ELECTRON DIFFRACTION STUDIES OF SERPENTINE MINERALS*

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Abstract

Electron microscope and single crystal electron diffraction methods have been used to examine the morphology and unit cell parameters of the serpentine minerals, and their inter-relations. Single tubular elements of silky chrysotile give electron diffraction patterns of clino- or ortho-chrysotile similar to the x-ray fibre diagrams; the two types are seen to exist in separate strands. Splintery varieties have a less disordered layer stacking than do silky fibres.

Massive serpentines giving the lizardite x-ray powder pattern are found to be essentially platy; two bastites give an electron diffraction pattern similar to that of lizardite from Kennack Cove.

Antigorites and picrolites are seen to be structurally similar giving characteristic superlattice spot patterns. The *a* parameter of antigorites can vary from one crystal to another and takes on "preferred" values.

A synthetic Mg-Ge serpentine and a serpentine from Unst, Shetlands, possess a 6-layered ortho cell. Comment is made on nomenclature of certain serpentine varieties.

Introduction

Much detailed x-ray diffraction work has been devoted to the elucidation of the crystal structures of the serpentine minerals and especially of chrysotile and antigorite. It is now generally accepted that both minerals have layer structures closely similar to that of kaolinite but with a trioctahedral Mg layer replacing the dioctahedral Al layer.

In the case of chrysotile, the fundamental layers may be curved so as to form hollow tubes or rolls. Electron micrographs of dispersed material have been interpreted as showing a tubular morphology (Turkevich and Hillier (1949); Bates, Sand and Mink (1950); Noll and Kircher, (1951)). The detailed analyses by Whittaker (1954, 1955a, 1955b) and by Jagodzinski and Kunze (1954) show a close similarity between the diffraction effects to be expected from cylindrical lattices and those obtained experimentally. On the other hand, Pundsack (1956) has shown that the measured density of compact bundles of chrysotile fibres is incompatible with both tubular and solid cylindrical formations. It may be that the x-ray data can be interpreted in terms of compact bundles of curved laths and that the hollow tubes are formed by curling when the material is dispersed.

In the case of antigorite, which has a platy morphology, interest cen-

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ters in the large a parameter (see below) which is considered to arise from a long period modulation of the simple layer structure, the precise nature of which has not been established, although various suggestions have been made (Aruja (1945); Onsager (1952); Zussman (1954)).

The term chrysotile has been widely used to describe fibrous serpentine, and the term antigorite for platy crystalline material. In addition, antigorite has often been applied to any non-fibrous serpentine. A more rigorous classification was suggested after a number of serpentine varieties had been studied by x-ray fibre and powder photographs (Whittaker and Zussman, 1956). This resulted in the recognition of a third variety, called lizardite (see Table 1). In addition a specimen from Unst (Brindley and von Knorring, 1954) and a synthetic Mg-Ge serpentine prepared by Roy and Roy (1954) appear to have a 6-layer orthocell. At this stage

TABLE 1. CELL PARAMETERS OF SERPENTINE MINERALS

	a, Å	b, Å	c, Å	β	Reference
1. Chrysotile (clino)	5.32	9.2	14.6	93°12′	Whittaker (1951)
Chrysotile (ortho)	5.32	9.2	14.6	90°	Whittaker (1953)
2. Antigorite	43.5	9.2	7.28	91°24′	Aruja (1945)
3. Lizardite	5.31	9.2	7.31	90°	Whittaker and Zussman (1956)
4. 6-layer ortho varieties:					
(material from Unst.)	5.32	9.22	43.6	90°	Brindley and von Knorring (1954); present text
(Synthetic Mg-Ge serpentine	5.44	9.42	44.7	90°	Present text

it will suffice to define the varieties of serpentine in terms of the data given in Table 1. Further discussion of nomenclature is given in a later section.

Because of the fine-grained nature of many serpentine varieties their characteristic morphology is unobservable in the light microscope, and structural information has been obtained only from x-ray powder patterns.

This paper describes the application of electron microscopy and electron diffraction to obtain further morphological and structural data on serpentine minerals. Dispersions were studied under the electron microscope to observe the morphology of different varieties and selected area diffraction patterns have been obtained from single crystals. These gave information about cell parameters and their relation to crystal morphology. It is not intended to discuss secondary morphological characteris-

tics seen in the electron micrographs; the varieties of tubular form described by other workers have been observed, but the descriptions given here are limited to recognition of tubes, rolled sheets, laths, plates, etc.

DESCRIPTION OF SPECIMENS

Specimens were chosen for study so that each structural type previously observed was represented. Moreover, within a given structural group specimens showing marked differences in texture and/or appearance were selected. Wherever possible, specimens were chosen for which chemical analyses were available.

(a) Clino- and ortho-chrysotiles

1. *A silky fibrous chrysotile* (Transvaal). #M 14676, Manchester University, Dept. of Geology collection. Pale yellow silky fibre of a cross-fibre vein in massive serpentine occurring in dolomitic rock. X-ray fibre photograph shows a mixture of clino-chrysotile with approximately 15% orthochrysotile, the components within a bundle being very well aligned with the fibre axis, which is parallel to *a*. Evidence of complete disorder in direction of *b* axis. Photograph resembles a rotation pattern.

2. *A silky fibrous chrysotile* (Nunyerry, W. Australia) with high ortho-chrysotile content.

3. *A coarse splintery clino-chrysotile* (Findeten Glacier, Zermatt) #0.9652, Oxford University Museum collection; listed as "Schweizerite." Greenish yellow splintery fibres with greasy feel. X-ray powder photograph similar to that of (1). X-ray fibre photograph shows a moderate spread of fibre axis (*a*-axis) orientation.

(b) Lizardites

4. *Massive serpentine* (Snarum, Norway). #0.17788, Oxford University Museum. Light green, massive; no texture observable by *x*-ray methods. Powder pattern that of lizardite.

5. *Platy serpentine* (Lizard, Cornwall). Described by Midgley (1951). White soft flaky material. Single crystals give *x*-ray diffraction patterns showing misorientations of plates and some randomness in stacking of successive structural units. Powder photograph is that of lizardite.

6. *Bastite* (Baste, Harz, Germany). B.M. 170.

7. *Bastite* (Baste, Harz, Germany). B.M. 67807. Both bastites are from the British Museum collection. They are platy pseudomorphs after orthopyroxene and each gives the lizardite powder pattern.

(c) Antigorites

8. *Platy antigorite* (Antigorio, Italy). #0.16327, Oxford University Museum. Hard dark green platy specimen, crystals showing sweeping extinction between crossed nicols.

9. *Platy crystalline antigorite* (Glen Urquhart, Scotland) #C.76095, Department of Mineralogy and Petrology, Cambridge University (Harker Collection). Dark green specimen with platy parting, associated with some yellow fibrous material. Described by Francis (1956). Crystals are very small plates, showing patchy or sweeping extinction between crossed nicols and giving *x*-ray patterns which demonstrate their composite character.

10. *Platy crystalline antigorite* (Mikonui, New Zealand). #011566 (Harker Collection). Small rectangular plates in a fine grained green rock. X-ray data by Aruja (1945) (see Table 1, also Zussman (1954)).

11. *Platy crystalline antigorite* (Caracas, Venezuela). Described by Hess, Smith and Dengo (1952). Similar in texture, x-ray and optical properties to No. 10.

12. *Platy crystalline antigorite* (Antigorio, Italy). #C 70520 (Harker Collection). Similar to Nos. 10 and 11.

13. *Massive antigorite* (Yu Yen Stone, Manchuria) #94356, U. S. National Museum. White massive material showing patchy extinction between crossed nicols.

X-ray powder photographs of the last six specimens are closely similar but show some variations.

14. *Coarsely fibrous picrolite* (Shipton, Quebec). #T.W. 2914, Department of Mineralogy and Petrology, Cambridge University. Light green, brittle, lath-like splinters. X-ray fibre pattern shows b axis along fibre length, with moderate spread of orientation of fibre axis.

15. *Coarsely fibrous picrolite* (Harford Co., Maryland, U.S.A.) #481.83, Genth Collection, College of Mineral Industries, The Pennsylvania State University, U.S.A. Similar to specimen 14.

Powder photographs of 14 and 15 have fewer lines but these correspond approximately with the strongest lines of No. 10.

(d) Other specimens

16. *Synthetic Mg-Ge serpentine.* Prepared by Roy and Roy (1954). Very small but well developed single crystals, exhibiting platy habit with hexagonal outline.

17. *Massive serpentine* (Unst, Shetland Isles). Described by Brindley and von Knorring (1954). Olive green, massive resinous appearance. Powder pattern shows series of weak lines indicating long spacing; unique interpretation not possible from powder diagram.

18. *Coarsely fibrous serpentine* (Unst, Shetland Isles). Described by Brindley and von Knorring (1954). Aggregates of hard blue-green fibres. Fibre photograph shows orthochrysotile type of cell but with evidence of greater order in structure than occurs in specimen 1. Powder pattern similar to that from specimen 17 but lacks series of weak lines.

ELECTRON MICROSCOPE AND DIFFRACTION TECHNIQUE

Prior to obtaining electron diffraction patterns from the listed specimens each of them was prepared as a platinum shadowed disperson on a collodion substrate and examined in the electron microscope (R.C.A. model: E.M.U. type 2D) in order to determine the homogeneity of the sample and its predominant morphological features.

Freshly prepared unshadowed dispersions were then used to obtain electron diffraction patterns, and selected areas for diffraction were those containing wherever possible only one crystal, of a suitable size and thickness to give a good diffraction pattern. Sometimes it was not possible to

achieve this ideal, and smaller crystals within the aperture area gave rise to superimposed but weaker patterns. Since prolonged exposure to the electron beam tends to weaken and broaden the diffraction spots, the pattern was photographed as quickly as possible, and immediately afterward an electron micrograph of the particular crystal was obtained. The instrument was such that its electron-optical system could be changed from microscopy to diffraction without disturbing the specimen.

Unfortunately there was no means for tilting the specimen holder and consequently the patterns obtained were from crystals in orientations acquired in settling on the substrate. Thus for platy and lath-like particles the beam was always appproximately parallel to their shortest dimension, but could not be made accurately so.

Measurements of electron diffraction patterns recorded on plates were made on a magnified projected image, and then converted to give cell parameters by reference to diffraction patterns of MgO particles, which for each plate were produced with identical settings on the instrument's controls.

DESCRIPTION AND DISCUSSION OF MICROGRAPHS AND DIFFRACTION PATTERNS

1. *Silky chrysotile* (Transvaal).

Electron micrographs (Fig. 1*a*) show elongated smooth-edged fibres frequently with a thin white axial line. One fibre and its electron diffraction pattern are shown in Fig. 1*b*. The diffraction patterns resemble closely those obtained by *x*-rays with the beam normal to a fibre bundle. Reflections are distributed along "layer lines," the spacing of which corresponds to the repeat distance $a = 5.32$ Å along the fibre axis. On the zero layer there occur 00l and 0k0 spots, which implies a randomness of orientation about the fibre axis which could be given by a bundle of fibres or by a cylindrical lattice. On the first layer line are seen 110 and 130 bands and on the second 20l and 20$\bar{l}$ spots. These reflections are in positions expected for the clino-chrysotile cell (see Fig. 2*e*) assuming rotation about the fibre axis. Similarly on the third layer there occur 310 and 330 bands and on the fourth 40l and 40$\bar{l}$ spots. Such features have been described and discussed for the corresponding *x*-ray patterns by Whittaker (1954, 1955*a, b*) who states that the absence of hkl and 0kl reflections and the shapes and positions of hk0 bands indicate complete disorder with regard to the b axis and also point to the curved nature of the lattice. An *x*-ray diagram of a bundle of fibres which is a mixture of ortho- and clino-chrysotile does not indicate whether the different cells are confined to separate smaller fibres, or are more intimately intergrown, perhaps within a fundamental unit. Single elements of specimen
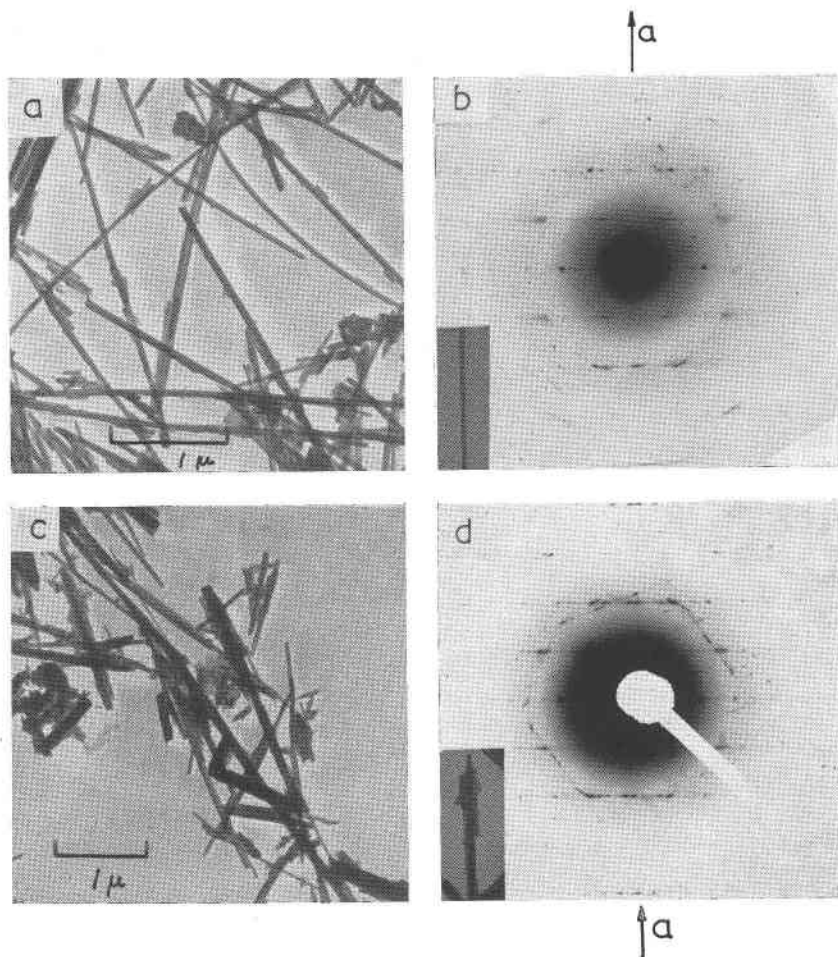
FIGS. 1a and b. Silky chrysotile: electron micrographs of dispersion and electron diffraction pattern from single fibre shown (Specimen No. 1).

FIGS. 1c and d. Splintery chrysotile: e.m. of dispersion and e.d. pattern from laths (Specimen No. 3).

(1) gave only the clino-chrysotile pattern, implying the separate existence of the two cell types.

2. Silky chrysotile.

The relation of ortho- to clino-chrysotile was tested more rigorously on a sample containing 60% ortho- and 40% clino-chrysotile. Some single fibres gave clino-chrysotile patterns (Fig. 2b) and others gave ortho-
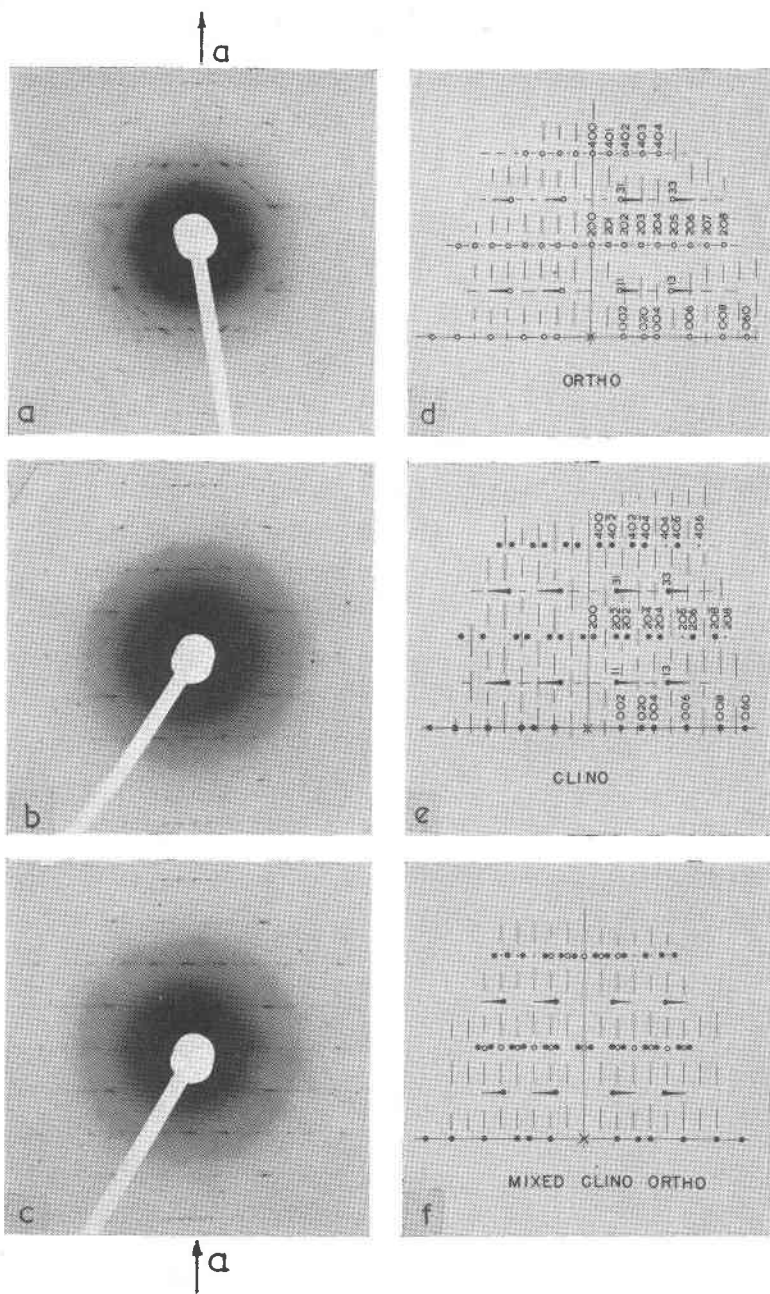
FIG. 2a. Ortho-chrysotile. e.d. pattern (Specimen No. 2).
FIG. 2b. Clino-chrysotile. e.d. pattern (Specimen No. 2).
FIG. 2c. Mixed ortho-, clino-. e.d. pattern (Specimen No. 9).
FIGS. 2d, e, f. Idealized patterns for ortho-, clino-, and mixture respectively.

chrysotile patterns (Fig. 2a). Small sheaves of fibres seen in electron micrographs also gave patterns of either one type or the other, so that it may be concluded that in this case the mixture of cells is on a comparatively coarse scale.

Figs. 2a, b and c present typical electron diffraction patterns from ortho-chrysotile, clino-chrysotile, and a mixture of the two. Alongside of them, Figs. 2d, e and f are the corresponding idealized diagrams. These are mainly to illustrate the positions of possible reflections, no account being taken of relative intensities. For ortho-chrysotile, spots on even layers lie at intersections of an orthogonal network and are represented by open circles. Clino-diagrams are best viewed by reference to this network since $h0l$ and $h0\bar{l}$ spots (closed circles) are grouped in pairs about the intersections, as can be seen in Fig. 2e. Reflection positions at which no spots were observed are represented by small dots, and to avoid complication clino-chrysotile reflections with l odd are omitted from Fig. 2e even though a few weak ones actually occur. The original negatives must be carefully examined to see some of the weaker reflections indicated in Figs. 2d, e, f.

With other materials or under different conditions it is possible that either more or fewer reflections may be observed.

### 3. *Splintery clino-chrysotile* (Zermatt).

Although this was seen from its x-ray powder pattern to be purely clino-chrysotile it was included in the present investigation because of its markedly different macroscopic appearance. Electron micrographs (Fig. 1c) show mainly elongated laths of widths ranging up to about 2000 Å. Only relatively few thin particles show the white central line so that it may be inferred that the specimen is a mixture of laths with a small number of tubes.

Fig. 1d shows the electron micrograph of the selected area and the diffraction pattern obtained from it. Owing to the tendency of particles to cluster together it was difficult to select an area containing a single lath so that here, as in other photographs, more than one set of diffraction spots is seen. Reflections on the zero and even layers are very similar to those in the pattern of the silky fibres but include some $20l$ reflections with l odd corresponding to the 2-layer cell. On odd layer lines, however, the $hk0$ bands are fainter and several hkl spots (of the type $13l$) appear. These observations indicate less disorder in the stacking of successive layers which may be associated with a lath-like rather than tubular morphology. The presence of $0k0$ as well as $00l$ spots on the zero layer and several hkl's on odd layers implies that within a lath there are smaller units in various orientations about the lath axis.

4. *Massive serpentine* (Snarum, Norway).

Electron micrographs (Fig. 3a) show the irregular plate-like morphology of the fine particles. Since no single crystal or fibre patterns were obtainable by x-ray methods there has been no previous indication as to whether or not the lizardite unit cell is incorporated in a fine scale tubular structure. Furthermore this typical matrix material in which fibre
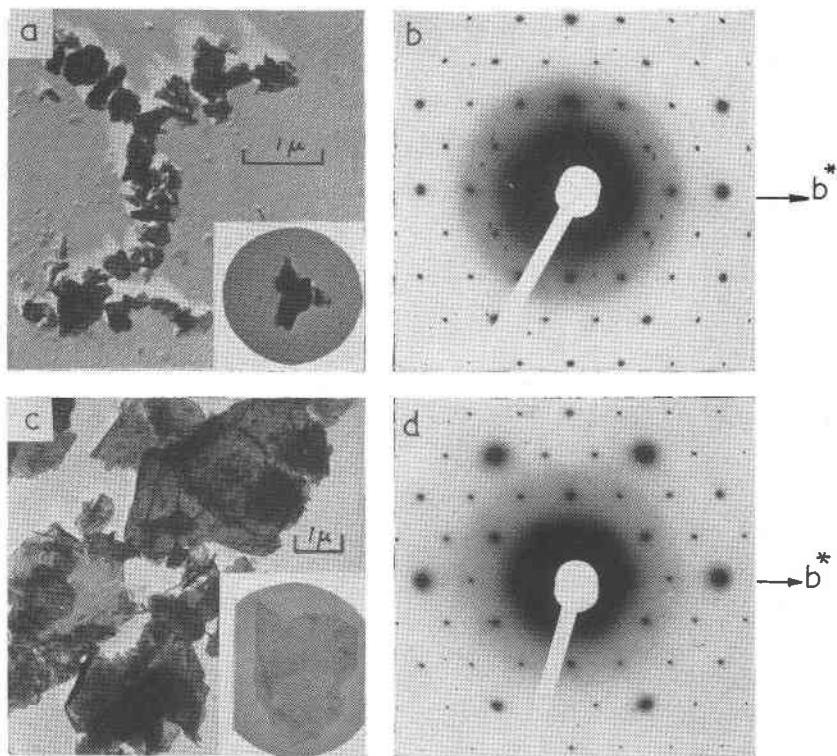
FIGS. 3a and b. Lizardite (massive). e.m. of dispersion and e.d. pattern from crystal shown (Specimen No. 4).

FIGS. 3c and d. Lizardite (platy). e.m. of dispersion and e.d. pattern from crystal shown (Specimen No. 5).

veins are often found is often designated as antigorite. The fallacy of this is shown by x-ray powder photographs and it is even more apparent from the electron diffraction patterns. (Compare Fig. 3b with those of the antigorite group, Fig. 4b and d.)

The pattern obtained from a single crystal of lizardite (Fig. 3b), is a hexagonal array of spots corresponding to a centered rectangular net of dimensions $a = 5.2$ Å, $b = 9.1$ Å in agreement with the x-ray powder pattern which gives $a = 5.31$ Å, $b = 9.20$ Å.

5. *White serpentine mineral* (Kennack Cove, Lizard, Cornwall).

This specimen, plate-like and flaky in hand specimen, gives electron micrographs (Fig. 3c) showing extensive thin plates, many with curled
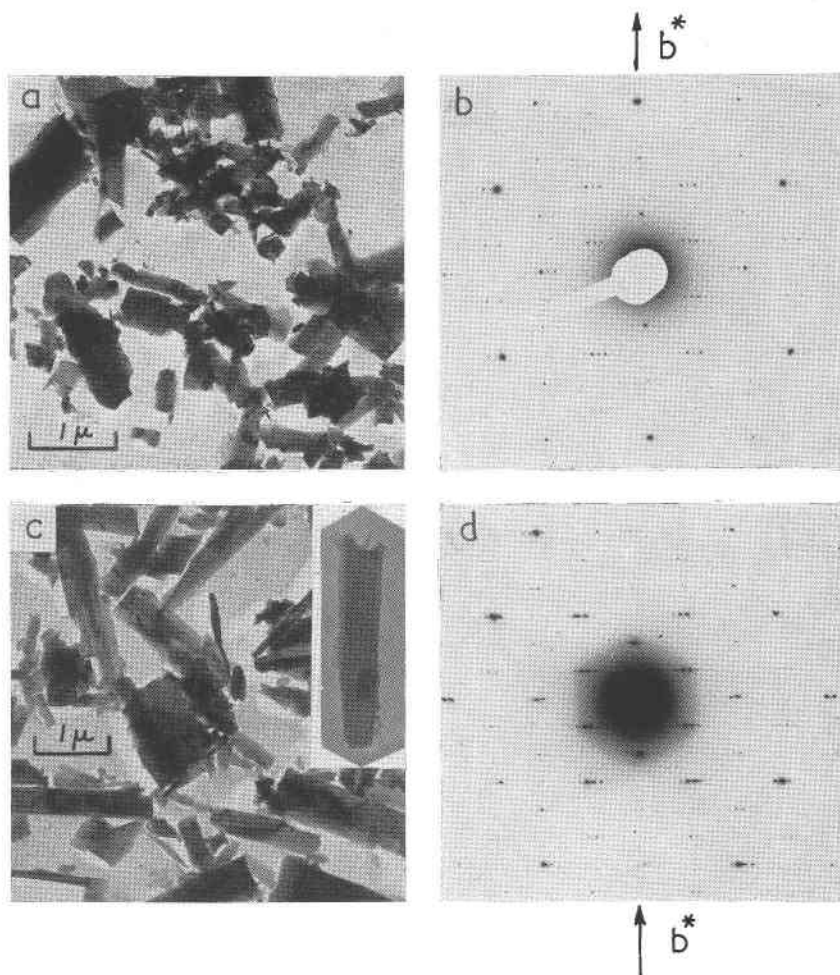
Figs. 4a and b. Antigorite (platy). e.m. of dispersion and e.d. pattern from single crystal (Specimen No. 8).

Figs. 4c and d. Antigorite (fibrous). e.m. of dispersion and e.d. pattern from single crystal (Specimen No. 15).

edges, and some small rod-like particles which may be rolled-up plates. The electron diffraction hexagonal array (Fig. 3d) yields the parameters $a = 5.28$ Å, $b = 9.15$ Å. These may be compared with values obtained by

the x-ray powder method, 5.31 and 9.20 Å, and from "single" crystal rotation photographs, 5.29 and 9.18 Å. Thus, although specimens (4) and (5) are so different in color and texture, both the x-ray powder patterns and the single crystal electron diffraction patterns show their structural similarity.

6. *Bastite* (Baste, Harz, Germany) B.M. 170.

7. *Bastite* (Baste, Harz, Germany) B.M. 67807.

X-ray powder patterns showed these to be lizardite and not antigorite.
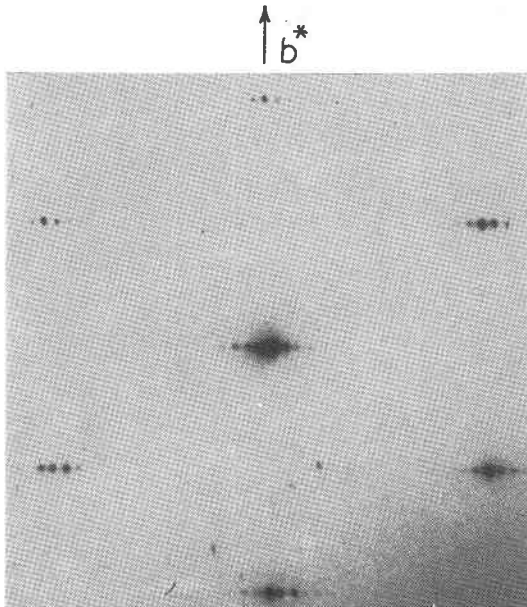

FIG. 5. Antigorite (massive). Part of e.d. pattern from single crystal of Yu Yen Stone, showing very closely spaced spots along a^* corresponding to $a \simeq 90$ Å. Scale $3 \times$ that of other diffraction patterns.

Electron micrographs and diffraction patterns confirm this and show the essential similarity between these and specimen No. 4.

8. *Antigorite* (Antigorio). Electron micrographs (Fig. 4a) show thin plates with approximately rectangular outline.

Electron diffraction patterns from single crystals are of the type shown in Fig. 4b. Layer lines are evident corresponding to a parameter $b = 9.30$ Å parallel to the longer morphological axis. Along each layer line, mainly grouped around reciprocal lattice points of a simple 5.3 Å

$\times 9.2$ Å rectangular net, are clusters of spots closely spaced at regular intervals corresponding to a cell parameter of approximately 38 Å. The pattern may be regarded as similar to those from plates of lizardite on which a superlattice periodicity along a^* has been superimposed.

9. *Antigorite* (Glen Urquhart, Scotland).

Electron micrographs of dispersions (Fig. 6) showed rectangular and irregular fragments accompanied in some cases by tube-like particles. This was difficult to understand in view of the plate-like nature of the gross material and it was later established that the fibrous particles came
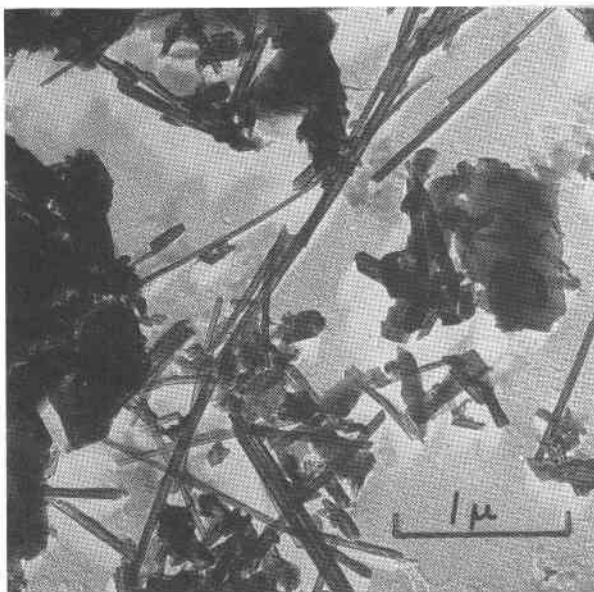

FIG. 6. Antigorite and chrysotile. e.m. of mixture (Specimen No. 9).

from an edge of the specimen which was yellow-brown and altered in appearance. Diffraction patterns of this tubular material identified it as clino-chrysotile. Some micrographs showed particles resembling wide tubes with wide bore or else elongated laths with curled edges. These too gave diffraction patterns of clino-chrysotile. A study of the fine structure in the $hk0$ bands appearing on patterns from single crysotile elements might reveal features characteristic of a particular curved formation (e.g., cylindrical, spiral, helical (Whittaker 1955c)). One pattern showed spots of both clino- and ortho-chrysotile (Fig. 2c) but the selected area contained more than one particle.

The plates of antigorite gave patterns similar to that shown in Fig. 4b yielding in most cases the values $b = 9.30$ Å, $a = 38$ Å, but some crystals gave $a = 34$ Å.

In order to investigate further the apparently variable a parameter of antigorite many more crystals from different specimens were examined and an analysis of these results is presented later.

10. *Antigorite* (Mikonui, New Zealand).

Patterns of the type shown in Figs. 4b and d were obtained from elongated, roughly rectangular platy crystals. Layer line spacing gave $b = 9.32$ Å (b parallel to crystal length), and the superlattice parameter was determined as $a = 43.1$ Å (c.f. x-ray single crystal measurements).

11 and 12. *Antigorites* (Caracas and Antigorio). These appeared in electron micrographs to have morphology similar to that of 10 and gave similar electron diffraction patterns exhibiting a variety of superlattice parameter values.

13. *Antigorite* (Yu Yen Stone). This very fine grained white material appeared in electron micrographs as irregular plate-like fragments sometimes showing a vaguely hexagonal outline. Many diffraction patterns (Fig. 5) show very closely spaced spots and yield parameters $a = 90$ Å to 110 Å, $b = 9.2$ Å; some yielded $a \simeq 41$ Å.

14. *Picrolite* (Shipton, Quebec).

Micrographs show plates and laths, but also some tubular material giving the diffraction pattern of clino-chrysotile. Diffraction from the plates yielded patterns similar to Fig. 4d.

15. *Picrolite* (Maryland, U.S.A.)

Electron micrographs show plates and broad laths (Fig. 4c), and the single crystal pictured gave the diffraction pattern in Fig. 4d ($b = 9.26$ Å, $a = 35.4$ Å).

16. *Synthetic (Mg-Ge) serpentine.*

Electron micrographs (Fig. 7a) show fairly thick plate-like crystals, some displaying sharp edges with a hexagonal outline. The diffraction pattern (Fig. 7b), comes from the thin crystals shown in the inset and resembles that of lizardite in being a hexagonal network. This yields the parameters $a = 5.40$ Å, $b = 9.40$ Å, which are larger than those of the Mg-Si serpentines.

The x-ray powder pattern from this synthetic serpentine contained very many closely spaced sharp lines indicating a large unit cell and a

well ordered crystal structure. The lines were all indexed using cell dimensions $a = 5.43_5$ Å, $b = 9.41_5$ Å, $c = 44.66 = 6 \times 7.44_5$ Å, $\beta = 90°$.

An $02l$ series of lines following closely on 020 (or 110) recalls the series which was reported for the specimen from Unst. In that case, Brindley and von Knorring (1954) suggested two possible explanations, namely that they could be indexed as $H20$ or as $02L$ lines corresponding to super-lattices $a = 43.6$ Å or $c = 3 \times 14.53$. These proposals have been further discussed by Zussman (1956). For the Mg-Ge serpentine, confirmation that the large parameter 44.66 Å is not associated with the a axis is provided by the electron diffraction pattern (Fig. 7b) since, unlike antigorites, it has no closely spaced spots in the a^* direction. It seems likely therefore that specimens 16 and 17 both contain a 6-layer cell.

17. *Massive Serpentine* (Unst, Shetlands).

Particles of this material are seen to be predominantly lath-like (Fig. 7c), and their electron diffraction patterns (Fig. 7d) differ from any of those previously described. Layer lines indicate a repeat distance along the lath axis, $a = 5.35$ Å $\pm 1\%$, and there is no indication of a long param-eter in this direction. On the zero layer are seen $00l$ and $0k0$ reflections and in some cases weak $0kl$ spots. On even layers $h0l$'s occur correspond-ing to a cell with $c = 14.5$ Å, including some strong reflections when l is odd and also some weak $hk0$ and hkl spots. On odd layers, $hk0$ and hkl spots appear which are consistent with a cell, $a = 5.35$, $b = 9.3$, $c = 14.5$ Å, $\beta = 90°$. Thus the pattern is one which may be derived by the rotation about a of a cell similar to that given for ortho-chrysotile by Whittaker (1951), and is compatible with the main reflections on the x-ray powder photograph presented by Brindley and von Knorring. However a few ad-ditional weak spots are sometimes observable on the first layer line which may correspond with some of the series of weak reflections fol-lowing 020 in the x-ray powder pattern. To summarize this discussion, the new evidence points clearly against this material having the antig-orite type cell, but provides only weak additional evidence for the 6-layer cell.

18. *Fibrous serpentine* (Unst, Shetlands).

Electron micrographs show slender lath-like fragments which give diffraction patterns similar to that shown in Fig. 7d.

ANALYSIS OF DATA FROM SINGLE CRYSTAL PATTERNS

The clusters of spots observed in electron diffraction patterns of antig-orites are similar to those obtained by x-ray diffraction from single crystals of antigorite from Mikonui (Aruja 1945, Zussman 1954), and

may be similarly interpreted as evidence of a large superlattice cell. However, the clusters also recall the unusual effects observed by other workers, e.g. from mica (Darbyshire and Cooper 1935), from ZnO (Rees and Spink 1950), from molybdenite (Finch and Wilman 1937, Uyeda, Ichinokawa and Fukano, 1954). In the case of mica, clusters of spots
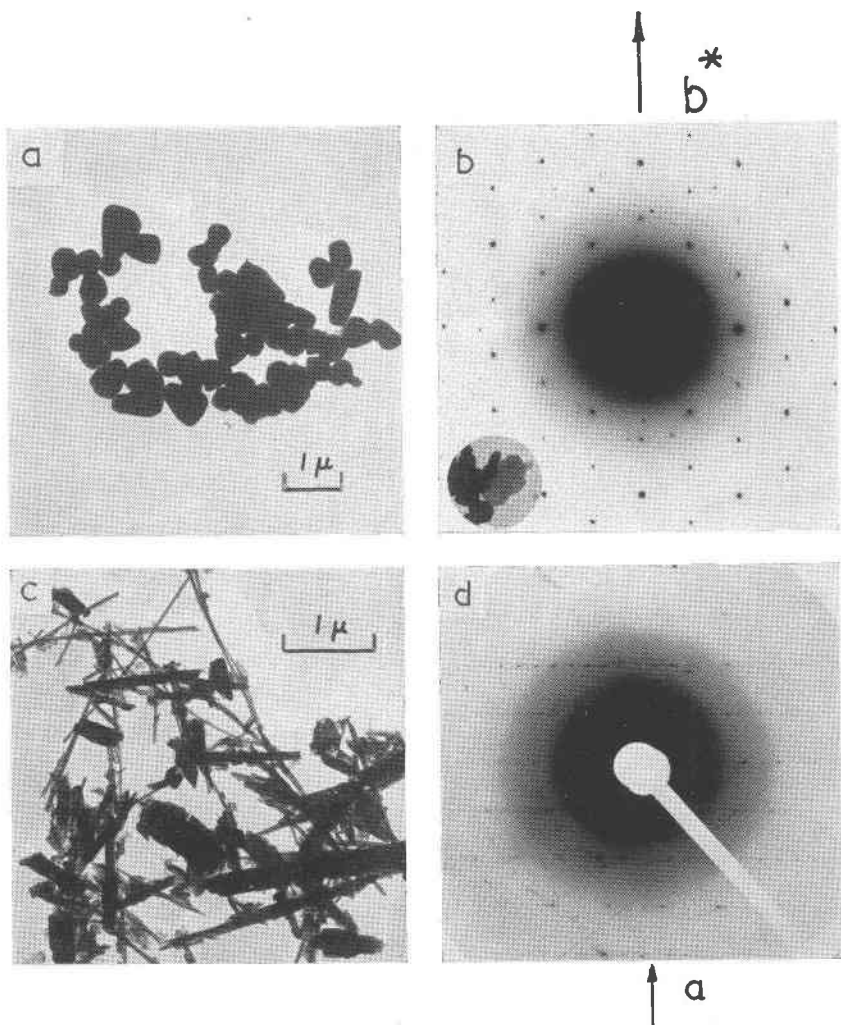
FIGS. 7*a* and *b*. 6-layer ortho-serpentine (synthetic Mg-Ge): e.m. of dispersion and e.d. pattern from crystals shown (Specimen No. 16).

FIGS. 7*c* and *d*. 6-layer ortho-serpentine (Unst): e.m. of dispersion and e.d. pattern from single lath (Specimen No. 17).

were attributed to *hkl* reflections occurring alongside of *hk*0's through bending or rotation of the crystal. In the case of ZnO and molybdenite, very close subsidiary maxima occur which are attributed to the limitation of crystal size. With these and other similar explanations in mind, the patterns of antigorite have been carefully examined, and it has been

TABLE 2. ANTIGORITES: *a* PARAMETER MEASUREMENTS, IN Å UNITS

Antigorio (O. 16327)	Antigorio (C. 70520)	Glen Urquhart	Mikonui	Caracas	Shipton, Quebec (Picrolite)	Harford Co., Md. (Picrolite)	Yu Yen Stone	Average
		33.4 33.5 33.9 33.9 34.0						33.7
	36.2					35.1 35.1 35.4 35.6 35.7 36.2 36.4		35.5
37.6 38.7 38.9	38.1 38.6 38.6 38.8	37.9 38.0 38.0 38.1 38.1 39.0						38.3
41.1	40.6		41.1 41.4 41.7	41.1 41.4	40.5 41.4	41.1 41.5		41.1
	42.3 42.6 43.0		42.7 43.1 43.5 43.7 44.0	42.4 42.4 42.8 43.2 43.6	43.9			43.1
							88.6 90.6 92.6 108 110	90.6 109

concluded that they are not explicable in such terms. They are entirely consistent with a structure involving a large *a* parameter which repeats with great regularity in successive cells of any given crystal.

In view of the variation from one pattern to another of the distances between the closely spaced spots in antigorite patterns, a study has been made of the sources of error involved, and the significance of the results has been evaluated.

Parameters derived from electron diffraction spot patterns are subject to errors introduced by the method of calibration and measurement, and possibly also by missetting of the crystal. Thin platy crystals can give a complete array of spots even when they are not exactly perpendicular to the beam, since reciprocal lattice points are in this case extended into "rods" in reciprocal space. If the $a \cdot b$ net plane is tilted about b by an angle ϕ, measurement of the spot pattern will give parameters b and $a \cos \phi$. Thus when control of crystal orientation is not possible, low values of the parameters may be obtained, the effect being most marked for distances measured normal to the axis of tilting. In the cases of the Mg-Ge serpentine and the lizardites, which produce hexagonal arrays of single spots, tilting can be detected by non-equivalence of spacings measured in symmetrically related directions; in some cases a tilted crystal can distort a rectangular spot pattern into an oblique one.

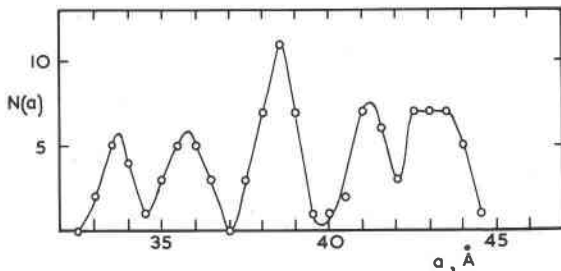In most cases described here, crystals tended to lie with the principal

Fig. 8. Distribution of a parameter values among antigorites.

net plane perpendicular to the beam, but orientation could not be further controlled. However, a crystal grossly tilted about b could be recognized by its effect on the average distance between clusters, and such patterns were disregarded.

Measurements of MgO powder rings indicated that a standard deviation of 1% in parameter value due to calibration and measurement errors could be expected. The mean value of the b parameter from a large number of determinations with a standard deviation of 1.1%, was 9.26 Å, indicating that there is little or no tilting affecting these measurements, and that b is more or less constant for all antigorites.

The values of a for antigorites were measured on many different patterns and are seen to fall into groups such that with one exception no member of a group differs by more than 2% from the mean (Table 2). It is certain that the differences in values recorded cannot be explained by crystal tilt, and that they are far greater than the estimated limits of experimental error. Table 2 also shows that not all possible values of a

are actually adopted in antigorite crystals but that certain values are "preferred." This is further illustrated in Fig. 8 where $N(a)$, the number of specimens with parameter $a \pm 0.5$ Å, is plotted against a, and peaks occur centered on 33.7, 35.8, 38.6, 41.2 and 43.0 Å. However, the difficulty of allowing for the fact that some crystals may give slightly low values through tilting makes it unwise to attach a too precise significance to the exact numbers quoted.*

DISCUSSION AND CONCLUSIONS

Electron microscope and electron diffraction studies have been used to examine the morphology, the unit cell parameters, and their interrelations in the serpentine minerals. They have been particularly useful where crystallite size has been too small for x-ray single crystal techniques, and have supplemented and sometimes modified previous concepts based on x-ray powder patterns alone. The main conclusions drawn from the presented results are summarized under appropriate headings below.

Chrysotile

Crysotile occurs in either silky or splintery fibres which in the dispersed state appear in electron micrographs as tubes and laths respectively. Electron diffraction patterns from single units of the silky variety still bear the features of a "rotation" pattern; they must therefore either contain smaller randomly oriented filaments, or else possess some tubular or roll-like configuration. Diffraction patterns from laths are also of the rotation type but indicate a greater degree of order in the fundamental crystallites.

Bundles of silky fibres were seen by x-ray diffraction to contain both ortho- and clino-chrysotile, but single elements of these gave electron diffraction patterns of either one cell or the other. Thus, it appears that ortho- and clino-chrysotile exist in separate strands.

Lizardite

The two specimens, #4 and #5, which are apparently very different, #4 being green and massive, #5 white and platy, are found to be fundamentally similar in that #4 is also platy on a fine scale, and both give similar x-ray and electron diffraction diagrams. The latter show hexagonal arrays of spots corresponding to the $a \cdot b$ net plane which lies in the plate and is perpendicular to the electron beam.

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* Not shown in Fig. 8 are values obtained from specimen 13 (Yu Yen Stone). Its patterns yield a parameters 41 Å, 90 Å and 110 Å. Furthermore, one specimen of a fibrous antigorite examined by J. A. Gard of Aberdeen University, yielded $a = 18.6$ Å.

Two bastites examined have similar morphology and give diffraction patterns similar to those of other lizardites.

Antigorites

Antigorites and picrolites were grouped together on the basis of x-ray powder patterns although the latter are fibrous, and it was thought (Whittaker and Zussman, 1956 (pt. 2)) that all possessed the same large cell with $a = 43.5$ Å. The present work shows that single picrolite crystals are lath-like and give electron diffraction patterns of the antigorite type. These patterns may be approximately described as those of an $a \cdot b$ net plane, with b parallel to the longer axis of the crystal, but with closely spaced spots of a superlattice in the a direction superimposed.

The superlattice parameter a is not constant, but takes a number of different values even among crystals from one specimen, and there are indications that certain values of a are preferred.

6-layer ortho-serpentines

A synthetic Mg-Ge serpentine has been allocated a six layered ($c = 6 \times 7.44_5$ Å) unit cell in order to index the many lines of its x-ray powder pattern (unpublished data). Confirmation that its large 44.7 Å axis is not of the antigorite type was provided by electron diffraction.

Micrographs of serpentine specimens from Unst, Shetlands, show laths which give spot patterns largely compatible with rotation of a 2-layered ortho-cell about the lath axis ($a = 5.3$ Å) but also showing faint indications of a 6-layer cell. This evidence, together with the absence of antigorite characteristics, and the previous x-ray evidence, all support the view that this material is structurally similar to the 6-layer Mg-Ge serpentine.

Nomenclature

In the light of the present studies some comment may be made concerning the naming of serpentine minerals. The classification presented by Whittaker and Zussman (1956) needs to be modified in some respects. As regards antigorite it was stated that only those specimens should be so called which give the x-ray powder pattern obtained from the variety from Mikonui. At that time this was the only variety from which single crystal x-ray patterns had been obtained. The principal features of the antigorite pattern are indeed shown by all of them but differences were noted which can now be attributed to the range of values adopted by the large a parameter. It seems reasonable that, for the present at least, the name antigorite should be applied to all serpentines possessing the large a parameter. Picrolites appear to be essentially antigorites with a splin-

tery fibrous character and therefore would be better termed "fibrous antigorite."

For the massive and columnar serpentine from Unst, Shetlands, it seems that their large parameter is $c = 6 \times 7.265 = 43.59$ Å and not the a parameter. Therefore, the name "ortho-antigorite" (Brindley and v. Knorring 1954) is no longer apposite. Such varieties can conveniently be called "6-layer ortho-serpentines."

The serpentine classification can now be represented as in Table 3. The table also indicates broadly the morphology (of each group) as seen in hand specimen and when dispersed in the electron microscope.

It is still premature to attempt to describe serpentine varieties with a systematic notation conveying symmetry and number of layers per cell

TABLE 3. SERPENTINE CLASSIFICATION

	Serpentines					
	Chrysotile	Lizardite	6-Layer Serpentine		Antigorite	
	Clino, Ortho, Para*				(various a parameters)	
Morphology (hand specimen)	fibrous; occasionally massive	massive or platy	massive, fibrous	platy	massive, platy	fibrous
Morphology (dispersed state, electron microscope)	tubes, laths	plates	laths	plates	plates	broad laths

* Para-chrysotile a component of silky fibre bundles was mentioned briefly by Whittaker and Zussman (1956) and its structure is to be further discussed by Whittaker in a future paper.

such as Levinson (1955) has developed for the micas because many details of the serpentine structures have yet to be evaluated.

In conclusion it is suggested that the terms "antigorite" and "chrysotile" should not be used loosely as being synonymous with "massive" and "fibrous." The four principal varieties can usually be identified by they x-ray powder patterns, but a more detailed designation can be achieved by careful examination of single crystal or fibre patterns obtained by x-ray and/or electron diffraction methods supplemented by electron micrographs.

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