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A REAPPRAISAL OF THE STRUCTURES OF THE SERPENTINE MINERALS

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ABSTRACT

The three theoretical stacking schemes for trioctahedral 1:1 layer silicates developed independently by Steadman, Zvyagin, and Bailey all assume ideal hydrogen bonding between successive layers, with polytypes developed through shifts of $\pm a/3$, $\pm b/3$ or zero, and rotations of 180° or zero. The three systems contain 16 distinct polytypes, and Bailey's nomenclature is extended to provide symbols for each one. If lizardite is redefined to include all serpentines with flat-layer structures, these can be designated as lizardite followed by the appropriate polytype symbol.

The above system cannot be applied to the chrysotile structures because the shifts between the layers show that the normal hydrogen bonding position is not achieved. The layer stacking depends on the fact that the basal oxygens form two sets, differing in z, and the lower one lies in the grooves between, and the upper one over the ridges formed by, the underlying hydroxyl rows. This stacking principle leads to a series of polytypes for which an analogous nomenclature is proposed, using subscript c to denote their essentially cylindrical character. Thus clinochrysotile, orthochrysotile and Zvyagin's 1-layer clinochrysotile become chrysotile $2M_{c1}$, $2Or_{c1}$ and $1M_{c1}$. The term parachrysotile is retained to describe the cylindrical structure with a 9.2Å fiber axis. The alternating wave structure of antigorite, with layer inversions and interconnections between successive layers at the inversions, destroys the possibility of systematic hydrogen bonding and makes the stacking dependent on the primary bonding at the interconnections, so that it cannot be discussed in terms of polytypes of either kind.

A review of the substitution in natural and synthetic chrysotiles and lizardites indicates that there is a compositional overlap between curved and flat-layer structures. Thus, as all flat-layer structures can be regarded as polytypes of lizardite and all cylindrical structures with a 5.3Å fiber axis can be regarded as polytypes of chrysotile, lizardite and chrysotile are polymorphs. Compositional data for parachrysotile are lacking. Antigorite is not a polymorph of the other serpentines because it has an essentially (though only slightly) different composition.

Because the mismatched tetrahedral and octahedral sheets in lizardite are respectively in tension and compression, it is suggested that it is the compression of the octahedral sheet that buckles the Mg plane so that the Mg atoms occupy two positions at different levels. This disturbance of the structure in turn tilts the tetrahedra in the way that is observed. In chrysotile the curvature only partly relieves the mismatch, and evidence is presented for a similar buckling in this structure, though to a smaller extent. This postulated buckling explains some hitherto obscure features of the structure. Antigorite appears to overcompensate the mismatch in the direction of curvature, but it has an anomalously thick octahedral sheet which is still unexplained.

INTRODUCTION

Because of their frequent sub-microscopic, fine-grained texture and close chemical relationships, an adequate classification of the serpentine minerals was delayed until structural information became available, and this was itself delayed by the unusual curved layers, superlattices and disordered stackings that occur in these minerals. It was not until 1956 that work on the structures of chrysotile by Whittaker (1952, 1953, 1954, 1955a, b, c, d, 1956a, b, c, 1957) and by Jagodzinski & Kunze (1954a, b, c) and of antigorite by Zussman (1954) and Kunze (1956, 1958, 1959) was advanced sufficiently for a viable classification to be put forward (Whittaker & Zussman 1956).

This classification divided the serpentine minerals into three structural groups based on cylindrical layers (chrysotile), corrugated layers (antigorite) and flat layers (lizardite). Chrysotile was further sub-divided into three varieties, clinochrysotile, orthochrysotile and parachrysotile. Antigorite was soon found to occur with a range of superlattice periods (corrugation wave-lengths) from 16 - 110Å as well as the original 43Å (Brindley *et al.* 1958; Chapman & Zussman 1959; Kunze 1961). Sub-division of the flat-layer serpentines was necessitated by the discovery of varieties with a 1-layer cell and a 2-layer cell (Rucklidge & Zussman 1965), a 6-layer cell (Zussman & Brindley 1957; Zussman, Brindley & Comer 1957; Olsen 1961; Müller 1963; Krstanović & Pavlovič 1967), a 6- (pseudo 2-) layer and a 6- (pseudo 3-) layer cell (Gillery 1959; Bailey & Tyler 1960), a 3-layer cell (Coats 1968) and a 9-layer cell (Jahanbagloo & Zoltai 1968)*. It has since become evident from the work of Zvyagin (1967) that a fourth variety of chrysotile, 1-layer clinochrysotile, must be added to the three chrysotiles of Whittaker & Zussman's classification.

Only two serpentine varieties have come to light whose relationship to the three-fold classification has been in doubt. One is the splintery serpentine (Povlen-type) found by Krstanovic & Pavlović (1964) which they suggested to have a modified clinochrysotile structure. More recently Middleton (1974) has investigated this further and found Povlen-type clinochrysotile to be composed of chrysotile-like layers. He has also found a Povlen-type orthochrysotile whose structure he has interpreted as an intergrowth of chrysotile and lizardite-like layers. The other serpentine variety is an unusual serpentine from the Tilly Foster mine, New York (Aumento 1967,) which may be a very intimate mixture of clinochrysotile and antigorite.

The purpose of the present paper is to discuss the differences between the internal structure of the layers of the main divisions of the serpentine minerals, and to relate them to one another and to other trioctahedral 1:1 layer silicates in terms of structure and crystal chemistry, and in this connection to develop further the discussion of Olsen (1961) and Radoslovich (1963b). The relationships of these structural features to the chemical differences that have been treated previously by Faust & Fahey (1962), Page (1968), and Whittaker & Wicks (1970) are also discussed. However, before proceeding to this discussion it is desirable to consider the relationships of the layer stacking of the serpentine minerals to the polytype classifications of Steadman (1964), Zvyagin (1967) and Bailey (1967a, 1969) for 1:1 layer silicates. Some confusion has been introduced into the literature by attempts to fit the serpentines into these classifications, which are not in fact directly applicable to the serpentine structures.

THEORETICAL POLYTYPES

Three theoretical stacking schemes for trioctahedral 1:1 layer silicates have been developed in recent years by (i) Steadman (1964), (ii) Zvyagin, Mischenko & Shitov (1966) and Zvyagin (1967) and (iii) Bailey (1967a, 1969). The terminology developed by the various authors differs and so do their basic assumptions, so that the same series of polytypes is not developed in each system, although there is considerable overlap (Table 1). The full details of the procedures are given in the original papers

TABLE 1. A COMPARISON OF POLYTYPES

			Steadman (1964)	Zvyagin (1967)				Bailey (1969)		
Space Group	No. of Layers in Unit Cell	Inter-layer Shifts	Structure Number	Trioctahedral Group Number	Structure Number	Structure Type	Modification	Group	Polytype	Extended Bailey Nomenclature
Cm	1	*a*/3	17	I^1	1	B	1M	A	1M	1M
Cc	2	*a*/3	18		2		$2M_1$		$2M_1$	$2M_1$
$P3_1$	3	*a*/3	19 & 20		3 & 4		3T		3T	$3T_1$
$Ccm2_1$	2	*a*/3+r	not considered	III^1	1	C	20	B	20r	20r
$P2_1$	2	*a*/3+r			2 & 3		$2M_3$	equivalent to 20r		
Cc	2	*a*/3+r			4		$2M_2$		$2M_2$	$2M_2$
$P6_{1\ \mathrm{or}\ 5}$	6	*a*/3+r			5 & 6		6H		6H	$6H_1$
P31m	1	None	1	IV^1	1	A	1T	C	1T	1T
R3	3	*b*/3	2 & 3	II^1	1 & 2		3T		3R	3R
P31c	2	*b*/3	8	II^1	3		2T		2T	2T
$P6_3cm$	2	None+r	9	VI^1	1	D	2H	D	$2H_1$	$2H_1$
$P6_3$	2	*b*/3+r	10 & 11	V^1	2 & 3		2H		$2H_2$	$2H_2$
R3c	6	*b*/3+r	16	V^1	1		6T		6R	$6R_1$
R3	6	None, *b*/3	4 & 5					affinities with		$6R_2$
P3	3	None, *b*/3	6 & 7					Bailey Group C		$3T_2$
R3	6	None+r *b*/3+r	12 & 13					affinities with		$6R_3$
$P6_3$	6	None+r *b*/3+r	14 & 15					Bailey Group D		$6H_2$

Where two structure numbers according to Steadman or Zvyagin are given on one line, they correspond to enantiomorphs.

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*Jahanbagloo & Zoltai (1968) analyzed what they called a hexagonal Al-serpentine with a 9-layer trigonal structure and a composition of $(Mg_{2.07}Al_{.72}Fe_{.07})(Si_{1.47}Al_{.53})O_5(OH)_4$. However, as this composition is closer to the amesite end of the lizardite-amesite solid-solution series this specimen will be called amesite *9T* in this paper.

and a detailed comparison of the methods is given in Wicks (1969).

For purposes of generating the various polytypes, the three systems assume an ideal tetrahedral sheet with hexagonal symmetry, linked through the apical oxygens without distortion to an ideal trioctahedral sheet with trigonal symmetry (Fig. 1). Stacking of successive layers is then assumed to occur in such a way that hydrogen bonding always develops between every basal oxygen of a given layer and the outer hydroxyls of the adjacent layer (see Fig. 2 of Bailey 1969). If such layers are stacked vertically above* one another such an optimum hydrogen-bonding system is developed, and the structure has a 1:1 layer trigonal unit cell. Equivalent hydrogen-bonding systems are developed if successive layers are shifted relative to one another by $-a/3$** along any of the three possible x-axes of the layer, or by $\pm b/3$ along a y-axis, rotated through ± 60°, ± 120° or 180°, or are subjected to combinations of such shifts and rotation. The number of alternatives is reduced by the fact that the layer symmetry makes it possible to describe all polytypes produced by $\pm b/3$ shifts in terms of a single y-axis (Fig. 1). It also makes rotations of ±120° equivalent to no rotation, and rotations of ±60° or 180° indistinguishable and therefore describable simply as rotation (r).

Zvyagin (1967) and Bailey (1969) have both classified the possible polytypes into four groups under the further limiting assumptions that:

(i) combined shifts of the type $a/3$ and $b/3$ do not occur

(ii) the relationship between every successive pair of layers involves the same kind of shift, or shift + rotation, although the direction of the shift may change in a systematic way to give multi-layer cells, as in the mica polytypes.

Both these authors classify the polytypes into four groups depending on the existence of interlayer relationships $a/3$, $a/3 + r$, $b/3$, and $b/3 + r$, with zero shift classified with the $b/3$ shifts. Their results are therefore virtually equivalent, but in comparing them it is important to note that Zvyagin and Bailey denote the groups by the same four letters but in a different way (Table 1). Bailey shows that Zvyagin's $2M_3$ polytype is equivalent to $2Or$ given the full symmetry of the layers. The members of each group are shown not only to share the same formal relationship but also to give rise to readily distinguishable diffraction intensities among their strong reflections (see Table 2, p. 361, Bailey 1969). Individual members of a group can be distinguished only by differences among their weak reflections (see Table 3, p. 362, Bailey 1969).

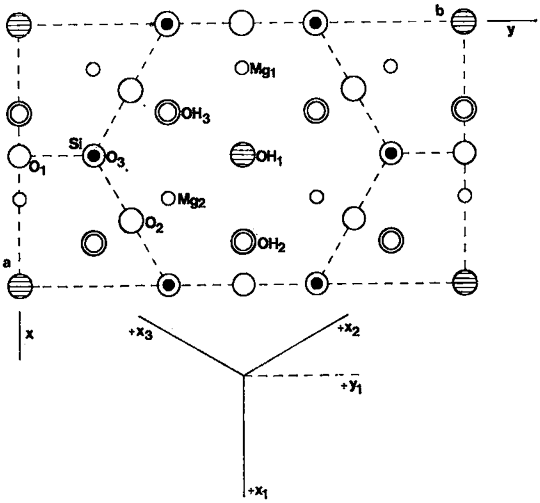

FIG. 1. [001] projection of the idealized serpentine layer with Mg in the II octahedral sites with respect to the x-axes, as defined by Bailey (1969). In the monoclinic chrysotile polytypes it is necessary to reverse the positive direction of the x-axis in order to satisfy the convention that β should be obtuse and as small as possible.

The earlier classification of Steadman (1964) is also shown in Table 1. Steadman did not divide the structures into groups, and he did not consider those based on shifts of $a/3 + r$, but he did include four more (enantiomorphic pairs of) structures not given by Zvyagin or Bailey because different kinds of shifts between alternate pairs of layers are involved. In fact Bailey has shown that structures exist which contain mixed shift sequences so that these structures listed by Steadman are not without interest. Steadman's numbers 4-7 have affinities to Bailey's group C and 12-15 to Bailey's group

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*The convention adopted by Steadman and Bailey, which is followed here, is to regard the outer hydroxyls to be on the top of the layers, and the silicate net at the bottom. In Zvyagin's discussion the opposite convention is adopted, but this makes no difference to the nomenclature and has been allowed for in the comparisons of the different classifications.

**There are two possible sets of octahedral sites in a 1:1 silicate layer, that occupied by Mg in Figure 1 (called II by Bailey) and another (I) which involves an interchange of the projected positions of Mg and the outer hydroxyls. If Mg occupies set I, the appropriate shifts are $+ a/3$.

D. Bailey's polytype nomenclature can be extended readily to take account of these, and other possible polytypes, as indicated in the last column of Table 1, and his extended system is used in this paper. Disordered crystals can usually be assigned to one of the major groups, A, B, C or D, Table 1, on the basis of their strong reflections.

ACTUAL POLYTYPES

Amesite and cronstedtite

The usefulness of the theoretical polytype schemes is illustrated most clearly by the structural studies on amesite and cronstedtite. In amesite, (polytypes $2H_1$ (Oughton 1957) $2H_2$ (Steinfink & Brunton 1956) and $6R_3$ (Steadman & Nuttall 1962), all in Bailey's group D, as well as a $9T$ polytype not developed in the theoretical schemes (Jahanbagloo & Zoltai 1968) have been described. In cronstedtite, polytypes $1M$, $2M_1$ and $3T_1$ (Group A), polytypes $1T$ and $2T$ (Group C), and polytypes $2H_1$, $2H_2$, $6R_3$ and $6H_2$ (Group D) have been found by Steadman & Nuttall (1963 and 1964). It is of interest to note that the $6R_3$ and $6H_2$ polytypes are developed only in Steadman's classification, but the others are found in all three classifications.

Lizardite

The name lizardite was proposed by Whittaker & Zussman (1956) to denote a serpentine mineral possessing a single-layer orthohexagonal cell and varying degrees of three-dimensional order; however, they noted that some specimens did not conform entirely to the single-layer cell but contained 180° rotations in some kind of random sequence. The flat-layer serpentines having multi-layer cells have hitherto been referred to simply as "multi-layer serpentines", with an implication that they are to be regarded as species distinct from lizardite. A simplification would be achieved if all flat-layer serpentines were termed lizardite, so that the 1-layer and 2-layer lizardites and the multi-layer varieties could all be regarded as polytypes. This nomenclature is therefore followed in the remainder of this paper. The problems raised in relation to the definitions of polymorphism and polytypism in the presence of small chemical differences are discussed below.

Detailed studies on the type lizardite from Kennack Cove, Cornwall, England, by Rucklidge & Zussman (1965) indicated that the crystals were composed of domains equivalent to the $1T$ and $2H$ polytypes (disregarding the $\pm b/3$ disorder). Krstanović (1968) has examined a number of lizardite samples from various Yugoslavian localities and selected those composed only of the disordered $1T$ polytype for detailed structural studies.

Although the structure of the individual layers in lizardite departs from the ideal in a number of ways, (discussed below), the stacking of the layers one on another is based on hydrogen bonding of the basal oxygens of one layer to the hydroxyls of the layer below in the manner assumed in the derivations of the theoretical polytypes. The use of the nomenclature discussed above is therefore fully justified.

The theoretical polytype classifications have their greatest application in the multi-layer varieties. These have been frequently classified in terms developed by Gillery (1959) as 6(2)-layer structures approximating a 2-layer structure, and as 6(3)-layer structures approximating a 3-layer structure. Most of the multi-layer lizardites described in the literature have some degree of disorder so that their diffraction patterns do not always fit Bailey's calculated diffraction patterns (Bailey 1969, Table 3, p. 362) and some have structures not included in Bailey's table. However, the main structural group A, B, C or D can often be determined by the use of Bailey's Table 2, p. 361, although elements of two structural groups may be present in some specimens.

It is interesting that the frequency of occurrence of the multi-layer lizardite polytypes recorded in the literature is: 2 in (Bailey's) group A, 1 in group B, 1 in group C and 4 in group D. When the one- and two-layer lizardites ($1T$ and $2H$) are included, however, group C becomes by far the most frequent group and the frequency of occurrence becomes C>D>A>B. This is the same relationship derived by Bailey (1969) from theoretical structure-stability estimations.

Bailey (1969) has indicated that further work is in progress on the multi-layer polytypes.

Chrysotile

Whittaker (1953, 1956a, b, c) has defined three types of chrysotile: clinochrysotile, orthochrysotile, and parachrysotile. Clinochrysotile has a 2-layer monoclinic cell (disregarding the cylindrical nature of the structure) with no rotation between the layers. Orthochrysotile and parachrysotile have 2-layer orthorhombic cells with rotations of 180° between the layers. In clinochrysotile and orthochrysotile the x-crystallographic axis is parallel to the fiber axis (the cylinder axis), whereas in parachrysotile the y-axis is parallel to the fiber axis. The cylindrical nature of clinochrysotile and orthochrysotile has been confirmed by electron microscope observation by Yada (1967), but the nature of parachrysotile is not as well-understood. Yada (1971) suggested that parachrysotile might be in the form of curved crystallites on the surface of clinochrysotile fibrils, but Middleton (1974) has shown that it must contain at least some cylindrical component.

Some confusion has developed in the literature as a result of the attempt to assign the chrysotile structures to polytypes in the various theoretical schemes. These schemes all make the fundamental assumption that each layer is stacked on the previous layer so that normal hydrogen bonding is developed (Fig. 2, Bailey 1969). However, in chrysotiles successive layers are stacked in such a manner that the normal hydrogen bonding does *not* take place (Whittaker 1953). The continuously changing register between adjacent layers in the circumferential direction inhibits systematic hydrogen bonding for all the basal oxygens, and not merely for ⅓ of them as assumed by Bailey (1969).

The structural refinements of both clinochrysotile (Whittaker 1956a) and orthochrysotile (Whittaker 1956b) indicate that the basal oxygens O_1 and O_2 are separated in the radial direction by 0.2Å, with O_1 projecting from the layer structure and O_2 withdrawn into it. The cylindrical curvature of the structure aligns the outer OH groups so that they form rows with grooves between them running around the circumference of the structure. Successive layers are stacked in such a way that the projecting O_1's fit into the underlying grooves and the withdrawn O_2's lie approximately over the OH rows. This arrangement involves a shift of 0.4Å (approximately $a/13$) away from the position of normal hydrogen bonding, assumed in the polytype schemes and found in many 1:1 layer structures. This shift, overlooked in general discussions of the chrysotile structures, eliminates chrysotile from any discussions of theoretical polytypes based on normal hydrogen bonding, and leads to a need for a different polytype nomenclature for chrysotile as discussed below.

The consequences of ignoring this unique stacking arrangement are illustrated by the confusion existing over the assignment of the standard polytypes to clinochrysotile and orthochrysotile. Steadman and Bailey consider clinochrysotile to be a distorted $1T$ polytype but Zvyagin considers it to be a distorted $1M$. Similarly, Steadman and Zvyagin consider orthochrysotile to be a distorted $2H$, but Bailey considers it to be a distorted $2Or$. This confusion is brought about by failing to appreciate that the interlayer shifts in chrysotile, although small, are significant and in the opposite direction to the shift in the standard polytypes. Also, the total lack of order along the y (circumferential) direction destroys the regular hydrogen bonding and reduces the effective repeat unit along x to $a/2$. Under these conditions it is possible to choose

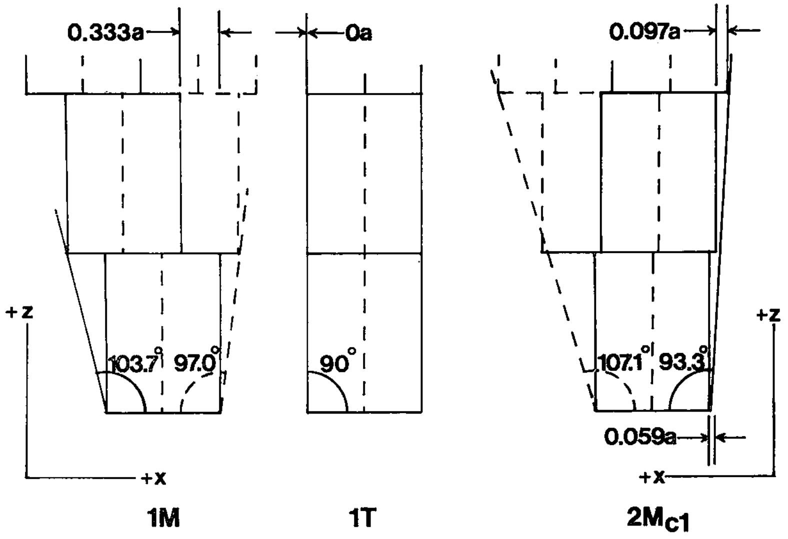

FIG. 2. Stacking relationships between chrysotile $2M_{c1}$ and disordered $1T$ and $1M$ polytypes in the [010] projection. The standard orientation of $2M_{c1}$ reverses the polarity of the x-axis in comparison to the standard polytypes. All β values are calculated on a basis of $a = 5.34\text{Å}$ and $c = 7.32\text{Å}$.

alternate origins for *a* which leads to further sources of confusion.

In order to distinguish the polytypes that arise in the chrysotile structure from those applicable to flat-layer structures, it is proposed to use a subscript *c* (for cylindrical) immediately following the main symbol (*e.g.* $2M_{c1}$, where $2 =$ the number of layers in the cell, $M =$ monoclinic, $c =$ cylindrical and $1 =$ polytype number), and to proceed to derive a number of expected polytypes.

In both the ortho- and clinochrysotile structures described by Whittaker the O_1 atoms not only project out of the layer in the radial direction, but are displaced by 0.10Å from their ideal position in the *x*-direction, *i.e.* parallel to the cylinder axis. In the discussion below, we suggest a mechanism for the production of this displacement which is an inevitable result of the compressive stress in the octahedral sheet of the serpentine structure. If it is accepted that the displacement always occurs, then a number of possible polytypes can be predicted.

As stated above, for a simple stacking of ideal layers with O_1 keyed into the grooves between rows of hydroxyls in the layer below, there would be a shift of the rows of hydroxyls on top of one layer with respect to those on the one below of approximately 0.4Å, which is in the opposite direction from the shift in Bailey's and Zvyagin's $1M$ disordered polytype (Fig. 2). If this situation were repeated in every layer, a $1M_c$ structure would result with $\beta = 93.3°$. If however O_1 is displaced by δ in the *x*-direction relative to the upper parts of its own layer, then because it is keyed into the groove of the layer below, the shift between one layer and the next will be changed to $0.4 \pm \delta$Å. When this shift is greater than and less than 0.4Å we propose to call the situation overshift and undershift respectively. In the known structure of clinochrysotile, which we now propose to denote $2M_{c1}$, δ is about 0.1Å and overshift and undershift occur in successive layers, with the result that β has the same value (93.3°) as if no undershift or overshift occurred, but of course the cell contains two layers.

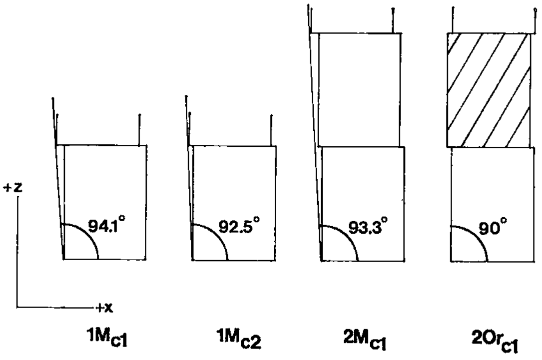

FIG. 3. Stacking relationships among the chrysotile polytypes $1M_{c1}$, $1M_{c2}$, $2M_{c1}$ and $2Or_{c1}$.

The stacking of ideal layers with a rotation of 180° between successive layers produces a separation of $a/6$ between the rows of hydroxyls from one layer to the next. In order to produce orthochrysotile with O_1 keyed into the grooves between the rows of hydroxyls in the layer below there must be a shift, from the ideal stacking position, of $0.4 \pm \delta$Å in the opposite direction to the shift necessary to produce Bailey's $2Or$ disordered polytype. This shift reduces the $a/6$ separation between hydroxyl rows in successive layers by $0.4 \pm \delta$Å. Either undershift or overshift in both layers would be compatible with the orthorhombic character; however, the structures would be different and would give significantly different $20l$ intensities. The known structure of orthochrysotile has undershift in both layers and we denote it $2Or_{c1}$. The theoretically possible structure with overshift in both layers may be denoted $2Or_{c2}$. Structures with alternate layers rotated by 180° but with alternating undershift and overshift can also be hypothesized, but they would be monoclinic with $\beta = 90.4°$ for a value of $\delta = 0.1$Å, and would constitute an enantiomorphic pair.

It is now important to consider the effect of over- and undershift in possible 1-layer structures. For $\delta = 0.1$Å these would have $\beta = 94.1°$ and 92.5° respectively, and we denote these as $1M_{c1}$ and $1M_{c2}$ respectively (Fig. 3) Zvyagin (1967) has published electron diffraction patterns of a 1-layer clinochrysotile fibril with $\beta = 106.5°$ which he suggests is the (disordered) ordinary $1M$ polytype. However, if $1M$ occurs, it would be expected to have $\beta = 103.7°$. Because of the complete circumferential disorder in chrysotile, it is always possible to choose an alternative β-angle due to the effective $a/2$ repeat along x (see Fig. 2). The alternative value for our $1M_{c1}$ polytype is 106.4°, in excellent agreement with Zvyagin's observation. We therefore conclude that his material has the $1M_{c1}$ stacking, and a β-angle that would be expressed more conventionally at 94.2°.

The high-resolution electron micrographs of chrysotile fibers sectioned perpendicular to the fiber axis (Yada 1967) give further support to the existence of a 1-layer clinochrysotile. The double spiral and concentric circular structures could possess a 2-layer clinochrysotile structure as defined by Whittaker (1956a) or an ortho-

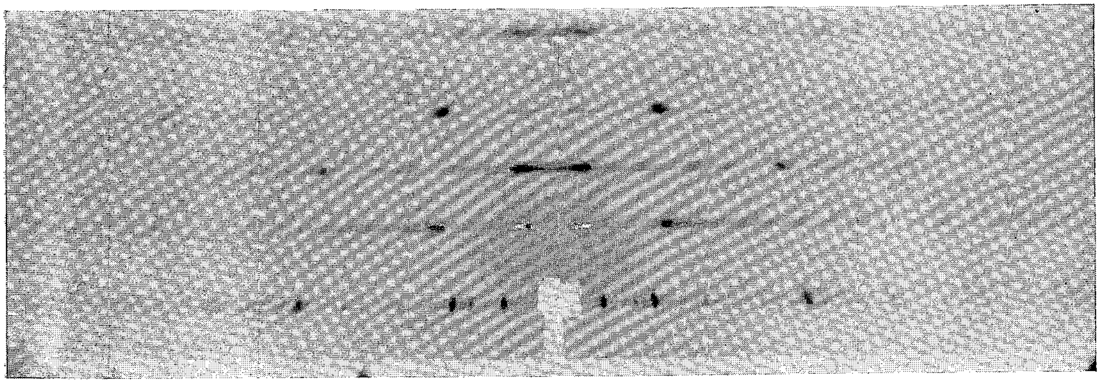

FIG. 4. Equi-inclination fiber photograph of chrysotile D_c from Krantz Kop, Natal.

chrysotile structure (Whittaker 1956b). However, multispiral structures with an odd number of layers, and those with numerous single-layer dislocations, cannot possess the 2-layer clinochrysotile structure. The 2-layer structure cannot form because the alternate positive and negative displacement of layers with respect to one another would be put out of sequence by each extra layer added by dislocation, or by the odd number of layers in multispiral structures. However, if the displacement is in the same direction in each layer so that the 1-layer clinochrysotile structure (Whittaker 1956a; Zvyagin 1967) develops, these multilayer spiral and single-layer dislocation growths would present no problem. Following the same reasoning, orthochrysotile or parachrysotile could not have multispiral growths with odd numbers of layers, or possess a high number of single-layer dislocations.

In addition to the three chrysotile polytypes $2M_{c1}$, $2Or_{c1}$ and $1M_{c1}$ that have now been observed, in many specimens there is evidence from the greater breadths of the $20l$ reflections relative to those of the $00l$ reflections that mistakes in the layer stacking may occur within a single fibril. In the extreme case there may be no discernible regularity in the stacking, and the $20l$ reflections are smeared into virtually continuous streaks along the layer lines. This disordered stacking is conveniently denoted as chrysotile D_c. An x-ray photograph of such a specimen from Krantz Kop, Natal (Whittaker 1956d) is shown in Figure 4.

With the introduction of an adequate polytype nomenclature it is no longer necessary to use the prefixes ortho- and clino- for chrysotile, as these can be more meaningfully replaced by the appropriate polytype symbol. However, all the polytypes discussed above have the x-direction parallel to the cylinder axis, and it is not possible to include parachrysotile in the scheme without introducing an additional symbol to denote the orientation of the layer axes. It is suggested that the name parachrysotile should therefore continue to be used as in the past. Thus chrysotile is a generic name for all the varieties; specific polytypes with x parallel to the cylinder axis can be unambiguously denoted as chrysotile with a polytype symbol, and material with y parallel to the cylinder axis can be unambiguously denoted by parachrysotile, to which a system of polytype symbols may also be added at some time in the future should this prove necessary. It is clear that parachrysotile must be regarded as a polymorph, and not a polytype, of chrysotile.

Antigorite

Zvyagin (1967) and Bailey (1969) have classified antigorite as a distorted $1T$ polytype. However, the curvature of the structure has the same effect as in chrysotile in precluding systematic hydrogen bonding between successive layers, and the control on the layer stacking is exerted by the direct interconnections between successive layers on the places $a = 0$ and $a = ½$ where the corrugations invert. Furthermore, the existence of the superlattice, and the changing relationship between successive layers over the half wavelength of the corrugated structure, change the diffraction pattern fundamentally from that calculated for the theoretical $1T$ polytype. Thus there is little value in discussing antigorite in terms of the theoretical polytypes.

CHEMICAL RELATIONSHIPS AMONG THE SERPENTINE MINERALS

Chrysotile and lizardite

It is generally accepted that the layer curva-

TABLE 2. AMOUNTS OF TRIVALENT SUBSTITUTION IN CHRYSOTILES AND LIZARDITES

Average x	Sample No.*	Average x	Sample No.*
0.01	C-3	0.11	L-1
0.03	C-4	0.13	S-2
0.035	C-1	0.14	C-6
0.045	C-2	0.16	L-5
0.08	L-4	0.20	L-3
0.09	C-5	0.23	L-2
0.10	C-7	0.35	S-3
0.105	S-1		

*C = chrysotile, L = 1- or 2-layer lizardite, S = multi-layer lizardite See Table 3, page 1034, Whittaker & Wicks (1970).

ture that occurs in both chrysotile and antigorite is due to the misfit between the octahedral and tetrahedral sheets with $b_{oct} > b_{tet}$, and neither chrysotile nor antigorite would be expected to form if the composition were such as to make $b_{oct} < b_{tet}$. However, if curvature is not the only conceivable way in which misfit might be accommodated when the composition is such as to make one expect $b_{oct} > b_{tet}$, then the converse assumption that lizardites cannot form under these circumstances need not be true. Flat-layer structures are expected when $b_{oct} = b_{tet}$, or when $b_{oct} < b_{tet}$, accommodation in the latter case depending mainly on tetrahedral rotations (Radoslovich & Norrish 1962; Radoslovich 1962).

The data available from analytical (Whittaker & Wicks 1970) and synthesis studies (Chernosky 1971, 1975) suggest that lizardite and chrysotile can indeed both form in overlapping composition ranges corresponding to $b_{oct} > b_{tet}$, and that the quest for a break in the composition range between chrysotile and lizardite pursued by Gillery (1959), Olsen (1961) and Radoslovich (1963b) is fruitless.

Radoslovich (1962) has shown that the for- $b_{oct} = b_{tet}$ when $x = 0.75$. This limit will be mula $(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8$* gives rise to raised by the presence of octahedral Fe^{2+} replacing Mg or octahedral Fe^{3+} replacing Al, and will be lowered by the presence of tetrahedral Fe^{3+} replacing Al. Therefore, it would be expected, and seems to be a fact, that chrysotiles can accept more Fe^{2+} than lizardite. On the basis of his synthesis work which gave lizardite and no chrysotile at $x = 0.25$ and above, and because of the statement by Nagy & Faust (1956) that natural chrysotile contains up to 2.9 ± 1.9 ($Al_2O_3 + Fe_2O_3$), Gillery suggested a compositional break between chrysotile and lizardite at $x = 0.2$. Olsen (1961) showed that Brindley & von Knorring's (1954) 6-layer lizardites had $x = 0.11$ and $x = 0.12$, and he proposed on the basis of these values, and of the analyses of Kalousek & Muttart (1957), that the assumed break is at $x = 0.10$. Subsequently, Radoslovich (1963b) concluded that "the high value, $x = 0.25$, was more acceptable". More recently Chernosky (1975) has synthesized chrysotile from $x = 0.0$ to 0.25 and lizardite from $x = 0.0$ to 2.0, demonstrating that there is no compositional break.

It is to be noted that even if a compositional break did exist at $x = 0.25$, there would still be a range of composition from $x = 0.25 - 0.75$ in which $b_{oct} > b_{tet}$ and yet flat layers are formed. It follows that there must be a mechanism of misfit relief other than curvature, and it is, therefore, perfectly feasible for alternative mechanisms of misfit relief to be operative over a given range of composition. Table 2 shows the value of x for the 15 specimens discussed by Whittaker & Wicks (1970) and among these specimens it may be seen that lizardites occur down to $x = 0.08$ and chrysotiles up to $x = 0.14$. In view of the small number of specimens studied, it would be surprising if the range of overlap were not appreciably greater than this.

The evidence from Gillery's and Chernosky's work suggests that multi-layer lizardites are favoured by high values of x, and the highest value of x in Table 2 corresponds to a specimen of this type. However, even if this trend exists, there is again no clear-cut distinction between the composition ranges of 1- and 2-layer lizardites and multi-layer lizardites.

The possibility that systematic compositional differences might exist among serpentine minerals and their varieties has led some authors to question the propriety of regarding them as polymorphs or polytypes. Within the range of their overlapping compositions now demonstrated, one need clearly have no inhibitions about this. Furthermore, it would be absurd to define polymorphism or polytypism so narrowly in respect of chemical identity that one part of an isomorphous series was regarded as polymorphic or polytypic with respect to another structure, whereas another part was not. It would seem almost inevitable that two polymorphic structures should have somewhat different capacities for accepting isomorphous replacement and therefore that close study should reveal incomplete equivalence in their chemical compositions. Equally, it would seem highly

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* Although the simple formula, corresponding to one structural formula unit, is used elsewhere in this paper a double formula is used in this section because it has been used as the basis of the discussions quoted from the literature.

probable that the occurrence of (possibly partly ordered) isomorphous substitution should modify the relative stability of different polytypes of a structure, and therefore that close study should reveal compositional differences (at least on a statistical basis) between polytypes. The appeal to small compositional differences to deny the existence of polymorphic or polytypic relationships therefore seems to be a profitless exercise.

In view of the above discussion it is suggested that all flat-layer serpentines, whether 1- or 2- or multi-layered types, should be regarded as polytypes of lizardite; that 1-layer clino-, 2-layer clino- and orthochrysotile should be regarded as polytypes of chrysotile; and that lizardite, chrysotile and parachrysotile should be regarded as polymorphs because their structures involve different processes of misfit relief, and their different stacking arrangements are consequences of this and not merely simple alternatives such as occur between polytypes.

Antigorite

The analyses discussed by Whittaker & Wicks (1970) indicate that antigorites have a higher SiO_2 content and a lower MgO and H_2O^+ content than the other serpentine minerals. This difference in composition is expected as a result of the alternating wave structure which reduces the Mg and OH content relative to Si at the points of inversion, as discussed by Zussman (1954) and Kunze (1956, 1958, 1961). Antigorite is therefore not a polymorph of the other serpentines in the strict sense, but is a phase of essentially (though only slightly) different composition. The departure of the composition from the ideal $Mg_3Si_2O_5(OH)_4$ must vary with the wavelength of the corrugations in the structure and antigorites which differ from one another in this way are therefore neither polymorphs nor polytypes; they are related in a similar way to one another (and to the ideal composition) as the integral members of nonstoichiometric oxide series are related to one another and to the stoichiometric compound. This has been fully demonstrated by Kunze (1961, Table 5, p. 239).

It follows from the discussion of chrysotile and lizardite that high-alumina antigorite with $b_{oct} \leq b_{tet}$ is not to be expected, as curving is essential to the antigorite structure, and none has been found. As shown by Whittaker & Wicks (1970), Fe^{2+} substitution in antigorite may be more extensive than in the other serpentines. This would be expected to raise the permitted Al + Fe^{3+} content before the flat lizardite structure supervenes over the curved structure, and the content of these ions often seems to be higher in antigorite than in chrysotile (Wicks & Whittaker 1970).

STRUCTURAL VARIATIONS

The available structural and chemical data

Radoslovich (1962) has pointed out that the calculated *b*-parameters of the octahedral and tetrahedral sheets of most trioctahedral 1:1 layer silicates rarely match, so that adjustments in the ideal atomic positions must occur. The nature of these adjustments is fairly well understood when $b_{oct} < b_{tet}$, but not when $b_{oct} > b_{tet}$. In this section we therefore seek to elucidate the adjustments and distortions involved in this latter case. The available data are rather inadequate, being confined to the results of two-dimensional refinements of the structures of lizardite $1T$ (Krstanovic 1968), chrysotile $2M_{c1}$ (clinochrysotile, Whittaker 1956a), chrysotile $2Or_{c1}$ (orthochrysotile, Whittaker 1956b), and antigorite (Kunze 1956, 1958, 1961). The lack of three-dimensional refinements is unfortunate, but is an inevitable result of the disorder present in lizardite and chrysotile, and the complexity of the antigorite structure has led to a similar limitation. Despite the uncertainties in calculations of bond lengths and angles that arise from these limitations, the trends in the variations from the ideal atomic positions are indicated clearly.

In order to make the calculations possible we assume ideal *y* coordinates throughout, and also make the following additional assumptions and approximations. Whittaker's Fourier maps give a single weighted mean position of O_3 and OH_1 and he suggested that these atoms may be at two levels separated by 0.22Å along z*. As this assumption is supported by the more recent refinement of lizardite $1T$ by Krstanovic, in which he found O_3 and OH_1 to be separated by 0.4Å, Whittaker's preferred *z* coordinates of O_3 and OH_1 are used in the following discussion. Whittaker's preferred *x* coordinate is also used for O_1. In the antigorite refinement no difference was assumed or detected between the O_3 and OH_1 coordinates or between the Mg_1 and Mg_2 coordinates, so the Mg_1 and Mg_2 octahedra are taken to be identical in this structure. Each half-supercell has 9 tetrahedra and 8 octahedra, each with slightly different bond lengths and

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* The standard 1:1 layer orientation of the *x*, *y* and *z* axes is used throughout this paper. In the original structure descriptions (Whittaker 1953, 1956a, b) *x* and *z* are reversed.

bond angles depending on their position. The results for one average tetrahedron and one average octahedron are presented.

With regard to chemical composition of the materials whose structure is to be discussed, no analysis has been given for the lizardite *1T* refined by Krstanović (1968) but he states "that the total amount of cations other than Si and Mg was found to be less than 1% by weight" (Krstanović 1968, p. 165), so it can be assumed it is very near the ideal composition $Mg_3Si_2O_5(OH)_4$.

The chemical compositions of the chrysotiles $2M_{c1}$ and $2Or_{c1}$ used for crystal structure determinations by Whittaker (1956a, b) are unfortunately not known, but the survey of serpentine chemical compositions by Whittaker & Wicks (1970) indicates that chrysotiles generally have low substitution, so that it is not unreasonable to assume that this is true of the samples studied by Whittaker.

The antigorite used by Kunze (1956, 1958, 1961) has been analyzed (Zussman 1954) and has the formula $(Mg_{2.87}Fe^{2+}_{.02}Fe^{3+}_{.03}Al_{.04})(Si_{1.99}Al_{.01})O_5(OH)_4$.

Distortions in lizardite

The dimensions of an uncompressed octahedral sheet are the result of the balance between these forces—" (I) cation-cation repulsion across shared octahedral edges, (II) anion-anion repulsion along shared edges, and (III) cation-anion bonds within octahedra." (Radoslovich 1963a, p. 80). Of these three forces, the first is considered to be the most significant. The divalent cations repel each other, causing the anion to move inwards along the sheet normal to produce a thinning of the octahedral sheet (Bailey 1967b). If trivalent cations substitute for the divalent cations the forces of repulsion will be stronger.

The ideal Mg-octahedral sheet would have $b = 8.78$Å and a thickness of 2.43Å (Table 3); both shared and unshared edges would have a length of 2.97Å, and all O-Mg-O angles would be 90°. However, in brucite the cation-cation repulsion between the Mg atoms extends b to 9.43Å and thins the sheet to 2.11Å, shortening the shared octahedral edges to 2.79Å by drawing the OH in along the z direction, and lengthening the unshared ones to 3.14Å. The corresponding O-Mg-O angles become 83.3° and 96.8° respectively. In this discussion the actual brucite sheet rather than the ideal brucite sheet will be used as a model of the unconstrained octahedral sheet.

When $b_{oct} < b_{tet}$ it is well-established that the main adjustments take place in the tetrahedral sheet by means of tetrahedral rotations (Radoslovich & Norrish 1962; Radoslovich 1962). The octahedral sheet is therefore likely to be under very little stress, and the available data on minerals of this type are of interest as a point of reference.

In amesite $2H_2$ (Steinfink & Brunton 1956), which is assumed to have a composition close to $(Mg_2Al)(SiAl)O_5(OH)_4$, b is 9.20Å and the calculated b_{oct} is 9.17Å, suggesting that there is not much stretching of the octahedral sheet (Radoslovich 1962). The *M-M* distances are 3.07Å (where $M = Mg_2Al$) and the sheet is 2.02Å thick (Table 3). The O and OH are coplanar, as are the hydroxyls of the OH plane, and the Mg and Al atoms occupy a single plane equidistant from the O,OH and OH planes. The *M*-O and *M*-OH bond lengths are 2.04Å. The shared edges of the octahedra are 2.69Å and unshared ones 3.07Å. The amesite *9T* structure (Jahanbagloo & Zoltai 1968) is less aluminous in the tetrahedral sheet but the octahedral sheet is similar to amesite except that it also has a small amount of iron of undetermined valence, and possibly some vacancies to maintain charge

TABLE 3. INTERATOMIC DISTANCES AND ANGLES

Bond Length, Angles etc.	Brucite Ideal	Brucite Observed	Amesite $2H_2$	Amesite 9T	Lizardite 1T	Chrysotile $2Or_{c1}$	Chrysotile $2M_{c1}$	Antigorite
calculated b_{oct}	8.78	-	9.17	9.19	9.45	9.45	9.45	9.29
calculated b_{tet}	-	-	9.56	9.35	9.15	9.15	9.15	9.15
b_{ob}	-	9.43	9.20	9.171	9.186	9.2	9.2	9.23
octahedral sheet thickness	2.43	2.11	2.02	2.05	2.20	2.08	2.08	2.44
M^*-M at 30° to x	2.93	3.14	3.07	3.06	3.08	3.08	3.08	3.11
M-M parallel to y	2.93	3.14	3.07	3.06	3.08	3.06	3.06	3.08
Average M_1-OH	2.10	2.10	2.04	2.04	2.03	2.06	2.06	2.17
Average M_2-OH					2.13	2.06	2.06	
tetrahedral sheet thickness	-	-	2.29	2.26	2.15	2.13	2.26	2.22
T^{**}-T at 30° to x	-	-	3.06	3.06	3.07	3.08	3.08	3.02
T-T parallel to y	-	-	3.06	3.06	3.06	3.07	3.07	3.08
Average T-O	-	-	1.68	1.66	1.61	1.62	1.64	1.64
Tetrahedra rotation	-	-	12.3°	8°	-	-	-	-

*M is occupied by Mg with or without lesser Al, Fe^{2+} or Fe^{3+}.

**T is occupied by Si with or without Al.

balance. The b_{oct} calculated with Radoslovich's formula is 9.19Å assuming all ferric and 9.20Å assuming all ferrous iron. The b is 9.17Å which may suggest that the octahedral sheet may be slightly compressed but it is more likely that b is smaller than 9.19Å because of the vacancies. The octahedral sheet is 2.05Å thick but in all other aspects the amesite $9T$ structure is similar to the amesite $2H_2$ structure. The cronstedtite $1T$, $3T$ and $6R_3$ (Steadman & Nuttall 1963) all show similar features.

The lizardite $1T$ (Krstanović 1968) represents the extreme case of $b_{oct} > b_{tet}$ with maximum compression along both the x and y axes. The octahedral sheet thickness of 2.20Å is (apart from the anomalous value for the antigorite discussed below) the thickest observed among trioctahedral 1:1 silicates (Table 3) and among trioctahedral 2:1 layer silicates (Bailey 1967b). The extreme compression buckles the plane of the magnesium cations, forcing them to occupy two structurally-distinct positions having z coordinates differing by 0.4Å. The Mg_1 remain in an almost central position 1.04Å from the average position of the O_3OH_1 plane and 1.16Å from the OH_2OH_3 plane, and the Mg_2 atoms are 1.45Å from the O_3OH_1 plane and 0.75Å from the OH_2OH_3 plane. This buckling of the Mg plane appears to be the key to understanding all the remaining adjustments.

As a direct result of the buckling, the average Mg_1-Mg_2 distance is increased from 3.06Å to 3.09Å (compare Mg-Mg distances of 3.14Å in brucite, Table 3), although there is little corresponding increase in Mg_2-Mg_2 distances.

It would be expected that as a result of the depression of Mg_1 relative to Mg_2, the three OH_2 and OH_3 hydroxyls would be displaced towards a point in their own plane having the x and y coordinates of Mg_1. Their y coordinates are unknown, and the displacements of their x coördinates are not significant in view of quoted errors. The displacements are, however, in the right direction on average.

There is a significant difference of about 0.3Å between the z coordinates of OH_1 and O_3, with OH_1 being the closer to the Mg atoms. It is suggested that this arises from a repulsion of the Si atoms (carrying their attached O_3 atoms with them) by the depressed Mg_1 atoms. The resulting depression of the O_3 atoms then permits an upward shift of OH_1. The average unshared edges of the octahedra (and the corresponding angles at Mg) are smaller than those found in brucite, and the average shared edges (and corresponding angles) are larger than those found in brucite. These differences are clearly the result of the compression of the octahedral sheet.

In spite of the buckling of the Mg plane, the extent of the compression of the octahedral sheet is rather small, and the tetrahedral sheet is therefore under considerable tension. Radoslovich (1962) calculated the mismatch along b for lizardites to be 0.22Å but since Krstanovic's specimen is nearly a pure Mg-lizardite, the mismatch must be near a maximum of 0.3Å (Table 3), the difference between brucite and the ideal tetrahedral sheet (Brindley 1967). The sheet is stretched and thinned to 2.15Å. The silicons maintain a near-hexagonal array but the Si-Si distances are increased to 3.07 and 3.06Å (Table 3).

It is important to emphasize at this point that although the lizardite is described as polytype $1T$, because this correctly describes the nature of the stacking, it is in fact orthorhombic and only pseudo-trigonal, and an explanation of this fact is needed.

The loss of equivalance between Mg_1 and Mg_2 that arises from the buckling of the Mg plane does not destroy the trigonal symmetry of the arrangement of Mg, but it increases the size of the trigonal unit, and when combined with the tetrahedral sheet the symmetry is lost. The greater proximity of Mg_1 to Si compared with Mg_2 will lead to unbalanced repulsion between Mg_1 and Si which will tend to rotate alternate tetrahedra about $|130|$ and $|\bar{1}30|$ axes. This should be manifested in a relative positive shift of the x coordinates of Si, O_1 and O_2 relative to O_3, and a separation between the z coordinates of O_1 and O_2 with O_1 going negative and O_2 positive. The observed difference in z between O_1 and O_2 is 0.40Å which is just significant (2.5σ). The corresponding shifts of Si, O_1 and O_2 relative to O_3 would be about 0.2Å, which is not observed, but as this value corresponds only to about 1.1σ this is not surprising.

The length of the T-O_3 bond in lizardite (where T = Si) is appreciably shorter than in amesite (where $T = Si_{0.5}Al_{0.5}$). The observed length of 1.56 ± 0.05Å in lizardite does not differ significantly from the expected value of 1.62Å. Thus, part of the apparent thinning of the tetrahedral sheet of lizardite relative to amesite (Table 3) is due to this compositional effect. The stretching effect may be expected to show most clearly in the thickness of the Si- (mean O_1, O_2) part of the sheet which is only 0.50Å compared with 0.58Å in amesite (which falls to 0.56Å when corrected for change of T occupancy). The T-O_1 and T-O_2 bond lengths cannot be calculated as reliably as T-O_3 in absence of y coordinates, but based on idealized y coordinates, the values obtained give a satisfactory average T-O bond length of 1.61Å (Table 3).

Curvature and distortions in chrysotile

Curvature of the layers has often been given as a means whereby misfit between sheets of different sizes can be accommodated without stress. For any given composition there is only one ideal radius of curvature, and thus in any individual chrysotile fiber there is only one layer that has the strain of mismatch completely relieved along the circumference of the curve. For the layers within this radius there will be overcompensation and for those outside there will be under-compensation.

Whittaker (1957) calculated the ideal radius for chrysotile to be 88Å and pointed out that the residual stress increases more slowly outwards than inwards. Yada (1967, 1971) observed that the minimum inner radius of chrysotile is 35 - 40Å and that the normal maximum outer radius varies from 135 - 140Å, but exceptional fibers have outer radii from 90 to 220Å. It is clear from these figures that the average structure in chrysotile fibers must usually correspond to material lying outside the ideal 88Å radius of curvature, and thus have mismatches only partly relieved by the curvature. Furthermore, since the curvature occurs about the x-axis, relief can only occur in the y-direction and the mismatch along the x-axis is completely uncompensated by the curvature. Therefore, in chrysotile (excluding parachrysotile) there is a very strong compressional stress in the x-direction in the octahedral sheet and there is also a lesser compressional stress in the y-direction in the average octahedral sheet.

Radoslovich (1962) calculated a mismatch of 0.12Å for chrysotile, but the basis of this is not clear and theoretically it could be as high as 0.3Å. Thus, one would expect the average compression in the octahedral sheet to be somewhat more than half of that in lizardite. In absence of precisely-known compositions for Whittaker's $2M_{c1}$ and $2Or_{c1}$ structures and in view of the uncertainties attached to some of their detailed parameters, the best test of this conclusion is to compare the mean of their relevant parameters with those of lizardite and amesite (see Table 3). The most important would seem to be the octahedral sheet thickness of chrysotile at 2.08Å against 2.20Å for lizardite and 2.02Å for amesite*, the mean tetrahedral sheet thickness of 2.19Å against 2.15Å for lizardite and 2.29Å for amesite; departure of the mean z coordinate of Mg from the centre of the octahedral sheet of chrysotile is 0.07Å compared with 0.21Å in lizardite and zero in amesite; the difference in z coordinates of O_1 and O_2 is probably about 0.2Å compared with 0.4Å in lizardite and zero in amesite, and the corresponding difference for O_3 and OH_1 is also estimated at about 0.2Å compared with 0.27Å in lizardite and zero in amesite. In the discussion of lizardite we have shown that all these parameters can be interpreted as arising either from the extension of the tetrahedral sheet or directly from the compression of the octahedral sheet, or indirectly from the buckling of the Mg plane that arises from that compression. No evidence has been given for such a buckling in chrysotile, but it has not hitherto been looked for. As two phenomena are present in chrysotile which, when they occur in lizardite, we have interpreted as due to this buckling, it seems very likely that it also occurs, though to a more limited extent, in chrysotile.

Curvature and distortion in antigorite

The antigorite structure refined by Kunze (1958) has b_{oct} = 9.29Å, calculated according to the formula of Radoslovich (1962), and has b_{tet} = 9.15Å because of the small amount of substitution of Al. The mismatch is therefore only 0.14Å. The superlattice repeat is 43.3Å and the radius of curvature varies from 72Å at one inversion to 50Å at the next inversion, with an average of 61Å (Kunze 1958), the curvature being along the x-direction instead of along the y-direction as in chrysotile.

Because every layer in the structure of antigorite is able to adopt the same radius of curvature, it might be expected that the radius adopted would be such as to relax the stresses completely in the x-direction. However, the calculated radius of curvature for a mismatch of 0.14Å is about 190Å, so that the curvature is substantially greater than would be expected, and must introduce a tension in the x-direction in the octahedral sheet at least as great as the compression in the y-direction. Such a balancing of tension and compression is perhaps not unreasonable, and its reality can be argued from the greater Mg-Mg distances (3.11Å) at 30° to the x-axis compared with those (3.08Å) parallel to the y-axis. The most surprising anomaly is the thickness of the octahedral sheet, which is greater than that in the other serpentines, whereas it would be expected to be less. This anomaly receives a contribution from the unusually long Mg-(O,OH) bonds (2.17Å) found

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* For the comparison of sheet thicknesses to be indicative of distortions in the sheets, the thicknesses should be corrected for the direct effect of the size of the ions. Therefore the thickness quoted for amesite would be more comparable with those of the serpentines if corrected in this way to 2.08Å (octahedral) and 2.20Å (tetrahedral).

by Kunze, but it is also due to unusually large (O,OH)-Mg-OH angles at shared octahedral edges, which would normally be interpreted as due to extreme compression of the octahedral sheet.

Because of the excessive curvature it would be expected that the tetrahedral sheet would be under tension along y but (unusually for a serpentine) under compression along x. This receives support from the Si-Si distances which are 3.08Å parallel to y and 3.02Å at 30° to x. These values are to be compared with the situation in lizardite and chrysotile where there is tension in both directions and the Si-Si disstances do not differ from one another by more than 0.01Å. The thickness of the tetrahedral sheet is not significantly different from that in the other serpentines, and there is no evidence for any difference in z coordinates of O_1 and O_2. There is thus no evidence for tilting of the tetrahedra, and consequently there is not even any indirect evidence for buckling of the Mg sheet.

Curvature and distortion in parachrysotile

Little detail is known of the structure of parachrysotile, but some predictions can be based on the variations found in the other structures. Parachrysotile and antigorite both curve along the x-axis so that the major compressive stress in the octahedral sheet occurs along the y-axis. However, as in the other chrysotiles, the curving of the structure will only partly relieve the mismatch, so that there will still be significant compressive stress along the x-axis in the octahedral sheet of parachrysotile. Therefore the conditions are unlike antigorite and similar to the other chrysotiles except that the major and minor stress directions are reversed. It is logical, therefore, to expect the variations from the ideal in parachrysotile to be similar to, although not identical with, the variations found in the other chrysotiles. In particular one would expect buckling of the Mg sheet, with the resultant displacement of O_1 to a lower z coordinate than O_2. This is consistent with the fact that Whittaker (1956c) found it necessary to postulate this same distortion as in the other chrysotiles in order to interpret the stacking in parachrysotile.

OVERSHIFT AND UNDERSHIFT IN CHRYSOTILE POLYTYPES

In the discussion of chrysotile polytypes above it was pointed out that overshift or undershift would occur if O_1 were displaced from its ideal position relative to the upper part of its own layer. In the original discussion of these displacements, Whittaker (1956a, b) discussed them in terms of a displacement of O_1 relative to the whole of the remainder of the layer including O_2, and found weak evidence that this existed. However, the process would be equally effective if O_2 (and even Si) partook of the same displacement relative to the octahedral layer. The discussion of the effects of buckling of the Mg sheet now provides us with a mechanism for producing a displacement, δ, of this kind. If δ is taken as positive when the displacement of O_1 is in the direction away from the nearest Mg atom in its own layer, then the tilting of the tetrahedra about axes through the O_3 atoms due to repulstion of Si by Mg_1 leads to a positive displacement δ amounting to about 0.2Å in lizardite, which applies equally to O_1 and O_2; since the relative z-displacements of O_1 and O_2 in chrysotile are about 0.2Å compared with 0.4Å in lizardite, we may expect a corresponding value of δ of about +0.1Å. This would lead directly to the observed overshift in chrysotile $1M_{c1}$ and in alternate layers of $2M_{c1}$, and to the observed undershift (because of the 180° rotations between layers) in $2Or_{c1}$. We can, however, offer no explanation of the observed undershift in the alternate layers of $2M_{c1}$.

DISCUSSION AND CONCLUSIONS

The various lizardites and multi-layer orthohexagonal serpentines can now be visualized as a single lizardite family with structural variations, and polytypes, varying with chemical composition. At the pure magnesium end of the composition range the lizardite structure is under extreme compression in the octahedral sheet and extreme stretching in the tetrahedral sheet, producing buckling of the Mg plane, downwarping of O_1 and uplifting of O_2, and reducing the layer symmetry to orthorhombic. These distortions may be the reason that the simple $1T$ or $2H$ stacking types, usually with considerably disordered $\pm b/3$ shifts, are the only ones known to form under natural conditions. A synthetic 6-layer polytype has been produced hydrothermally by Jasmund & Sylla (1971, 1972).

The substitution of Al, as is well-known, relieves the misfit, first to produce $b_{oct} = b_{tet}$ and then $b_{oct} < b_{tet}$, on the way towards the amesite composition. With the reduction in the mismatch, not only do the internal structural deformations become smaller and smaller until with $b_{oct} < b_{tet}$ only simple tetrahedral rotations occur, but also the number of possible polytypes increases significantly because the better- formed structures have more stacking possibilities than the deformed structures.

The substitution of Fe^{3+} for Mg and Si has the same effect as Al substitution, but is less effective in the octahedral sheet and more effective in the tetrahedral sheet. Ferric-rich serpentines have been recorded (L2 and L3 of Whittaker & Wicks 1970; ferrian lizardite, Ping-Wen & Che 1968), but they do not reach the $b_{oct} = b_{tet}$ condition, let alone approach the ferric-iron analogue of amesite. However, it is theoretically possible for $(Mg_2Fe^{3+})(SiFe^{3+})O_5(OH)_4$ to exist. With greater and greater ferric substitution it is presumably possible for the lizardite structure to accept more and more ferrous iron (see S-3, Fig. 6 Whittaker & Wicks 1970) until the cronstedtite composition, $(Fe_2^{2+}Fe^{3+})(SiFe^{3+})O_5(OH)_4$ is reached.

The substitution of trivalent cations Ni^{3+}, Co^{3+}, Mn^{3+} and Cr^{3+} for Mg would also reduce the mismatch, but extensive substitution would require the substitution of Al or Fe^{3+} in the tetrahedral sheet to balance the charges.

Probably the only suitable divalent cation smaller than Mg is Ni^{2+}, and it seems that this can substitute freely for Mg. The nickel analogue of lizardite, nepouite (Maksimovic 1973), is known and intermediate members between lizardite and nepouite exist (Springer 1974) suggesting a solid-solution series. If the *b* parameter of $4Ni(OH)_2{\cdot}NiOOH = 9.21$Å (Jambor & Boyle 1964) can be taken as *b* for the octahedral sheet of nepouite, it can be seen that $b_{oct} > b_{tet}$ for the entire series. This suggests that the polytypes will be limited to disordered 1*T* or 2*H* under natural conditions. The nepouite (ROM number M18475) noted in Springer (1974) is the 1*T* polytype. A synthetic 6-layer polytype has been produced hydrothermally by Jasmund & Sylla (1971, 1972).

It would be expected that the substitution of Fe^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, and Cr^{2+} would be extremely limited because they would increase the mismatch in a structure already near the limits of structural adjustment. The survey of lizardite compositions (Whittaker & Wicks 1970) indicates that these have very low Fe^{2+} contents. Because of this, it would be expected that no lizardite analogue containing large amounts of these cations would exist. However, greenalite (Steadman & Youell 1958) seems to be the Fe^{2+}-analogue and caryopilite* (Peacor *et al.* 1974) seems to be the Mn-analogue, although neither is understood well. In ferrous hydroxide, $Fe(OH)_2$, *b* is 9.72Å so the mismatch in a Fe^{2+}-lizardite would be 0.57Å, and in pyrochroite, $Mn(OH)_2$, *b* is 9.97Å so the mismatch in a Mn-lizardite would be 0.82Å (Donnay & Ondik 1973). These seem too large to be overcome by the variations found in the Mg-lizardite 1*T* structure. Perhaps there are vacancies in the octahedral sheets of these minerals, with some trivalent ions to maintain charge balance, that help to decrease the mismatch. In kellyite, the Mn-analogue of amesite (Peacor *et al.* 1974), and in zinalsite, the Zn-analogue of amesite (Chukhrov & Petrovskaia 1971) the Al substitution produces a condition of $b_{oct} < b_{tet}$.

A pure magnesium chrysotile has a fully stretched tetrahedral sheet and a highly but not completely compressed octahedral sheet. Thus chrysotile could be expected to accept some Al or Fe^{3+} substitution in both sheets, but the compositional limit would be expected to be considerably less than that corresponding to $b_{oct} = b_{tet}$ since significant mismatch is needed to produce curving. The substitution of trivalent cations such as Ni^{3+}, Co^{3+}, Mn^{3+} and Cr^{3+} (together with balancing tetrahedral Al or Fe^{3+}) would be restricted by the same limitations.

The substitution of Ni^{2+} for Mg would reduce the mismatch slightly and allow a larger "ideal" radius of curvature to develop. The Ni analogue of chrysotile $2M_{c1}$ (pecoraite) has been described by Faust *et al.* (1969) and it would appear that a solid solution exists between the two end-members.

The substitution of divalent cations larger than Mg is limited by the amount of curving the structure will accept. Noll *et al.* (1958) have synthesized Co-chrysotile, but attempts to synthesize Zn- and Mn-chrysotile have failed (Roy & Roy 1954). The observed diameters of the Co-chrysotile tube were smaller than the diameter of synthetic Mg- and Ni-chrysotiles, as would be expected because Co^{2+} would have a smaller radius of "ideal" curvature than the other two. An ionic radius larger than Co^{2+} may well be too large to allow the chrysotile structure to form.

The antigorite structure, like chrysotile, is necessarily limited to compositions producing $b_{oct} > b_{tet}$. Although Fe^{2+} tends to dominate over Fe^{3+} in the analyzed specimens reviewed by Whittaker & Wicks (1970), there is no obvious reason why appreciable Fe^{3+} should not be present, and the compositions noted may simply reflect a reducing environment of formation. Substitutions generally would be expected to be subject to limitations similar to those in chrysotile, although in fact they seem to be less

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[*] Kato (1963) has shown that ektropite = caryopilite, and that bementite is structurally similar to the friedelite group of minerals.

TABLE 4. TRIOCTAHEDRAL 1:1 LAYER SILICATES

<table>
<tr><th colspan="6">SERPENTINE GROUP</th></tr>
<tr><th>Serpentine</th><th>Ni-Serpentine</th><th>Fe-Serpentine</th><th>Mn-Serpentine</th><th>Zn-Serpentine</th><th>Co-Serpentine</th></tr>
<tr><td>antigorite</td><td>?</td><td>?</td><td>?</td><td>?</td><td>?</td></tr>
<tr><td>chrysotile</td><td>pecoraite</td><td>?</td><td>?</td><td>?</td><td>synthetic</td></tr>
<tr><td>parachrysotile</td><td>?</td><td>?</td><td>?</td><td>?</td><td>?</td></tr>
<tr><td>lizardite</td><td>nepouite</td><td>greenalite</td><td>caryopilite</td><td>?</td><td>?</td></tr>
<tr><td colspan="6">Substitution of Al in 1/3 of the octahedral sites and 1/2 of the tetrahedral sites produces $b_{oct} < b_{tet}$ and eliminates curved structures such as chrysotile, antigorite, pecoraite, etc.</td></tr>
<tr><td>amesite</td><td>?</td><td>berthierine</td><td>kellyite</td><td>zinalsite</td><td>?</td></tr>
<tr><td colspan="6">Substitution of Fe^{3+} in 1/3 of the octahedral sites and 1/2 of the tetrahedral sites also produces $b_{oct} < b_{tet}$.</td></tr>
<tr><td>?</td><td>?</td><td>cronstedtite</td><td>?</td><td>?</td><td>?</td></tr>
</table>

rigorous. Ferroan antigorites have been reported by Frondel (1962) and Dietrich (1972). Complete substitution by Ni^{2+} would be expected to be possible, and a specimen with a high Ni content has been reported by Faust (1966). Because of the cross-linking between the layers in antigorite, it is not expected to be able to form different polytypes.

The structures and chemistry of the serpentine group of minerals discussed above, together with some related trioctahedral 1:1 layer silicates, are summarized in Table 4.

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