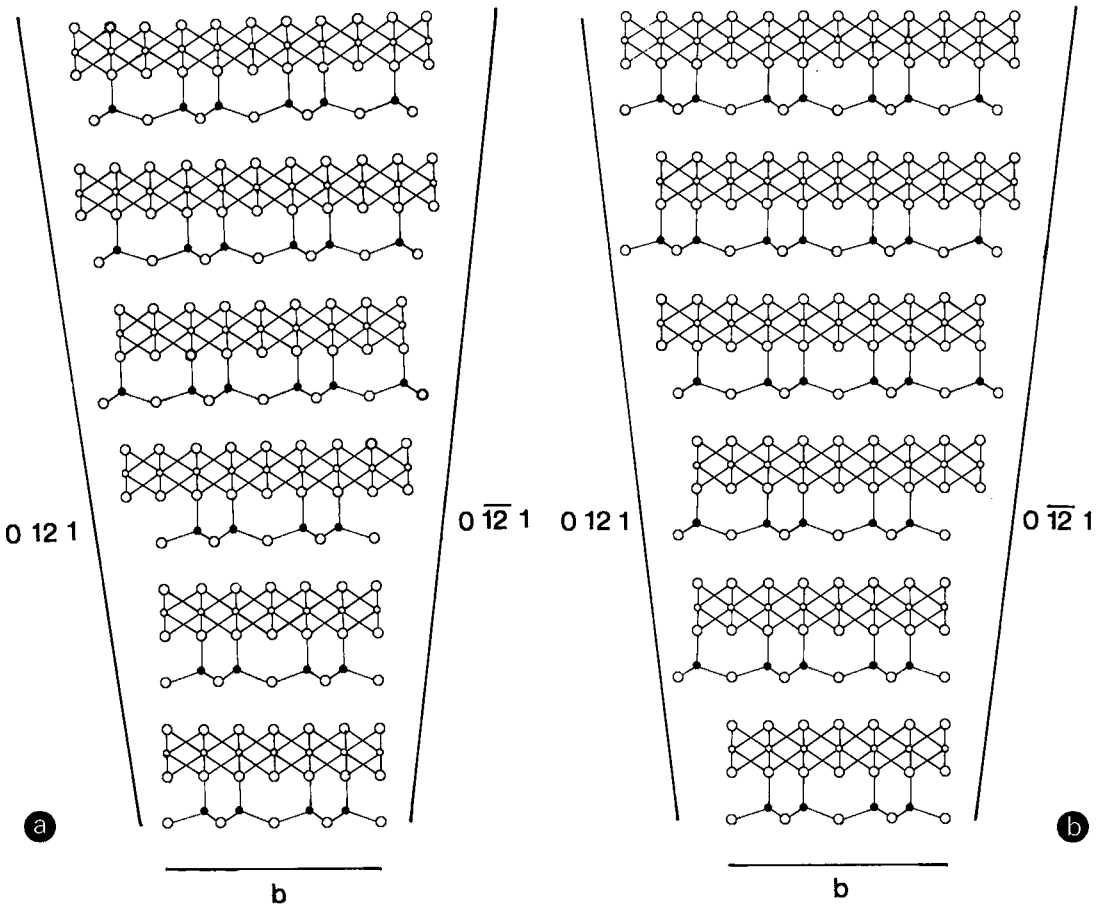


FIG. 3. Serpentine layers in one 12° sector of an idealized polygonal structure with 30 equal sectors in the complete polygon. At each new layer, on average, half an $Mg(O,OH)_6$ octahedron is added to each edge of the sector, corresponding to sector boundaries {0,12,1}. This may be done either (a) by adding one octahedron to both sides at every second layer, or (b) by adding one octahedron at each new layer alternately on the left-hand and right-hand edges of the sector. To maintain the serpentine composition, one SiO_4 tetrahedron must on average be added to each edge of the sector at one out of three layers. In (a), a SiO_4 tetrahedron is shown as being added to both edges of every third layer, but this is only one of the possible arrangements. Similarly, in (b), only one of the possible arrangements is shown, in this case the addition of a SiO_4 tetrahedron alternately to the left-hand and right-hand edges of the sector at two layers out of three. Small open circles Mg, small filled circles Si, large open circles O,OH.

some of the larger variations in sector angle, it would also lead to varying numbers of sectors in the complete polygon because the sector angles then are not all the same. But the observations of Yada & Wei (1987) show that the actual number of sectors is virtually confined to 15 or 30, which implies that the average number of octahedra added at successive layers must be the same in all the sectors. There is no structural requirement that this should be so. But, if the polygonal structure developed as an overgrowth on a nucleus of cylindrical chrysotile, the circular symmetry of that nucleus should lead to the development of equal sectors. Cases of a polygonal serpentine with a core of cylindrical chrysotile have been observed (Cressey & Zussman 1976, Mellini 1986, Mitchell & Putnis 1988), and the presence of such cores was inferred from diffraction evidence by Middleton & Whittaker (1976). But there are also examples of polygonal serpentine without a chrysotile core (Cressey & Zussman 1976). The large variations in sector angle for incomplete polygonal sections and

specimens in which the sectors do not have a common center may result from the lack of a nucleus with a circular cross-section or from some other lack of circular symmetry in the growth conditions.

An alternative explanation for the occurrence of 15 or 30 polygonal sectors might be provided by the addition of different numbers of octahedra to the two sides of each sector, giving two kinds of boundary plane. For $n = 15$, the first sector might be bounded by (010) and (03$\bar{1}$), the second by (031) and (010), the third by (010) and (0$\bar{3}$1), and so on. But the final plane of the fifteenth sector would be (0$\bar{3}$1) and would not match the (010) plane of the first sector. The indices of the first and last boundary plane would be the same for an arrangement with boundary planes alternately {010} and {061} for $n = 30$. The sector angle would then be (010):(061) = 11.84° instead of 11.97° where all the boundary planes are {0,12,1}. Sectors with two kinds of boundary plane would therefore fit together less well than sectors with only one. The lower strain energy would therefore favor arrangements with equal sectors and identical boundaries between sectors. On the high-resolution electron micrograph of Yada & Wei (1987), the sector boundaries are symmetrical with respect to the 001 lattice fringes and therefore all of the same kind.

The addition of octahedra to the Mg–O,OH sheets has been implicitly described in terms of regular arrangements of sectors that should have straight boundaries. Random arrangements also are possible so long as, on average, the correct numbers of octahedra are added equally to both sides of the sector. But such irregular arrangements would be expected to have sector boundaries with zig-zags on a unit-cell scale. The actual boundaries observed on electron micrographs are straight, so far as can be seen, but this should not be taken as positive evidence for regular addition of octahedra to the layers in each sector. The steps in a zig-zag boundary should be multiples of 1.5 Å, the step for one octahedron ($b/6$). HRTEM is therefore only capable of resolving the coarser steps (with at least three or four octahedra added to the layer), and even those will only be seen on micrographs if there is sufficient contrast. There is no conclusive direct evidence for either random or regular addition of octahedra to the layers in each sector.

Relationship Between Polygonal Layers Stacked in Sectors and the Concentric Layers of Chrysotile

There is a special geometrical relationship between the microstructure of flat layers in polygonal serpentine and the concentric wrapping of curved layers in chrysotile. Consider a cylindrical layer of chrysotile, of radius r, in which there are N b-repeats in the circumference:

$$2\pi r = Nb$$

The next layer out has a radius $(r + c\sin\beta)$ and contains an additional number δN of b-repeats in its circumference:

$$2\pi(r + c\sin\beta) = (N + \delta N)b$$

By subtraction,

$$\delta N = (2\pi c\sin\beta)/b.$$

δN is equal to 4.995 for the single-layer subcell of chrysotile-2M_{cl} with a b of 9.2, a c of 7.325 Å, and a β of 93°16′. The same requirements in fact also applies to layers that are wrapped as spirals instead of concentric cylinders, as shown in Appendix 1.

Thus, each successive cylindrical layer must contain five more b-repeats in its circumference than the previous layer, as first noted by Whittaker (1954). Expressed in terms of the sheets making up the structural layer, successive sheets of octahedra and tetrahedra must contain 30 more octahedra and 20 more tetrahedra. The observations of Yada & Wei (1987) show that polygonal growth also requires the addition of five b-repeats to the perimeter of the polygon. In the 30-sector polygon, successive layers have $2 \times b/12 = b/6$ added in each of the 30 sectors, making $5b$ around the perimeter. In the 15-sector polygon, the extra $5b$ around the perimeter is made up of $2 \times b/6 = b/3$ added to successive layers in each of the 15 sectors. This corresponds to the addition of one octahedron to each successive sheet in each of the 30 sectors, or of two octahedra in each of the 15 sectors.

But could there be cases of fewer and larger sectors, *e.g.*, five sectors with a 72° angle and one b-repeat added to successive layers in each sector? In general, n sectors require a sector angle $360/n$ and $5/n$ b-repeats, $30/n$ octahedra, $20/n$ tetrahedra added to each successive layer in each sector. Each layer would extend laterally by an extra $5b/2n$ on either side of the normal to (001) and be bounded by planes {0kl} with $k/l = 2n/5$. But the angle (0kl):(0$\bar{k}l$) between the bounding planes is $2\arctan[(b/c\sin\beta)(5/2n)]$, and is not exactly the same as the sector angle $360/n$.

No cell dimensions have been reported specifically for polygonal serpentine. The cell dimensions for both chrysotile and lizardite are now considered, mainly for comparison, but also because monoclinic polygonal serpentine has flat layers with a curved-layer stacking sequence (Middleton & Whittaker 1976, Cressey & Zussman 1976), and it is not clear which cell is most appropriate in that case.

Table 1 gives the angle (0kl):(0$\bar{k}l$) calculated using the cell dimensions for three different samples of lizardite (with flat layers) and chrysotile-2M_{cl} (with curved layers). For flat layers with the cell

TABLE 1. SECTOR ANGLES, SECTOR BOUNDARIES AND OVERALL MISFIT FOR IDEAL POLYGONAL STRUCTURES WITH DIFFERENT NUMBERS OF SECTORS

Number of sectors	Sector angle	In each sector: Average number of b-repeats (5/n), Mg octahedra (30/n) and Si tetrahedra (20/n) added at each new layer			Indices of boundary plane	Angle between boundary planes (0kl):(0$\bar{k}$l)				Overall misfit for complete polygon n[(0kl):(0$\bar{k}$l)] - 360			
n	360/n	5/n	30/n	20/n	{0kl}	1	2	3	4	1	2	3	4
5	72	1	6	4	021	65.11	64.85	64.70	64.34	-34.45	-35.75	-36.50	-38.30
6	60	5/6	5	3.33	0,12,5	56.03	55.79	55.66	55.32	-23.83	-25.26	-26.04	-28.08
10	36	1/2	3	2	041	35.41	35.24	35.15	34.92	-5.93	-7.60	-8.50	-10.80
15	24	1/3	2	1.33	061	24.03	23.91	23.85	23.68	+0.41	-1.35	-2.25	-4.80
20	18	1/4	1.5	1	081	18.14	18.05	18.00	17.87	+2.72	+1.00	0	-2.60
30	12	1/6	1	0.67	0,12,1	12.15	12.09	12.05	11.97	+4.41	+2.70	+1.50	-0.90
40	9	1/8	0.75	0.5	0,16,1	9.13	9.08	9.05	8.99	+5.01	+3.20	+2.00	-0.40
45	8	1/9	0.67	0.44	0,18,1	8.11	8.08	8.05	8.00	+5.17	+3.60	+2.25	0
60	6	1/12	0.5	0.33	0,24,1	6.09	6.06	6.04	6.00	+5.44	+3.60	+2.40	0

1. Calculated for an orthohexagonal cell with b 9.235, c 7.233 A corresponding to the trigonal cell of lizardite-1T (a 5.332, c 7.233 A; Mellini 1982).
2. Calculated for an orthohexagonal cell with b 9.223, c 7.259 A corresponding to the trigonal cell of lizardite-1T (a 5.325, c 7.259 A; Mellini & Zanazzi 1987).
3. Calculated for an orthohexagonal cell with b 9.211, c 7.270 A corresponding to the hexagonal cell of lizardite-2H1 (a 5.318, c 14.541 A; Mellini & Zanazzi 1987).
4. Calculated for the single-layer cell with c 7.325 A derived from that of chrysotile-2Mc1 (a 5.34, b 9.2, c 14.65 A, β 93°16'; Whittaker 1956).
Angles are expressed in degrees.

dimensions of lizardite, the sector angle, $360/n$, and the angle between the boundary planes $(0kl):(0\bar{k}l)$ are close for values of $n \geq 15$; for such arrangements, the sectors would be expected to fit together reasonably well. For fewer sectors, there is a discrepancy between the sector angle, $360/n$, and the angle between the boundary planes $(0kl):(0\bar{k}l)$; such large sectors will not fit together without gaps. This explains why polygons with $n < 15$ have not been found.

The overall fit for the complete polygon may be gauged from the difference between the sum of the angles $(0kl):(0\bar{k}l)$ and 360°, *i.e.*, $n[(0kl):(0\bar{k}l)] - 360$. Values of this difference (given in Table 1) demonstrate that the best overall fit is obtained for values of n between 15 and 30, which depend on the exact cell-dimensions. For small values of n, there would be a gap left if the sectors were fitted together. For large values of n, there would be insufficient room for all the sectors. In this case, although each individual sector is only slightly too big, the overall misfit is large enough to be significant. This fuller analysis suggests that polygonal structures with n = 15, 20 and 30 are those most likely to be found.

Layers with the dimensions of the curved layers in chrysotile show different behavior, as would be expected: both the misfit between $360/n$ and $(0kl):(0\bar{k}l)$ and the overall misfit decrease as $n \rightarrow \infty$ and the polygon becomes a circle. But the distinction in behavior between flat and curved layers may not be as well established as Table 1 suggests. The accuracy to which b can be determined for chrysotile is limited by the displacements of the $hk0$ maxima from the ideal positions, in diffraction from a cylindrical lattice (Whittaker 1955a). To that extent, the way in which the chrysotile data in Table 1 exemplify the expected behavior may be fortuitous.

The analysis in Table 1 suggests that polygonal structures with n = 15, 20 and 30 are those most likely to be found. Why then have structures with n = 20 not been observed? The sectors will fit together satisfactorily for n = 20, better for some cell dimensions than for n = 15 or 30. The case n = 20 corresponds to the addition of a complete tetrahedron at each layer in each sector but not a whole number of octahedra, whereas n = 15 and n = 30 correspond to the addition of whole numbers of octahedra. For other values of n (16 to 19 and 21 to 29), an irrational number of both octahedra and tetrahedra would have to be added. The restriction of polygonal structures to 15 and 30 sectors suggests that it is the addition of octahedra to the "brucite" sheet that controls sector development. If so, this would eliminate polygonal structures with n = 20 and others in which the number of added octahedra in each sector, $30/n$, is not an integer. Only n = 15 and

n = 30 then remain to yield polygonal microstructures with minimum strain.

For polygons with 15 or 30 sectors, the fitting of the sectors to form a polygonal structure is unlikely to be perfect and will depend on the cell dimensions of the flat layers. Some strain across sector boundaries will remain and will have to be accommodated. This residual strain may account for the departures of sector angles from the ideal values and from perfect regularity, and in more extreme cases for the absence of a sector or the presence of an extra one. The need to accommodate this residual strain may also explain why the sectors sometimes lack a single common center.

Geometry of Polygonal Wrapping of Layers

An alternative view is obtained if the geometry of polygonal wrapping of layers in equal sectors is considered. If there are n sectors each at a distance r from the center of the polygon measured normal to the (001) plane, the perimeter of that layer is $2nr\tan(180/n)$, where $180/n$ is half the sector angle. The next layer out is at a distance $(r + c\sin\beta)$ from the center, and its perimeter will have increased by $2nc\sin\beta\tan(180/n)$. The number of additional b-repeats in the perimeter of each successive layer is then $[2nc\sin\beta\tan(180/n)]/b$.

The numbers of extra b-repeats in successive layers calculated for various values of n are shown in Table 2 for the same four sets of cell dimensions as in Table 1. For the cell dimensions of lizardite (flat layers), five extra b-repeats at each new layer can be accommodated with minimal strain in polygonal arrangements with n between 15 and 30, depending on the exact cell-dimensions. For larger numbers of sectors, there would be insufficient room, whereas for smaller numbers of sectors, there would be a large gap. As noted above, polygonal structures with n = 20 have not been found, and the common occurrence of structures with n equal to 15 or 30 shows the controlling influence of the addition of a whole number of octahedra to the Mg–O sheet in each sector.

For the cell dimensions of chrysotile (curved layers), the incorporation of five b-repeats at the perimeter of each new layer would leave a gap that becomes progressively smaller as n becomes larger, approaching an exact fit for cylindrical or spiral wrapping ($n \rightarrow \infty$). But as noted earlier, the way in which the chrysotile data follow the expected trend may be fortuitous because of the limited accuracy of b.

TABLE 2. NUMBER OF POLYGON SECTORS AND INCREASE IN PERIMETER AS EACH NEW LAYER IS ADDED

Number of sectors	Number of additional b-repeats in perimeter of each successive new layer			
n	1	2	3	4
5	5.69	5.72	5.73	5.77
6	5.43	5.45	5.47	5.51
10	5.09	5.11	5.13	5.17
15	4.99	5.02	5.03	5.07
20	4.96	4.99	5.00	5.04
30	4.94	4.96	4.98	5.01
40	4.93	4.96	4.97	5.00
45	4.93	4.95	4.97	5.00
60	4.93	4.95	4.96	5.00

1. Calculated for an orthohexagonal cell with b 9.235, c 7.233 A corresponding to the trigonal cell of lizardite-1T (a 5.332, c 7.233 A; Mellini 1982).
2. Calculated for an orthohexagonal cell with b 9.223, c 7.259 A corresponding to the trigonal cell of lizardite-1T (a 5.325, c 7.259 A; Mellini & Zanazzi 1987).
3. Calculated for an orthohexagonal cell with b 9.211, c 7.270 A corresponding to the hexagonal cell of lizardite-$2H_1$ (a 5.318, c 14.541 A; Mellini & Zanazzi 1987).
4. Calculated for the single-layer cell with c 7.325 A derived from that of chrysotile-$2M_{c1}$ (a 5.34, b 9.2, c 14.65 A, β 93°16′; Whittaker 1956).

Strain Energy and the Growth of Polygonal Serpentine

Some insight into the formation of polygonal serpentine may be gained by considering the strain energy of serpentines with curved and flat layers. The local strain energy associated with a single curved layer of radius r is made up of two components: (a) intralayer strain arising from the difference in cell dimensions between the sheets of tetrahedra and of octahedra. This strain is zero at only one radius of curvature, that for which $b_{oct} = b_{tet}$. At higher radii, the curvature of the layer will be insufficient to compensate for the mismatch between b_{oct} and b_{tet}, and the intralayer strain will increase and approach the value for flat layers as $r \rightarrow \infty$ (Fig. 4a). At lower radii, the curvature will overcompensate for the mismatch, and the intralayer strain will increase steadily as the radius falls (Fig. 4a). (b) interlayer strain that arises because concentric layers must be out of register along the b axis as a result of the extra b-repeats inserted at each layer. The interlayer strain will be $5b/2\pi r$ and will fall steadily to zero as r increases (Fig. 4b). The interlayer strain for flat layers is of course zero.

The intralayer and interlayer strain energies must be similar in magnitude. If the intralayer strain were very small at all radii, curved layers would never occur; if the interlayer strain were very small at all radii, flat layers would never be found.

The total local strain energy at a curved layer is the sum of the intralayer and interlayer components. How it varies with the radius will depend on the relative magnitudes of the two components

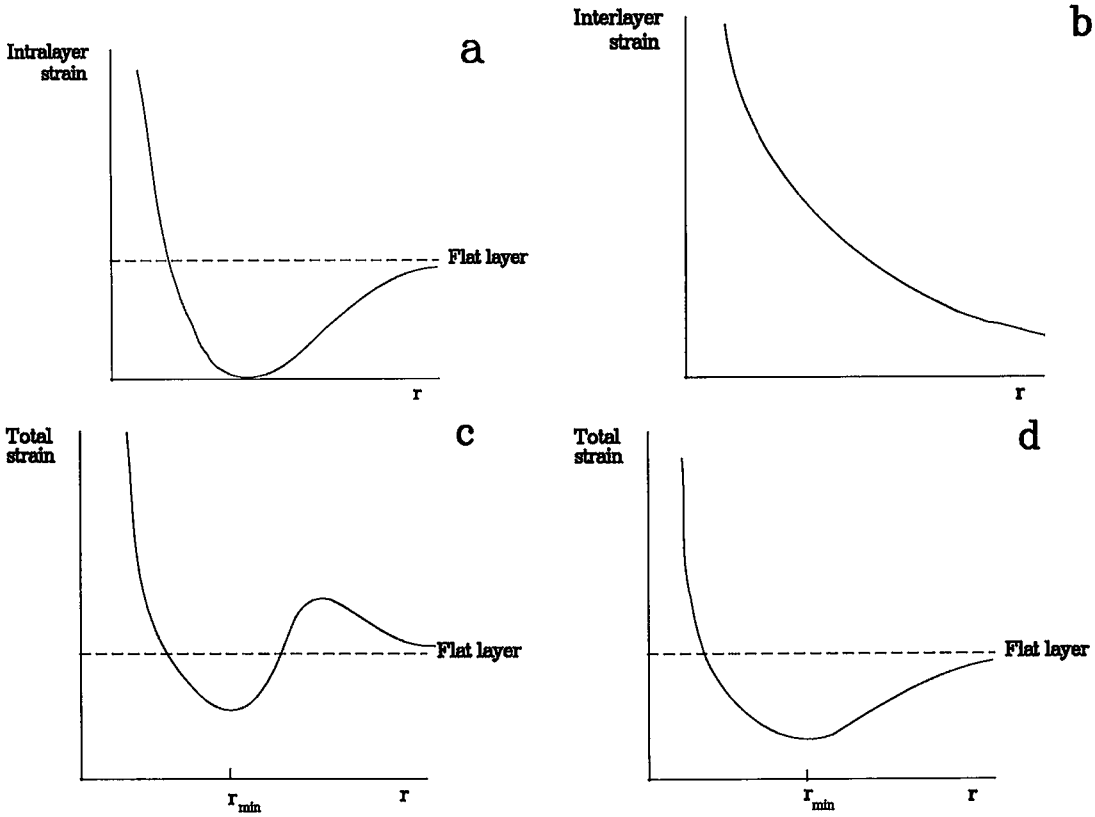


FIG. 4. Qualitative variation of the local strain associated with a single layer as a function of its radius r for (a) the intralayer strain arising from the mismatch in b between the sheets of octahedra and tetrahedra; (b) the interlayer strain arising from the lack of register along the b axis in adjacent sheets; (c) the total strain if the interlayer component is sufficiently large to make the total strain at larger radii exceed the intralayer strain for a flat layer (dashed line); polygonal structures with flat layers should occur for larger "radii" in this case; (d) the total strain if the interlayer strain is too small for the total strain to exceed that for a flat layer (dashed line); polygonal structures should not occur in this case.

(Figs. 4c and d). In Figure 4c, at larger radii, the interlayer strain is sufficiently large relative to the intralayer component to make the total local strain energy for a curved layer exceed that for a flat layer. As such, flat layers will be preferred at larger radii, and this will account for the occurrence of polygonal structures almost exclusively in fibrils of large diameter and around centers with cylindrical or spiral layers (Cressey & Zussman 1976, Mellini 1986, Mitchell & Putnis 1988). Figure 4d shows the case in which the interlayer strain is too small to make the total local strain for a curved layer exceed that for a flat layer. Polygonal growth of flat layers should not occur in this case.

It is important to distinguish the local strain energy associated with one particular layer and the strain energy for the bulk material. The strain energy of a chrysotile fibril depends on the area under the curve describing local strain between r_{int} and r_{ext}, the internal and external radii of the fibril. Theoretically, the arrangement having the lowest strain energy will consist of many fibrils, each of which consists of a single layer whose radius corresponds to the minimum total local strain energy in Figures 4c or d. But this ignores the contribution of surface energy to the free energy, which would be excessively large for a single-layer fibril. In practice, the minimum in the curve describing total local strain will lead to an energetically favorable arrangement consisting of many fibrils with r_{int} and r_{ext} close to r_{min}. This should be so whether the curve describing local strain energy follows Figure 4c or Figure 4d. Such a microstructure is what is found in normal chrysotile.

Which microstructure actually occurs must

depend on the relative rates of nucleation of new fibrils and of radial growth of existing fibrils (*i.e.*, addition of material at the outer circumference of the fibril, increasing its outer diameter). The occurrence of normal chrysotile implies growth conditions with a relatively high rate of nucleation, whereas formation of polygonal serpentine would require a relatively high rate of radial growth, so that the fibril radius becomes large enough for flat layers to be preferred (right-hand region of Fig. 4c).

Conclusion and Discussion

Polygonal microstructures in serpentine ideally develop around a nucleus with circular cross-section, which could well be a fibril of ordinary chrysotile with concentric cylindrically or spirally curved layers. The central zone, having circular symmetry, should ensure the development of an outer polygonal structure with equal sectors.

For cases of polygonal serpentine with perfectly equally developed sectors, the number of sectors and the sector angle are controlled by the increase in the perimeter of each new layer and the increase in the length of the new layer in each sector. Just as five extra *b*-repeats must be incorporated around the circumference of a new concentric cylindrical layer or around each new turn of a spiral layer, any arrangement of sectors must incorporate five extra *b*-repeats around the perimeter of each new layer with minimal misfit. Depending on the exact cell-dimensions, only arrangements with 15 and 30 sectors can do this, and these are the structures observed in natural polygonal serpentines. In those arrangements, each new layer in each sector increases in length by a multiple of $b/6$ as a result of the addition of a whole number of octahedra; this controls the development of polygonal sectors. These geometrical requirements constitute a model for the development of regular polygonal microstructures in serpentine that satisfactorily explains the observation of Yada & Wei (1987) concerning the number of sectors in the polygon, restricted to 15 or 30 in most cases. Small departures from regular sectors and from the ideal number of sectors may arise in order to relieve residual strain in the ideal polygonal microstructures.

The sectors observed in polygonal serpentines are not perfectly regular; the sector angles vary within $\pm$ 3° of the ideal values. Departures of the sector boundaries from the ideal {0*kl*} plane may be related to the way the atoms adjust their positions at the interface. But there may also be more complex structures at the sector boundaries, in which the change in orientation of the flat layers takes place *via* a region with curved layers, such as in Figure 6b of Mellini (1986) or one with "antigorite offsets", in which the tetrahedra switch from one side of the octahedral layer to the other (Mitchell & Putnis 1988).

The model for polygonal microstructures described is purely geometrical and tells us nothing of how the atoms actually fit together at the interface between two sectors. The fit is likely to require considerable departures from the crystal structure of lizardite expected for flat layers. In the lizardite structure itself, the $Mg(O,OH)_6$ octahedra are distorted, the plane of Mg atoms is buckled, and the SiO_4 tetrahedra are tilted out of the (001) plane. These features differ in the other serpentine polymorphs, chrysotile and antigorite (Wicks & Whittaker 1975). Figures 1 and 2 suggest that the $Mg(O,OH)_6$ octahedra near a sector boundary are likely to be highly distorted. The boundary itself may be thought of as a local severe buckling of the plane of Mg atoms, accompanied by tilting of the SiO_4 tetrahedra out of the (001) plane.

Acknowledgements

I thank Dr. Keiji Yada for showing me his electron micrographs and describing his and Dr. Liu Wei's observations on sectors in Povlen-type chrysotile shortly after the Euroclay 87 meeting. I am also grateful to Professor Jack Zussman, Fred Wicks and an anonymous referee for their valuable criticism and suggestions for improving this paper.

References

Cressey, B.A. (1979): Electron microscopy of serpentinite textures. *Can. Mineral.* **17**, 741-756.

_____ & Zussman, J. (1976): Electron microscopic studies of serpentinites. *Can. Mineral.* **14**, 307-313.

Eckhardt, F.-J. (1956): Röntgenographische Untersuchungen am Schweizerit. *Neues Jahrb. Mineral. Monatsh.*, 32-43.

Krstanović, I. & Pavlović, S. (1964): X-ray study of chrysotile. *Am. Mineral.* **49**, 1769-1771.

_____ & _____ (1967): X-ray study of six-layer ortho-serpentine. *Am. Mineral.* **52**, 871-876.

Mellini, M. (1982): The crystal structure of lizardite 1T: hydrogen bonds and polytypism. *Am. Mineral.* **67**, 587-598.

_____ (1986): Chrysotile and polygonal serpentine from the Balangero serpentinite. *Mineral. Mag.* **50**, 301-305.

_____ & Zanazzi, P.F. (1987): Crystal structures of

lizardite-1T and lizardite-2H_1 from Coli, Italy. *Am. Mineral.* **72**, 943-948.

MIDDLETON, A.P. & WHITTAKER, E.J.W. (1976): The structure of Povlen-type chrysotile. *Can. Mineral.* **14**, 301-306.

MITCHELL, R.H. & PUTNIS, A. (1988): Polygonal serpentine in segregation-textured kimberlite. *Can. Mineral.* **26**, 991-997.

WEI LIU & SHAOYING JIANG (1984): The discovery of Povlen-type hydroxyl-chrysotile and its mineralogy. *Acta Mineral. Sinica* **2**, 111-116.

WHITTAKER, E.J.W. (1954): The diffraction of X-rays by a cylindrical lattice. I. *Acta Crystallogr.* **7**, 827-832.

_____ (1955a): The diffraction of X-rays by a cylindrical lattice. II. *Acta Crystallogr.* **8**, 261-265.

_____ (1955b): The diffraction of X-rays by a cylindrical lattice. IV. *Acta Crystallogr.* **8**, 726-729.

_____ (1956): The structure of chrysotile. II. Clino-chrysotile. *Acta Crystallogr.* **9**, 855-862.

_____ & ZUSSMAN, J. (1971): The serpentine minerals. *In* The Electron-Optical Investigation of Clays (J.A. Gard, ed.). *Mineral. Soc., Monogr.* **3**, 159-191.

WICKS, F.J. & O'HANLEY, D.S. (1988): Serpentine minerals: structures and petrology. *Rev. Mineral.* **19**, 91-167.

_____ & WHITTAKER, E.J.W. (1975): A reappraisal of the structures of the serpentine minerals. *Can. Mineral.* **13**, 227-243.

YADA, K. (1967): Study of chrysotile asbestos by a high resolution electron microscope. *Acta Crystallogr.* **23**, 704-707.

_____ (1971): Study of microstructure of chrysotile asbestos by high resolution electron microscopy. *Acta Crystallogr.* **A27**, 659-664.

_____ & WEI LIU (1987): Polygonal microstructures of Povlen chrysotile observed by high resolution electron microscopy. *Euroclay 87 (Sevilla, Spain), abstr.*

ZUSSMAN, J., BRINDLEY, G.W. & COMER, J.J. (1957): Electron diffraction studies of serpentine minerals. *Am. Mineral.* **42**, 133-153.

Received February 26, 1990, revised manuscript accepted December 10, 1991.

APPENDIX 1.

INCORPORATION OF ADDITIONAL b-REPEATS AT EACH TURN OF A SPIRALLY WRAPPED LAYER OF CHRYSOTILE

In polar coordinates a spiral is represented by the equation $r = k\theta$, where k is a constant depending on how tightly the spiral is wound.

If p denotes the length along the line of the spiral from the center, then for a small increment $\delta\theta$

$$\delta p = r\delta\theta = k\theta \bullet \delta\theta$$

The length of n complete turns of the spiral must then be

$$\int_0^{2\pi n} k\theta \bullet d\theta = 2\pi^2 k n^2.$$

The length of the nth turn alone of the spiral is easily shown to be $2\pi^2 k(2n - 1)$. The increase in length of the $(n+1)$th turn over the nth is $4\pi^2 k$ and is independent of n, *i.e.*, the same at each turn.

For one turn of the spiral, r increases by $2\pi k$, the radial spacing of the spiral, which, in chrysotile, is the layer spacing $c\sin\beta$. Therefore $k = (c\sin\beta)/2\pi$, and the increase in length around succssive turns of the spirally wrapped layer is $2\pi c\sin\beta$. The number of extra b-repeats added at each turn, δN, is thus $(2\pi c\sin\beta)/b$ and has the same value, 5, as for the concentric cylindrical wrapping of layers.

High-resolution electron micrographs (Yada 1967, 1971) show examples of both single and multiple spiral layers in sections of chrysotile, but in none are the 020 lattice fringes resolved around the complete fibril. For multiple layers with m layers in the spiral, δN is equal to $(2\pi mc\sin\beta)/b$, and so a multiple of 5 extra b-repeats must be incorporated into each turn of the multiple spiral.

The case of helical wrapping of layers in chrysotile, for which there is evidence from both X-ray and electron diffraction and HRTEM images (Whittaker 1955b, Whittaker & Zussman 1971, Yada 1971), is more problematical. The length around a turn in the helix depends not only on the layer spacing but also on the pitch of the helix. If there is indeed a requirement that the increase in length around each successive turn of the helix should be a whole number of b-repeats, then this will restrict the pitch of the helix to specific values.