Canadian Mineralogist
Vol. 14, pp. 314-321 (1976)

THE STRUCTURE OF UNST-TYPE 6-LAYER SERPENTINES

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ABSTRACT

Six-layer orthohexagonal serpentines similar to that described from Unst in the Shetland Islands are now known from six other localities and have been made synthetically in the Mg-Ge, Mg-Si, Ni-Si, and Mg-Al-Si systems. The strong X-ray powder reflections of index $k=3n$ are similar to those in amesite, and indicate (1) alternate occupation of the I and II sets of possible octahedral positions in adjacent layers, and (2) interlayer shifts involving some alternation of zero, $+b/3$, and $-b/3$ vectors. The weak supercell reflections of index $k \neq 3n$ indicate that (3) the symmetry cannot be rhombohedral. There are 21 possible 6-layer models fulfilling these three characteristics. Comparison of calculated structure amplitudes with those obtained by corrections applied to a densitometer trace of the powder pattern of the Mg-Ge synthetic serpentine gave three best-fit models. One model is favored because it not only gives the lowest residual *R* value but also is a relatively simple structure that most closely resembles the amesite-$2H_2$ structure. The model can be described as a stacking of two unit cells of the standard $2H_2$ polytype (with $-b/3$ and $+b/3$ interlayer shifts in each cell) plus one cell of the $2H_1$ polytype (with zero shifts), and is designated as lizardite-$6T_1$.

SOMMAIRE

Des serpentines orthohexagonales à 6 couches, semblables à celles provenant de Unst des Iles Shetland, ont été trouvées dans six autres environnements naturels et elles ont été synthétisées dans les systèmes Mg-Ge, Mg-Si, Ni-Si et Mg-Al-Si. Les réflexions intenses de clichés de poudre qui ont l'indice $k=3n$ sont semblables à celles de l'amésite, et indiquent (1) une occupation alternante des ensembles I et II des positions octaédriques possibles dans des couches adjacentes, et (2) des déplacements entre les couches avec alternation des vecteurs zéro, $+b/3$ et $-b/3$. Les faibles réflexions de supermaille qui ont l'indice $k \neq 3n$ indiquent que (3) la symétrie ne peut être rhomboédrique. Il y a 21 modèles à six couches possibles ayant ces trois caractéristiques. Une comparaison des amplitudes de structure calculées avec celles obtenues par des corrections faites à une trace de densitomètre d'un diagramme de poudre de la serpentine synthétique Mg-Ge nous donne les trois modèles préférés. Un des modèles est favorisé parce qu'il donne non seulement l'indice résiduel R le plus bas, mais aussi une structure relativement simple qui ressemble beaucoup à la structure de l'amésite-$2H_2$. On peut la décrire comme un amoncellement de deux mailles élémentaires du polytype standard $2H_2$ (avec $-b/3$ et $+b/3$ de déplacements entre les couches de chaque maille) plus une maille du polytype $2H_1$ (avec zéro de déplacement), ce qui est désigné par lizardite-$6T_1$.

(Traduit par le journal)

INTRODUCTION

Six-layer orthohexagonal serpentine from Unst in the Shetland Islands was described by Brindley & von Knorring (1954). According to these authors, the X-ray powder pattern resembles that of 2-layer amesite but is differentiated by a series of closely spaced extra lines following the 020 reflection. The periodicity of 43.8Å determined from these superlattice lines suggested an analogy to the 43.39Å lateral periodicity along *X*, as determined for antigorite by Aruja (1945). However, the authors could not discount the possibility of a multi-layer periodicity along *Z*. Zussman & Brindley (1957) showed later by electron diffraction that the Unst serpentine did not have a lateral superlattice, and they concluded that the superlattice must be along *Z*.

Since the description of the Unst material, other natural 6-layer serpentines with very similar X-ray patterns have been identified from the Tracy mine, Michigan, by Bailey & Tyler (1960), Thompson Lake, Labrador, by Olsen (1961), Piz Lunghin, Switzerland, by Müller (1963), Korab Mtn., Yugoslavia, by Krstanović & Pavlović (1967), Lord Brassey mine, Tasmania, and Silversheen mine, Western Australia, by I. M. Threadgold (pers. comm., 1960, 1975). Most of these serpentines are Mg-rich, but the Tracy mine material is Al-rich and approaches amesite in composition. Six-layer structures that give similar X-ray patterns (with small differences probably due to compositional variations) have been made synthetically by Roy & Roy

(1954) with the composition $Mg_3Ge_2O_5(OH)_4$, by Jasmund & Sylla (1971, 1972) with the probable compositions $Mg_3Si_2O_5(OH)_4$ and $Ni_3Si_2O_5(OH)_4$, and by Shirozu & Momoi (1972) at Al-rich compositions.

The Unst serpentine is described as massive with a conchoidal fracture on a macroscopic scale but lath-like and elongate along *X* on a microscopic scale. Electron diffraction of an apparent single lath gave a composite diffraction pattern simulating rotation of an orthohexagonal structure about *X* (Zussman *et al.* 1957). The pattern is different than that of the known chrysotiles, however, and does not have the azimuthal disorder that is typical of a curled, tubular structure. Several flat laths in different orientations parallel to *X*, rather than curling, would explain the composite pattern. Electron diffraction photographs of several different lath-like fragments of the Unst serpentine taken in the present study were similar to that shown by Zussman *et al.* (1957) in their Figure 7d. The sample was prepared for electron microscopy by taking loose material, obtained by scraping the sample with a steel file, and placing it on a glass slide that had been coated previously with a monolayer of soap. After carbon coating, the sample was floated off the slide, washed repeatedly in distilled water, and mounted on a copper grid for microscopy. Diffraction patterns from different lath-like fragments showed different assemblages of reflections along the *Y** row lines, and this lends support to the view that these actually are composite patterns due to laths oriented in a zone semi-parallel to *X*. Specimens from Thompson Lake and the Silversheen mine examined by electron microscopy in the present study also were found to consist of lath-like fragments. The more Al-rich Tracy mine serpentine, however, takes the form of small hexagonal platelets similar to the synthetic Mg-Ge serpentine of Roy & Roy (1954). Jasmund & Sylla (1971, 1972) noted in their study that curled tubes of Mg-chrysotile and Ni-chrysotile formed first, but were converted to hexagonal platelets of the 6-layer form after annealing at 320°-350°C and 200-500 atm for several weeks.

Gillery (1959) has reported hydrothermal synthesis of a second form of platy 6-layer serpentine, which increases in amount at the expense of 1-layer serpentine as tetrahedral and octahedral Al increase. The *X*-ray powder pattern of this material is quite different in detail from that of the Unst-type serpentine. The Unst serpentine has *hkl* reflections for which the intensity relationship is $I_{l=3n} \gg I_{l=3n\pm1}$, so that the structure approximates a 2-layer cell [termed by Gillery a 6(2) structure]. The Gillery synthetic 6-layer serpentine has *hkl* reflections for which the intensity relationship is $I_{l=2n} \gg I_{l=2n\pm1}$, so that the structure approximates a 3-layer cell [termed a 6(3) structure]. Shirozu & Momoi (1972) have confirmed Gillery's hydrothermal results, in which the amount of 6(3) structure increases at the expense of the 1-layer structure with increase in Al-substitution. But they also found on raising the temperature from 300°-400°C to 590°C, and the pressure from 18,000 psi to 35,000 psi, that the 6(2) Unst-type structure formed instead of the 6(3) structure. Natural serpentine similar to the synthetic 6(3) material has been described from the Tracy mine intermixed with 6(2) serpentine. These are the type F and type B materials, respectively, of Bailey & Tyler (1960). Bailey (1969) subsequently realized that the powder pattern of the type F serpentine did not have the extra reflections indicative of a 6-layer cell and could be correlated instead with his ideal 1*M* or 3*T* polytypes. The latter two polytypes give identical powder patterns and cannot be differentiated except by single crystal study. Single crystals of aluminian serpentine from the Lake Superior region give patterns similar to those of both the synthetic 6(3) and natural type F serpentines, but with weak reflections indicative of a 9-layer or 18-layer cell (Jahanbagloo & Zoltai 1968). None of these serpentines is considered further in this paper.

STRUCTURE DETERMINATION

The structure of the Unst-type 6-layer serpentine has been of interest in this laboratory since the discovery of the similar Tracy mine serpentine. Further work on the type B sample of Bailey & Tyler by R. A. Eggleton (unpublished), however, showed it to be a mixture of two type B phases of slightly different compositions. The small differences in *d*-values became apparent only by using Fe$K\alpha$ X-radiation rather than Cu$K\alpha$. Further structural work, therefore, has been concentrated on the type material from Unst and on the synthetic Mg-Ge material prepared by Roy & Roy (1954), both kindly supplied by G. W. Brindley. In addition, the Thompson Lake and Silversheen mine specimens have been made available to us by E. J. Olsen and I. M. Threadgold, respectively. All specimens are very fine grained, and single crystals suitable for individual study have not been discovered to date.

Brindley & von Knorring (1954) noted the similarity of the strongest reflections in the Unst X-ray powder pattern to those of amesite.

TABLE 1. GROUP D 6-LAYER SERPENTINES

Model No.	Interlayer Shifts*	Space Group
1	- + - + 0 0	$P3$
2	- - + - + +	$P3$
3	+ + - - 0 0	$P3$
4	0 - + - 0 +	$P3$
5	0 0 0 0 + -	$P3$
6	0 - + 0 + -	$P6_3$
7	0 + - + + +	$P3$
8	0 - - + 0 +	$P3$
9	0 + + + + -	$P3$
10	0 + 0 + - -	$P3$
11	0 0 + + 0 +	$P3$
12	0 0 + 0 + +	$P3$
13	0 + - - - -	$P3$
14	- - 0 + + 0	$P6_3$
15	- - - + + +	$P6_3$
16	0 0 + 0 0 -	$P6_3$
17	0 + + - + +	$P3$
18	0 + + + - +	$P3$
19	0 0 0 + + +	$P3$
20	0 0 0 + 0 -	$P3$
21	0 + - 0 + -	$P3c1$
22	- - - - - -	$R3c$
23	0 - 0 - 0 -	$R3$
24	0 0 + - - +	$R3$

* Interlayer shifts of zero, $+b/3$, and $-b/3$ relative to the axes of Fig. 1 are listed as 0, +, and -, respectively. Octahedral cation sets II and I are occupied in alternate layers.

Bailey (1969) has pointed out that these strong reflections correspond closely in intensities to those of his theoretical group D polytypes, of which amesite is one example, but that the weaker reflections which define the 6-layer periodicity do not fit those of any of the three standard polytypes within group D (namely $2H_1$, $2H_2$, and $6R$). The group D structures are those characterized by occupancy of octahedral cation sets I and II in alternate 1:1 layers (equivalent to octahedra slanting in opposite directions), and by interlayer shifts either of zero, $+b/3$, or $-b/3$, rather than of $\pm a/3$. For simplicity, Bailey (1969) assumed in the derivation of his standard polytypes that interlayer shifts of zero and $\pm b/3$ were not intermixed in the same crystal. This constraint must now be relaxed and the exact stacking sequence determined from its effect on the weak reflections of index $k \neq 3n$ (orthohexagonal indexing). The strong reflections are all of index $k = 3n$ and hence are insensitive to shifts of zero or $\pm b/3$ (i.e. are invariant within group D).

It was concluded for purposes of experimental model construction that Unst-type 6-layer serpentines

(1) are based on platy trioctahedral 1:1 layers of the serpentine type,

(2) are characterized by occupancy of octahedral cation sets I and II in regular alternation in adjacent layers (because calculations show that regular I, I, I, II, II, II alternation, irregular permutations such as I, II, I, I, II, II, sequences, or unequal numbers of the two sets cause recognizable deviations from observed group D intensities),

(3) have interlayer shifts that are of magnitude zero, $+b/3$ or $-b/3$ between layers, but always preserving long hydrogen bond contacts between adjacent oxygen and hydroxyl surfaces of the layers, and

(4) are based either on an orthohexagonal or hexagonal-shaped cell, but do not have rhombohedral symmetry (because the observed continuous succession of superlattice lines does not have systematic rhombohedral absences).

As a first attempt to solve the structure, Moore (1972) derived five non-rhombohedral 6-layer group D sequences by trial-and-error variation of interlayer shift vectors of 0, $+b/3$, and $-b/3$. Calculation of $k \neq 3n$ intensities showed moderate agreement with observed values for one model (model 2 in this paper). As a second stage in this process, a computer program was written to derive all possible permutations of these interlayer shifts that would give a 6-layer repeat. This resulted in 21 possible models, including the five derived previously by Moore (Table 1). Enantiomorphs have been excluded. Three rhombohedral structures also derived by the computer program were not considered further.

TESTING OF MODELS

Because the synthetic Mg-Ge serpentine gives an X-ray powder pattern that is sharper and has more superlattice lines than given by the other available specimens, it has been used as the principle source of reflection data of the Unst-type for testing of the 21 possible models. The best model then was compared in detail to the natural Unst sample. For both the Mg-Ge synthetic serpentine and the natural Unst sample, X-ray powder pattrens were taken without prior sample grinding in a 114.6 mm diameter camera with Cu$K\alpha$ radiation. A thin, solid needle-shaped specimen was cut by razor blade from the massive Unst serpentine. The synthetic serpentine was already in powder form, and was placed in a Lindemann glass capillary tube. The resulting powder arcs were smooth and homogeneous for both samples, indicative of tiny particles in random orientation. Intensities were measured as peak heights above background from scanning transmittance microdensitometer charts. Intensities were corrected for Lorentz-polarization factors and multiplicities to yield observed structure amplitudes (F_o) for comparison with calculated values (F_c) for the test models.

Ge is approximately the size of Al in tetrahedral coordination so that considerable tetrahedral rotation can be expected in order to reduce the lateral dimensions of the tetrahedral sheet to fit those of the octahedral sheet. Bond lengths of Ge^{IV}—O = 1.75Å and Mg^{VI}—O, OH = 2.09Å were assumed, and the tetrahedra were rotated until they would fit in a cell having the observed lateral dimensions of the Ge serpentine. The tetrahedral rotation value predicted by this procedure was 18.55°. The same direction of rotation was assumed as was found for amesite by Hall (1974), namely, movement of the basal oxygens in a direction that is both toward the nearest OH-groups in the adjacent layer and toward octahedral cations in the same layer. For the Si-rich Unst serpentine the same model of the layer used by Bailey (1969) for derivation of his standard polytypes was used. This model has a planar hexagonal network with no tetrahedral rotation and is assumed to be of ideal composition $Mg_3Si_2O_5(OH)_4$. Table 2 lists the atomic positions of the first layer for the two specimens, as based on a 6-layer primitive hexagonal cell.

TABLE 2. ATOMIC COORDINATES FOR UNST-TYPE SERPENTINES

Atom	Mult.	*x*	*y*	*z*(Ge)	*z*(Si)
T(1)	1	1/3	2/3	.0128	.014
T(2)	1	2/3	1/3	.0128	.014
Mg	3	.6667	.0000	.0753	.078
O(1)	1	1/3	2/3	.0519	.053
O(2)	1	2/3	1/3	.0519	.053
O(3)	3	.5969;.500	.0000;.000	0	0
OH(1)	1	0	0	.0519	.053
OH(2)	3	.3333	.0000	.0986	.101

Coordinates listed only for first layer of a primitive hexagonal cell, with coordinates of subsequent layers determined by stacking sequences. For the basal oxygen O(3) the *x* and *y* coordinates for the Ge analogue are listed first, followed by those for the Si analogue. The *z* coordinates for the two analogues are listed separately.

For convenience, all models were assumed to be triclinic and to be based on an orthohexagonal cell. Computer programs were used to generate atomic coordinates and to calculate structure amplitudes for each model. The strong reflections of index $k=3n$ were found to have identical F values for all of the models so that further differentiation was made by means of non-overlapping $k \neq 3n$ reflections. Of the 21 possible models, eight (#14-21 in Table 1) could be eliminated at once because of numerous calculated (non-rhombohedral) structural absences among the observed continuous sequence of $02l$ reflections (orthohexagonal indexing). Of the remaining 13 models, six (#1-6) predicted $F(0kl)=F(0k\bar{l})$ and seven (#7-13) predicted $F(0kl)\neq(0k\bar{l})$. The latter seven structures were rejected due to very poor agreement between observed F^2 values and those calculated by $0kl$ and $0k\bar{l}$ in the superimposed reflections. taking into account the non-equivalence of Within the remaining group of six structures, three gave a better fit than the other three by 5 to 10 percentage points in comparison of the residual R values. These three best-fit models are listed below.

INTERLAYER SHIFTS	RESIDUAL *R* VALUES all reflections	 $k \neq 3n$ reflections
(1) $-b/3$, $+b/3$, $-b/3$, $+b/3$, 0, 0	14.5%	30.6%
(2) $-b/3$, $-b/3$, $+b/3$, $-b/3$, $+b/3$, $+b/3$	15.1	33.5
(3) $+b/3$, $+b/3$, $-b/3$, $-b/3$, 0, 0	15.2	33.7

The comparison above excludes only overlapping reflections and those to which several non-equivalent sets of spectra contribute, such as hkl. Some of the weakest $k \neq 3n$ reflections are barely visible above background (intensity values of 0.6 in Table 3), however, and cannot be measured accurately. If these reflections are deleted, the residual R values for $k \neq 3n$ reflections are 23.4% for model 1, 30.1% for model 2, and 29.1% for model 3. Thus, the best measurements for these diagnostic reflections clearly indicate model 1 as the correct structure. The stronger $k=3n$ reflections are invariant within group D so that all of the models have the same residual of 10.5% for these reflections. Although not required by space-group symmetry, $F(h0l)=F(h0\bar{l})$ for all 13 models. The higher R values for the weaker $k \neq 3n$ reflections are believed to result from (1) poorer precision inherent in the measurement of the smaller peaks on the densitometer trace, and (2) lack of any detailed structural refinement.

Figure 1 compares the three best-fit stacking models with that of amesite-$2H_2$ in YZ projection. All three models belong to space group $P3$. As mentioned, model 1 is considered correct because it clearly gives the smallest residual

TABLE 3. OBSERVED AND CALCULATED POWDER DATA

Synthetic Mg-Ge Serpentine						Unst Serpentine				
d_{calc}	I_{calc}		I_{obs}	d_{obs}	$hk.l$	d_{obs}	I_{obs}		I_{calc}	d_{calc}
7.449	95.4		77	7.460	00.6	7.270	100		100.0	7.268
4.706	16.2	24.3	34	4.696	01.0	4.585	34	30.8	15.8	4.609
4.680	8.1				01.1				7.6	4.584
4.605	8.0		w	4.606	01.2				7.4	4.509
4.487	29.9		34	4.490	01.3	4.402	7.3		27.6	4.393
4.337	6.8		17	4.336	01.4	4.251	3.9		6.2	4.245
4.164	6.2		18	4.166	01.5	4.074	5.0		5.4	4.075
3.978	21.8		18	3.983	01.6	3.890	6.1		19.8	3.892
3.788	4.8		w	3.784	01.7	3.637	84	73.1	4.0	3.705
3.725	54.2		66	3.728	00.12				69.1	3.634
3.599	4.1		13	3.597	01.8	3.521	3.9		3.3	3.520
3.416	14.2		19	3.413	01.9	3.340	3.4		11.1	3.340
3.241	3.1		7.5	3.241	01.10	3.170	2.8		2.3	3.168
3.075	2.6		6.9	3.076	01.11	3.004	2.2		1.9	3.006
2.921	9.3		5.7	2.923	01.12	2.859	1.7		6.2	2.854
2.776	1.9		3.8	2.778	01.13	2.710	2.2		1.3	2.712
2.717	22.0		26	2.720	11.0	2.659	w		3.1	2.661
2.673	12.0		13	2.673	11.3	2.617	14		10.1	2.618
2.642	1.6		1.3	2.640	01.14	2.585	w		1.0	2.580
2.552	100.0		100	2.552	11.6	2.502	72		90.4	2.499
2.517	5.6		w	2.517	01.15	2.457	2.8		3.2	2.459
2.483	10.7		10	2.484	00.18	2.424	1.1		5.3	2.423
2.402	1.2		0.6	2.404	01.16					
2.383	4.0		7.5	2.386	11.9	2.333	26		30.7	2.332
2.324	1.8		ww	2.325	02.3	2.274	w		1.0	2.276
2.302	0.4		ww	2.305	02.4					
2.295	1.0		ww	2.298	01.17	2.200	w	1.8	0.5	2.197
2.244	1.8		ww	2.239	02.6				1.3	2.197
2.196	3.4	18.9	19	2.196	01.18	2.148	17	19.4	1.7	2.144
2.195	15.5				11.12				17.7	2.147
2.168	0.5		0.6	2.168	02.8					
2.126	1.8		4.4	2.124	02.9	2.090	w		1.6	2.081
2.104	0.7		0.6	2.103	01.19	2.020	w	1.2	0.4	2.054
2.082	0.5		0.6	2.084	02.10				0.4	2.038
2.036	0.5		0.6	2.032	02.11				0.4	1.992
2.008	18.1		25	2.006	11.15	1.962	27		31.8	1.963
1.989	1.8		0.6	1.992	02.12					
1.942	0.4	2.6	6.3	1.941	02.13	1.895	w	1.3	0.4	1.899
1.939	2.2				01.21				0.9	1.893
1.894	0.4		0.6	1.894	02.14					
1.862	3.4		5.0	1.863	00.24	1.817	3.4		1.5	1.817
1.847	1.6		0.6	1.847	02.15					
1.833	17.9		31	1.834	11.18	1.792	4.5		10.7	1.791
1.800	0.4		2.5	1.800	02.16					
1.796	0.4		0.6	1.796	01.23					
1.779	1.2	2.6	0.6	1.778	12.0	1.742	4.5	2.2	1.4	1.742
1.777	1.4				12.1				0.8	1.741
1.773	0.9		0.6	1.772	12.2					
1.766	3.6		11	1.765	12.3	1.728	w		2.8	1.730
1.756	0.9	1.3	2.5	1.756	12.4					
1.753	0.4				02.17					
1.732	1.4	4.7	3.1	1.730	01.24					
1.730	3.3				12.6					
1.713	0.8		ww	1.712	12.7					
1.695	0.8		1.3	1.695	12.8					
1.675	3.9	6.7	15	1.675	11.21	1.638	12	20.2	18.8	1.637
1.674	2.8				12.9				1.4	1.639
1.653	0.7		ww	1.653	12.10					
1.620	0.3	0.6	1.3	1.618	02.20					
1.615	0.3				01.26					
1.605	2.4		1.9	1.604	12.12					
1.580	0.6	1.8	1.9	1.579	12.13					
1.578	1.2				02.21					
1.569	26.7		41	1.569	03.0	1.536	35		28.3	1.536
1.536	22.0	28.3	36	1.536	11.24	1.502	20	32.3	19.3	1.501
1.535	6.3				03.6				13.0	1.503
1.512	0.2		ww	1.511	01.28					
1.500	0.2	0.5	ww	1.501	12.16					
1.498	0.3				02.23	1.462	ww		0.3	1.464
1.490	2.2		w	1.491	00.30	1.453	2.2		1.8	1.454
1.460	1.0		ww	1.462	02.24					
1.446	12.4	14.0	16	1.446	03.12	1.415	3.9	7.0	6.3	1.415
1.446	1.6				12.18				0.7	1.414
1.424	0.2	1.2	ww	1.421	02.25					
1.420	0.6				01.30					
1.419	0.4				12.19					
1.414	4.0		5.0	1.414	11.27	1.381	5.6		7.6	1.381
1.358	2.7		4.4	1.358	22.0	1.327	1.7	4.3	2.0	1.331
1.354	0.8	1.4	ww	1.354	02.27				0.9	1.323
1.353	0.6				22.3				1.4	1.325
1.336	11.1		16	1.336	22.6	1.309	16		13.8	1.309
1.326	7.7		5.7	1.326	03.18	1.298	1.7		3.5	1.297
1.310	0.7	10.3	13	1.306	22.9					
1.306	8.4				11.30	1.276	6.1		5.3	1.276
1.305	0.8				13.0					
1.305	0.4				13.1					
1.291	0.3	2.9	3.9	1.288	13.5					
1.289	0.2				02.29					
1.286	1.4				13.6					
1.286	1.0				12.24					
1.276	3.2		3.9	1.276	22.12	1.250	ww		0.6	1.249
1.262	1.2	2.1	2.2	1.261	13.9					
1.261	0.3				12.25					
1.259	0.6				02.30					
1.242	0.9		ww	1.242	00.36	1.210	3.4	4.8	1.2	1.211
1.236	1.7	1.9	2.2	1.236	22.15				3.6	1.210
1.236	0.2				12.26					
1.212	0.4	1.2	ww	1.212	11.33	1.183	w	2.1	1.9	1.184
1.212	0.8				12.27				0.2	1.184
1.200	3.3		4.2	1.200	03.24	1.168	mw	4.1	0.9	1.173
1.195	0.9	4.6	5.7	1.193	13.15				0.4	1.170
1.192	3.7				22.18				2.8	1.166
1.176	0.2	0.9	ww	1.175	04.0					
1.176	0.1				04.1					
1.175	0 1				04.2					
1.174	0.5				02.23					
1.145	0.8	1.1	1.9	1.145	22.21	1.121	w		3.7	1.120
1.145	0.3				04.9					
1.130	0.1	3.0	3.3	1.129	04.11					
1.129	2.7				11.36					
1.127	0.2				13.20					
1.114	0.2	0.8	ww	1.113	01.39					
1.113	0.6				13.21					
1.098	0.4	5.9	5.5	1.097	02.36	1.074	mw	3.8	0.4	1.072
1.097	5.5				22.24				3.4	1.073
1.080	4.5	4.8	5.2	1.080	03.30	1.056	mw		4.6	1.056
1.080	0.2				23.0					
1.079	0.1				23.1					
1.064	0.2		ww	1.063	00.42					
1.055	0.4	0.5	ww	1.053	23.9					
1.054	0.1				13.25					
1.050	0.8		ww	1.050	22.27	1.028	w		1.8	1.027
1.027	1.9		ww	1.026	14.0					
1.018	0.4	8.1	m	1.017	12.36					
1.017	7.7				14.6	0.9965	m		5.2	0.9963
1.006	0.7	3.5	w	1.005	14.9	0.9850	w		1.7	0.9848
1.004	2.8				22.30					
0.9909	3.4	6.8	mw	0.9903	11.42	0.9680	w	2.7	1.3	0.9673
0.9900	0.4				23.18				0.2	0.9691
0.9899	3.0				14.12				1.2	0.9693
			+21 indexed lines				+8 indexed lines			

Synthetic Mg-Ge serpentine: a = 5.4337±(7)Å, c = 44.697±(8)Å
Unst serpentine: a =5.322±(1)Å, c = 43.61±(1)Å

R value for those reflections that differ among the three models. It also is a relatively simple structure that most closely resembles the amesite-$2H_2$ structure. It can be described as a stacking of two unit cells of the amesite $2H_2$ polytype (with $-b/3$ and $+b/3$ interlayer shifts in each cell) plus one cell of the $2H_1$ polytype (with zero shifts). Another way to describe the structure is that of the $2H_2$ polytype with one stacking fault interrupting the sequence such that the 6th layer is projected onto the 1st layer, rather than being offset by $-b/3$.

For the natural Unst serpentine specimen there are fewer lines and less resolution of individual reflections on the powder pattern than for the synthetic Mg-Ge specimen. When model 1 is used (incorporating the Mg-Si structural unit with no tetrahedral rotation), a residual R value of 19.5% for all non-overlapping reflections is obtained for the Unst serpentine, which is considered reasonable in view of the quality of the powder pattern and the lack of structural refinement of the model. Table 3 lists the observed powder patterns for the Unst serpentine

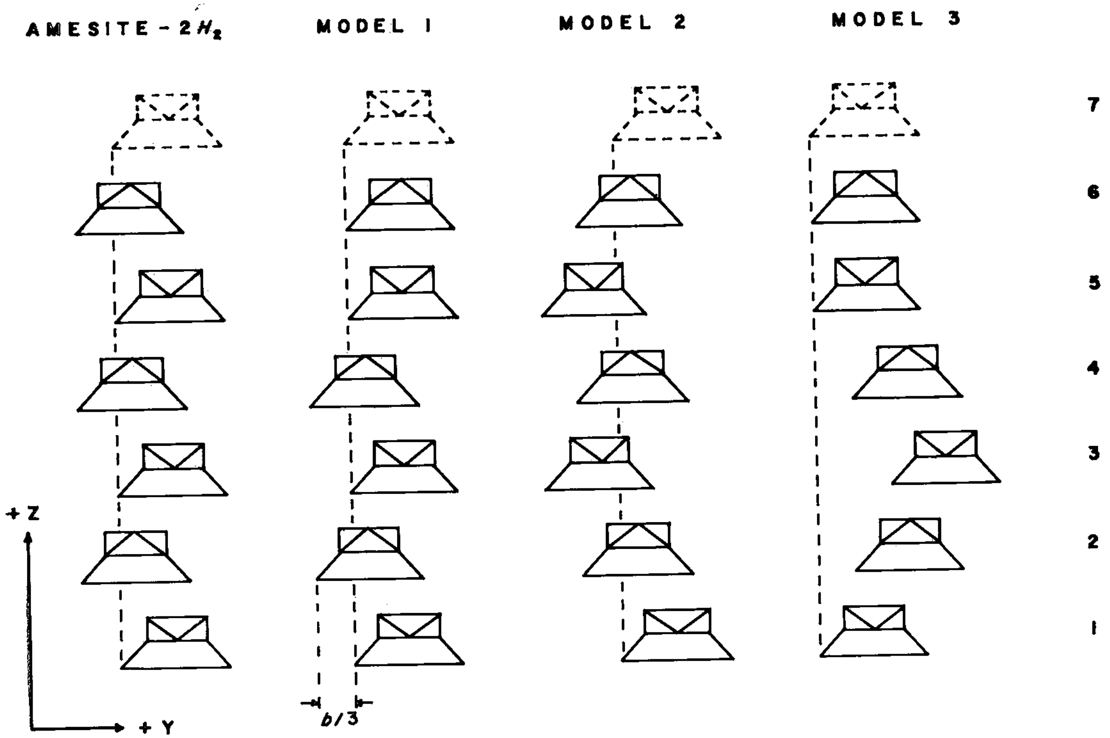

FIG. 1. Diagrammatic representation of layer sequences in three best-fit models for Unst-type serpentine, relative to that in amesite-$2H_2$. Octahedral cation sets II and I alternate in successive layers.

and its Ge analogue, along with the patterns calculated from model 1. A few minor changes have been made in the indexing originally given by Zussman & Brindley (1957), including several reflections not previously recorded. These latter reflections were seen to have significant intensity on densitometer scans, and were indexed using a least-squares convergence procedure based upon observed d values and cell dimensions.

In fine-grained materials of this sort it is possible that different structures may be intermixed, either as individual crystallites or as domains within crystallites. Single crystal study would be necessary to identify the latter situation as well as to recognize complex stacking variants of a more simple structural motif of the sort described by Jahanbagloo & Zoltai (1968).

Note should be taken that the $k \neq 3n$ reflections usually are not observed in powder patterns from group D serpentines that are not of the Unst-type. Gandolfi patterns taken of known examples of $2H_1$, $2H_2$, and $6R$ single crystals of amesite and cronstedtite confirmed that the $k \neq 3n$ reflections are too weak to show up on powder patterns even though they are observable on single crystal photographs. This means that these polytypes cannot be distinguished from one another by means of powder patterns. Disordered layer stacking, if present, would not be detectable either, because it affects only these same unobserved $k \neq 3n$ lines. If all other group D conditions are satisfied, however, the strong $k = 3n$ reflections diagnostic of group D would be observed and would indicate 2-layer periodicity. Randomly stacked 2-layer packets of this sort have been identified and illustrated for Cr-chlorite by Lister & Bailey (1967). For these reasons, group D serpentines that do not show Unst-type long-periodicity lines cannot be characterized as to regularity or randomness of stacking from powder patterns, and Mg-rich varieties also might be misidentified as the more Al-rich amesite unless careful attention is paid to the positions of the basal reflections. Two such examples have been found in the present study.

NOMENCLATURE

Wicks & Whittaker (1975) have suggested that the ideal $6H$ polytype of space group $P6_1$ derived by Bailey (1969) in his group B struc-

TABLE 4. SIX-LAYER POLYTYPE SYMBOLS

Space Group	Steadman (1964) Model Number	Bailey (1969)		Wicks & Whittaker (1975) Symbol	Present Paper	
		Group	Symbol		Model	Symbol
$P6_{1,5}$	--	B	$6H$	$6H_1$	--	$6H_1$
$P6_3$	14 & 15	D	--	$6H_2$	14	$6H_2$
$R3c$	16	D	$6R$	$6R_1$	22	$6R_1$
$R3$	4 & 5	C	--	$6R_2$	--	--
$R3$	12 & 13	D	--	$6R_3$	23	$6R_2$
$P3$	--	D	--	--	1	$6T_1$

tures be designated $6H_1$ and that the ideal $6R$ polytype of space group $R3c$ be designated $6R_1$. Further designations $6H_2$, $6R_2$, and $6R_3$ were suggested for several 6-layer structures derived by Steadman (1964). It would be impractical to assign similar designations to the large number of theoretical 6-layer structures derived in the present study for group D serpentines, however, or to the large number of structures that preliminary calculations indicate can be developed by similar permutations of stacking shifts involving the X directions. It is proposed, therefore, that polytype designations beyond those given by Bailey (1969) for the simple polytypes be limited to structures actually observed in natural or synthetic specimens.

If the proposal above is followed, the designations $6H_1$ and $6R_1$ as given by Wicks & Whittaker would be retained for Bailey's ideal $6H$ and $6R$ polytypes. Although no natural or synthetic examples of the $6H_1$ polytype are known, there are at least two minerals based on the $6R_1$ structure (model 22 of this paper). Nacrite is a dioctahedral derivative that has the $6R_1$ stacking sequence. A trioctahedral example has been found in amesite by Hall & Bailey (1976), but because of suspected twinning a more accurate symbol for that particular specimen would be $6PR_1$ (where P=pseudo). The enantiomorphic 6-layer structures 12 and 13 generated by Steadman (1964) in space group $R3$ have been identified in amesite and in cronstedtite by Steadman & Nuttall (1962, 1964) and in kellyite by Peacor *et al.* (1974). This polytype is designated here as $6R_2$, thus superceding the $6R_3$ symbol given by Wicks & Whittaker to a different and as yet unobserved Steadman polytype (Table 4). The $6R_2$ structure as designated here corresponds to model 23 of the present paper. For the amesite and cronstedtite specimens studied by Steadman & Nuttall a symbol $6PR_2$ is more appropriate because of observed twinning and reduced symmetry. The symbol $6H_2$, suggested by Wicks & Whittaker for Steadman's enantiomorphic structures 14 and 15 of space group $P6_3$, can be retained because this polytype has been identified in cronstedtite by Steadman & Nuttall (1964). The $6H_2$ structure corresponds to model 14 of the present paper.

The Unst serpentine is based on model 1 of the present paper, and has trigonal symmetry $P3$. The appropriate structural symbol, therefore, is $6T_1$. Following the recommendation of Wicks & Whittaker that the name lizardite be extended to include other flat-layer serpentines, the entire name of Unst-type serpentines would be lizardite-$6T_1$ with adjectival modifiers as needed to indicate compositional variants. Due to lack of information as to symmetry, no structural symbol can be assigned at present to the 6(3) aluminian serpentine synthesized by Gillery (1959) and by Shirozu & Momoi (1972).

ACKNOWLEDGEMENTS

This research was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, PRF grant 4899-AC2, and in part by the Earth Sciences Section, National Science Foundation, NSF grant GA-34918. Specimens were kindly provided by G. W. Brindley, E. J. Olsen, and I. M. Threadgold.

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Manuscript received March 1976.