

Aggregate Refractive Indices and Unit Cell Parameters of Synthetic Serpentine in the System $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}^1$

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Abstract

Variation of synthetic serpentine, $(\text{Mg}_{6-x}\text{Al}_x)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$, unit cell parameters, molar volume (V), and aggregate refractive index (\bar{n}) as a function of the substitution $2\text{Al}^{3+} = \text{Si}^{4+} + \text{Mg}^{2+}$ were investigated for the compositions $x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, 0.75, 1.0, 1.5,$ and 2.0 . Regression equations relating variation in these parameters with composition are:

$$\begin{aligned} a &= 5.3132(28) + 0.0169(87)x - 0.0219(55)x^2 && \underline{0.99} \\ b &= 9.1990(64) + 0.0425(138)x - 0.0354(71)x^2 && \underline{0.975} \\ c &= 7.3115(69) - 0.2277(254)x + 0.0553(155)x^2 && \underline{0.975} \\ V &= 205.030(255) + 9.899(.328)x && \underline{0.75} \\ \bar{n} &= 1.5504(5) + 0.0239(16)x - 0.0032(9)x^2 && \underline{0.99} \end{aligned}$$

Figures in parentheses represent the estimated standard deviation; underlined figures represent the significance of the regression coefficients. The best determinative curve for estimating serpentine composition from measured values of d_{002} (in Å) is: $x = 2.4949 - 7.1247 \sqrt{d_{002} - 8.5277}$; the significance of the regression coefficients in this equation is greater than 0.975. The linear variation of molar volume with composition suggests that aluminous serpentines form an ideal solid solution series.

Introduction

The variation of aggregate refractive indices and unit cell parameters with composition has been used to construct determinative curves for monitoring the alumina content of synthetic serpentine in hydrothermal experiments. The effects of the coupled substitution $2\text{Al}^{3+} = \text{Si}^{4+} + \text{Mg}^{2+}$ were studied for 11 serpentines whose compositions correspond to values of $x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, 0.75, 1.0, 1.5,$ and 2.0 in the formula $(\text{Mg}_{6-x}\text{Al}_x)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_8$.

Synthetic tubular serpentine having the composition $0 \leq x \leq 0.05$ is referred to as clinochrysotile; platy serpentine restricted to the compositional limits $0.05 < x < 1.0$ is referred to as lizardite; and platy serpentine restricted to the compositional limits $1.0 < x < 2.0$ is referred to as aluminous serpentine. Aluminous serpentine has also been referred to as septechlorite (Nelson and Roy, 1958) and 1- or 6-layer orthoserpentine (Gillery, 1959). Although clinochrysotile and lizardite contain one formula unit and 6-layer orthoserpentine contains six formula

units per unit cell, all compositions are expressed in terms of two formula units in order to facilitate comparison with the results of previous studies.

The cell parameters obtained in the present study agree favorably with values for natural (Deer, Howie, and Zussman, 1962; Page, 1966) and synthetic (Yoder, 1952; Nelson and Roy, 1958; Gillery, 1959; Shirozu and Momoi, 1972) serpentines. The results presented in this paper have been reported orally (Chernosky, 1974) and supercede preliminary data (Chernosky, 1971) for the compositions $0 \leq x \leq 0.25$.

Starting Materials and Experimental Procedures

Clinochrysotile, lizardite, and aluminous serpentine were synthesized hydrothermally under controlled conditions of pressure and temperature (Table 1). Hydrothermal experiments were performed both at the Massachusetts Institute of Technology and at the Geophysical Laboratory, Carnegie Institution of Washington. Although experimental procedures differed slightly (see Chernosky, 1973), pressures are probably accurate to within ± 2 percent and temperatures to $\pm 5^\circ\text{C}$ (M.I.T.) and $\pm 10^\circ\text{C}$ (G.L.) of the stated values.

Starting materials for the experiments were either

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TABLE 1. Synthesis Conditions for Serpentine on the Join $Mg_6Si_4O_{10}(OH)_8-Mg_4Si_2Al_4O_{10}(OH)_8^*$

Composition x^{**}	Experiment No.	P (kb)	T (°C)	Duration (hours)	Starting material	Products
0	195M	2	412	470	OM	chr, tr. fo
0	212M	2	431	1400	195M	clinochrysotile
0	241M	2	413	2400	OM	plates
0.05	42M	2	365	620	gel	chr, liz, tr. fo
0.05	76G	10	400	238	42M	chr, liz, tr. fo
0.10	43M	2	365	620	gel	chr, liz, tr. fo
0.10	75G	10	433	238	43M	chr, liz, tr. fo
0.15	41M	2	365	620	gel	chr, liz, tr. fo
0.15	73G	10	433	238	41M	chr, liz, tr. fo
0.20	67M	1	401	73	gel	chr, liz, tr. fo
0.20	68M	1	401	73	gel	chr, liz, tr. fo
0.20	72G	10	470	162	67M	chr, liz, tr. fo
0.20	87G	6.9	477	244	68M	chr, liz, tr. fo
0.25	50M	2	363	504	gel	chr, liz, tr. fo
0.25	70G	10	470	162	50M	chr, liz, tr. fo
0.50	369M	2	463	312	OM	liz, tr. fo
0.50	402M	2	480	336	369M	liz, tr. fo
0.75	349M	2	487	312	OM	serp, tr. fo
0.75	351M	2	492	304	OM	serp, tr. fo
0.75	368M	2	480	316	OM	serp, tr. fo
1.0	366M	2	480	316	OM	serp, tr. fo
1.0	384M	2	647	357	OM	serp, tr. fo
1.0	391M	4	580	576	OM	serp, tr. fo
1.5	390M	2	478	576	OM	serp, tr. fo
2.0	367M	2	480	316	OM	serp, tr. fo

*Abbreviations: OM—oxide mix, G—Geophysical Lab, M—Mass, Inst. of Tech., fo—forsterite, liz—lizardite, serp—aluminous serpentine, chr—chrysotile, tr—trace (less than 1%).

**composition in terms of x (see text)

stoichiometric mixtures of oxides or coprecipitated gels. Details concerning the preparation of starting materials have been given by Chernosky (1973). It was necessary to use gel starting materials for compositions $0.05 \leq x \leq 0.25$ despite the presence of about 0.5 wt percent excess Na_2O . When oxide mixes in this compositional range were used as starting materials, clinochrysotile tubes formed rapidly from the MgO and SiO_2 components of the mix, which are apparently more soluble than Al_2O_3 in the fluid phase. Unreacted Al_2O_3 in the experimental products was eliminated by using gel starting materials. Al_2O_3 is apparently more reactive in gels than in oxide mixes because it is finer grained and hence more soluble in the fluid phase.

Experimental products were studied with oil immersion, powder X-ray diffraction, and electron microscope techniques. Due to the fine grain size of synthetic serpentines, only aggregates, consisting of numerous randomly-oriented serpentine grains, could be observed with a petrographic microscope. The precision with which the refractive index of each aggregate can be measured is a function of the number and orientation of serpentine crystals within the aggregate. It was found that the aggregate or average index of refraction (\bar{n}) could usually be

bracketed by two oils whose refractive indices differed by 0.002. Indices of refraction were determined in sodium light, using liquids whose refractive index was checked with an Abbe refractometer. Aggregate indices of refraction are probably accurate to within ± 0.002 of the stated value. Unit cell parameters were calculated by refining powder patterns obtained with an 11.46 cm Debye-Scherrer camera and $CuK\alpha$ radiation; least squares unit cell refinements were performed with the program LCLSQ (MIV) written by Burnham (1962). Linear and quadratic least squares regression equations were calculated for the unit cell parameters with the program REGRESSION written by L. W. Finger. Two criteria were used to decide whether the linear or quadratic equation fit the data "best": (1) the sum of the squares of the deviations about the regression should be a minimum, and (2) an F -test (Draper and Smith, 1966, p. 25) was used to test which equation was the most significant.

Results

Experiments conducted for relatively short periods on the composition $x = 0$ generally yielded a mixture of platy serpentine + clinochrysotile. A mixture of clinochrysotile + plates was recrystallized to 100 percent clinochrysotile (Table 1, 212M) at $431^\circ C$, 2 kbar, suggesting that clinochrysotile is the stable phase for the composition $x = 0$ at these conditions. An oxide mix with the composition $x = 0$ was converted to 100 percent plates at $413^\circ C$, 2kbar (Table 1, 241M). A powder pattern of the platy phase resembles a pattern of lizardite rather than chrysotile (Table 2).

Experiments performed within the serpentine stability field consistently yielded the two-phase assemblage clinochrysotile + lizardite (Chernosky, 1971) for compositions in the range $0 < x \leq 0.25$. This two-phase assemblage was persistent over a pressure range from 0.5 to 10 kbar in experiments of more than 100 days duration. Attempts to reverse the high-temperature assemblages (forsterite + talc or forsterite + talc + chlorite) within the serpentine stability field consistently yielded lizardite + clinochrysotile for compositions with $x \leq 0.25$. Examination of the experimental products with an electron microscope revealed that the long slender clinochrysotile tubes synthesized on the composition $x = 0$ gradually become shorter, thicker, and less abundant as the bulk composition of the charge becomes more aluminous. The powder pattern of synthetic clinochrysotile ($x = 0$) has broad peaks and

TABLE 2. Powder Patterns of Natural Clinochrysotile, Synthetic Clinochrysotile, and Platy Serpentine with the Composition $Mg_6Si_4O_{10}(OH)_2$ *

hkl	Natural clinochrysotile		Synthetic clinochrysotile (212M)		Serpentine plates (241M)				
	d(calc)	I	d(obs)	d(calc)	hkl	d(obs)	d(calc)	I	
002	7.36	VS	7.380	7.313	VS	001	7.209	7.237	VS
020	4.58	M	4.559	4.588	M	020	4.544	4.602	M
004	3.66	VS	3.660	3.656	VS	002	3.615	3.619	S
024			2.808	2.859	VW				
130	2.66	MW	2.655	2.648	W				
201	2.594	MW	2.589	2.580	W	201	2.496	2.493	VS
202	2.549	M	2.538	2.538	W				
202	2.456	S	2.450	2.445	S	202	2.143	2.141	M
203	2.282	W				203	1.783	1.706	MW
204	2.215	W	2.208	2.207	VW				
204	2.096	M	2.091	2.098	WM				
008	1.829	W	1.828	1.828	VW,B				
206	1.748	M	1.742	1.744	W				
						310	1.730	1.739	VVW
						311	1.697	1.691	VW
060	1.536	S	1.530	1.529	S,B	060	1.537	1.534	MS,B
						061	1.500	1.501	M,B
0,0,10	1.465	W	1.463	1.463	W	005	1.448	1.447	VVW
						062	1.410	1.412	VW
402	1.317	MW	1.317	1.317	W	401	1.307	1.306	W,B
						205	1.270	1.271	W
						402	1.249	1.247	VW
0,0,12			1.221	1.219	VW,B	403	1.164	1.163	VW
						404	1.070	1.071	VVW
						510	1.052	1.055	VVW
0,0,14			1.045	1.045	VW,B	531	0.996	0.994	VW,VB
						532	0.967	0.967	VW,B
						533	0.927	0.926	VVW,B

*The powder pattern for natural clinochrysotile was recorded by Whittaker and Zussman (1956). The powder patterns for synthetic clinochrysotile (212M) and platy serpentine (241M) were recorded with a 11.46 cm camera using filtered Cu K α radiation. Synthetic clinochrysotile was indexed on the basis of a cell with $a = 5.309$, $b = 9.181$, $c = 14.648$ Å and $\beta = 93^\circ$. Platy serpentine was indexed on the basis of an orthorhombic cell with $a = 5.312$, $b = 9.204$ and, $c = 7.237$ Å.

resembles the pattern of natural clinochrysotile; powder patterns of phases with compositions $x = 0.20$ and 0.25 have sharp peaks and resemble patterns of natural lizardite, even though the content of tubes in the charge is significant ($\sim 10 - 20$ percent). The presence of 20 percent clinochrysotile in a lizardite + clinochrysotile mixture could not be detected with X-ray powder techniques.

A one-layer aluminous serpentine (Gillery, 1959) was synthesized from oxide mixes with the compositions $x = 0.50$ and 0.75 . A six-layer aluminous serpentine was synthesized from the compositions $x = 1.0$, 1.5 , and 2.0 .

Aggregate Indices of Refraction

A plot (Fig. 1) of the data contained in Table 3 shows that \bar{n} of synthetic serpentine increases smoothly with increasing alumina content. A quadratic regression relating \bar{n} to composition (Table 4) is significant at the 0.99 level, *i.e.*, the probability of obtaining such a large deviation by chance is 0.01. The aggregate index of refraction for alumina-poor serpentines ($x \leq 0.25$) is independent of the pressure-temperature conditions at which the serpentine was synthesized; the effect of pressure and temperature on

\bar{n} for serpentines more aluminous than $x = 0.25$ was not investigated.

The aggregate refractive index of synthetic clinochrysotile (#212M, Table 3) is 1.553, whereas the aggregate refractive index of the platy serpentine with the same composition (#241M, Table 1) is 1.549. This difference may be accounted for by two factors: (1) the denser polymorph of a material always has a higher refractive index than the less dense one, and (2) there is a contrast in morphology between the two polymorphs. The morphology of chrysotile tubes is such that the tube ends constitute a relatively small part of the crystallite mass. As a result, \bar{n} is dominated by the high index (γ) which has its vibration direction parallel to the tube length. In contrast, the morphology of lizardite plates is such that the low index (α), which has its vibration direction normal to the plates, contributes more to \bar{n} , thereby decreasing the effect of (γ).

Observed values for \bar{n} of serpentine are comparable to the mean refractive indices (Table 3) calculated with the rule of Gladstone and Dale (1864), using the specific refractive energies of the constituents of minerals (Larsen and Berman, 1934, p. 31), the weight percentages of these constituents, and the density (Dx) calculated from the unit cell parameters

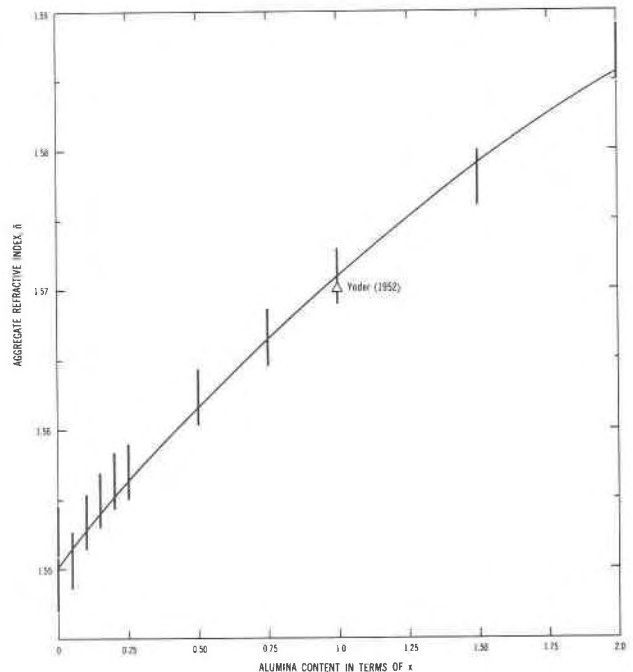


FIG. 1. Plot of aggregate index of refraction against composition of synthetic chrysotile and lizardite. Solid line is least squares regression for synthetic serpentines. Length of bar represents precision of measurement.

TABLE 3. Unit Cell Parameters, Density, Molar Volume, Aggregate Refractive Indices, and d_{002} of Synthetic Chrysotile and Lizardite*

		Alumina content in terms of x (experiment number)						
		0(212M)	0(241M)	0.10(75G)	0.15(73G)	0.20(72G)	0.20(87G)	0.25(70G)
a	Å	5.306 (6)	5.312 (4)	5.326 (11)	5.319 (7)	5.317 (4)	5.324 (5)	5.315 (1)
b	Å	9.176 (12)	9.204 (17)	9.222 (30)	9.204 (14)	9.219 (11)	9.219 (11)	9.207 (6)
c	Å	14.650 (8)	7.237 (15)	7.276 (31)	9.274 (12)	7.238 (11)	7.257 (9)	7.251 (3)
V	Å ³	712.13 (1.77)	353.81 (1.12)	357.32 (2.78)	356.10 (1.23)	354.81 (92)	356.16 (94)	354.83 (28)
Dx	g/cm ³	2.585 (6)	2.601 (1)	2.576 (20)	2.586 (9)	2.595 (7)	2.586 (7)	2.596 (2)
v	cm ³	214.44 (53)	213.01 (19)	215.20 (1.68)	214.46 (74)	213.69 (56)	214.50 (56)	213.70 (17)
\bar{d}_{002}	Å	3.6564	3.6186	3.6379	3.6368	3.6192	3.6284	3.6253
\bar{n}_{obs}		1.553	1.549	1.553	1.555	1.556	1.556	1.557
\bar{n}_{calc}		1.570	1.574	1.568	1.570	1.571	1.569	1.572
		Alumina content in terms of x (experiment number)						
		0.75(349M)	0.75(368M)	1.0(366M)	1.0(391M)	1.5(390M)	2.0(367M)	
a	Å	5.317 (2)	5.318 (3)	5.306 (2)	5.302 (4)	5.285 (5)	5.269 (7)	
b	Å	9.210 (9)	9.204 (16)	9.210 (3)	9.200 (5)	9.175 (7)	9.148 (9)	
c	Å	7.189 (10)	7.207 (13)	42.024 (51)	42.607 (79)	42.607 (79)	42.387 (78)	
V	Å ³	352.03 (72)	352.81 (95)	2093.92 (3.03)	2088.60 (424)	2065.97 (5.37)	2042.87 (6.84)	
Dx	g/cm ³	2.620 (5)	2.614 (7)	2.645 (4)	2.651 (5)	2.684 (7)	2.718 (9)	
v	cm ³	212.01 (43)	212.48 (57)	210.18 (30)	209.64 (43)	207.37 (54)	205.05 (69)	
\bar{d}_{002}	Å	3.5944	3.6037	3.5709	3.5687	3.5506	3.5322	
\bar{n}_{obs}		1.567	1.567	1.571	1.571	1.577	1.577	
\bar{n}_{calc}		1.574	1.573	1.578	1.581	1.5840	1.601	

* Abbreviations: V-unit cell volume, v-molar volume, and Dx-density calculated from V. β for 212M, is 93.34°. Numbers in parentheses are errors and represent standard deviations calculated by the program used to refine the unit cell parameters. Synthesis conditions for the samples are in Table 1. Alumina contents are represented by x in the formula: $(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8$.

(Table 3). Values of \bar{n}_{calc} are consistently about 0.7 percent greater than the values of \bar{n}_{obs} (Table 3). Hazen and Wones (1972) noted consistently positive deviations of as much as +0.087 in the quantity ($\bar{n}_{calc} - \bar{n}_{obs}$) and suggested that Larsen and Berman (1934) had overestimated the specific refractive energy of H₂O (0.3355). A value of 0.3 for $k(H_2O)$ would bring

the calculated and observed mean refractive indices of synthetic serpentine into agreement.

Unit Cell Parameters

The average natural lizardite structure is 1-layer trigonal (Rucklidge and Zussman, 1965), whereas natural clinochrysotile is approximately 1-layer trigonal (Bailey, 1969). The unit cell parameters reported in this study were refined on the basis of a 2-layer monoclinic cell for clinochrysotile, on the basis of a 1-layer ortho cell for the compositions $0.10 \leq x \leq 0.75$, and on the basis of a 6-layer ortho cell for the compositions $1.0 \leq x \leq 2.0$. The actual unit cell parameters obtained by least squares regression of synthetic serpentine powder patterns are listed in Table 3. In order to compare them directly with the data of Nelson and Roy (1958), Gillery (1959), and Shirozu and Momoi (1972), the unit cell parameters were normalized on the basis of a 1-layer ortho cell and plotted (Fig. 2). Calculated least-squares regression equations (Table 4) suggest that *a*, *b*, and *c* vary smoothly though nonlinearly with composition (Fig. 2); the error bars shown on Figure 2 represent estimated standard deviations obtained from the least-squares cell-refinement program and reflect precision only. Although *a*, *b*, and *c* vary nonlinearly with composition, note that the variation in unit cell volume

TABLE 4. Regression Equations for Serpentine X-Ray Parameters and Bulk Indices of Refraction against Composition*

Regression equation with standard errors of coefficients	Significance of regression coefficients
$\bar{n}_D = 1.5504 + 0.0239x - 0.0032x^2$ ±0.0005 ± 0.0016 ± 0.0009	.99
<i>a</i> = 5.3132 + 0.0169x - 0.0219x ² ±0.0028 ± 0.0087 ± 0.0055	.975
<i>b</i> = 9.1990 + 0.0425x - 0.0354x ² ±0.0064 ± 0.0138 ± 0.0071	.975
<i>c</i> = 7.3115 - 0.2277x + 0.0553x ² ±0.0069 ± 0.0254 ± 0.0155	.975
V = 356.958 - 8.046x ±0.304 ± 0.422	.99
v = 205.030 + 9.899 ±0.255 ± 0.328	.975
Dx = 2.5783 + 0.0682x ±0.0021 ± 0.0030	.975
\bar{d}_{002} = 3.6507 - 0.0979x + 0.0196x ² ±0.0024 ± 0.0070 ± 0.0036	.975

* Abbreviations: x-alumina content in serpentine (see text); z-mole fraction chrysotile; a, b, c, \bar{d}_{002} given in Å; V given in Å³; v given in cm³; Dx given in g/cm³.

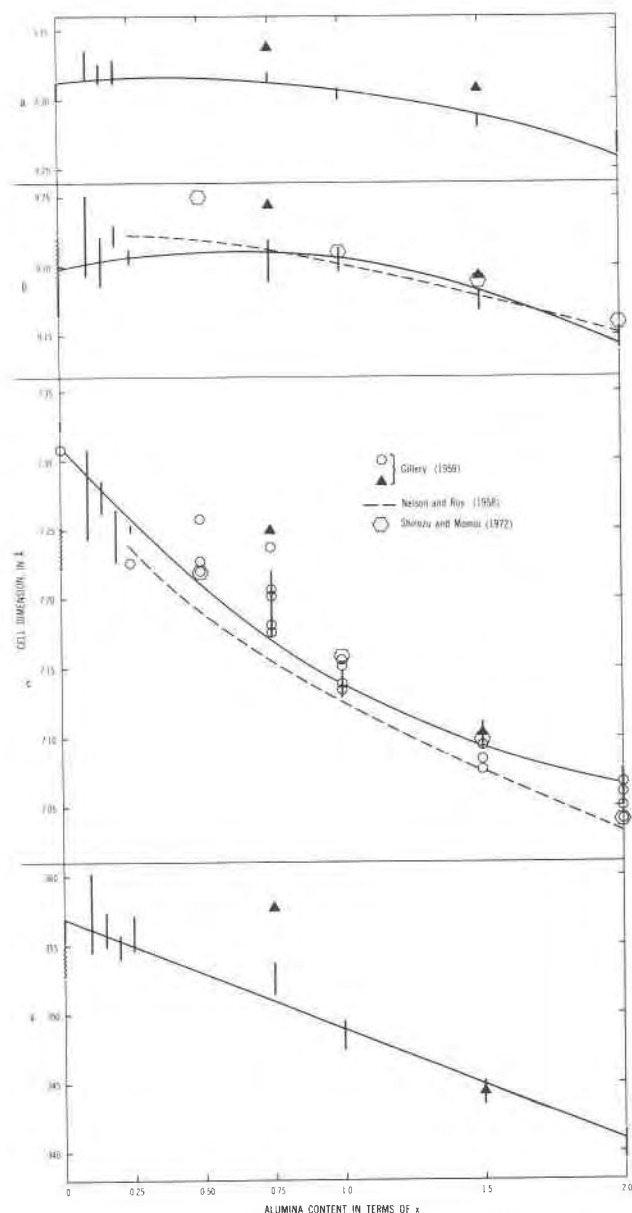


FIG. 2. Plot of synthetic serpentine unit cell parameters (a , b , c) and unit cell volume (V) against composition. Dashed lines represent the data of Nelson and Roy (1958); solid lines represent least squares regression equations calculated from the data contained in Table 3. Length of bar represents calculated error of observation. Solid triangle represents a value obtained by refining a powder pattern; open circle or hexagon represents a value calculated by using the position of 001 reflections. Wavy bar represents values obtained for a platy phase with the composition $x = 0$ (241M).

(V) is linear. Also note that the c parameter of synthetic serpentine is affected to a greater extent than the a or b parameters when Al_2O_3 is added.

Agreement between the unit cell parameters ob-

tained in this study and those obtained by Nelson and Roy (1958) and Shirozu and Momoi (1972) is good in view of the fact that these investigators used only d_{060} and d_{002} to calculate the variation in b and c with composition. Refined unit cell parameters for the compositions $x = 0.75$ and $x = 1.5$ (Gillery, 1959) are somewhat greater than the values obtained in this study (Fig. 2); however, Gillery (1959, Table 1) also reported values for c which are comparable with those obtained in this study.

Serpentine Determinative Curve

A sufficient number of reflections for a complete unit cell refinement generally cannot be obtained from serpentine in a polyphase synthetic assemblage, so that plots of unit cell parameters against composition cannot be used to estimate the alumina content of serpentine. Fortunately, d_{002} varies smoothly though not linearly with composition (Fig. 3). Because reflections from phases other than chlorite do not interfere with d_{002} , Figure 3 may be used to estimate the compositions of synthetic serpentines coexisting with other phases in hydrothermal experiments. The regression equation relating d_{002} to composition (Table 4) can be cast in the following more useful form for estimating composition from measurements of d_{002} :

$$x = 2.4949 - 7.1247\sqrt{d_{002} - 3.5277}.$$

Caution must be exercised if this equation is used to estimate the composition of natural lizardite or

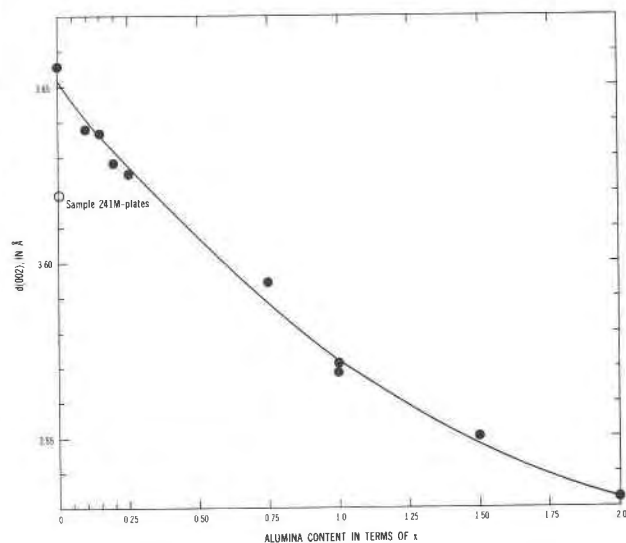


FIG. 3. Plot of d_{002} against composition of synthetic chrysotile and lizardite. Solid line is least squares regression for synthetic serpentines.

clinochrysotile. Even though the substitution of divalent cations for Mg^{2+} will primarily affect a and b , the substitution of trivalent cations other than Al^{3+} in the tetrahedral sheet will markedly affect c and hence d_{002} .

Serpentine Density and Molar Volume

The density (Dx) and molar volume (v) of synthetic serpentines were calculated using the relations

$$Dx = \frac{MZ}{VN_A} \quad \text{and} \quad v = \frac{VN_A}{Z}$$

where Dx is in grams per cubic centimeter and v is in cubic centimeters. M is the formula weight in grams, Z is the number of formula units per unit cell, V is the unit cell volume, and N_A is Avagadro's number. The calculated densities vary smoothly with composition (Table 3, Fig. 4). Molar volume is a linear function of composition expressed in mole fractions (Table 3, Fig. 5), suggesting that aluminous serpentines form an ideal solid solution series (Thompson, 1967).

Discussion

Mismatch between the lateral dimensions of the octahedral and tetrahedral sheets, and polytypism, or both, may account for the structural differences

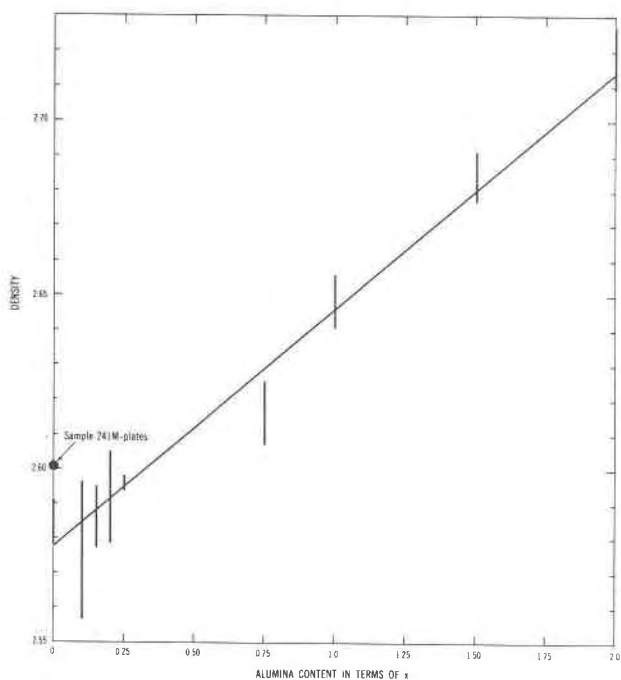


FIG. 4. Plot of density against composition of synthetic chrysotile and lizardite. Solid line is least squares regression for synthetic serpentine. Length of bar represents calculated error of observation.

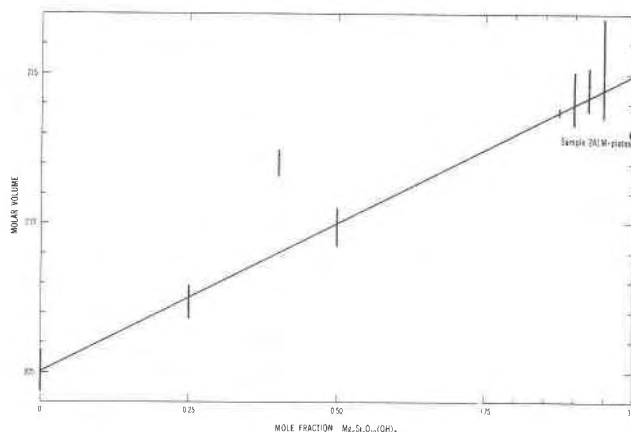


FIG. 5. Plot of synthetic serpentine molar volume against mole fraction chrysotile. Solid line is least squares regression for synthetic serpentines. Length of symbol represents calculated error of observation. The value for $Chr_{0.375}$ was not used in calculation of the regression equation.

between the serpentine-group minerals. Polytypism, or the regular and irregular stacking of layers, will not be discussed because the fine-grained synthetic serpentines are not suitable for single-crystal studies needed to characterize polytypes. The alumina content influences the structure and hence the aggregate refractive indices (Fig. 1) and unit cell parameters (Fig. 2) of serpentine because it controls the relative dimensions of the tetrahedral and octahedral sheets.

Cell Parameters

Variation in unit cell parameters of synthetic serpentine (Table 3, Fig. 2) can be explained by examining the calculated variation in lateral dimensions of the octahedral and tetrahedral sheets as a function of their alumina content (Table 5). The formula for serpentine was recast to $(Mg_{1.5-z}Al_z)(Si_{1-z}Al_z)O_{2.5}(OH)_2$, where z is the amount of alumina in the octahedral and tetrahedral sheets. Assuming that (1) the theoretical distances for Si-O and Al^{IV} -O bonds are $1.61 \pm 0.01 \text{ \AA}$ and $1.76 \pm 0.01 \text{ \AA}$, respectively, (2) the tetrahedra are strictly regular, Al^{3+} substituting randomly for Si^{4+} , and (3) the linear dimensions of the tetrahedral sheet proportionately increase with the addition of alumina, then the variation in a and b with alumina content can be calculated (Table 5) with the equations (Brindley, 1967):

$$b(Si_{1-z}Al_z) = 9.15 + 0.91z, \quad \text{and} \\ a = \frac{b}{\sqrt{3}}$$

TABLE 5. Calculated Variation in Octahedral and Tetrahedral Sheet Lateral Dimensions with Alumina Content*

Composition		Tetrahedral sheet		Octahedral sheet		Δ
x^*	z^{\dagger}	a	b	a	b	
0	0	5.28	9.15	5.40	9.36	-7.04
0.2	0.05	5.31	9.20	5.39	9.34	-1.49
0.5	0.125	5.35	9.26	5.37	9.30	-0.40
0.75	0.188	5.38	9.32	5.35	9.27	+0.55
1.0	0.25	5.41	9.38	5.33	9.24	+1.50
2.0	0.50	5.55	9.61	5.27	9.12	+5.28

*Alumina content in terms of x (see text); \dagger the relation: $(Mg_{1.5-z}Al_z)(Si_{1-z}Al_z)$ is used to define z ; Δ -area of tetrahedral sheet minus area of octahedral sheet.

The lateral dimensions of the octahedral sheet (Table 5) were calculated by assuming a linear decrease in the size of the brucite sheet ($5.4 \text{ \AA} \times 9.36 \text{ \AA}$) where alumina is added in the form of gibbsite ($4.99 \text{ \AA} \times 8.64 \text{ \AA}$), according to the relation: $(Mg_{1.5-z}Al_z)$. The calculated values for the unconstrained sheets (Table 5) are somewhat larger than the observed values for a and b in lizardite and are therefore qualitative at best. Because the lateral dimensions of the octahedral sheet are about 4.4 percent larger than the dimensions of the tetrahedral sheet (Table 5) for the composition $x = 0$, there is a tendency for tetrahedral tilting along all hexagon edges. Barring additional structural constraints, the layers curl to form chrysotile tubes with the octahedral sheet on the convex side and the tetrahedral basal oxygens on the concave side. Because the octahedral and tetrahedral sheets as well as the layer as a whole are neutral, only weak, long-hydrogen bonds ($\sim 3 \text{ \AA}$) between the apical tetrahedral oxygens in one layer and the hydrogen of the hydroxyl groups in the next layer and very weak Van der Waals forces bind the individual layers together.

The progressive addition of alumina ($2Al^{3+} = Mg^{2+} + Si^{4+}$) has two effects on the serpentine structure: (1) the lateral dimensions of the tetrahedral sheet increase, and the lateral dimensions of the octahedral sheet decrease (Table 5); and (2) the replacement of Mg^{2+} by Al^{3+} increases the positive charge on the tetrahedral sheet, even though the layer as a whole remains neutral. As a consequence of the first effect, both sheets uncurl to produce platy lizardite. In response to the second effect, c decreases (Fig. 2) as the magnitude of the charge difference between the octahedral and tetrahedral sheets increases.

Because the lateral dimensions of the octahedral and tetrahedral sheets change in an inverse way as a

function of alumina content, there is a unique composition at which these dimensions are identical. Based on the calculations for unconstrained sheets (Table 5), it is predicted that the octahedral and tetrahedral sheets will have identical lateral dimensions at the composition $x = 0.5$.

Rather than curling in a direction opposite to that of clinochrysotile, aluminous serpentines articulate because the lateral dimensions of the tetrahedral sheet contract as a result of tetrahedral rotation. Donnay, Donnay, and Takeda (1964) have shown that an alternate clockwise and anticlockwise twist of the tetrahedra about a vector normal to the sheets will reduce the lateral dimensions according to the expression

$$\cos \alpha = \frac{b(\text{obs})}{4\sqrt{2}d_t}$$

where α is the angle of rotation, $b(\text{obs})$ is the observed b parameter, and d_t is the mean tetrahedral bond length. The value for d_t has been estimated from the relation between mean Si, Al-O distance and mean tetrahedral bond length proposed by Smith and Bailey (1963). The accuracy of the calculations in Table 5 may be ascertained by determining the actual composition for which $\alpha = 0$, *i.e.*, where both sheets have identical lateral dimensions. The composition for which α becomes zero is $x = 0.25$ rather than $x = 0.5$ as predicted in Table 5.

Poor agreement between the predicted and actual composition at which the octahedral and tetrahedral sheets have identical lateral dimensions suggests that at least one other factor, in addition to tetrahedral rotation, influences articulation. Because lateral contraction tends to bring the tetrahedral actions closer together, it is likely that some adjustment is also made by thickening of the tetrahedral sheets and thinning of the octahedral sheets, thereby decreasing and increasing, respectively, their lateral dimensions.

Because the ionic radius of Fe^{2+} (0.74) is 10.8 percent greater than the ionic radius of Mg^{2+} (0.66), the magnitude of the difference between the lateral dimensions of an octahedral and tetrahedral sheet should increase as octahedral Fe^{2+} content increases. In an alumina-free system, lizardite will not crystallize unless another trivalent cation such as Fe^{3+} enters the structure and serves to adjust the lateral dimensions of both the octahedral and tetrahedral sheets by a substitution such as $2Fe^{3+} = (Mg^{2+}, Fe^{2+}) + Si^{4+}$. It is not surprising that natural lizardites contain high to moderate Fe^{3+} contents and that FeO makes up less than 7 percent of the total of

the three oxides $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ (Whittaker and Wicks, 1970).

Gillery (1959) has shown in synthesis experiments that the ratio of 6-layer to 1-layer serpentine increases as alumina content and pressure increase. Because the c dimension decreases slightly as the percent of 6-layer serpentine increases, Gillery (1959) postulated that the 6-layer serpentine has a slightly smaller volume than the 1-layer serpentine. The curvature in the plot of c against composition (Fig. 2) is partly explained by a progressive increase in the percent of 6-layer serpentine as alumina content increases. A linear extrapolation of the decrease in c shown by the alumina-poor compositions would result in a value for c about 4 percent smaller than the one observed for the composition $x = 2.0$. The plot of c against composition (Fig. 2) is curved because the tendency to contract is progressively overcome by cation repulsion.

Attempts to synthesize serpentine having an alumina content greater than $x = 2.0$ have produced assemblages of aluminous serpentine (whose c dimension corresponds to an aluminous serpentine with an alumina content $x = 2.0$) + corundum or aluminous serpentine + spinel + corundum (Nelson and Roy, 1958; Gillery, 1959). Bailey (written communication) has suggested that the failure to synthesize serpentine having an alumina content $x > 2.0$ is due to instability of octahedral sheets with higher charges.

Optical Properties

The planar arrangement of hydroxyls in the octahedral sheet of layer silicates such as the serpentine group minerals renders them particularly susceptible to secondary polarization by adjacent hydroxyls. The electric vector of light whose propagation direction is normal to the sheets vibrates parallel to the sheets and distorts or polarizes neighboring hydroxyls. Light propagating parallel to the sheets, on the other hand, has its vibration direction normal to the sheets and hence induces less secondary polarization. As a result of secondary polarization, the velocity of light propagating normal to a sheet is decreased, causing an increase in the refractive indices β and γ ; *i.e.*, negative birefringence (one low and two high refractive indices) is produced.

The substitution of Al^{3+} for Mg^{2+} in the octahedral sheet results in an increased degree of polarization because small highly charged cations have greater polarizing powers than larger cations having smaller charge; the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet results in less polarization because

oxygen is not as polarizable as is a hydroxyl group. The lesser influence on the tetrahedral anions may be balanced to some extent by the higher charge on the sheet, so that the net effect of both tetrahedral and octahedral substitutions is an increase in total polarization.

Phase Equilibria

The nature of the two-phase, lizardite + clinochrysotile field which exists for compositions in the range $0 < x \leq 0.25$ and for synthetic iron-bearing serpentines along the join $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ – $\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ (Page, 1966) is still not clearly understood. The assemblage clinochrysotile + lizardite is probably stable, although experimental studies have neither proved or disproved this contention. Coexisting lizardite + clinochrysotile at Burro Mountain (Page, 1967) and on the Tiburon Peninsula (Page, 1968) in California were interpreted as equilibrium situations and tend to suggest that the assemblage clinochrysotile + lizardite is stable. Unfortunately, reaction kinetics at the temperatures in question are so slow that conversion from one morphology to another has not been experimentally feasible; however, current experimental work does offer an indirect means of testing the hypothesis that the assemblage clinochrysotile + lizardite is an equilibrium one.

Electron photomicrographs of synthetic clinochrysotile show that the tubes become shorter and thicker as the alumina content of the bulk composition is increased, suggesting that alumina is incorporated in synthetic clinochrysotile. If it could be demonstrated that the proportions but not the compositions of clinochrysotile and lizardite changed as a function of temperature, the phases would have to be considered polymorphs whose coexistence is metastable except along a univariant curve. If, however, both the proportions and compositions of coexisting clinochrysotile and lizardite changed as a function of temperature, they would not be polymorphs, and the two-phase assemblage would probably be stable.

Owing to the fine-grained nature of the synthetic products, only an indirect means of monitoring possible compositional variations in coexisting phases is possible. The variation in cell parameters, determined by electron diffraction of individual plates and aggregates of tubes within a two-phase assemblage, will be used to study the compositions of coexisting clinochrysotile and lizardite.

A rather puzzling problem is posed by platy

serpentine with the composition $x = 0$. Theoretically, platy serpentine with a lizardite-like structure should not form because of the large amount of mismatch between the octahedral and tetrahedral sheets (Table 5). The only way to achieve articulation without allowing any curling is to distort the sheets severely. The unit cell parameters do not suggest an explanation; b and c are smaller for the platy serpentine, whereas a is the same for both species. Hopefully, electron diffraction studies will help to deduce the structure of the platy serpentine.

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