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SERPENTINES: NATURAL MIXTURES OF CHRYSOTILE AND ANTIGORITE¹

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ABSTRACT

Chemical, physical, and mineralogical investigations show that the serpentine group of minerals are natural mixtures of various proportions of the two "end-members," chrysotile and antigorite. Mineral species names other than chrysotile and antigorite or their polymorphs, are not justified and should be abandoned. It is suggested that serpentines other than the two "end-members" should be defined in terms of their percentage chrysotile-antigorite content. An *x*-ray diffraction method providing semiquantitative estimates of the chrysotile-antigorite content of the serpentine minerals is described.

INTRODUCTION

The serpentine group of minerals are hydrous magnesium silicates having the general formula $Mg_6Si_4O_{10}(OH)_8$ and entering into a rather wide range of substitutional solid solutions involving other divalent cations. These relationships are now known to be further complicated by polymorphism. For the interpretation of the chemical analyses of the serpentine samples it may be permissible to assume certain hypothetical end-members:

The chrysotile group

$Mg_6Si_4O_{10}(OH)_8$ chrysotile
 $Fe_6Si_4O_{10}(OH)_8$ ferro chrysotile
 $Ni_6Si_4O_{10}(OH)_8$ nickel chrysotile
 $Mn_6Si_4O_{10}(OH)_8$ manganese chrysotile

The antigorite group

$Mg_6Si_4O_{10}(OH)_8$ antigorite
 $Fe_6Si_4O_{10}(OH)_8$ ferro antigorite
 $Ni_6Si_4O_{10}(OH)_8$ nickel antigorite
 $Mn_6Si_4O_{10}(OH)_8$ manganese antigorite

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Chemical analyses of minerals of the serpentine group show that, in addition to the ions considered in the above end-members, the following can be present: Al^{+++} , Fe^{+++} , Cr^{+++} and possibly Ca^{++} , Ti^{++++} , Co^{++} , Cu^{++} and Na^+ . It is not known in what state of association some of these ions are in the serpentine minerals or whether they (or some of them) are only components of impurities intimately mixed with the fine-grained serpentine minerals. These end-members are not proposed as new mineral names as it is recognized that some of the names have already been applied to specific minerals.

This paper is confined almost entirely to the study of the magnesium rich end-members, chrysotile and antigorite, which, following traditional usage, we will refer to collectively as serpentine.

X-ray diffraction, electron microscopical studies, differential thermal analysis, and optical investigations made on a large number of serpentine samples have shown that serpentine is composed of the two "end-members," chrysotile and antigorite. The antigorite content of the chrysotile-antigorite mixtures, as shown in this paper, was estimated by an x-ray diffraction method. Additional data relating to the natural mixtures is being prepared for presentation at a later date.

REVIEW OF PREVIOUS STUDIES ON SERPENTINE

Mineralogical and crystallographical studies

The crystal structure of the serpentines is very similar to that of kaolinite. Recent investigations have proved beyond much doubt that the structural scheme presented by Warren and Bragg (1930) is not correct. Warren and Hering (1941) found that chrysotile has a layer-structure which is composed of the same units as the kaolinite structure with the exception that in the octahedral layer two aluminum ions are replaced by three magnesium ions. Whittaker (1951, 1952, 1953) differentiated two varieties of chrysotile, both identical in structure type but different in the stacking of unit layers and, accordingly, in symmetry. Whittaker has named the two varieties ortho-chrysotile and clino-chrysotile. The crystal structure of antigorite was first determined by Aruja (1945) who suggested that the antigorite structure is essentially a magnesium analogue of the kaolinite type structure and thus is very similar to chrysotile. Ito (1950) concluded that antigorite has a kaolinite-like structure, and Midgley (1951) has also proposed still another monoclinic structure. Brindley and von Knorring (1954) found an orthorhombic variety of antigorite and named it ortho-antigorite. These studies suggest that analogous to chrysotile there may also be several different polymorphous forms of antigorite. The detailed x-ray studies on the

polymorph of chrysotile and antigorite by Whittaker and Zussman appeared while this paper was in press.

In spite of the great similarity between the crystal structures of the two minerals the morphologies of chrysotile and antigorite are markedly different. Chrysotile is fibrous and antigorite is flaky. Turkevich and Hillier (1949) observed with the electron microscope that chrysotile fibers are hollow tubes. As early as 1930 Pauling predicted that a serpentine layer-structure would tend to curve; he wrote:

"The non-existence of a magnesium analogue of kaolinite is accounted for by the large values of the fundamental translations in the brucite layer (with $a=5.40 \text{ \AA}$), which would cause the kaolinite-type layer to curve."

According to this concept, tubular chrysotile fibers are built up of curved kaolinite-type sheets. Noll and Kircher (1950, 1951) made electron micrographs of chrysotile fibers sliced perpendicular to the fiber axes; the photographs showed a few ring-like objects. Jagodzinski and others (1953, 1954) made further studies on the tubular structure of chrysotile, relating it to the crystal structure. Bates and Mink (1950) suggested that the flaky habit of antigorite might be caused by the replacement of some of the magnesium ions in the octahedral sheet by trivalent cations, chiefly Al^{+++} and Fe^{+++} , resulting in a decrease of the strain that is believed to be responsible for the curvature of the kaolinite-type layers of chrysotile. It is difficult to prove that such a relationship exists, although most of the chemical analyses available indicate that antigorite samples have a higher Al_2O_3 content than the chrysotiles.

Selfridge (1936) has shown that the various textures of the serpentines indicate only different modes of formation and that on the basis of x -ray diffraction and optical evidence the many varieties could be reduced to two species, antigorite and chrysotile.

In 1951 B. Nagy and T. F. Bates conferred with G. T. Faust on the work that the latter was doing on the serpentine group of minerals. Faust had found by optical, differential thermal analysis, and other studies that a number of specimens he studied were natural mixtures of antigorite and chrysotile. Nagy and Bates (1952) made independently a detailed study of this part of the problem and obtained quantitative data which led them to propose that serpentines other than chrysotile and antigorite are natural mixtures of these two minerals.

Chemical-geological studies

Hydrothermal studies have contributed to the understanding of the genesis of serpentine. The first recorded attempt to synthesize the serpentine group of minerals was made by Ipatieff and Mouromtseff as early

as 1927. Van Nieuwenburg and Blumendal (1930) reported a synthetic product which appeared to be serpentine. Jander and Wuhrer (1938) and Jander and Fett (1939) obtained serpentine and talc from a "charge" containing MgO , SiO_2 and H_2O and Strese and Hofmann (1941) attempted to synthesize serpentines, especially antigorite, by adding alkali salts to the starting mixture. None of these early studies resulted in definite evidence as to the exact nature of the synthetic products.

Noll (1944) was the first to study the products of the hydrothermal synthesis experiments under the electron microscope and observed fibers that were approximately 1μ long and had diameters ranging from 0.01μ to 0.03μ . Introduction of KOH to the system resulted in a flaky substance; the properties of both the flaky and fibrous materials appeared to resemble chrysotile. Epprecht (1947) performed further experiments related to the synthesis of the serpentine minerals and suggested that the addition of KOH may aid the development of antigorite. Balduzzi, Epprecht, and Niggli (1951) made attempts to lengthen synthetic chrysotile fibers. They reported some success but were unable to produce synthetic fibers of economic quality.

The study of Bowen and Tuttle (1949) represents a major contribution to the understanding of the genesis of the serpentines. These authors determined the phase equilibrium relationships in the system $MgO-SiO_2-H_2O$ and found that chrysotile is a stable phase below $500 \pm 10^\circ C.$ and at pressures ranging between 2000 and 40,000 psi, but they were unable to synthesize antigorite. The results of recent hydrothermal studies have shown that chrysotile can be readily synthesized but not antigorite. The work of Yoder (1952), with the system $MgO-Al_2O_3-SiO_2-H_2O$, seems to be significant in respect to the synthesis of antigorite. He found that a flaky "aluminous" serpentine crystallizes out below $520^\circ C.$ and water vapor pressures ranging from 2,000 to 30,000 psi. The properties of this flaky serpentine are somewhat different from those of natural antigorite.

The lack of specific information as to the formation of antigorite is unfortunate because this mineral is most commonly the main constituent of natural serpentine deposits. Study of field deposits and field relationships may help to solve the problem of the formation of antigorite. Sobolev (1945) noted that chrysotile may recrystallize into antigorite. Hess, Smith, and Dengo (1952) described antigorite from Venezuela which was derived from chrysotile under dynamothermal metamorphism. Nagy (1953) suggested that the recrystallization of chrysotile into antigorite may be more common than generally thought. He further suggested that the natural mixtures of chrysotile and antigorite might have developed by the following processes: (1) in the presence of

available Al^{+++} and Fe^{+++} ions the crystallization of antigorite was followed by the crystallization of chrysotile generally around or between the already formed antigorite grains, (2) formation of antigorite by partial recrystallization of chrysotile, and (3) by the combination of both of these processes.

CHRYSOTILE AND ANTIGORITE

Differentiation of chrysotile and antigorite

The studies listed above have proved that chrysotile and antigorite are two distinct serpentine minerals. These two minerals are chemically and structurally similar but they have different particle morphologies. Furthermore, chrysotile is decomposed by less severe physical and chemical treatment than is antigorite. Table 1 lists the more prominent physical and chemical properties of chrysotile and antigorite that can be used for identifying these two minerals.

Figures 1 and 2 show electron micrographs of the tubular chrysotile fibers and flaky antigorite particles. It is often difficult to see certain features which are indicative of the tubular morphology. A photograph

TABLE 1. PROPERTIES OF CHRYSOTILE AND ANTIGORITE

Property	Chrysotile	Antigorite
1. Electron microscopical morphology	Tubular fibers	Flakes, laths
2. Indices of refraction (range)	1.53-1.56	1.56-1.58
3. Distinctive α -ray diffraction lines on powder photographs	Data given by Whittaker and Zussman, 1956	Data given by Whittaker and Zussman, 1956
4. Chemical composition	$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ (may contain $2.9\% \pm 1.9\%$ Al_2O_3 and Fe_2O_3) ¹	$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ (may contain as much as $6.5\% \pm 2.9\%$ Al_2O_3 and Fe_2O_3) ¹
5. Effect of leaching in hydrochloric acid	One normal HCl treatment results in structural collapse ²	Concentrated HCl treatment results in structural collapse ²
6. Effect of exposure to the electron beam of electron microscope	Rapidly disintegrates in the electron beam	Electron beam does not affect it appreciably

¹ Arithmetic mean and standard deviation, respectively, calculated from chemical analyses found in the literature.

² HCl treatment consists of heating the samples at 95° C. for a period of one hour. The differential rate of solubility is believed to be valid only if the specific surface areas of the samples are similar. The term "structural collapse" is used only for brevity to denote a condition where, as the result of the HCl treatment, the sample ceases to give an α -ray diffraction pattern with easily definable diffraction maxima.

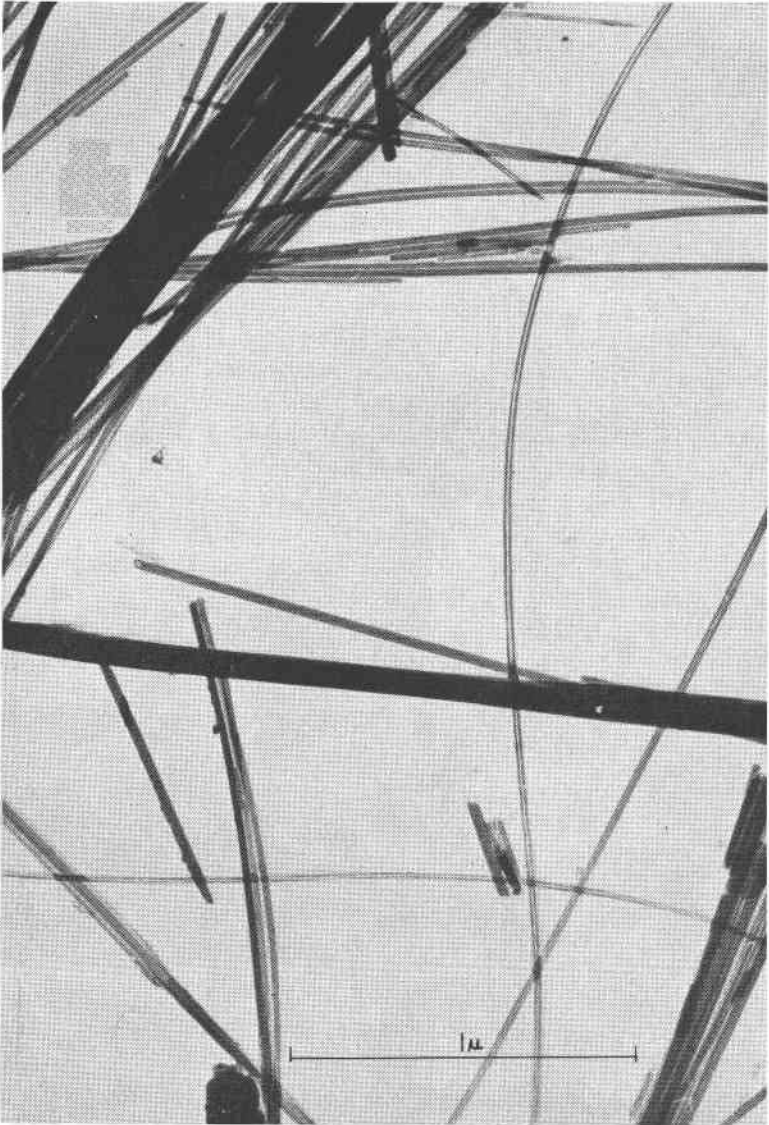


FIG. 1. Electron micrograph showing fibers of chrysotile from Globe, Arizona.
Magnification 45,500 \times .

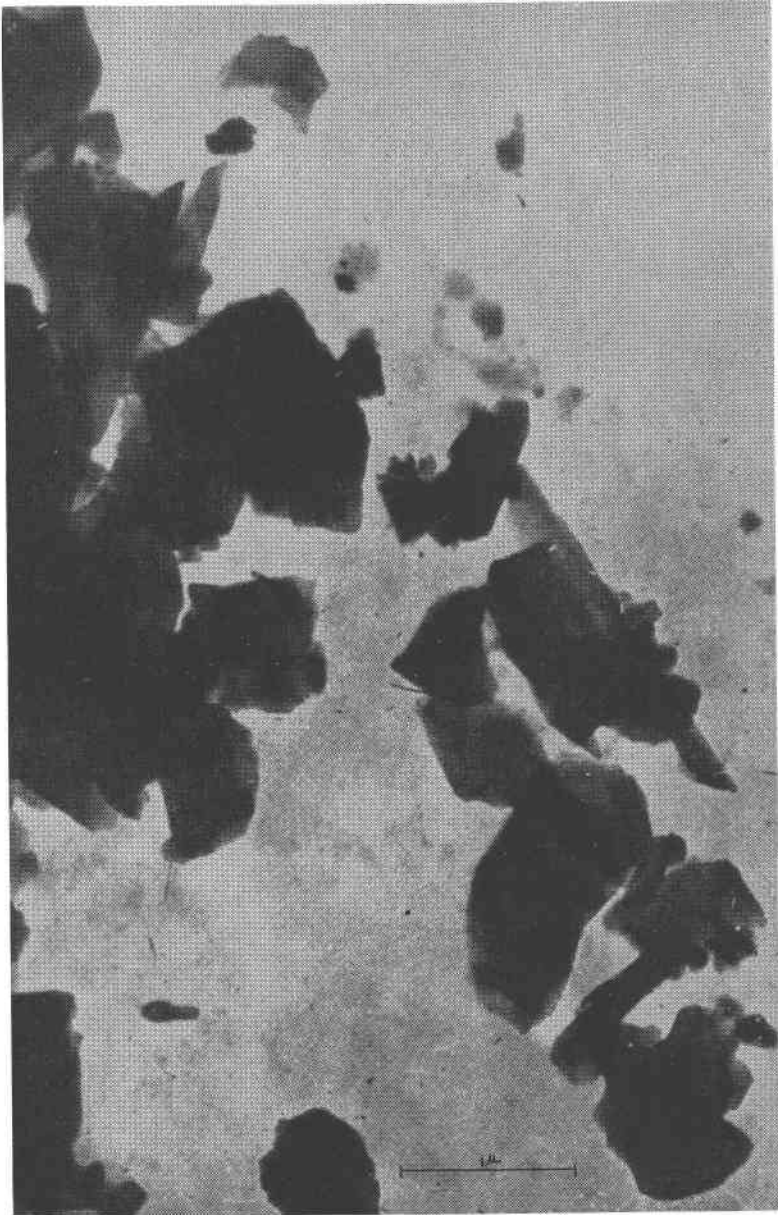


FIG. 2. Electron micrograph showing flake shaped particles of antigorite from Antigorite Valley, Italy. Magnification 23,000 \times .

taken of a transparent glass tube and of a solid glass rod is shown in Fig. 3. The dark bands parallel to the fiber axis of the chrysotile fibers may be optically similar to the dark bands parallel to the long axis of the glass tube. The glass rod does not show the same features.

SERPENTINE MINERALS FORMERLY CLASSIFIED AS
INDEPENDENT SPECIES

Selfridge found that most minerals of the serpentine group which were regarded as individual species (williamsite, picrolite, etc.) exhibited only

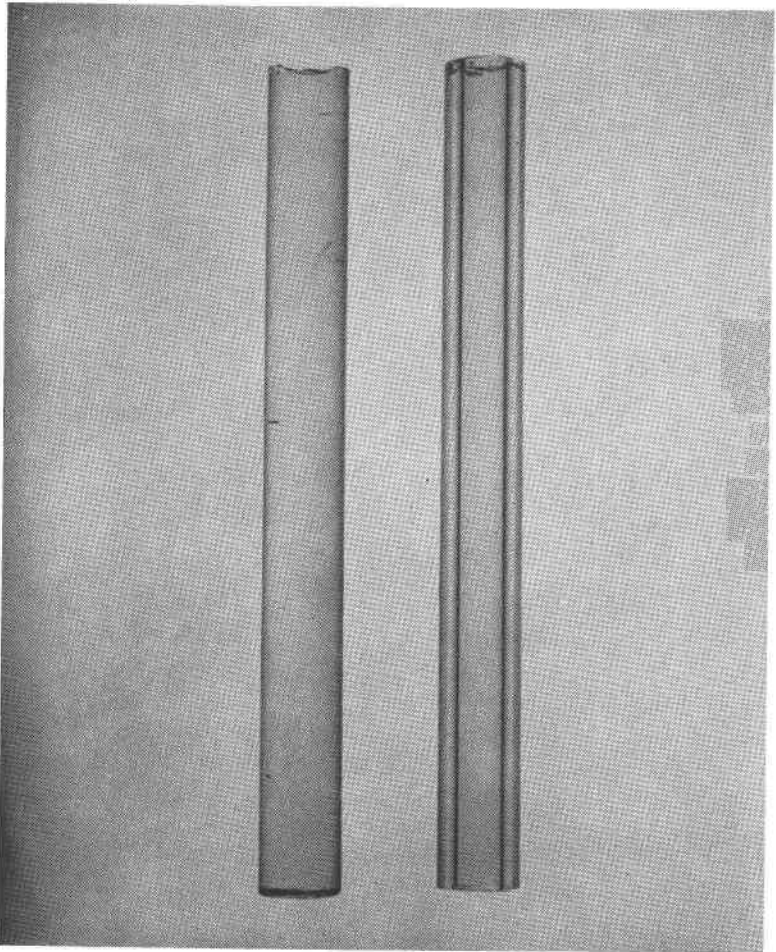


FIG. 3. Laboratory glass rod and glass tube (outside diameter: 8 mm.) as seen in transmitted light. The glass tube shows two, double dark bands parallel to the long axis. These might be similar to the dark bands seen in the chrysotile fibers parallel to the fiber axis which, one may speculate, might not be completely resolved.

minor differences in textures when examined in thin section. During the present studies a large number of serpentine samples were investigated; the results confirmed Selfridge's conclusions. In addition it was found that all serpentines examined are either chrysotile or antigorite or natural mixtures of the two.

Chemical composition

The chemical composition of all serpentine minerals is similar to that of chrysotile and antigorite. A survey of the chemical analyses in the literature shows that chrysotile may contain $2.9\% \pm 1.9\%$ Al_2O_3 and Fe_2O_3 , and antigorite may contain $6.5\% \pm 2.9\%$ Al_2O_3 and Fe_2O_3 . These figures are the arithmetic mean and standard deviation, respectively, calculated from forty-five chemical analyses. The chemical compositions of serpentines formerly regarded as different species are between or close to these limits and do not show a significant deviation from the chemical composition of chrysotile and antigorite. The chemical compositions of five purified and recently analyzed serpentines are shown in Table 2. One has to keep in mind that serpentines are fine-grained minerals, and, therefore, it is often impossible to decide whether the small amounts of certain constituents are present in the crystal structure or are caused by the presence of admixed impurities.

Crystal habit

Crystal habit of the serpentines can be studied only under high magnification. Electron micrographs of serpentines (natural mixtures) show fibrous (tubular) or irregular or flaky particles or both. The irregular particles are believed to be fragments of antigorite flakes crushed during the grinding of the samples. The irregular particle morphology can also be caused by poor dispersion of very fine-grained, flaky antigorite particles. Figure 4 is an electron micrograph of a serpentine which shows the presence of both fibers and flakes.

Optical properties

Optical properties of the serpentine samples are similar to the optical properties of chrysotile and antigorite. The indices of refraction were determined by the oil immersion method at controlled temperatures; the resultant maximum and minimum values are listed in Table 5. These indices seem to range between the indices of refraction of pure chrysotile and antigorite. The same table also lists the antigorite content in per cent of each of the samples, determined with the aid of a special x-ray diffraction method. There may be a correlation between antigorite content and indices of refraction. However, it is believed that such a correlation would be justified only if one knew the chemical composition of each of the

TABLE 2. CHEMICAL ANALYSES OF SOME SERPENTINE MINERALS

Constituent	F-1	F-14	F-19	F-20	F-40
SiO ₂	44.50	44.70	43.53	42.02	44.25
Al ₂ O ₃	1.41	.50	1.89	.52	.24
Fe ₂ O ₃	None	.07	.49	.19	1.34
FeO	.35	.29	4.21	.11	.60
MgO	41.56	42.05	37.52	41.44	39.02
CaO	.02	.12	None	None	—
Na ₂ O	None	—	None	—	—
K ₂ O	None	—	None	—	—
H ₂ O ⁻	None	.06	.55	1.64	2.06
H ₂ O ⁺	12.36	12.43	11.69	14.04	12.54
TiO ₂	None	None	None	None	.07
Cr ₂ O ₃	.06	—	.01	—	—
NiO	.095	—	.20	—	—
CoO	—	—	None	—	—
MnO	None	—	.04	.03	.02
Σ	100.36	100.22	100.13	99.99	100.14
<i>Analyst</i>	Joseph J. Fahey	Joseph J. Fahey	K. J. Murata	Joseph J. Fahey	Joseph J. Fahey

Localities

- F-1. Antigorite, variety-williamsite: State Line pits, (Lowes Mine) approximately 1.2 miles west-northwest of Rock Springs, Cecil County, Maryland.
- F-14. Serpentine, variety—"Yu-Yen Shi Stone," Pei-wa-ku and Lao-yeh-ling, Hsiu-yen Hsien, Liaoning Province, Manchuria.
- F-19. Serpentine, variety-baltimoreite: Bare Hills, Baltimore County, Maryland.
- F-20. Chrysotile: asbestos deposits: Gila County, Arizona.
- F-40. Serpentine, variety-deweylite: Prairie Creek area of peridotite in T. 8 S., R. 25 W., 2½ miles south-southeast of Murfreesboro, Pike County, Arkansas.

samples. Chemical analyses were not available for all samples subjected to the *x*-ray diffraction test, and, therefore, it is not possible to decide whether the indices of refraction are related to the antigorite content, Fe⁺⁺⁺ content, or some other factors.

Differential thermal analysis

The differential thermal analysis curves of the minerals of the serpentine group are characterized by the two basic patterns of the end-members antigorite and chrysotile. The *DTA* curves in Fig. 5 were obtained as photographs. The samples were heated in a nickel block at the rate of 12° C. per minute according to the methods described by Faust, (1948 and 1950). Crystalline alumina, specially prepared for carbon de-

terminations, free from surface alkali, and of 60 mesh size was used as the thermally neutral body. The purified minerals were crushed to pass a 58 mesh bolting cloth sieve and re-examined for impurities.

The basic *DTA* curve for antigorite is represented by number C-64 in Fig. 5, which was obtained from a specimen from the type locality, North of Domodossola in Val Antigorio, Novara Province, Piedmont Region, Italy. The basic *DTA* curve for chrysotile is best represented by curves C-489 obtained from the synthetic chrysotile prepared by Bowen and Tuttle (1949), and C-84 obtained from chrysotile (asbestos) from Gila County, Arizona. Curve C-120 is a *DTA* curve of a natural mixture of 75 per cent antigorite and 25 per cent chrysotile (see Table 5, number 11). This curve was obtained from the gem material from Liaoning Province, Manchuria.

The *DTA* patterns of the natural mixtures of the serpentine group can be interpreted on the basis of these standard curves.

The existence of distinct serpentine minerals, other than chrysotile and antigorite (or their polymorphs), is not confirmed on the basis of chemical, morphological, optical, differential thermal analysis, and x -ray diffraction data. The properties of all of the different varieties seem to lie between the properties of chrysotile and antigorite.

A SEMIQUANTITATIVE METHOD FOR THE DETERMINATION OF THE ANTIGORITE-CHYRSOTILE CONTENT OF NATURAL MIXTURES

Quantitative x -ray analysis methods of crystalline mixtures have received considerable attention in the past. A thorough description may be found, among others, by Alexander and Klug (1948). It can be proved mathematically that the diffraction intensity is a function of the weight fraction and density of the components in the mixtures, and the absorption coefficients of the unknown and of the matrix, etc. In experiments involving natural serpentine mixtures some of these factors cannot be realized with the desired accuracy and, therefore, one must be content with a method which provides semiquantitative estimates. Such a method, however, is thought to be sufficient for the purpose of analyzing the natural serpentine mixtures.

Chrysotile is more readily affected by treatment with hydrochloric acid than is antigorite. Nagy and Bates (1952) found that after leaching with one normal hydrochloric acid for one hour at 95° C., chrysotile gave an x -ray diffraction pattern which showed only a very broad, weak, and diffuse reflection at low angle values; to achieve the same results they had to treat antigorite with concentrated HCl. This differential rate in solubility is believed to be valid only if the two minerals have similar

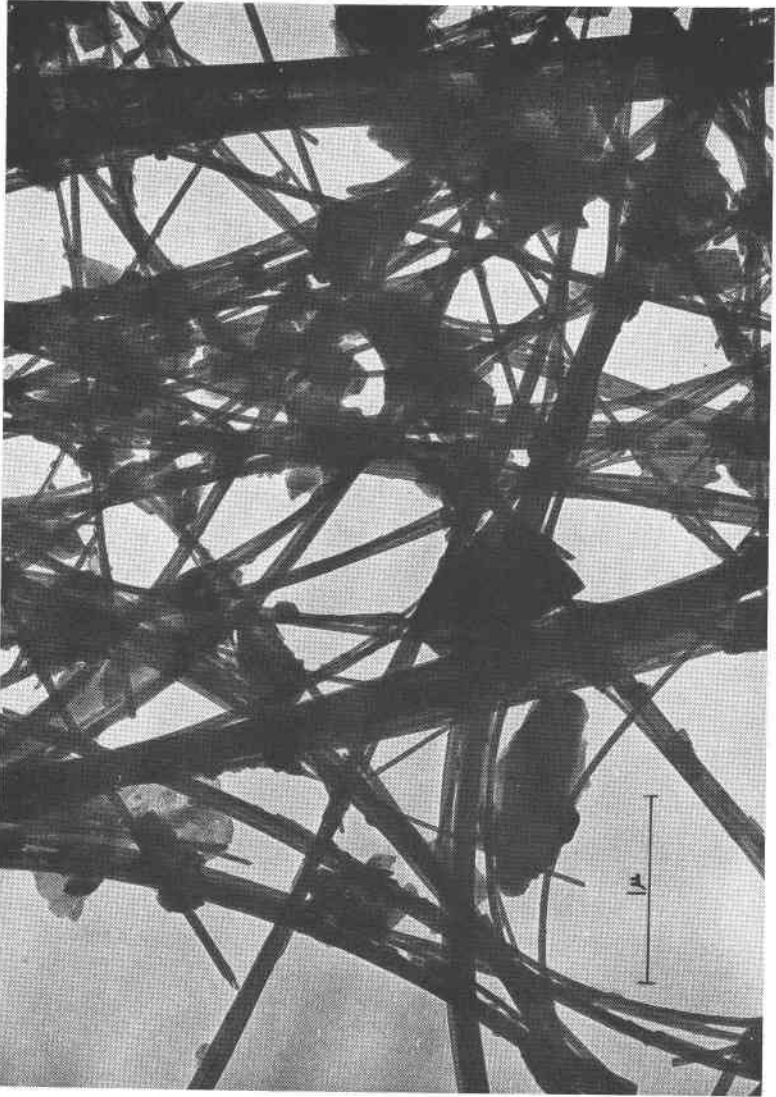


FIG. 4. Electron micrograph of serpentine from near Montville, Morris County, New Jersey, showing a natural mixture of chrysotile fibers and antigorite flakes. 25,000 \times .

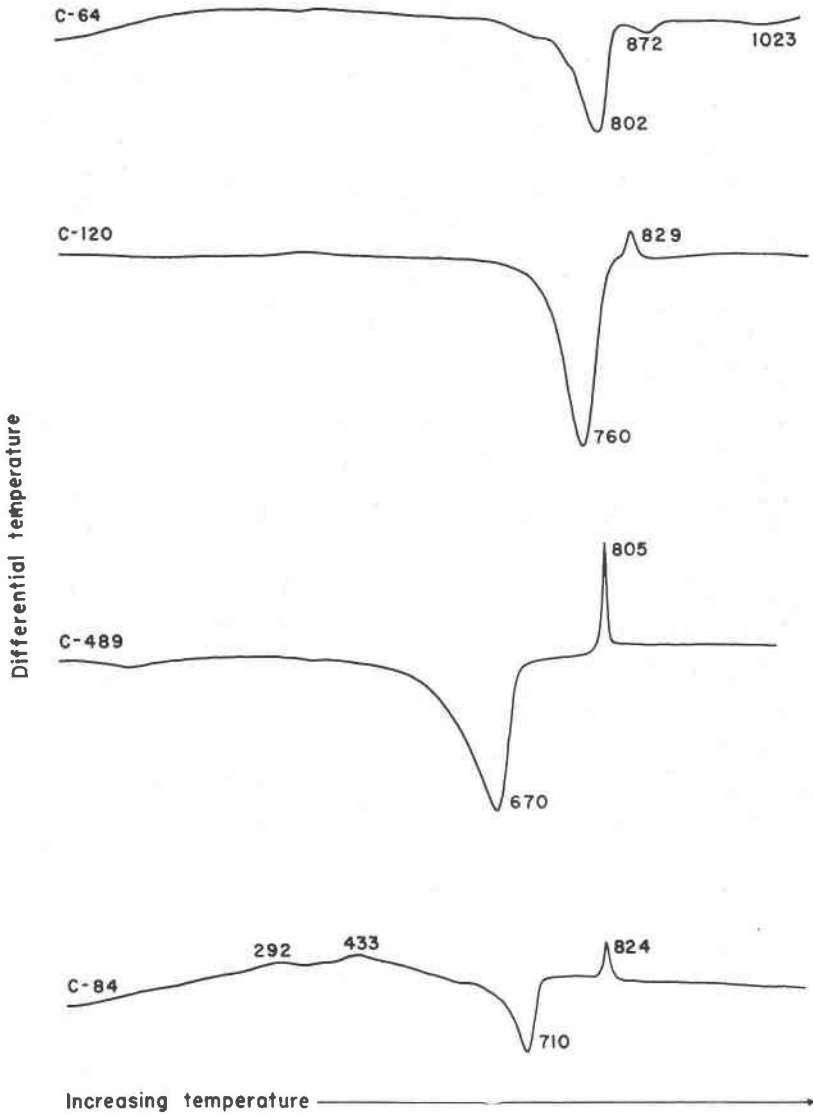


FIG. 5. Differential thermal analysis curves. C-64, antigorite, Val Antigorio, Italy; C-120, natural mixture of antigorite with some chrysotile, Manchuria; C-489, chrysotile, synthetic, Bowen and Tuttle preparation T2-29C; C-84, chrysotile, Gila County, Arizona. All temperatures are given in degrees Centigrade. These curves were all obtained with a resistance of 600 ohms in the galvanometer circuit, and at a heating rate of 12° C. per minute.

specific surface areas. Nagy and Bates (1952) measured the surface areas of antigorite from Antigorio Valley, Italy, and chrysotile from Thetford, Quebec, by the Brunauer-Emmett-Teller method using nitrogen as the adsorbent and found that they are of similar magnitude.

It is possible to devise a semiquantitative method for determining the composition of serpentine minerals in terms of chrysotile and antigorite content by treating the sample with one normal hydrochloric acid and then examining the x -ray diffraction pattern of the dried residue. The diminution in the intensity of the 001 reflection of the acid-treated sample is an estimate of the chrysotile-antigorite content of the mixture. The change of intensity of the 001 reflection of the HCl treated mixtures was studied chiefly because this reflection is the most prominent and easiest detected reflection on the x -ray diffraction patterns of most natural serpentines and because the 001 reflections of the chrysotile and antigorite correspond to very similar interplanar spacings.

The semiquantitative analysis method is based on a relationship found between the intensities of the 001 reflections of synthetic mixtures and the proportions of the acid treated chrysotile and the antigorite content of these mixtures. The relationship found between the 001 intensity and the amount of antigorite present in the synthetic mixtures was then applied to the estimation of the proportions of chrysotile and antigorite in the natural mixtures. This method was developed solely for the purpose of studying serpentines; its usefulness for other systems was not investigated. The synthetic mixtures (weight percentage) were prepared from chrysotile from Thetford, Quebec, and from antigorite from Unionville, Pennsylvania, both treated with one normal hydrochloric acid. The samples were x -rayed in a "Norelco" x -ray spectrometer unit by using filtered copper radiation. The samples were supported in hollow slides and were thoroughly homogenized; precautions were taken to exclude oriented textures. An arc of approximately 4° was recorded; peak heights were related to the peak height of untreated antigorite. The observed I/I_0 values are referred to as intensities, I_{001} . The relationship found between intensity and the antigorite content has been evaluated by means of a statistical test of the data. During the statistical study Dr. J. C. Griffiths of the Pennsylvania State University and Dr. M. A. Rosenfeld of the Magnolia Petroleum Company offered valuable suggestions and furnished help (especially in the development of the analysis of variance model). For their contributions the authors express their appreciation.

It has been assumed that for the given experimental conditions the

factors influencing the intensities of the 001 reflections may be grouped as follows:

- (1) antigorite content of the mixtures,
- (2) packing of the samples in the hollow slides,
- (3) all residual variation, chiefly "machine" error.

An experiment was designed to evaluate variations in intensity due to the different sources. The experimental plan called for two steps: first for the definition of the influence of the three different sources of variation on intensity, and secondly for a correlation between intensities and proportions of antigorite and chrysotile. An estimate of the extent of total variation in a set of data attributable to one or more assignable causes of variation may be obtained with the aid of the analysis of variance method. The method also provides tests of significance, by which it is possible to decide whether the assignable causes have probably resulted in real variation or whether the apparent variation ascribed to them is the result only of the chance causes which produce the error variation. Accordingly, each mixture was sampled three times to obtain three subsamples. The subsamples show the affect of variations caused by differences in packing while the proportions of the components remained relatively constant. Subsamples were x-rayed three times. Since there were no changes in either proportions or packing the results were considered to be indicative of variations caused by all other sources, essentially by "machine" error. Consequently the intensity of each mixture is the mean of nine determinations.

Sixteen mixtures varying from 0 to 100% antigorite were prepared, resulting in a total of 102 runs. (The subsamples of seven mixtures were run only once.) The results are shown in Table 3.

The analysis of variance resulted in a variance ratio or F distribution indicative of the sources of variation. The mathematical model, shown in Table 4, was designed according to models presented among others by Dixon and Massey (1951); the F values were obtained from the tables of Fisher and Yates (1948). Comparing the intensity variation arising from subsamples with the variation arising from "runs," the variance ratio or F test yielded a value of 15.09; such a value or larger will occur much less frequently than one time in one-hundred on the average when there is no real effect of subsamples. It is concluded that intensity differences arising from subsamples (i.e. packing) are very much greater than the differences arising from "runs" (i.e. chiefly "machine" error). For this reason it was permissible to pool the experimental error, i.e. to

TABLE 3. OBSERVED 001 INTENSITIES OF SYNTHETIC CHRYSOTILE-ANTIGORITE MIXTURES

First set										
Per cent Antigorite (Proportions)										
Subsamples	run	0%	10%	20%	30%	40%	60%	80%	90%	100%
1	1	3	2	13	16	20	48	67	65	93
	2	6	5	10	17	20	43	69	59	99
	3	2	4	10	19	23	43	73	67	95
2	1	3	6	19	18	28	63	80	87	104
	2	6	5	15	18	30	59	92	77	101
	3	2	6	16	8	30	60	83	74	98
3	1	2	8	23	8	43	64	75	87	95
	2	3	1	12	8	40	65	75	84	97
	3	4	2	11	7	45	64	77	85	96

Second set								
Per cent Antigorite (Proportions)								
Subsamples	25%	35%	45%	55%	65%	75%	85%	
1	29	10	33	68	59	69	87	
2	19	27	36	35	69	64	87	
3	21	14	36	58	70	58	96	

TABLE 4. MATHEMATICAL MODEL OF ANALYSIS OF VARIANCE FOR THE SERPENTINE EXPERIMENT

Source of Variation	Degree of Freedom	Sum of Squares (ss)	Mean Square
Proportions (p) (Between percentages)	$(p-1)$	$SS_p = \sum_1^p \left(\sum_1^{rs} x \right)^2 / rs - C.T.$	$\frac{SS_p}{(p-1)}$
Packing (s) (Between subsamples)	$p(s-1)$	$SS_s = \sum_1^{ps} \left(\sum_1^r x \right)^2 / r - C.T. - SS_p$	$\frac{SS_s}{p(s-1)}$
"Machine" error (r) (Between runs)	$ps(r-1)$	$SS_r = \sum_1^{psr} x^2 - C.T. - SS_p - SS_s$	$\frac{SS_r}{ps(r-1)}$
Total	$psr-1$	$\sum_1^{psr} x^2 - C.T.$	

Abbreviations: p=proportions (i.e. percentage antigorite), s=packing (subsamples), r="machine" error, ss=sum of squares and C.T.=correction term.

add its effect to that arising from packing; accordingly it is sufficient to make only one run of each of the subsamples. The second set (seven mixtures) of runs shown in Table 3 was made in accordance with this conclusion. Making use of the F test again for comparing the differences arising from samples (i.e. antigorite content or proportions) and from subsamples (i.e. packing) an F value of 75.85 was obtained. This value shows that intensity differences arising from measurements of different composition ranges are much greater than those arising from packing. Intensity differences of equal variance arising from both samples and subsamples would occur by chance very much less often than one time in one-thousand.

Plotting the raw data on arithmetic graph paper indicates a linear relationship between antigorite content and intensities in the 30–85% antigorite range. The line of regression was determined for this range by the least squares method.

The standard error of estimate (s_y) determines the scatter about the line of regression, s_y was found to equal 8 percentage antigorite units. These are indicated by the two dashed parallel lines on Fig. 6.

The coefficient of correlation (r) expresses the degree of association (perfection of a relationship on a comparative basis). r was found to be 0.896, (1.000 is a perfect association). The probability that this coefficient of correlation occurs by chance is less than one in one-hundred.

The coefficient of determination (r^2) is 80.3%, which indicates that approximately 80% of the relationship is accounted for in the regression line but the remaining 20% variation is due to unassigned source.

A large number of natural serpentine samples were investigated by this method. All specimens were first examined with x -ray diffraction and optical methods and the impure samples were discarded (i.e. those which contained fine grained non-serpentine minerals in such intimate association that separation was not possible). The results of the analysis are shown in Table 5. In the same table the maximum index of refraction is also listed together with a short description of the macroscopic properties.

CONCLUSIONS

These experimental studies show that minerals classified as serpentines are either chrysotile or antigorite or natural mixtures of these two minerals. An x -ray diffraction method based on a study of the product resulting from the differential rate of reaction of chrysotile and antigorite with one normal hydrochloric acid was found to provide semiquantitative estimates of the composition of chrysotile-antigorite mixtures (both

TABLE 5. ANTIGORITE CONTENT (IN PER CENT) OF VARIOUS MINERALS IN THE SERPENTINE GROUP

(arranged according to increasing amounts of antigorite)

No.	Names formerly assigned to samples	Locality	Macroscopic appearance	n_{\max}	Antigorite content (in per cent) as determined by the x-ray method. (The remainder is chrysotile)
1	Chrysotile (F-20)	Asbestos deposits, Gila County, Arizona	fibrous	1.540	1
2	Chrysotile	Templeton Township, Papi-neau County, Quebec, Canada	fibrous	1.550	8
3	Porcello-phite	Coleraine Township, Megantic County, Quebec, Canada	massive	1.561	47
4	Chrysotile	Near Montville, Morris County, New Jersey	fibrous	1.555	50
5	Baltimore-ite (F-19)	Bare Hills, Baltimore County, Maryland	fibrous	1.574	50
6	Picrolite changing to chrysotile	Shipton Township, Richmond County, Quebec, Canada	fibrous	1.556	55
7	Marmolite	Castle Point, Hoboken, Hudson County, New Jersey	massive	1.558	58
8	Williamsite	Dublin, Harford County, Maryland	massive	1.563	58
9	Antillite	Havana, Havana Province, Cuba, West Indies	massive showing a few flakes	1.563	67
10	Antillite	Havana, Havana Province, Cuba, West Indies	massive together with a few flakes	1.564	68
11	Serpentine (F-14)	Pei-wa-ku and Lao-yeh-ling, Hsiu-yen Hsien, Liaoning Province, Manchuria	massive	1.564	75
12	Picrolite	Cullakee mine, Buck Creek, Clay County, North Carolina	fibrous	1.564	78
13	Picrolite	"Blue Hill," North Carolina	fibrous, some parts are massive	1.570	82

TABLE 5—(continued)

No.	Names formerly assigned to samples	Locality	Macroscopic appearance	n_{max}	Antigorite content (in per cent) as determined by the x-ray method. (The remainder is chrysotile)
14	Aphrodite	Grenville, Argenteuil County, Quebec, Canada	massive	1.569	88
15	Serpentine	Near Lafayette Station, Philadelphia County, Pennsylvania	massive	1.577	90
16	Marmolite	Blandford, Hampden County, Massachusetts	massive	1.561	95
17	Picrolite	Dublin, Harford County, Maryland	fibrous, flaky	1.565	96
18	Williamsite (F-1)	Woods Chrome mine, Open quarry, Little Britain Township, Lancaster County, Pennsylvania	massive	1.568	98
19	Serpentine	Hull County, Quebec, Canada	massive	1.584	98
20	Antigorite	North of Domodossola in Val Antigorio, Novara Province, Piedmont Region, Italy	flaky	1.576	100

The samples were obtained from the Genth Mineralogical collection of the Pennsylvania State University and from the U. S. Geological Survey, Washington, D. C.

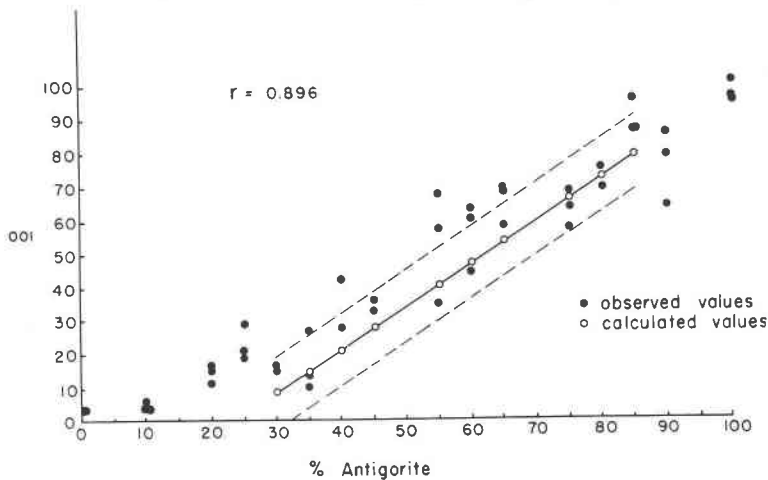


FIG. 6. Relationship between the intensity of the 001 reflection (I/I_0) and the antigorite content of the HCl treated chrysotile-antigorite mixtures.

mechanical and natural). It is suggested that serpentines should be defined in terms of the relative proportions of antigorite and chrysotile.

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REFERENCES

- ALEXANDER, L., AND KLUG, H. P. (1948), Basic aspects of x -ray absorption in quantitative diffraction analysis of powder mixtures: *Anal. Chem.*, **20** (10) 886-889.
- ARUJA, E. (1945), An x -ray study of the crystal structure of antigorite: *Mineral. Mag.*, **27**, p. 65-74.
- BALDUZZI, F., EPPRECHT, W., AND NIGGLI, P. (1951), Weitere Versuche zur Synthese von Chrysotilasbest: *Schweizer. min. pet. Mitt.*, **31**, 293-305.
- BATES, T. F., AND MINK, J. F. (1950), Morphology and structure of the serpentine minerals antigorite and chrysotile (abst.): *Geol. Soc. Am. Bull.*, **61**, 1442-1443.
- BOWEN, N. L., AND TUTTLE, O. F. (1949), The system $MgO-SiO_2-H_2O$: *Geol. Soc. Am. Bull.*, **60**, 439-460.
- BRINDLEY, G. W., AND VON KNORRING, O. (1954), A new variety of antigorite (ortho-antigorite) from Unst, Shetland Islands: *Am. Mineral.*, **39**, 794-804.
- DIXON, W. J., AND MASSEY, F. J. (1951), Introduction to statistical analysis: New York, McGraw-Hill Book Co., 370 p.
- EPPRECHT, W. (1947), Versuche zur Synthese von Serpentin-Mineralien: *Schweizer. min. pet. Mitt.*, **27**, 1, 1-20.
- FAUST, G. T. (1948), Thermal analysis of quartz and its use in calibration in thermal analysis studies: *Am. Mineral.*, **33**, 337-345.
- FAUST, G. T. (1950), Thermal analysis studies on carbonates I, Aragonite and calcite: *Am. Mineral.*, **35**, 207-224.
- FISHER, R. A., AND YATES, F. (1948), Statistical tables for biological, agricultural and medical research: New York, Hafner Publishing Co., 112 p.

- HESS, H. H., SMITH, R. J., AND DENGU, G. (1952), Antigorite from the vicinity of Caracas, Venezuela: *Am. Mineral.*, **37**, 68-75.
- IPATIEFF, W., AND MOUROMTSEFF, B. (1927), Formation de silicates cristallisés en millier aqueux sous pressions et à températures élevées: *Acad. sci. Paris Comptes rendus*, **185**, 647-649.
- ITO, T. I., in collaboration with SADANAGA, R. and TAKEUCHI, Y. (1950), X-ray studies on polymorphism: Tokyo Maruzen, 251 p.
- JAGODZINSKI, H., AND BAGCHI, S. N. (1953), Die Gerollte Struktur des Chrysotils: *Neues Jahrb. Mineral., Monatsh.*, **1953**, Abt. A, 97-100.
- JAGODZINSKI, H., AND KUNZE, G. (1954), Die Röllchenstruktur des Chrysotils. I Allgemeine Beugungstheorie und Kleinwinkelstreuung: *Neues Jahrb. Mineral., Monatsh.*, **1954**, 95-108.
- JANDER, W., AND FETT, R. (1939), Hydrothermale Reaktionen II Magnesiumsilikate: *Zeits. anorg. und allg. Chemie.*, **242**, 145-160.
- JANDER, W., AND WUHRER, J. (1938), Hydrothermale Reaktionen I Die Bildung von Magnesiumhydrosilikaten: *Zeits. anorg. und allg. Chemie*, **235**, 273-294.
- MIDGLEY, H. G. (1951), A serpentine mineral from Kennack Cove, Lizard, Cornwall: *Mineral. Mag.*, **29**, 526-530.
- NAGY, B. (1953), The textural pattern of the serpentines: *Econ. Geology*, **48**, 591-597.
- NAGY, B., AND BATES, T. F. (1952), Stability of chrysotile asbestos: *Am. Mineral.*, **37**, 1055-1058.
- NOLL, W. (1944), Anwendung der Elektronenmikroskopie beim Studium hydrothermaler Silikatreaktionen: *Kolloid. Zeits.*, **107**, 181-190.
- NOLL, W., AND KIRCHER, H., (1950), Zur Morphologie des Chrysotilasbestos: *Naturwiss.* **37**, 540-541.
- NOLL, W., AND KIRCHER, H. (1951), Über die Morphologie von Asbesten und ihren Zusammenhang mit der Kristallstruktur: *Neues Jahrb. Mineral., Monatsh.*, **10**, 219-240.
- PAULING, L. (1930), The structure of the chlorites: *Nat. Acad. Sci. Proc.*, **16**, 578-582.
- SELFDRIDGE, G. C. (1936), An x-ray and optical investigation of the serpentine minerals: *Am. Mineral.*, **21**, 463-503.
- SOBOLEV, N. D. (1945), Microtexture of serpentinites: *Akad. Nauk U.S.S.R. Doklady*, **50**, 455-456; *Chem. Abs.* (1950), **44**, 5282f.
- STRESE, H., AND HOFMANN, U. (1941), Synthese von Magnesiumsilikat-Gelen mit Zweidimensionalen Regelmässiger Struktur: *Zeits. anorg. und allg. Chemie*, **247**, 65-95.
- TURKEVICH, J., AND HILLIER, J. (1949), Electron microscopy of colloidal systems: *Anal. Chemistry*, **21**, 475-485.
- VAN NIEUWENBURG, C. J., AND BLUMENDAL, H. B. (1931), The pneumatolytic synthesis of silicates: Part I; *Rec. travaux chim.*, **50**, 129-138.
- WARREN, B. E., AND BRAGG, W. L. (1930), The structure of chrysotile $H_4Mg_3Si_2O_9$: *Zeits. Krist.*, **76**, 201-210.
- WARREN, B. E., AND HERING, K. W. (1941), The random structure of chrysotile asbestos (abst.): *Phys. Rev.*, **59**, 925.
- WHITTAKER, E. J. W. (1951), An orthorhombic variety of chrysotile: *Acta Crystallographica*, **4**, pt. 2, 187-188.
- WHITTAKER, E. J. W. (1952), The unit cell of chrysotile: *Acta Crystallographica*, **5**, pt. 1, 143-144.

- WHITTAKER, E. J. W. (1953), The structure of chrysotile: *Acta Crystallographica*, **6**, pt. 8-9, 747-748.
- WHITTAKER, E. J. W., AND ZUSSMAN, J. (1956), The characterization of serpentine minerals by x-ray diffraction: *Mineral. Mag.*, **31**, 107-126.
- YODER, H. S., JR. (1952), The MgO-Al₂O₃-SiO₂-H₂O system and the related metamorphic facies: *Am. Jour. Sci.*, *Bowen Volume*, pp. 569-627.

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