STUDIES ON THE CHRYSOTILE AND ANTIGORITE COMPONENTS OF SERPENTINE

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ABSTRACT

The fiber (chrysotile) and adjoining layer of matrix of several specimens of serpentine were compared for differences in chemical compositions, x-ray diffraction, specific volume, loss on heating, differential thermal analysis, thermal balance analysis and electron microscopy. The significant difference in composition was a lower Al_2O_3, and also generally Fe_2O_3 and FeO, content of the fiber compared to the matrix. Results of computation of the structural formulas using the method of Duncan McConnell suggested that a small difference occurs in the distribution of the extraneous ions (Al^{3+}, Fe^{3+}, etc.) in the structure of chrysotile and the matrix. The computations indicated that in the case of the fiber, the only extraneous substituent in the silica layer was tetrahedral water (($H^+)_4$ for Si^{4+}), the other ions apparently assuming octahedral coordination. The silica layer of the matrix, on the other hand, contained small amounts of ions together with the tetrahedral water. Thermal balance and static loss-on-heating results indicate clearly that a small portion of the water is liberated at a higher temperature than that from the brucite layer, and this high-temperature water could be the tetrahedral water suggested by results of the computations.

Electron microscope examinations showed that specimens of the matrix contained "fibers" in form of laths of probably different degrees of curvature, including tubes. The occurrence of chrysotile in tubular crystals was confirmed with a variation not previously reported. The specimen from Eden Mills exhibited curling of lath-like crystals from both edges which apparently resulted in formation of twin tubes. Results of specific volume measurements on a massive sample of this mineral indicated negligible voids precluding a tubular morphology. Since the subdivided fibers occurred in form of tubes it may be assumed that these form during the grinding of the specimen.

I. INTRODUCTION

Results of investigations in recent years (1, 2, 3, 4, 5, 6) on the morphology of chrysotile show that the fibers occur in the form of tubular crystals. Antigorite on the other hand in microscopically detectable particles occurs in platy crystals. Bates and Mink (7) advanced the hypothesis, on the basis of Pauling's (8) theory of "misfit" between layers as being the fundamental cause of curvature; that the crystals of antigorite tended to be flat because of the presence of extraneous ions which relieved the stress. Roy and Roy (9) studied the effects of substitutions of

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ions on the morphology of synthetic serpentines and showed that the crystal habit, platy or tubular, was related to the size of the substituent ion.

The present study was undertaken to examine the possible effects of the extraneous constituents in mineral serpentines on their properties. The specimens, from different localities, consisted of veins of chrysotile between adjoining layers of the matrix. The results of complete chemical analysis, x-ray diffraction, electron microscopy, differential thermal analysis, thermal balance analysis, static loss on heating and specific volumes are given in this report.

II. MATERIALS AND PROCEDURES OF TEST

1. Materials

The minerals used in this study and related information on them are given in Table 1. As noted, most of the fiber and matrix pairs were ob-

TABLE 1. MINERALS USED IN PRESENT STUDY

Designation or name	Locality	Supplier and supplier's No.
Fiber and Matrix	Eden Mills, Vt.	Wards[a]
Fiber and Matrix	Delaware Co., Pa.	N.M.[b] R 4658
Fiber and Matrix	Aboutville, N. Y.	N.M. 9143
Fiber and Matrix	Globe, Arizona	N.M. R 4654
Fiber and Matrix	———, Quebec	N.M. 18,879
Fiber and Matrix	———, Quebec	N.M. 107,853
Fiber and Matrix	Montville, N. J.	N.M. R 4656
Yu Yen Stone	Manchuria, China	N.M. 94356

[a] Ward's Natural Science Establishment.
[b] National Museum, Washington, D. C.

tained from the National Museum, others were purchased from Ward's Natural Science Establishment. Fibers for special tests were purchased on the open market. The specimens from Quebec varied considerably one from the other in physical characteristics.

The matrix immediately adjoining the veins of fibers was cut to a thickness of $\frac{1}{4}$ inch and then crushed finely. These are the samples, with one exception, to be mentioned, used in the present study.

2. Procedures

X-ray diffraction was recorded with either a North American Philips wide angle Geiger-counter unit or with cameras of 57.3 mm. radius. Filtered CuKα radiation obtained with excitation of 35 K.V.P. at tube

current of 17 ma. was used exclusively. Rates of scan for Geiger-counter recording ranged from 1° to 1/8° per minute, in 2θ.

The matrix specimen for the electron microscope mounts were finely subdivided by repeated grinding in a mortar with a pestle. The fibers for this purpose were dispersed in aqueous suspension with a Waring Blendor. The photographs were taken using an R.C.A., Universal Model, Electron Microscope at magnifications up to 9,900 ×.

Specific volumes were determined with Gay Lussac flasks of 10 ml. and 100 ml. capacity in water at 35° C., controlled to ±0.05° C. Water and CCl_4 were used alternately as density media, and the samples ranged from one to five grams in weight. Temperatures were recorded to ±0.025° C. and weighings to about 0.1 mg.

Precautions, as follows, were observed in this phase of the study. Each flask was standardized with both density media, at the temperature used. To insure surface wetting of the samples, one drop of "Tergitol"[a] was added to the water in each determination. The liquids were admitted to the flasks containing the specimen under partial vacuum. A stoppered desiccator provided with a thistle tube and stopcock was used for filling the flasks. The fiber-matrix pairs were always tested concurrently.

Specimens used for determining the specific volume of massive chrysotile (in compact condition as occurring in the vein) were cut into pieces of 0.7 to 1.0 inch-square cross sections parallel to the fibers, the fibers being held intact by the layers of matrix still present at the extremities of the fibers. The matrix was then trimmed back so that the fibers had a protective layer of about 1/16 to 3/32 inch of the matrix. The veins ranged from 5/8 to 7/8 inch in thickness. The specimens, after overnight drying at 100° C., were exposed to the laboratory air for about two weeks before weighings and measurements were taken. After completion of these tests, the specimens, wrapped in glazed paper, were crushed carefully in a vise in order to separate matrix from fibers. The volume of the matrix, assumed to be void free, was computed from its weight and density and the value obtained subtracted from the measured volume of the composite specimen.

The differential thermal analysis (DTA) equipment used in the present study has been described (10). In order to obtain results that could be compared without need of allowing for variations due to equipment, all samples were tested in the same cell starting with a cold furnace. The same weight of fiber and matrix obviously could not be used at a fixed volume due to the bulking effects inherent in the fibers. The samples for tests, amounting to 1.00 ± 0.10 g. of matrix (passing a No. 20 sieve and

[a] Sulfate derivative of 3.9 diethyl tridecanol-6.

retained on No. 50 sieve) and 0.60 ± 0.05 g. of fibers were packed in the cell with a minimum of crushing of "bundles" about 0.02 to 0.05 inches in diameter, following a set procedure to minimize possible variations in degree of compaction from sample to sample.

Chemical analyses were made according to standard methods.

Loss-on-heating curves were determined in a laboratory furnace, the temperatures being obtained with chromel-alumel thermocouples located near the crucibles. A period of twenty-four hours was allowed for attainment of equilibrium at each temperature. Some small deviation from equilibrium may have occurred between temperatures of about 500 to 600° C., but because the samples were heated together, the data are comparable.

III. Results and Discussions

1. Oxide Composition of Minerals

The results of chemical analysis of the serpentines for 19 constituents are given in Table 2. These data show that the Al_2O_3 content of the matrix was always higher than that of the fibers for each serpentine sample. Also, the sum of the moles of the extraneous constituents was invariably higher for the matrix than for the fibers for any given serpentine. One correlation based on the total amounts of Al^{3+}, Fe^{3+} and Fe^{2+} ions is given later in this report.

In order to ascertain how the composition of a given serpentine might vary from one section to another, a specimen consisting of a layer of matrix between two veins was analyzed. The 3.0 inch thick layer of Eden Mills matrix was cut into five sections of equal thickness and these are marked consecutively *M-1* to *M-5*. The results are given in Table 3. The fiber-matrix pairs at the two extremities of the specimen showed the same trends as manifested by those listed in Table 2. The variations in the amounts of the constituents in zones *M-2*, *M-3*, and *M-4* were large, indicating possible presence of some other phase, probably a chlorite. One may note especially the high magnesia and low water contents of samples *M-3* and *M-4*.

In the application of analytical data, the possible presence of impurities becomes a problem. The serpentine specimens from Globe, Arizona, and Eden Mills, Vermont, contained a second phase, possibly chlorite and magnesite, respectively. The Montiville fiber also probably contained an unidentified impurity. The other specimens were assumed to be homogeneous phases, that is, the extraneous ions were considered to be lattice constituents. On such assumption, the following computations were made.

Attempts to calculate structural formulas from the analytical data

TABLE 2. OXIDE COMPOSITIONS OF FIVE PAIRS OF SERPENTINE AND ONE ANTIGORITE

	Delaware Co. Pa. N.M. R 4658		Aboutville, N. Y. N.M. 9143		Globe, Arizona N.M. 4654		Quebec, Canada N.M. 18879		Montville, N. J. N.M. 4656		Antigorra N.M. 96917
	Matrix	Fiber	Matrix	Fiber	Matrix	Fiber	Matrix	Fiber	Matrix	Fiber	Matrix
SiO_2, %	42.40	42.50	41.80	41.80	26.80	43.00	41.52	41.70	42.02	41.88	41.30
Al_2O_3	.74	.32	.19	.11	.42	.27	.57	.24	.49	.19	1.59
Fe_2O_3	.48	.50	.93	.68	1.13	1.08	.36	.30	1.50	.81	3.61
FeO	.043	.010	.06	.05	.22	.17	.06	.05	.057	.05	4.51
MgO	42.70	42.50	42.67	42.82	25.00	40.00	42.80	42.85	42.05	41.38	36.30
Ign., Loss	13.52	13.46	13.88	14.04	14.85	13.17	14.36	14.23	13.74	14.22	11.19[a]
SO_3	.00	.00	.08	.09	.00	.01	.02	.02	.07	.31	.06
TiO_2	.070	.021	.10	.05	.022	.020	.06	.03	.073	.036	.15
CO_2	.11	.14	.04	.01	9.98	.78	.00	.07	.06	.02	.03
Cr_2O_3	.008	.004	.003	.003	.006	.005	.01	.005	.001	.005	.30
CaO	.01	.04	.19	.10	21.00	1.43	.11	.05	.26	.47	.43
MnO	.02	.02	.04	.04	.12	.16	.04	.02	.024	.05	.11
NiO	.00	.00	.00	.00	.00	.00	.00	.00	.002	.00	.26
CuO	.05	.01	.00	.00	.05	.03	.05	.02	.00	.00	nd.
Na_2O	.03	.04	.02	.03	.03	.03	.03	.07	.02	.06	.04
K_2O	.02	.02	.01	.01	.03	.02	.02	.01	.014	.023	.02
Loss at 110° C.	.26	.65	.24	.28	.16	.53	.60	.83	.32	.60	nd.
Total, %	100.55	100.23	100.25	100.11	99.82	100.71	100.55	100.51	100.70	100.10	99.90

[a] Includes loss at 110° C.

TABLE 3. OXIDE COMPOSITIONS OF SERPENTINE SPECIMEN FROM EDEN MILLS CONSISTING
OF A LAYER OF 3 INCHES OF MATRIX BETWEEN TWO VEINS OF FIBERS
CUT INTO LAYERS .6 INCH THICK

	Fiber	M-1	M-2	M-3	M-4	M-5	Fiber
SiO_2	38.38	36.78	37.96	40.56	40.42	36.88	39.96
Al_2O_3	0.44	1.67	1.47	1.53	0.34	1.48	.64
Fe_2O_3	6.19	6.01	3.83	3.50	1.81	5.87	4.30
FeO	1.30	1.81	2.09	2.78	2.42	1.69	1.30
MgO	39.90	39.75	41.90	43.10	43.90	39.80	41.00
Loss (1100° C.)	13.26	13.26	11.94	8.81	10.21	13.69	12.88
SO_3	0.14	0.14	0.10	0.12	0.11	0.10	0.10
TiO_2	0.03	0.05	0.02	0.02	0.02	0.03	0.072
CO_2	—	—	0.19	0.18	0.18	0.14	0.00
Cr_2O_3	0.11	0.31	0.25	0.26	0.24	0.33	0.12
CaO	—	—	0.03	0.03	0.04	0.03	0.04
MnO	0.08	0.09	0.12	0.15	0.13	0.10	0.08
NiO	0.10	0.22	0.18	0.13	0.12	0.10	0.06
Na_2O	0.02	0.03	0.03	0.04	0.02	0.04	0.02
K_2O	—	—	0.04	0.03	0.03	0.03	0.02
Loss (110° C.)	0.28	0.21	—	—	—	—	.38[a]
Total, %	100.23	100.33	100.15	100.26	99.99	100.31	100.97

[a] Loss at 150° C.

following conventional methods gave unsatisfactory results. Application of the method of McConnell (11) which is based on the assumption that a portion of the water, designated as tetrahedral water, is substituted for the silica $((H^+)_4$ for $Si^{4+})$ similarly as in the hydrogarnets, gave some striking results. The data are given in Table 4. In these computations, it is assumed that the silica layer is completely filled, there being 2.000 moles of the cations. Since the analytical results did not give the indicated total, the deficiency was made up by assuming that the excess water, as indicated in the calculations, was substituted in the silica layer. Any further deficiency from the required value of 2.000 was subtracted from the sum of the cations in the brucite layer without regard to kind.

The computed results in Table 4 show that tetrahedral water is the only substituent for Si^{4+} in the silica layer of chrysotile, the total of cations being very close to a value of 2.000. The calculations of the antigorite formula indicate, on the other hand, that a small but apparently real amount of substituents other than the water are present in the silica layer of this mineral.

After the deductions were made, the brucite layer of both minerals

TABLE 4. ION DISTRIBUTIONS IN OCTAHEDRAL AND TETRAHEDRAL POSITIONS IN ANTIGO-
RITE AND CHRYSOTILE CALCULATED BY THE METHOD OF DUNCAN MCCONNELL (11)

Ion	Delaware Co., Pa.		Aboutville, N. Y.		Quebec #18879		Montville, N. J.	
	Matrix	Fiber	Matrix	Fiber	Matrix	Fiber	Matrix	Fiber
Mg^{2+}	2.924	2.937	2.922	2.937	2.915	2.935	2.873	2.820
Fe^{3+}	.017	.017	.032	.024	.012	.010	.052	.021
Fe^{2+}	.002	.003	.003	.001	.003	.002	.002	.001
Al^{3+}	.040	.017	.007	.006	.031	.012	.027	.013
$R \pm R^{4+}$[a]	.009	.007	.026	.016	.027	.017	.034	.064
	2.992	2.981	2.990	2.984	2.988	2.976	2.989	2.919
Tetrah. Reg.[b]	.012	.001	.013	.000	.004	.000	.008	.001
Octah. Total	2.980	2.980	2.977	2.984	2.984	2.976	2.981	2.918
Si^{4+}	1.950	1.961	1.921	1.921	1.900	1.915	1.940	1.914
$(H^+)_4$	.038	.038	.066	.079	.096	.085	.052	.085
Debit[c]	.012	.001	.013	.000	.004	.000	.008	.001
Tetrah. Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

[a] Summation of all ions other than those listed in the table.

[b] The amounts of ions required for completing the silica layer are subtracted from the total amount assumed to occupy the octahedral position.

[c] Amount of ion required to fill all tetrahedral positions.

showed a balance very close to a value of 2.980 except for the Montville fiber, this being 2.919. Some uncertainty regarding the computed result occurs because of the relatively large amounts of CaO (0.47%) and SO_3 (0.31%), the SO_3 was not counted in either the fiber or matrix computations. Because of the uncertainty regarding the manner in which the CaO and SO_3 are combined, the computed results on the fiber of the Montville serpentine cannot be interpreted rigorously.

2. X-ray Data

The x-ray data of five fiber-matrix pairs are given in Table 5. Each result represents the average value of 2 to 5 measurements. A distinguishing feature of these data is a generally richer and sharper pattern for the matrix compared to that of the fiber. Also small spacing differences in the 4.3 to 4.8 Å region are evident in the results of the matrix samples.

A specific feature of the data generally serving to differentiate between the chrysotile and matrix is the ratio of the intensities of the line at 7.3

TABLE 5. X-RAY DIFFRACTION DATA FOR FIBROUS AND MATRIX COMPONENTS OF SERPENTINE FROM DIFFERENT LOCALITIES. EACH PATTERN IS THE AVERAGE OF 2 TO 5 MEASUREMENTS OBTAINED ON FILM OR WITH GEIGER-COUNTER RECORDER

Delaware, Pa.				Aboutville, N.Y.				Globe, Ariz.				(N.M. 18879) Quebec, Canada				Montville, N. J.			
Fiber		Matrix		Fiber		Matrix		Fiber		Matrix[a]		Fiber		Matrix		Fiber		Matrix	
I/103[b]	d, Å	I/77	d, Å	I/36	d, Å	I/80	d, Å	I/35	d, Å	I/45	d, Å	I/108	d, Å	I/125	d, Å	I/138	d, Å	I/158	d, Å
				.15	13.4			.1	11.3							.01	11.1	.08	11.1
		.05	8.1	.15	10.2			.1	8.7										
1.0	7.37	1.0	7.32	.06	7.8			1.00	7.31	1.00	7.31	.91	7.34	1.00	7.35	1.0	7.11	1.0	7.25
				1.0	7.28	1.0	7.28												
vw[c]	6.6	vvw	6.8	.08	6.8			.1	6.6							.04	5.8		
vw	5.75																		
								.1	4.77										
.15	4.53	.25	4.58	.10	4.51	.2	4.60	.15	4.53	.13	4.53	.15	4.60	.25	4.63	.04	4.55	.15	4.55
		.14	4.53	.11	4.45	.2	4.52					.10	4.48	.10	4.52				
.15	4.47			.10	4.37	.1	4.42	.2	4.41			.15	4.45	.05	4.48	.13	4.37		
.15	4.44			.05	4.29	.05	4.31					.15	4.43						
								.1	3.95										
1.0	3.66	.66	3.64	.88	3.64	.69	3.65	.85	3.63	.67	3.66	.89	3.66	.73	3.63	.92	3.63	.59	3.63
								.05	3.20										
								.1	3.02										
								vvw	2.88										
vw	2.93																		
				.05	2.58	.01	2.63							.05	2.66	.07	2.61	.28	2.50
w	2.45	.35	2.46	.10	2.42	.10	2.54	ms	2.42			.07	2.44	.40	2.51	.10	2.42	.03	2.43
				.05	2.37	.25	2.50							.05	2.62				
						.20	2.46												
		.1	2.15			.08	2.16							.10	2.16			.12	2.14
w	1.84	.05	1.85	.05	1.82	.06	1.83	m	1.82			.03	1.83	.05	1.80	.06	1.82	.05	1.86
																.03	1.77		
m	1.54	.2	1.54	.10	1.53			ms	1.52					.05	1.55	.13	1.53	.15	1.58
vw	1.46	.1	1.50	.05	1.46			m	1.46					.25	1.54			.08	1.57
		w	1.31	.05	1.31													.06	1.34
vw	1.22							mw	1.22									.04	1.31

[a] Pattern not completely reported because of large amount of impurity

[b] Intensities are given as the ratio of each line to the strongest line, which is designated in counts per second.

[c] The abbreviations: w—weak, m—medium, s—strong, and v—very, apply to the comparative intensities of lines in film recording.

Å to that at 3.6 Å, referred to as the $I_{7.3}/I_{3.6}$ ratio. In Fig. 1 these ratios are plotted against the total number of moles of Al^{3+}, Fe^{3+} and Fe^{2+} for seven fiber-matrix pairs. The values for each pair are connected by a line. The values of the ratios ranged from about 1.0 to 1.2 for the fibers and about 1.3 to 1.8 for the matrix specimens. Four other fiber-matrix
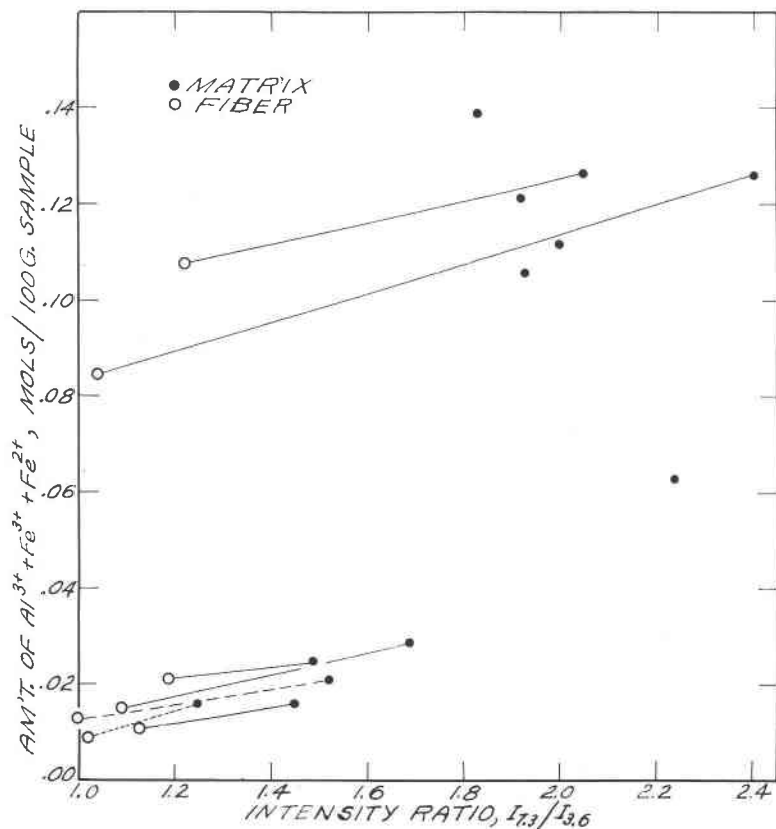

Fig. 1. Plot of the total Al^{3+}, Fe^{3+} and Fe^{2+} contents of serpentine samples and the ratios of the intensities of lines at 7.3 Å and 3.6 Å ($I_{7.3}/I_{3.6}$).

pairs of other serpentines, which were not analyzed, were also observed to manifest a similar variation in the $I_{7.3}/I_{3.6}$ ratios. The values for all specimens ranged from 0.80 to 1.40 for the fibers and 1.27 to 2.40 for the matrix. Because of the overlapping of the values for the fiber and matrix in the range between about 1.27 and 1.40, these values alone are not suitable for differentiating between fibers and matrix. However, in every

sample of serpentine examined, the value of the $I_{7.3}/I_{3.6}$ ratio was invariably higher for the matrix than for the fiber.

3. Specific Volume

The specific volume values for the three fiber-matrix pairs containing the lowest amounts of impurities were consistent and the average value of 15 determinations on the fibers was 0.392, and average of six values on the matrix was 0.398. It appeared worthwhile to compare these values with those calculated from the unit cell on a product of ideal composition, $3MgO \cdot 2SiO_2 \cdot 2H_2O$, and the values so calculated are given in Table 6.

TABLE 6. TABULATION OF UNIT CELL SIZES, IN Kx UNITS, BY WHITTAKER (12) AND COMPUTED DENSITY FUNCTIONS OF CHRYSOTILE AND ANTIGORITE

(In these calculations, 1 Å = 1.00202 Kx)

Parameter or function	Warren & Bragg chrysotile	Warren & Hering chrysotile	Aruja chrysotile	Padurow chrysotile	Whittaker chrysotile	Aruja antigorite
a_0	14.66	7.33	14.62	7.36	14.65	7.265
b_0	18.50	9.24	9.2	9.26	9.2	9.238
c_0	5.33	5.33	5.32	5.33	5.33	5.42[a]
α	90°	90°	90°	92°50′	90°	90°
β	93°16′	93°16′	93°12′	93°11′	93°7′	91°24′
γ	90°	90°	90°	89°50′	90°	90°
Calculated Density[b]	2.533	2.535	2.558	2.522	2.548	2.513
Specific Volume	0.3948	0.3945	0.3909	0.3965	0.3925	0.3979
Ratio Specific Volumes Matrix: Fiber	1.008	1.009	1.018	1.004	1.014	(Unity)

[a] The eight-fold multiplication along the c axis gives a value of $c_0 = 43.39$.

[b] Calculations were performed using Avagadros number, $N = 6.06 \times 10^{-23}$ so that direct comparison with Aruja's original results may be made.

The results of 0.394 and 0.398 for chrysotile and matrix (antigorite) are in good agreement with the experimentally determined values. Results of 0.381 and 0.378 for the specific volume of the fiber and matrix, respectively, of the Eden Mills, Vermont, serpentine are lower than those given because of the higher amounts of iron present in this sample.

The results obtained with water and CCl_4 showed good agreement, within 1.0 per cent, for the fibers only. The matrix specimens gave consistently higher values in CCl_4, by 3.00 ± 0.75 per cent, than in water. The only apparent explanation which can be made is that all voids in

fibers and matrix were filled with water, but not all with CCl_4 in the matrix.

The apparent specific volumes of three massive chrysotile specimens are given in Table 7. The Eden Mills fibers contained only 1.0 per cent voids compared to 12.5 per cent for the Globe fibers. One may safely assume that the Eden Mills fiber with so low an amount of voids could not occur as tubular fibers or even solid round rods (the void volume for rods of uniform diameter in closest possible packing amounts to 9.3 per cent). On the other hand, the entire Globe specimen, and a portion of the Delaware specimen could occur as small bore capillaries. Pundsack (13)

TABLE 7. APPARENT AND ABSOLUTE SPECIFIC VOLUMES OF SPECIMENS OF SERPENTINE CONSISTING OF THICK LAYERS OF FIBERS BETWEEN THIN LAYERS OF MATRIX, AND AMOUNTS OF VOIDS IN THE FIBERS

Specimen	Specific volume		Amount fibers % by vol.	Voids by % of app. vol.
	Apparent, cc./g.	Absolute, cc./g.		
Eden Mills	.386	.383	77	1.0
Delaware County	.422	.394	80	8.2
Globe, Ariz.	.440	.394	84	12.5

who used a different technique in preparation of the test specimens than described here for void-volume measurements observed voids amounting to only few per cent of total volume.

4. *Loss on Heating*

Representative loss-on-heating curves are presented for two samples of fiber-matrix components of serpentine in Fig. 2. The losses are referred to a constant weight obtained on drying at 135° C. Two other specimens of fiber and matrix (Globe, Arizona and commercial grade of Quebec chrysotile) showed curves intermediate between the respective ones shown in Fig. 2.

The two matrix specimens manifested a small continuous loss up to about 450° C. and this was followed by a large loss in the temperature interval from 450° to about 550° C. These specimens also showed a second but comparatively small inflection between approximately 550° and 600° C. This suggests that a portion of the water was held somewhat more strongly than that given off at the lower temperature. Such a two-step dehydration was not observed for the fiber. In comparing further the curves of the fiber to those of the matrix, it is seen that the fibers in

both pairs of specimens lost the water at higher temperatures than did the matrix specimens. It follows, therefore, that the major amount of water is more tightly bound in the chrysotile component than in the matrix.

The loss-on-heating curves indicate a small but apparently real difference in the binding strength of water in the fiber and matrix.
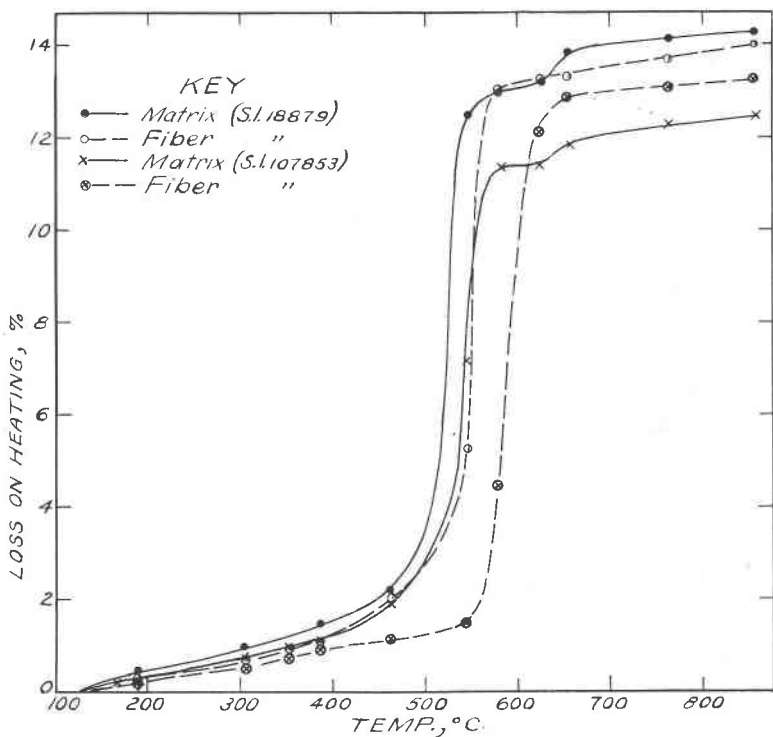

FIG. 2. Loss on heating curves.

5. Differential Thermal Analysis

The DTA results on six pairs of serpentine specimens did not show any definite trends which could serve to differentiate between fiber and matrix. The principal thermal effects, accompanying the dehydration of the brucite water, and the subsequent exothermic peak, varied about equally among the samples with no relation to sample origin. In general, the temperature interval between completion of dehydration of the brucite water and the start of the exothermic reaction was slightly larger for the fiber than for the matrix. However, due to the uncertainties of definitely measuring this difference, reproduction of the DTA results does not appear to be justified.

6. Thermal-Balance Analysis

In view of the loss-on-heating results, and the possible difference in the temperature gap, just mentioned, between the fibers and matrix, it seemed desirable to obtain further information on the dehydration of the serpentine pairs in the form of thermal-balance curves. The thermal-balance gives the loss in weight, in a continuously recorded curve, as a function of temperature. The tests were performed on three serpentine pairs at the Bureau of Reclamation, Denver, Colorado, under direction of Dr. R. C. Mielenz. The samples were heated at a temperature-rise rate of 5° C. per minute.

The result of most interest is the amount of water lost at high temperatures. The thermograms were examined for inflections in regions of high temperatures, and the temperature at which the "high-temperature" water started to be driven off was taken at the point where the tangent to the curve first begins a negative (clockwise) rotation. These points generally were not easily located but may be considered to represent fairly closely the temperature at which the liberation of the high-temperature water started. The results are summarized in Table 8 along with the identification of the specimens. The temperatures at which the high-temperature water started to come off were approximately the same for the two components of each serpentine sample, but varied among the serpentines. Dehydration was complete at about 900 to 940° C. The amounts of the high-temperature water ranged from 0.60 to 0.93 per cent by weight of the sample exposed to laboratory air.

The curves for the Quebec serpentine (National Museum 18879) are presented in Fig. 3 in terms of percentage loss in weight in order that

TABLE 8. SUMMARY OF THERMAL BALANCE RESULTS ON SERPENTINE SAMPLES

Sample	Loss on ignition %[a]	Temp. range of "high-temp. water" ° C.	Amount "high-temp. water" %[a]	Calc. amt. of $(H^+)_4$ in mols, (Table 4)
Quebec Matrix N.M. 18,879	14.59	745–1000	.93	.096
Quebec Fibers N.M. 18,879	14.80	763–1000	.74	.085
Delaware Co., Pa. Matrix	13.33	816–1000	.67	.038
Delaware Co., Pa. Fibers	13.58	811–1000	.76	.038
Eden Mills, Matrix	12.77	788–1000	.71	
Eden Mills, Fibers	12.17	796–1000	.60	

[a] The amount of water, in per cent, is based on the weight of the sample in equilibrium with air in the laboratory.

direct comparison to the loss-on-heating curves could be made. These curves, and those of the remaining samples, failed to show a second step dehydration as did two of those shown in Fig. 2 in static loss-on-heating tests. Apparently the rate of heating affects the manner in which the high-temperature water is lost.
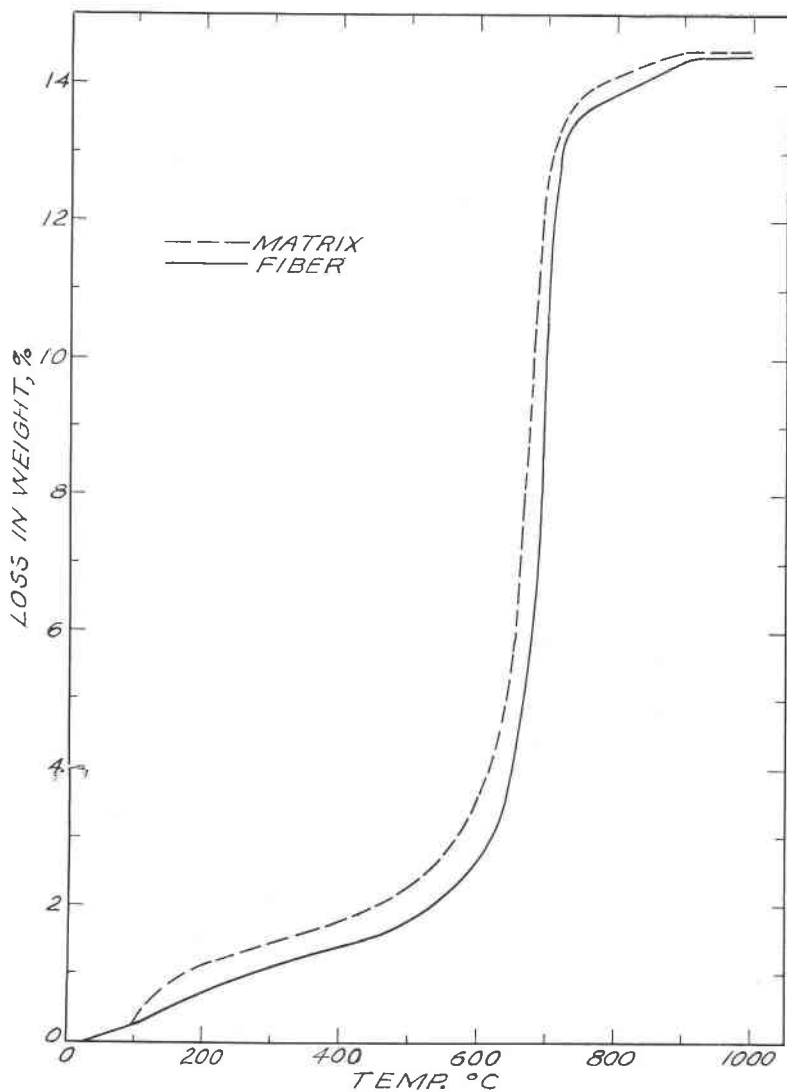

FIG. 3. Thermal-balance results on serpentine (Quebec, N.M. 18879), the loss being expressed in percentage.

The amount of high-temperature water can be determined only approximately because the temperature at which this water starts to be given off probably coincides with that at which loss of the other is still occurring. The possibility that the high-temperature water and tetrahedral water are the same, as suggested by computations based on McConnell's methods would seem to merit further study. Quantitative substantiation of the hypothesis based on the observed and calculated amounts of high-temperature water is not indicated by the present data. This is not surprising because of possible variations in amounts of surface adsorbed water at time of testing the samples, and the possible simultaneous loss of high-temperature water and the principal water of hydration. Nevertheless, there can be little doubt, if any, that the dehydration takes place in two stages and there is a qualitative relationship as indicated by a comparison of the last two columns of Table 8 which suggests the presence of tetrahedral water in the serpentines.

7. *Electron Microscopy*

The pairs of serpentine from Eden Mills, Delaware County, Quebec (N.M. 18879), the Globe fibers and Yu Yen Stone were examined with the electron microscope. The examinations confirmed the previously observed (1, 2, 3, 4, 5, 6) tubular crystalline habit with exception of certain variations in the Eden Mills fibers to be described.

The Yu Yen Stone, microscopically of a clearly platy crystalline habit, was examined after prolonged grinding. The crystals in massive form and in fragments manifested the usual laminar habit. However, crystals having appearance of tubes or curved laths were abundantly present in the lighter fraction of the suspended sample. The electron micrograph in Fig. 4 illustrates the morphology of this mineral. The Eden Mills matrix contained a high proportion of fibrous crystals which at highest magnification appeared like partially curved laths. The fibers also contained some crystals manifesting a trough-like appearance. The required higher resolution for study of this detail was realized by Joseph G. Sayre on the electron microscope at Owens-Corning Glass Company, who examined this specimen and the Globe and Delaware County chrysotile.

The examination of the Globe and Delaware County specimens revealed presence of capillaries of apparently small bore as illustrated in Fig. 5. The specific volumes of massive specimens of these two minerals suggested presence of voids which could be those between fibers and the pores.

In Fig. 6 is shown a fiber, between two others, of the Eden Mills chrysotile which is considered to manifest a cross section similar to a trough. Curvature apparently occurred simultaneously from both edges
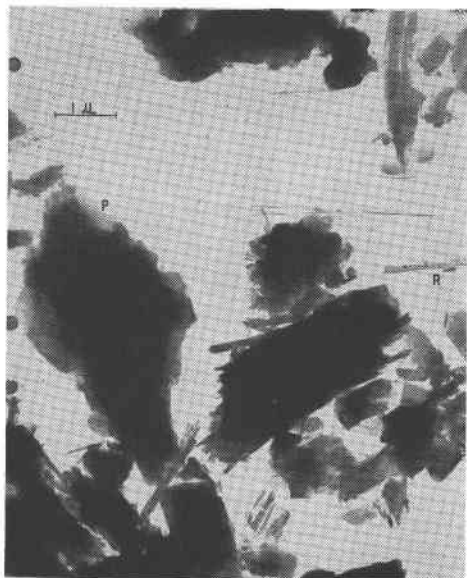
FIG. 4. Electron micrograph of finely powdered Yu Yen Stone (*P*=plate and *R*=rolled plate or lath).
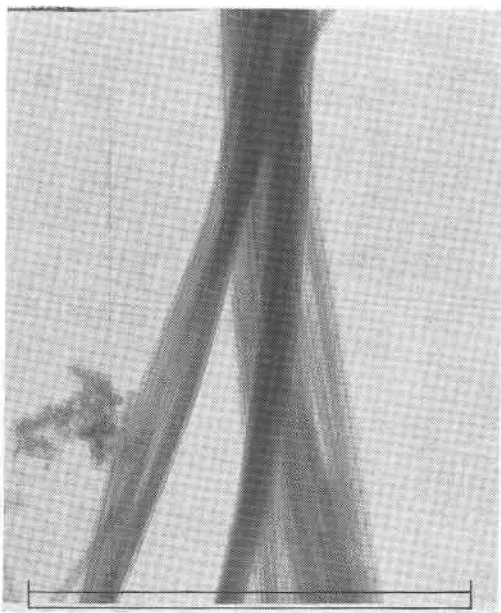

FIG. 5. Electron micrograph of tube-like fibers of Globe, Ariz., chrysotile.

of a lath but was arrested. If curling of a lath from two edges occurs the individual crystals for completely rolled crystal should consist of two tubes. Figure 7 includes some of the assumed double tube fibers which had been twisted. The immediate area of the twisted fiber is reduced in size and the photographic image is darker. The observed effect could be due to the presence of a double tube fiber rolled from the edges of a single crystal. Figure 6 also contains possibly a shred of a single fundamental layer which is apparent in the form of a twisted ribbon-like fiber in the upper part of the figure and extends from the first to the third fibers.

In the bottom of Fig. 8 are seen six fibers which further illustrate the apparent double tube morphology of the Eden Mills chrysotile. The first three fibers from the left are smaller in diameter and also of reduced photographic intensity compared to the next two. Judging by the increased size and darkness of the image, it may be that the latter two fibers consist of two elemental crystal sheets. The sixth fiber appears also to consist of two layers, one of the single layers on the left being incompletely curled.

A total of 209 measurements were made of the fiber diameters of both chrysotile and matrix using micrographs at $50,000\times$ magnification. Statistical treatment of the data, through size distribution frequencies, indicate that two (or perhaps even three) sizes obtained for the fibers as shown in Fig. 9. The lower distribution mode of fiber diameters for both the chrysotile and matrix, centered at about 340 Å, represents the range in apparent fiber diameter. The upper mode, centered at about 650 Å, is possibly a function of "fibril" size distribution. The presence of two functions may indicate, as already deduced, that the fibers were double tubes or formed from sequential layers. The previously reported fiber diameters (3, 14) fall only somewhat below the most probable size of 340 Å shown in Fig. 9. The fiber size probably is dependent, at least in degree, on the specimen origin. The data of this study indicate an upper value of about 400 to 500 Å and a lower value of about 100 Å for diameters of single fibers.

IV. INTERPRETATIONS

Results of oxide compositions and structural formulas computed by the McConnell method suggest that small but real differences exist between chrysotile and matrix of a given serpentine. The matrix may contain a higher concentration of extraneous ions in the brucite layer and possibly also a small amount in the silica layer. The chrysotile on the other hand may contain only $(H^+)_4$ as a subsituent for the Si^{4+} ion, no other substitution occurring in the silica layer. The computations and results of experiments on water content indicate that the amount of the high-temperature
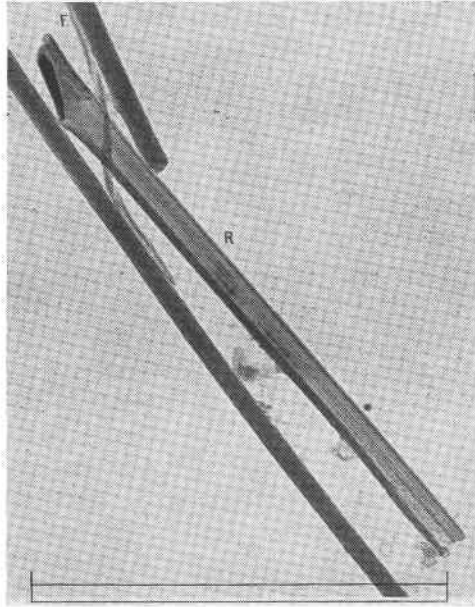
FIG. 6. Electron micrograph of Eden Mills chrysotile showing a partially rolled lath (*R*) and fragment of single layer (*F*).
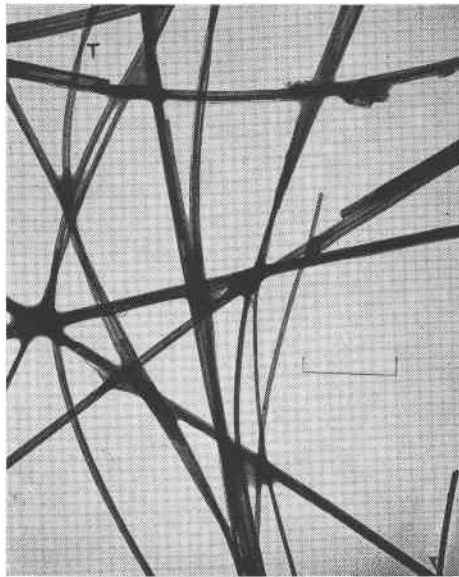

FIG. 7. Electron micrograph of Eden Mills chrysotile showing apparent double tube crystals, some being twisted (*T*).

(supposedly tetrahedral) water are about the same for both matrix and fibers of a given serpentine, and therefore would not be expected to affect the morphology.

The small differences in the amounts of Al^{3+} (and Fe^{3+}, Fe^{2+}, etc.) ions apparently correlate with crystal habit. These results substantiate at least qualitatively, the hypothesis by Bates and Mink (7) that the Al^{3+} ions stabilize the laminar structure of the matrix. Roy and Roy (9)
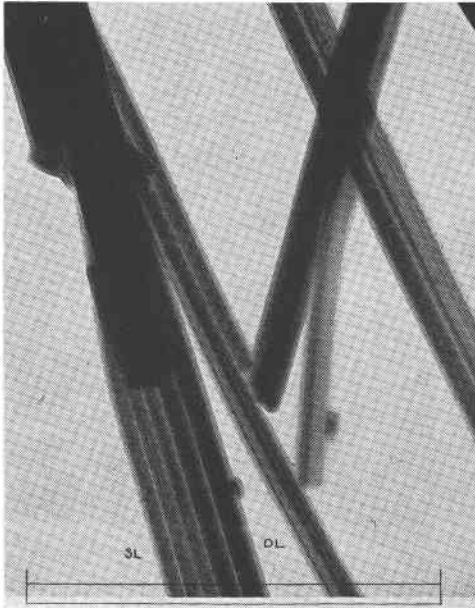

Fig. 8. Electron micrograph of six fibers, three of single layer rolls (*S.L.*), two of double layer rolls (*D.L.*) and one of double layer in which one layer is incompletely rolled.

advanced the hypothesis that the R_2O_3 content of natural antigorite (matrix) should be higher than that of the chrysotile. The present results confirm that theory. In this connection, the results on the Eden Mills chrysotile which probably contained more structurally bound Al^{3+} and other ions than the other serpentines studied, are interesting because of the general tendency of this chrysotile to occur in laminar crystals.

The measurements in this study and by Pundsack (13) on the specific volume of massive chrysotile fiber revealed generally a porosity far too low compared to that required for a massive specimen consisting of tubular crystals. It would follow that chrysotile could occur largely in the form of lath or sheet crystals in native form. If such laths or sheets

contain internal strains due to misfit between layers, curling of the sheets into laths or tubes should occur. The present studies suggest that such a mechanism may apply to the formation of chrysotile in tubular crystals, but the evidence does not preclude the occurrence of tubular crystals in massive chrysotile (Globe, Ariz., in present studies). It may be speculated that the "fibers" in the matrix could also originate during grinding. More detailed study, however, of the matrix in both massive and subdivided form will be required before any conclusion may be drawn.
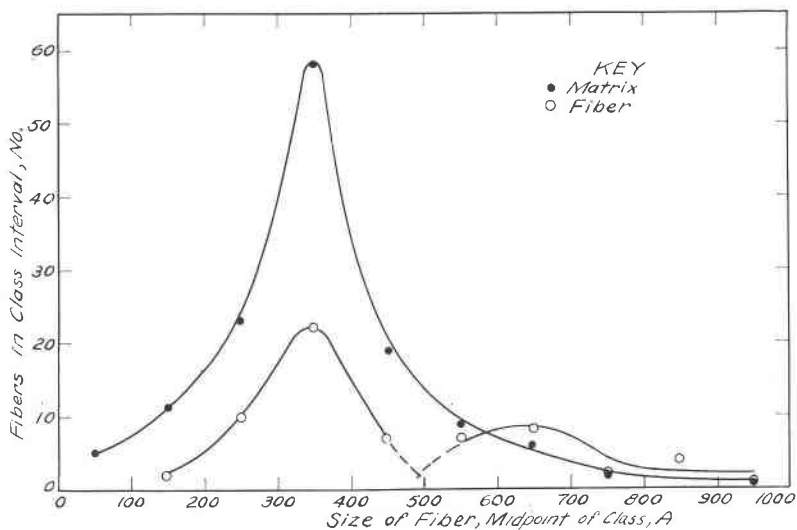

FIG. 9. Frequency distribution of sizes of fibers in seven serpentine samples.

SUMMARY

1. Results of chemical analysis showed that, for each serpentine examined, the fibers contained less Al_2O_3 and generally also less Fe_2O_3 and FeO than did the matrix.

2. Computations of structural formulas by the method of Duncan McConnell indicates that the silica layer of the fiber contains only tetrahedral water as a substitutent, but that of the matrix also contains a small amount of other ions in addition to the tetrahedral water.

3. X-ray patterns of the matrix were richer and sharper than those of the fiber. An outstanding feature of the x-ray data was the ratio of the intensities of the line at 7.3 Å to that at 3.6 Å ($I_{7.3}/I_{3.6}$ ratio), which ranged in value from about 0.8 to 1.4 for the fibers and 1.3 to 2.4 for the

matrix. In the 4.5 to 4.6 Å range of the pattern, the matrix generally showed longer spacings than did the fibers.

4. The values of the $I_{7.3}/I_{3.6}$ ratio were found to increase with increasing total contents of Al_2O_3, Fe_2O_3, and FeO, the matrix being richer in these constituents for a given serpentine composite of fibers and matrix. Although these differences appear real, no rigouous interpretation of the data could be made.

5. The specific volumes of the purest fibers and matrix specimens agreed closely with the values calculated from the published unit cell size.

6. Thermal balance and static-loss-on-heating results indicated that a small amount of the total water is liberated at temperatures higher than those required for dehydrating the brucite layer.

7. Electron microscope views showed that the matrix specimens contained varying amounts of "fibers" apparently ranging in shape from flat laths to complete tubes. Statistical analysis of 209 measurements of fiber sizes in enlarged photomicrographs indicated that the most probable fiber diameter (or cross section) for both the matrix and fiber components was 340 Å.

8. Specific volume measurements on three massive samples of chrysotile indicated porosities of 1.0, 8.5, and 12.5 per cent. The sample of low-porosities could not contain fibers in the form of capillaries, but because the sample after grinding contained tube-like crystals it may be assumed that these were formed by spontaneous rolling of the laths into tubes during the grinding.

ACKNOWLEDGMENTS

REFERENCES

1. TURKEVICH, J., AND HILLIER, J., *Analytical Chemistry*, **21**, 475 (1949).
2. BATES, T. F., SAND, L. B., AND MINK, J. F., *Science*, **111**, 512–513 (1950).
3. NOLL, W., AND KIRCHER, H., *Naturweiss*, **10**, 233–234 (1952).
4. BATES, T. F., *Denison University Bulletin*, **51**, 83–92 (1951).
5. YODER, H. S., *Am. Jour. Sci.* (Bowen Vol.), 569–627 (1952).
6. ILER, RALPH K., Colloid Chemistry of Silica and Silicates, p. 209 (1955), Cornell University Press.

7. BATES, T. F., AND MINK, J. F., *Am. Mineral.*, **36**, 310–311 (1951).
8. PAULING, LINUS, *Proc. National Academy of Science*, **16**, 578–582 (1930).
9. ROY, D. M., AND ROY, R., *Am. Mineral.*, **39**, 957–975 (1954).
10. KALOUSEK, G. L., DAVIS, C. W., JR., AND SCHMERTZ, W. E., *Jour. Am. Concrete Institute, June 1949, Proc.*, **45**, 693.
11. McCONNELL, DUNCAN, *Clay Minerals Bulletin*, **1**, 178–188 (1951). See also: *Am. Mineral.* **39**, 830–831 (1954).
12. WHITTAKER, E. J. W., *Acta Crystallographica*, **5**, 143 (1952).
13. PUNDSACK, F. L., *Jour. Physical Chemistry*, **59**, 892–895 (1955), and **60**, 361–364 (1956).
14. FANKUCHEN, I., AND SCHNEIDER, M., *Jour. Am. Chemical Society*, **66**, 500 (1944).