

AN EXPERIMENTAL STUDY OF THE FORMATION AND PROPERTIES OF SYNTHETIC SERPENTINES AND RELATED LAYER SILICATE MINERALS

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ABSTRACT

The hypothesis that the formation of tubular crystals of chrysotile is the result of misfit of the alternate brucite and silica layers, is tested by means of chemical substitution. Increasing the size of the tetrahedral layer by substituting Ge^{4+} for Si^{4+} results in the formation of hexagonal platy crystals of the serpentine phase, $\text{Mg}_6\text{Ge}_4\text{O}_{10}(\text{OH})_4$. Decreasing the size of the octahedral layer and at the same time increasing the size of the tetrahedral layer is accomplished by partial substitution of Al^{3+} into the structure to form platy aluminian serpentine, $\text{Mg}_5\text{AlAlSi}_3\text{O}_{10}(\text{OH})_4$. The replacement of Mg^{2+} by the similar-sized Ni^{2+} ion yields a serpentine $\text{Ni}_6\text{Si}_4\text{O}_{10}(\text{OH})_4$ which is either tubular or platy, depending on other factors. Another serpentine phase synthesized, $\text{Ni}_6\text{Ge}_4\text{O}_{10}(\text{OH})_4$, forms hexagonal platy crystals. Other substitutions using the following ions: Mn^{2+} , Zn^{2+} , Co^{2+} , Fe^{3+} , Cr^{3+} , and Ga^{3+} , fail to yield a serpentine type structure.

A number of other hydrosilicate type structures have been synthesized, and comparisons are made of the phase equilibrium relations determined to be present among phases in the systems, $\text{MgO-SiO}_2\text{-H}_2\text{O}$, $\text{NiO-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-GeO}_2\text{-H}_2\text{O}$.

I. INTRODUCTION

One of the mineralogical problems which has attracted considerable attention in recent years concerns the structure, morphology and synthesis of the serpentine minerals chrysotile and antigorite. The structure of chrysotile, although known in outline, has been the subject of much debate, the choice between a kaolinite type sheet structure and an amphibole chain structure being relatively difficult and not resolved till relatively recent times. Acceptance of the sheet structure makes possible the consideration of the curving of these sheets, first suggested by L. Pauling (1930), as the means of compensating for any slight strain among the layers. The diffraction effects (both x -ray and electron) to be expected from curved sheets were studied both theoretically and experimentally by Fock and Kolpinsky (1940). Comprehensive work by Aruja (1945) and Whittaker (1952) greatly enlarged our understanding of these minerals. Most recently on the basis of direct observation in the electron microscope numerous investigators have shown these chrysotile crystals not only to be curved but to actually occur as cylindrical or tubular crystals. (See Bates, Sand and Mink, 1950; Noll, 1950; Hillier, 1949; and Turkevitch and Hillier, 1949.) Whereas previous investigators have relied on physical proofs for the concept of the tubular crystals being caused by the misfit of layers, a "chemical" method for adducing evidence to this same

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end may be devised on the basis of synthesizing a series of such structures containing ions of slightly different size. At the same time interesting data may be obtained on the formation and stability of various structures containing different ions.

In earlier work Bowen and Tuttle showed electron micrographs of synthetic chrysotile ($\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_4$) with apparently tubular habit although they did not recognize these as "tubes," while Bates, Sand and Mink (1950), Hillier (1949), and Noll (1950) have demonstrated the tubular habit of natural chrysotile using the electron microscope. Tu (1949) claimed that he had prepared "antigorite" with a platy habit from magnesia-silica mixtures containing small amounts of Al_2O_3 , and Roy (1952) and Yoder (1952) presented evidence for solid solution with 2 Al replacing Mg+Si in chrysotile, giving rise to a phase with platy hexagonal habit—probably the same phase as Tu's "antigorite." Since the inception of this work, Noll prepared synthetic Ni-serpentine in the presence of Na^+ and Cl^- ions, and showed these to be tubular. Van Eyk Voorthuysen (1952) had also reported the preparation of synthetic Ni-serpentine but did not describe its morphology. The present work was carried out in an attempt to obtain comparative data on several synthetic serpentine with respect to morphology.

Incidental to the work on morphology, by studying a few compositions in each of the systems investigated it was possible to obtain information on the existence, properties and stability range of other phases which form in these systems. A comparison of the stability of the various analogous phases (isomorphs) can provide useful geochemical data.

II. EXPERIMENTAL

In the present study the phases were prepared by now well-established hydrothermal techniques (Roy and Osborn, 1952; Roy, Roy, and Osborn, 1950). For such preparations it is very desirable if not essential to start with the components in a very finely divided and if possible "amorphous" form. To this end mixtures were prepared by one or more of the following techniques: (a) as coprecipitated gels; (b) by mixing alcohol soluble salts or compounds in solution and evaporating; or (c) mixing finely divided salts which would decompose easily, such as hydroxides and carbonates by wet grinding in agate mortars. All chemicals used were of reagent grade purity. Such mixtures are wrapped in gold or platinum foil and treated at the appropriate temperature and pressure. The temperature range was from 150°C .– 900°C . and the pressure range from 500 psi–30,000 psi. Runs varied in length from $\frac{1}{2}$ day to 60 days. More complete details of the experimental technique are omitted here since they have been given in earlier papers (Roy and Osborn, 1952; Roy, Roy,

and Osborn, 1950). Some 250 runs were made to obtain these data. After hydrothermal treatment, the products were identified largely by their optical properties and x -ray diffraction patterns—all the products being so examined. Either Norelco 90° Geiger-counter “diffractometers” or a GE XRD-3 165° diffractometer were used, with filtered Cu or Fe radiation. The petrographic microscope proved to be of limited use with such fine-grained material, and most of the material was studied under the electron microscope (RCA Model EMU). Latterly, some work was done with single crystal electron diffraction patterns to determine unit cell dimensions. Where x -ray data are listed, they were obtained on the high angle instrument, although in some cases only the few low-angle spacings were obtained. Instead of using calibrants in the latter cases, the instrument zero was checked and the low-angle spacings read directly. Under such conditions reliable data are obtained for calibrating materials. Reproducibility in most cases was better than $.01^\circ \theta$. The frequently large discrepancies between 001 and higher order reflections were absent.

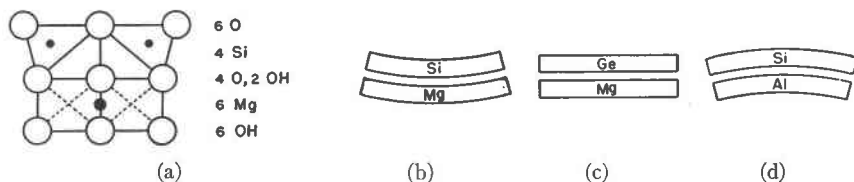


FIG. 1. Schematic representation of serpentine-type structures. (a) Chrysotile structure; (b) Chrysotile structure, silica and brucite layers, showing curvature due to larger size of brucite layer; (c) Magnesia-germania serpentine layers, not curved; (d) Gibbsite and silica layers in halloysite, curved in opposite direction from serpentine.

III. RESULTS

A. RELATION BETWEEN MORPHOLOGY AND COMPOSITION:

1. *Misfit due to composition.* In Fig. 1 (a) we represent (according to the scheme used by Pauling): the structure of magnesium chrysotile and in Fig. 1 (b) the structure is illustrated very schematically as two sheets (one of brucite and one of silica) of slightly different length. Due to the “misfit” between these layers there is a tendency to curvature with the brucite layer on the outside. This curving tendency is the apparent cause for the tubular nature of chrysotile and endellite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$).^{*} It is desirable to obtain further information to show whether this is indeed the case. In order to obtain a closer fit of the layers, we can change the size of either the brucite or silica layers, eliminating any tend-

^{*} A detailed illustrated treatment of the “misfit” idea has been given by Bates, Hildebrand, and Swineford (1950).

ency to curvature due to misfit. In Fig. 1 (c) the size of the silica layer is increased by the replacement of Si^{4+} by Ge^{4+} , to show an approximate fit. (A quantitative figure is not available directly for the expected size of the "GeO₂" layer.) Whereas complete replacement of 3Mg^{2+} in the brucite layer by 2Al^{3+} (to produce endellite, Fig. 1 (d) gives the opposite type of misfit with the silica layer on the outside, partial substitution should cause a condition of good fit for some compositions. Roy (1952) has shown there is no substitution of 2Al^{3+} for 3Mg^{2+} in the octahedral position *only*, but that substitution takes place, on the other hand, when the equivalent amount of Al^{3+} enters the tetrahedral position simultaneously. This makes Al^{3+} doubly effective, since it contracts the brucite layer and expands the silica layer simultaneously; and hence, only a

TABLE 1. MORPHOLOGY OF SERPENTINES

Starting Material Composition	Temp. ° C.	Press. (psi)	Time (hrs.)	Electron Microscope Observations
3 MgO · 2 SiO ₂ †	392	10,000	408	long fibrous "jointed" tubes, curved
3 MgO · 2 SiO ₂ †	230	5,000	648	short stubby tubes
3 MgO · 2 GeO ₂ †	500	10,000	92	hexag. plates, thin and thick
3 MgO · 2 GeO ₂ †	450	20,000	120	hexag. plates, some thick
3 NiO · 2 SiO ₂ + NaCl‡	325	5,000	48	good tubes
3 NiO · 2 SiO ₂ + NaCl‡	325	5,000	172	v.* fine plates, few tubes
3 NiO · 2 SiO ₂ + NaCl‡	445	10,000	22	good tubes, some plates
3 NiO · 2 SiO ₂ + KCl‡	220	5,000	24	few tubes, v. fine particles
3 NiO · 2 SiO ₂ + KCl‡	450	10,000	24	good tubular crystals
3 NiO · 2 SiO ₂ ‡	325	5,000	26	v. fine plates, some poor tubes
3 NiO · 2 SiO ₂ ‡	325	5,000	190	v. fine plates
3 NiO · 2 SiO ₂ ‡	500	10,000	90	platy
3 NiO · 2 SiO ₂ ‡	400	8,000	215	platy
3 NiO · 2 GeO ₂ ‡	300	10,000	144	v. fine-grained platy
3 NiO · 2 GeO ₂ + KCl‡	230	5,000	24	fairly large hexag. plates
5 MgO · 1 Al ₂ O ₃ · 3 SiO ₂ §	515	23,000	384	good hexag. plates
5 MgO · 1 Al ₂ O ₃ · 3 SiO ₂ †	515	23,000	384	fairly good hexag. plates
5 MgO · 1 Al ₂ O ₃ · 3 SiO ₂ ‡	605	10,000	384	good hexag. plates
57 MgO · 1 Al ₂ O ₃ · 40 SiO ₂ †	450	10,000	276	v. thin plates, possibly few tubes

* Abbreviations used: v. = very, hexag. = hexagonal, xls = crystals.

† Mixtures of C.P. oxides.

‡ Co-precipitated gels.

§ Nitrate-ethyl silicate type mixture.

relatively small amount of Al^{3+} should be required to cause a good fit. Most of the other feasible substitution in the brucite layer of Ni^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , etc., should retain or increase the misfit.

2. *Experimental results.* The results of the experiments relating to morphology are summarized in Table 1, and are described briefly below; *x*-ray data for the serpentine phases formed are given in Table 2.

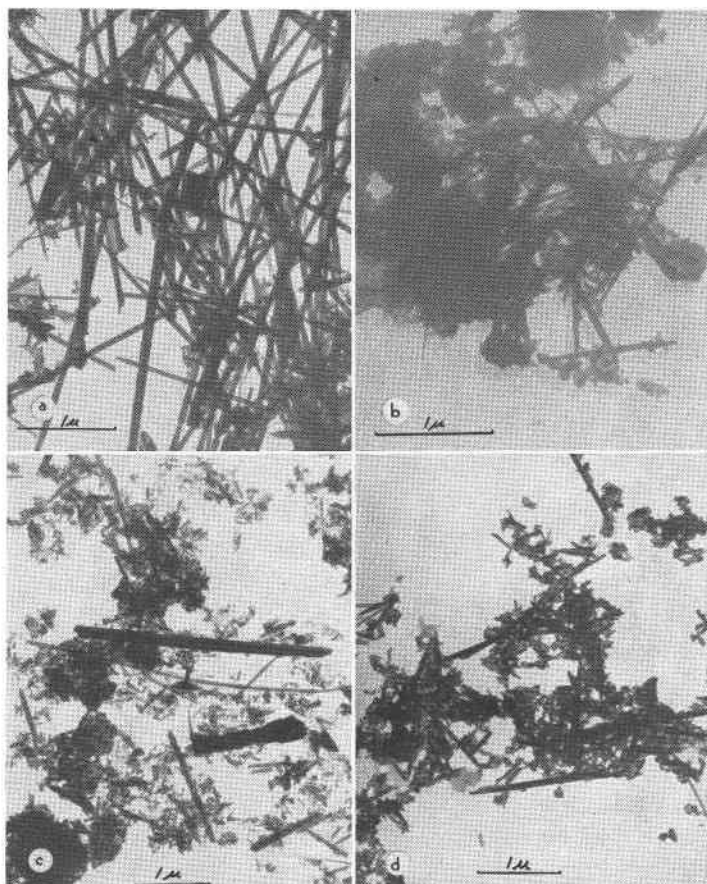
TABLE 2. X-RAY DATA FOR SYNTHETIC SERPENTINE PHASES*

Aluminian Serpentine $5 \text{ MgO} \cdot \text{Al}_2\text{O}_3$ $\cdot 3\text{SiO}_2 \cdot 4 \text{ H}_2\text{O}$		Magnesia-Germania $3 \text{ MgO} \cdot 2 \text{ GeO}_2$ $\cdot 2 \text{ H}_2\text{O}$		Nickel-Germania $3 \text{ NiO} \cdot 2 \text{ GeO}_2 \cdot 2 \text{ H}_2\text{O}$		Nickel-Silica $3 \text{ NiO} \cdot 2 \text{ SiO}_2 \cdot 2 \text{ H}_2\text{O}$	
<i>d</i> (Å)	<i>Int.</i>	<i>d</i> (Å)	<i>Int.</i>	<i>d</i> (Å)	<i>Int.</i>	<i>d</i> (Å)	<i>Int.</i>
7.17	s	7.46	vs	7.49	vs	7.26	vs
		4.70	m				
4.59	ms	4.62	mw	4.62	s, br		
		4.50	m			4.2	vw
		4.34	w				
		4.17	w				
		4.02	vw				
3.574	vs	3.73	vs	3.680	vs	3.629	s
		3.13	w				
2.64	w	2.76	w				
				2.690	m, br		
2.50	mw						
2.39	w	2.553	s	2.540	vs	2.50	ms
		2.488	w				
		2.332	vw				
2.000	vw	2.201	vw			2.14	m
		2.017	w				
		1.835	w				
1.536	vs						
1.502	w	1.569	m	1.559	s	1.52	m
1.412	w						

* Powder data obtained on GE-XRD-3 diffractometer using filtered Cu radiation.

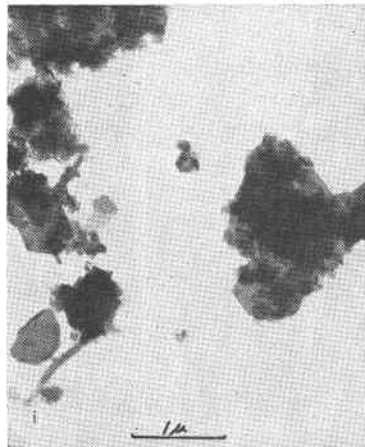
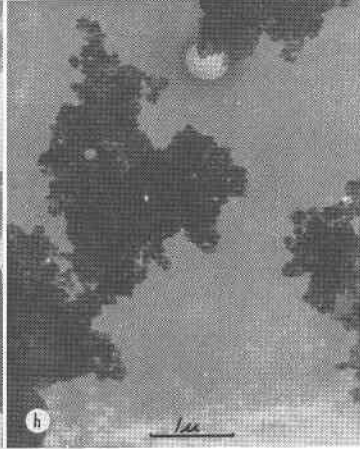
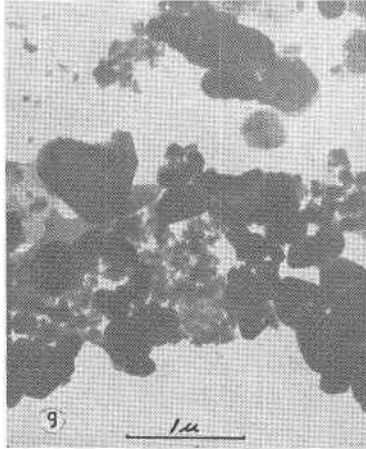
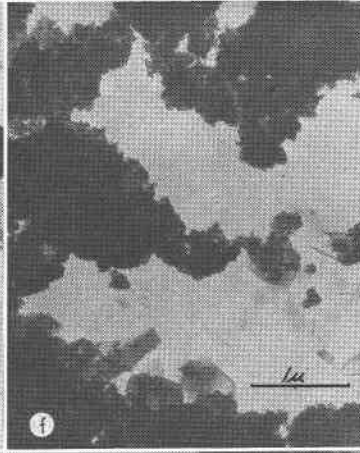
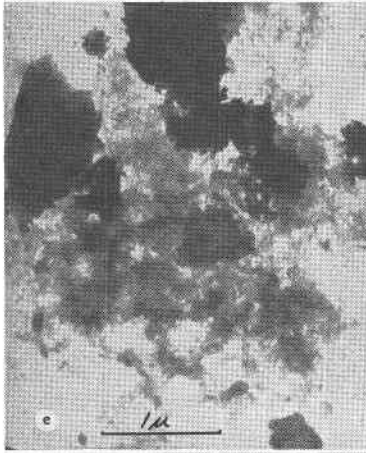
(a) *Substitution for Si.* The substitution of Ge^{4+} for Si^{4+} yielded a magnesia-germania serpentine, formed easily in euhedral hexagonal plates, which in some instances were even visible in the light microscope. Electron micrographs, Plate 1 (g) show this clearly and the sharp *x*-ray diffraction patterns confirm a plate-like rather than tubular, habit.

(b) *Substitution for both Si^{4+} and Mg^{2+} .* Al^{3+} was found to enter the serpentine structure, substituting for both Si^{4+} and Mg^{2+} , producing an "aluminian serpentine" of composition, $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$, which con-



EXPLANATION OF PLATE I

- (a) Synthetic Chrysotile, $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, formed at 390°C ., 10,000 psi, 408 hours.
- (b) Tubular serpentine, $3\text{NiO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ formed in presence of NaCl, 445°C ., 10,000 psi, 22 hours.
- (c) $3\text{NiO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ formed in presence of NaCl, 325°C ., 5,000 psi, 48 hours.
- (d) $3\text{NiO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ formed in presence of KCl, 450°C ., 10,000 psi, 24 hours.
- (e) $3\text{NiO}_2 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, no NaCl, formed at 325°C ., 5,000 psi, 190 hours.
- (f) $3\text{NiO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, no NaCl, formed at 500°C ., 10,000 psi, 90 hours.
- (g) $3\text{MgO} \cdot 2\text{GeO}_2 \cdot 2\text{H}_2\text{O}$, formed at 500°C ., 10,000 psi, 92 hours.
- (h) $3\text{NiO} \cdot 2\text{GeO}_2 \cdot 2\text{H}_2\text{O}$, formed in presence of KCl, 230°C ., 5,000 psi, 24 hours.
- (i) $5\text{MgO} \cdot 1\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$, formed at 600°C ., 10,000 psi, 384 hours.



sistently yields a sharp x -ray pattern and forms euhedral platy crystals (Plate 1 (*i*)). This phase is undoubtedly related to that reported in the more qualitative work by Tu (1949) and Bates, Sand and Mink (1950) wherein alumina-containing serpentines were prepared with a platy habit. Tu has referred to these as "antigorite" on the basis of morphology. Indeed, if morphology is the only criterion used to distinguish chrysotile from antigorite, it would be quite possible that natural antigorites should also be characterized by compositional differences such as increased R_2O_3 content (over that of chrysotile). The data in the literature are insufficient to confirm or deny such a hypothesis.

(*c*) *Substitution of divalent ions for Mg^{2+}* . Inasmuch as Mg^{2+} is about the smallest divalent ion which exists normally in sixfold coordination, the substitution of Mn^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} on the basis of size alone should yield tubular serpentine crystals. Ni^{2+} did yield a serpentine phase, as has been reported before (Voorthuysen and Franzen, 1950*a*, 1950*b*, 1951), but even in the absence of foreign ions—a condition not observed in other investigations. (See Plate 1 (*e*), (*f*).) In distilled water its habit was non-tubular, but no well-formed platy crystals were observed either. The misfit in this case would be expected to be as great or greater than with Mg^{2+} and if greater, perhaps the strain is so large that only very small curved fragments result. Mn^{2+} and Zn^{2+} do not form any layer lattice phase at all with Si, yielding only tephroite or hemimorphite, respectively, at the lowest temperatures (*vide infra*). The formation of tephroite was an indication that failure to form a serpentine at all cannot be ascribed to oxidation of the Mn^{2+} . Co^{2+} did not yield a serpentine-like phase, but this may be the result of failure to react at low temperatures.* Thus, it appears that Mn^{2+} , Zn^{2+} , and Co^{2+} are either too large or too polarizable to form a serpentine structure at all and that Ni^{2+} represents the largest divalent ion which can replace Mg^{2+} completely in the structure.

(*d*) *Further substitutions*. Inasmuch as a platy serpentine had been formed from MgO - GeO_2 mixtures, other oxides in combination with GeO_2 were tried to further delineate the possible chemical substitutions. NiO - GeO_2 mixtures yielded a definite 1:1 layer structure with a basal spacing of 7.50 Å (which is very close to that for the MgO - GeO_2 serpentine). Its habit was definitely non-tubular, but fine-grained platy. MnO - GeO_2 mixtures failed to yield any hydrous phase, and like in the MnO - SiO_2 system an olivine type structure (Ge-tephroite) was formed instead. Ga_2O_3 - GeO_2 mixtures did not yield any clay phase—possibly due to the

* Mixtures containing cobalt were prepared only by decomposing cobalt nitrate-ethyl silicate mixtures. It is possible that mixtures made from gels might react better at low temperatures, providing the cobalt remains in the divalent oxidation state.

experimental difficulties arising from the enormous differences in solubility; the mixture was made up by three different methods with no improvement in results. Ga_2O_3 - SiO_2 mixtures were tried, in attempt to form a kaolinite type structure which would serve as a possible end-member for substitution in the serpentine structure. No two-layer hydrosilicate was formed; but, a montmorillonite-type phase was synthesized from pure Ga_2O_3 - SiO_2 - H_2O mixtures. A close analogy between Ga^{3+} and Al^{3+} containing structures would be expected, since the former is only slightly larger, and should decrease the misfit in the octahedral layer—however it may be just too large to fit in the structure at all. (See Roy and Osborn, 1953, for discussion of Al-montmorillonite.)

B. INFLUENCE OF OTHER FACTORS ON MORPHOLOGY

That the layer-size is not the only and sufficient consideration in the formation of tubular crystals is suggested by the different results obtained by different workers. Noll and Kircher (1952) using a concentrated NaCl solution obtained well-formed tubes whereas in "neutral" water we were unable to do so. It was therefore considered worthwhile to investigate the influence of three other variables usually associated with this work: the temperature of growth, the length of time of growth and the presence of foreign ions. Results of the experiments are summarized in Table 1. The effect of pressure was not investigated extensively, although in only one system, $\text{MgO-Al}_2\text{O}_3$ - SiO_2 - H_2O , was there any indication that pressure played a role.*

1. *Presence of foreign ions.* NaCl solutions were added in concentrations up to 10% to the pure Ni-Si end member and the runs repeated. This yields, of course, a very much lower concentration of Na^+ and Cl^- than those used by Noll (op. cit.). However, an immediate and distinct difference was made in the habit of the resultant serpentine-phase; the rather poorly formed crystals of the pure end member were replaced by distinct tubes (see Plate 1 (b), (c)). The reason for this striking change is not at all clear. Whether the Na^+ ion acts merely as an "impurity" (such as methylene blue in the case of alums) which modifies the habit, or whether it is actually admitted into the structure, thus enhancing the misfit is not known. KCl additions were used in attempt to clarify this point. Ni-Si serpentine formed as tubular crystals in the presence of KCl (Plate 1 (d)); and in the case of Ni-Ge the platy structure was not

* Investigation of the polymorphism of the composition $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ (Roy and Roy, 1952) suggested that aluminian serpentine of this composition is metastable at higher temperatures, and yields to clinocllore. High pressures facilitate the conversion and clinocllore was not formed at all at pressures below 10,000 psi.

altered, but improvement in the size and shape of the hexagonal plates was observed (Plate 1 (*h*)).

The data in any case clearly showed the rather surprising influence of the presence of foreign ions on the morphology of these crystals. That the "misfit" is necessary to the formation of curved crystals is shown by the fact that Ni-Ge mixtures did not yield tubes with NaCl additions.

2. *Temperature.* Both pure and NaCl-containing Ni-Si mixtures were treated at successively higher temperatures to see whether the temperature of formation would have any influence on the morphology. No tubes were obtained from the pure member at any temperature, nor was there much evidence for enhancement of crystal size (Plate 1 (*e*), (*f*)). With the NaCl-containing mixtures, tubes were formed at both high and low temperatures in runs of short duration.

3. *Time.* Longer periods of time favored the formation of platy, rather than tubular crystals. In NaCl-containing samples treated for several days very few tubes remained, whereas one- or two-day runs yielded good tubular crystals. This may be the result of removal of Na^+ from the system, or may suggest that the tubes are really less stable, eventually yielding to the more stable platy structure.

C. SYNTHESIS AND STABILITY OF LAYER SILICATES

1. *MgO-SiO₂-H₂O.* Magnesium silicate serpentine ($3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) was prepared synthetically* by Bowen and Tuttle in their original study of the system MgO-SiO₂-H₂O and its limit of stability was reported to be $490 \pm 10^\circ \text{C}$. (at 10,000 psi). Our results were in agreement with this value; other relevant data are given elsewhere (Roy and Roy, 1952). The phase thus obtained was tubular. A remarkable "cone-in-cone" habit was noticed in several cases and may be seen in Plate 1 (*a*).

2. *MgO-Al₂O₃-SiO₂-H₂O.* The substitution of Al into the chrysotile structure has been demonstrated to produce a structure which is distinctly platy (see Plate 1 (*i*)), yet having an *x*-ray pattern characteristic of serpentine. As little as 1 mol. per cent alumina produced a distinct tend-

* In spite of this synthesis a rather surprising result was reported by Nagy and Bates (1952, 1953) in that an apparent so-called "weight loss" of nearly 20% is reported for natural chrysotile in water, which would of course preclude the possibility of its hydrothermal synthesis. However, chrysotile from Thetford, Que., dried at 110°C . was dispersed as long fibres by blending, re-dried and the weight loss determined after heating in distilled water at 80°C . for 2 hours. Expressed in gms./100 ml. this amounted to 0.16. Another sample (weighing 8 gms.) of chrysotile from Globe, Ariz., was dispersed in a similar manner, dried weighed and boiled at 100°C . with 400 ml. of distilled water. The total loss of weight amounted to 0.65% checked both on the residue and filtrate. This reasonable weight loss was probably due to ferruginous and organic impurities, as shown from the "amorphous to *x*-rays" nature and reddish color of the material obtained by evaporation of the filtrate.

ency toward a platy structure, although in the electron micrographs there was some indication of being mixed in part with tubular crystals. Substitution of 2Al for Mg+Si in the chrysotile formula gives the formula $Mg_5Al(AlSi_3)O_{10}(OH)_8$, which is the same as clinochlore. This composition indeed yielded a serpentine structure, consisting of well-developed hexagonal plates under the electron microscope.

Evidence that substitution of Al may extend even beyond the clinochlore composition is seen in the fact that compositions high in alumina yield an aluminian serpentine with a slightly smaller basal spacing than that of the clinochlore composition. Aluminian serpentine from the 5:1:3 composition had a basal spacing of 7.161; that from 75:15:10 was nearly the same, 7.163; whereas a higher alumina composition 50:30:20 had a spacing of 7.06, indicating further substitution of Al beyond the clinochlore composition, probably extending as far as the amesite composition (4:2:2 MgO:Al₂O₃:SiO₂). Electron microscopic examination of these mixtures indicated the absence of any tubular crystals.

Prolonged heating of the 5:1:3 composition at temperatures above 450° C. and pressures of greater than 15,000 psi produced partial conversion of aluminian serpentine to the presumably stable clinochlore structure. The true stability range of aluminian serpentine could not be definitely established, since reaction at low temperatures is very slow. Conditions favoring the stability of aluminian serpentine would no doubt be lower temperatures and relatively low pressures.

3. *MgO-GeO₂-H₂O*. The germanium serpentine, $3MgO \cdot 2GeO_2 \cdot 2H_2O$ is formed easily from intimate mixtures of very fine MgO and the quartz form of GeO₂ under conditions similar to those under which the silicon analogue grows. The decomposition temperature was found to be $520 \pm 15^\circ$ C. at 10,000 psi. This phase gives a well-defined powder x-ray pattern not showing the diffuseness of the chrysotile pattern, and has a basal spacing of 7.47 Å and a mean refractive index for the basal section of 1.600. Above the decomposition temperature the phases which appeared were $Mg_3Ge_4O_{10}(OH)_4$ (germanium talc) and Mg_2GeO_4 . The former had an x-ray pattern similar to magnesia-silica talc, except for the fact that the 001 line is not observed at all, with an expanded cell, whereas the latter was found to be isotropic, and with a spinel-like structure, having a refractive index of 1.76. No reference was found to such a phase in the standard tables or textbooks although it was later found that Goldschmidt (1931) in a study of the crystal chemistry of germanium had found that Mg_2GeO_4 has an olivine structure at high temperatures. In a footnote he refers to the fact that he was later able to prepare a spinel-like form at low temperatures with $a_0 = 8.3$. The inversion of the spinel

form to the olivine form was reported to take place (Jander, 1932) at 1065° C. We were able to prepare well-formed single crystals (octahedra) of the spinel form and also of the olivine form. The inversion is very sluggish and by the quenching technique using runs of 12-24 hrs. duration was found to be 1005° C. (see Table 2). X-ray measurements yielded a unit cell edge of 8.255 for the spinel form, and $a_0=4.915$, $b_0=10.295$, $c_0=6.020$ for the olivine form. Mason (1952) has noted the possible importance of the increase in density when olivine transforms to spinel as a mechanism for explaining both the second-order discontinuities in seismic data used to obtain information on the earth's structure. A figure of 9% is given (without reference) for the increase in density. From our data a value of 8.16% calculated on the olivine density basis is obtained. However, unless a compositional gradation is assumed it is unlikely that the olivine-spinel inversion could "begin to change—at a depth of 413 km and the change would become complete at a depth of 984 km" as stated by Mason (*loc. cit.*).

4. $NiO-SiO_2-H_2O$. Garnierite, the nickel-containing serpentine occurs in nature, and the synthetic phase may be regarded as an end-member or pure nickel garnierite. Mixtures were made by coprecipitating gels from weighed amounts of nickel nitrate and sodium silicate solutions, and electrolysing to remove the adsorbed Na^+ . Here also a serpentine structure ($3NiO \cdot 2SiO_2 \cdot 2H_2O$) is formed in a wide range of temperatures and pressures. The decomposition temperature at 10,000 psi was found to be much higher than expected, and indeed exceeded that of the magnesium analogue; a value of $530 \pm 15^\circ$ C. was assigned to this equilibrium temperature. The Ni-serpentine has a basal spacing of 7.35 Å, and on decomposition yields Ni-talc and Ni-olivine. The basal spacing of nickel-talc was 9.50 Å compared to 9.41 for the magnesian member.

Further investigation of the morphology of nickel serpentines revealed that the tubular structure (Noll and Kircher, 1952) was formed only when Na^+ was present. Sodium chloride was added to the nickel-silica gel in a ratio of about 1:10, and such mixtures treated hydrothermally for short periods yielded a serpentine structure having tubular crystals. Prolonged heating of similar mixtures, however, yielded no apparent tubes; and the electrolysized gels produced a platy, or non-tubular structure (*vide supra*).

5. $MnO-SiO_2-H_2O$. This system offered greater experimental difficulties than the ones mentioned earlier due to the easily variable oxidation state of manganese. Mixtures were made by mixing manganous carbonate with finely precipitated silica. No serpentine-like phase was encountered at any time during this study; this does not preclude the existence of such a phase in nature—as it has not been possible to synthesize many

naturally occurring minerals—but since the other serpentine structures form so easily this does indicate that such a structure is unlikely in nature. It was moreover surprising that no other hydrate of manganese and silica was encountered; instead tephroite was found to be stable in the presence of water as low as 250° C.; and no appreciable reaction was obtained at much lower temperatures.

6. $ZnO-SiO_2-H_2O$. Although no layered zinc silicate hydrates are known in nature we hoped to be able to synthesize such a phase. The mixtures were made by evaporating an alcohol-water solution of zinc nitrate and ethyl orthosilicate, and decomposing the product to leave only the oxides. Hemimorphite was the only hydrated phase encountered and this was identical with the natural mineral. Its decomposition temperature at 10,000 psi was found to be about 200° C., where it is replaced by willemite + water.

7. $CoO-SiO_2-H_2O$. In this system also no serpentine-like structure was obtained at all, the phase appearing most commonly being the olivine Co_2SiO_4 , with lattice dimensions very close to that of the magnesium olivine, forsterite. At low temperatures oxidation of Co^{2+} took place, giving rise to the spinel Co_3O_4 . It is possible that a serpentine phase might still be formed, however, if sufficiently reactive mixtures were used, providing the oxidation state of cobalt could be controlled.

8. $Ga_2O_3-SiO_2-H_2O$. The other family of layered silicates derive from the alumina-silica-water system, and the obvious ion which may be substituted here is Ga^{3+} for Al^{3+} . This was done in an attempt to prepare a gallium kaolinite, which in turn might be expected to form solid solutions with one of the serpentine minerals. Mixtures were made by two methods: (1) the coprecipitation of gallium nitrate and sodium silicate solutions, and electrolysing the gel and (2) mixing alcohol solutions of gallium nitrate and ethyl silicate and decomposing the evaporate.

No gallium-kaolinite was synthesized under any conditions tried, from 200° to 500° C. and pressures of 6,000 to 10,000 psi. However, a gallium montmorillonite containing essentially no other cations besides Ga^{3+} and Si^{4+} was obtained. This montmorillonite produced a fairly sharp x-ray diffraction pattern, and the basal spacings were expandable with ethylene glycol from 13.2 Å (dried at 110° C.) to 17.0 Å. Under the electron microscope the crystals showed a fairly typical montmorillonite habit, extremely thin plates and fuzzy particles, sometimes rolled around the edges.

9. $NiO-GeO_2-H_2O$. The composition, $3NiO \cdot 2GeO_2$ yielded a platy serpentine-like structure, similar to that in the system $MgO-GeO_2-H_2O$ system. The mixture was made by coprecipitating GeO_2 dissolved in water with a nickel sulfate solution. No appreciable amount of GeO_2 was pres-

ent in the filtrate, suggesting quite complete co-precipitation. The presence of KCl did not change the crystal habit, but developed larger plates. This phase was stable up to $358 \pm 16^\circ$ C. at 10,000 psi, above which it decomposed to yield a talc and a spinel phase.

10. *MnO-GeO₂-H₂O*. Inasmuch as Mn^{2+} was apparently too large to form a serpentine phase with Si^{4+} , combination with Ge^{4+} was tried instead. $MnCO_3$ and the quartz-form of GeO_2 were mixed, and at temperatures as low as 200° C. only an anhydrous orthosilicate resembling tephroite was formed, while below 150° C. no reaction was obtained. Hydrrous Mn^{2+} germanates must therefore exist, if at all, only at very low temperatures.

11. *Ga₂O₃-GeO₂-H₂O*. The composition $Ga_2O_3:2GeO_2$ was investigated for a possible kaolinite-type end member structure, in the hope that this might serve as a basis for substitution into the serpentine structure. Inasmuch as Ga^{3+} was apparently too large to form a kaolinite-type structure with Si^{4+} , it was thought that increasing the size of the four-coordinate ion also might result in a stable structure of this type. Several different methods of making mixtures were tried, but in no case was a hydrrous gallium germanate obtained. Gallia gels are rapidly converted to Ga-diaspore (Roy, Hill and Osborn, 1951), which is recrystallized under hydrothermal treatment at relatively low temperatures, while the GeO_2 is largely dissolved in the water before sufficient reaction takes place. At higher temperatures (about 415° C.) an apparently anhydrous gallium germanate was obtained, resembling one of the aluminosilicates of the sillimanite family.

12. *Fe₂O₃-SiO₂-H₂O*. Mixtures in this system were made up by coprecipitating gels from potassium silicate and ferric ammonium sulfate solutions, washing, and in one case electro dialyzing the samples. A mica-type phase was formed through hydrothermal treatment of the non-electro dialyzed samples at relatively low temperatures; i.e., about 300° C., due to the presence of K^+ as impurity. This phase is therefore a pure Fe^{+++} muscovite, with the Fe^{+++} in both octahedral and tetrahedral coordination. Electro dialyzed samples treated above about 350° C. did not form any compound, but yielded a mixture of cristobalite and hematite. At lower temperatures no crystallinity was observed in runs as long as two weeks.

13. *Cr₂O₃-SiO₂-H₂O*. Mixtures in this system were made up by various methods: coprecipitating gels from potassium silicate and chromium nitrate solutions; and by decomposing an alcohol solution of chromium nitrate and ethyl silicate. The results are only preliminary, like those in the Fe_2O_3 - SiO_2 - H_2O system, but no kaolinite type compound or other identifiable layer lattice compound was formed at temperatures as low

as 200° C. CrO(OH) was crystallized from some of the runs between 200° C. and 275° C.

D. COMPARISON OF EQUILIBRIA IN THE VARIOUS SYSTEMS

In Fig. 2 are given a series of triangles suggesting equilibria for the systems studied which show a general similarity. The data for MgO-SiO₂-H₂O are taken from Bowen and Tuttle (1949)* and the other systems are drawn very approximately for comparison, from the data obtained in the present study (see Table 3).

The small triangles denote combinations of three phases in equilibrium, throughout a given temperature range, for a constant water pressure of about 10,000 psi. For example, triangle II of the system NiO-SiO₂-H₂O shows the following equilibrium assemblages of three phases: Ni serpentine-Ni talc-H₂O and Ni serpentine-Ni forsterite-H₂O. At 530° C., with a constant water pressure of 10,000 psi the following four phases are in equilibrium: Ni serpentine \rightleftharpoons Ni forsterite + Ni talc + H₂O. Univariant curves describing the change in temperature of such reactions with change in pressure may be drawn, but the effect of pressure in the range used (between 2000 and 20,000 psi) was so small that this was not considered significant.

Significant transitions include the upper stability temperatures (Triangles II-III) for the serpentines (at 10,000 psi) which are (1) 490° C. for Mg-Si, (2) 520° C. for Mg-Ge, (3) 530° C. for Ni-Si, which are remarkably close; and (4) 360° for Ni-Ge, which is considerably lower. Stability limits for talc, show marked differences. Mg-Si talc is stable up to 780° C., whereas the Mg-Ge talc decomposes at about 600° C., and Ni-Si talc appears to be stable to a much higher temperature, about 850° C. (or slightly higher). The decomposition temperature of Ni-Ge talc was not determined. A comparison is shown in Fig. 2 (triangles III-IV).

The magnesia-silica amphibole, anthophyllite, exists in nature, but was produced only metastably in the hydrothermal studies of Bowen and Tuttle (i.e., it was never formed in equilibrium with excess H₂O). No anthophyllite phase was found in the NiO-SiO₂ system, but with MgO-GeO₂ a structure similar to anthophyllite was produced, consisting of well-formed long needle-like crystals of this phase. Difficulty in pursuing further the stability relations in the system MgO-GeO₂-H₂O was encountered because of the high solubility of GeO₂ in water at elevated temperatures and pressures.

The similarity among the upper stability temperatures for the ser-

* The only modification of the data of Bowen and Tuttle is the temperature for the reaction, brucite \rightleftharpoons periclase + H₂O (Roy, Roy and Osborn, 1953) which has been lowered from 890° C. to 635° C. at 10,000 psi.

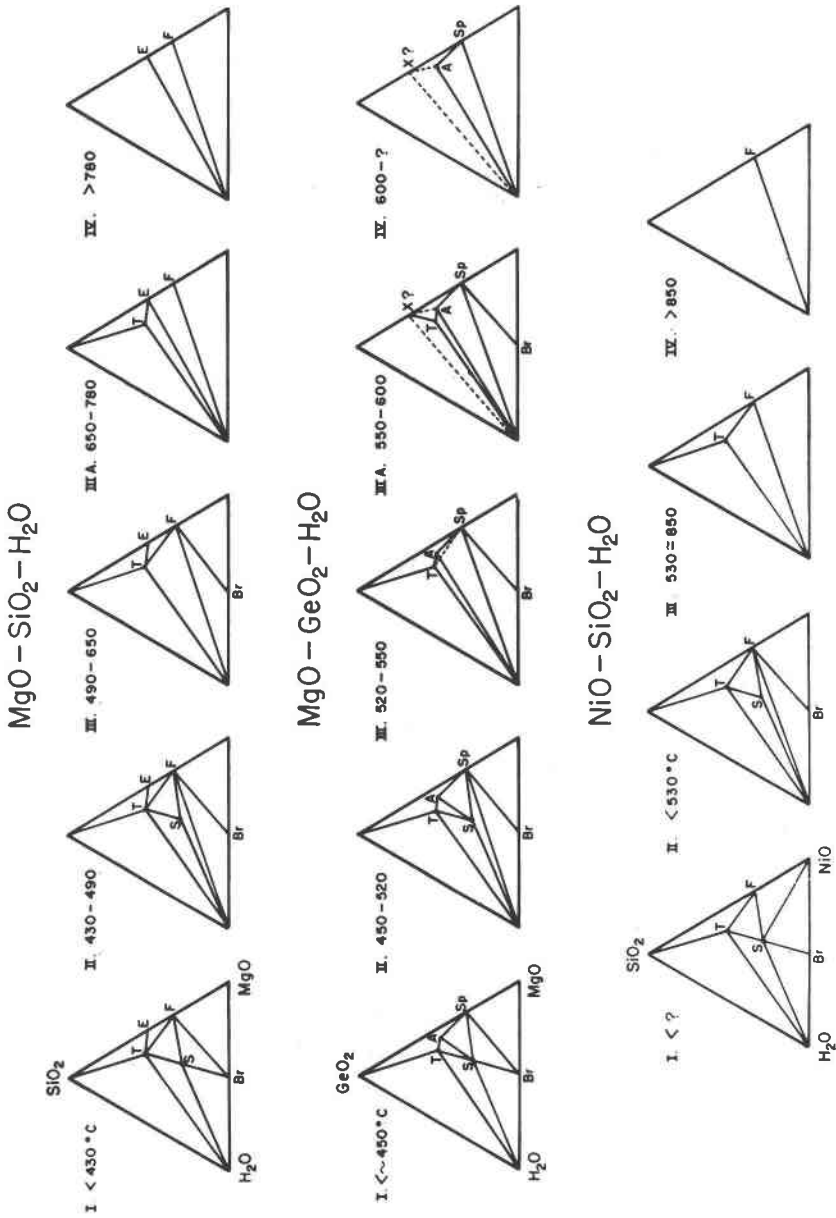


Fig. 2. Comparison of phase equilibria in the systems MgO-SiO₂-H₂O, MgO-GeO₂-H₂O and NiO-SiO₂-H₂O. Abbreviations used: T = talc, E = enstatite, F = forsterite, S = serpentine, Br = brucite, A = anthophyllite, Sp = spinel, X = unknown.

TABLE 3. PHASE EQUILIBRIUM DATA FOR THE SYSTEMS
MgO-GeO₂-H₂O, NiO-SiO₂-H₂O and NiO-GeO₂-H₂O

Composition Mol. Ratio	Temp. ° C.	Press. psi.	Time hrs.	Phases Present*
MgO-GeO ₂ -H ₂ O				
3 MgO:4 GeO ₂	200	10,000	24	talc
3 MgO:4 GeO ₂	370	4,000	24	talc
3 MgO:4 GeO ₂	500	10,000	74	talc+l. serp.
3 MgO:4 GeO ₂	550	10,000	49	talc+l. anth.
3 MgO:4 GeO ₂	650	10,000	24	anth+?
3 MgO:4 GeO ₂	800	5,000	½	spinel-?
3 MgO:2 GeO ₂	500	10,000	92	serp.
3 MgO:2 GeO ₂	450	20,000	120	serp.
3 MgO:2 GeO ₂	520	10,000	96	talc+l. serp.
3 MgO:2 GeO ₂	530	10,000	96	spinel+anth.
3 MgO:2 GeO ₂	650	10,000	24	anth.+spinel+?
2 MgO:GeO ₂	400	10,000	18	serp. mostly
2 MgO:GeO ₂	500	10,000	74	spinel+l. serp.
2 MgO:GeO ₂	550	10,000	49	spinel+l. anth.
2 MgO:GeO ₂	900	2,000	1	spinel
2 MgO:GeO ₂	1003		12	spinel+olivine
2 MgO:GeO ₂ (spinel) †	1003		12	spinel
2 MgO:GeO ₂	1012		36	olivine
2 MgO:GeO ₂ (spinel) †	1012		36	olivine
2 MgO:GeO ₂	1030		12	olivine
2 MgO:GeO ₂ (spinel) †	1030		12	olivine
3 MgO:GeO ₂	400	10,000	18	serp.+bru.
3 MgO:GeO ₂	645	5,000	18	spinel+per.
NiO-SiO ₂ -H ₂ O				
3 NiO:2 SiO ₂	180	5,000	29	serp.
3 NiO:2 SiO ₂	325	5,000	190	serp.
3 NiO:2 SiO ₂	400	8,000	216	serp.
3 NiO:2 SiO ₂	500	10,000	90	serp.
3 NiO:2 SiO ₂	520	10,000	25	serp.+talc+NiO?
3 NiO:2 SiO ₂	525	8,000	192	talc+ NiO? +olivine
3 NiO:2 SiO ₂	540	7,000	48	talc mostly
3 NiO:2 SiO ₂	650	5,000	24	talc+olivine
3 NiO:2 SiO ₂	835	5,000	5	talc+olivine
3 NiO:2 SiO ₂	900	5,000	1½	olivine+l. talc
3 NiO:2 SiO ₂	1200		14	olivine+trid.
NiO-GeO ₂ -H ₂ O				
3 NiO:2 GeO ₂	230	22,000	24	serp.
3 NiO:2 GeO ₂	318	10,000	144	serp.
3 NiO:2 GeO ₂	318	10,000	24	serp.
3 NiO:2 GeO ₂	342	10,000	24	serp.
3 NiO:2 GeO ₂	375	10,000	72	spinel+talc
3 NiO:2 GeO ₂	400	10,000	24	talc+spinel
3 NiO:4 GeO ₂	230	22,000	24	talc
3 NiO:4 GeO ₂	310	10,000	24	talc

* Abbreviations: l.=little, serp.=serpentine, anth.=anthophyllite, bru.=brucite, per.=periclase, trid.=tridymite.

† Starting material was spinel form; others were mixed oxides.

pentine structures in the MgO-SiO₂, NiO-SiO₂ and MgO-GeO₂ systems was not expected, especially in view of the similarity in decomposition products; i.e., they all give rise to talc+an orthosilicate type (either olivine or spinel type)+H₂O. One would naturally expect the higher covalency in the case of Ni to be reflected in a pronouncedly lower stability temperature, and similarly a lower temperature might also be expected for the stability limit of the Mg-Ge phase. Only in the case of NiO-GeO₂ was the expected lower stability temperature realized. In a very qualitative way this might indicate that the bonds responsible for the break-up of the serpentine structure are not M-OH bonds, but some bond or group common to all the serpentines and influenced only to a minor extent by the octahedrally coordinated ion. In other words, the weakest link in the chain may be the weak interlayer bonds, which are influenced only to a minor extent by the ions within the layers. The strength of the interlayer bonds will undoubtedly be affected by the extent of contrapolarization of the OH or O ions by the cation "within" the layer; but this should be relatively small.

The talc decompositions on the other hand, give rise to different products in each case, and generalizations as to the explanation for differences in maximum stability temperatures would involve very complex considerations, which will not be discussed here.

SUMMARY

A number of synthetic phases with the serpentine structure have been prepared hydrothermally. A comparison of their morphology supports the thesis that in such structures a "misfit" between layers is the basic cause for the formation of tubular crystals.

Other data show the secondary importance of the presence of foreign ions, temperature of formation, and length of run in conditioning this basic requirement.

A series of composition triangles are presented showing the sequence of phase assemblages stable at various temperatures for the systems MgO-SiO₂-H₂O, MgO-GeO₂-H₂O, and NiO-SiO₂-H₂O. A large number of new phases has been synthesized, and these are described briefly inasmuch as they affect the equilibria.

REFERENCES

- ARUJA, E. (1945), An x-ray study of the crystal structure of antigorite: *Mineral. Mag.*, **27**, 65-74.
- BATES, T. F., HILDEBRAND, F. A., AND SWINEFORD, A. (1950), Morphology and structure of endellite and halloysite: *Am. Mineral.*, **35**, 463-484.
- BATES, T. F., SAND, L. B., AND MINK, J. F. (1950), Tubular crystals of chrysotile asbestos: *Science*, **111**, 512-513.

- BOWEN, N. L., AND TUTTLE, O. F. (1949), The system $MgO-SiO_2-H_2O$: *Bull. Geol. Soc. Am.*, **60**, 439-460.
- FOCK, V. A., AND KOLPINSKY, V. A. (1940), *J. Phys. (USSR)*, **3**, 194.
- GOLDSCHMIDT, V. A. (1931), Zur Kristallchemie des Germaniums: *Nachr. Gesellsch. d. Wissensch. Göttingen, Math. Phys. Kl., Fachgr. IV*, Bd. I, 184.
- HILLIER, J. (1949), New worlds for study: *Scientific Monthly*, **69**, 161-168.
- JANDER, W., AND STAMM, W. (1932), The inner structure of solid inorganic compounds at higher temperatures. V. Electrical conductivity, diffusion, and reactivity of magnesium orthosilicate and magnesium orthogermanate in the solid state: *Zeit. anorg. Chem.*, **207**, 289-307.
- MASON, B. (1952), Principles of Geochemistry. John Wiley and Sons, Inc., New York.
- NAGY, B., AND BATES, T. F. (1952), Stability of chrysotile asbestos: *Am. Mineral.*, **37**, 1055-1058.
- NOLL, W. (1950), Zur Morphologie des Chrysotilasbestos: *Naturwiss.*, **37**, 540-541.
- NOLL, W., AND KIRCHER, H. (1952), Synthese des Garnierites: *Naturwiss.*, **10**, 233-234.
- PAULING, L. (1930), The structure of the chlorites: *Pro. Nat. Acad. Sci.*, **16**, 578-582.
- ROY, D. M. (1952), Phase equilibria in the system $MgO-Al_2O_3-H_2O$ and in quaternary systems derived by the addition of SiO_2 , CO_2 and N_2O_5 . *Ph.D. Thesis*, The Pennsylvania State University, Jan. 1952.
- ROY, D. M., AND ROY, R. (1952), Studies in the system $MgO-Al_2O_3-SiO_2-H_2O$: *Am. Mineral.*, **38**, 358. (Abstract).
- ROY, D. M., ROY, R., AND OSBORN, E. F. (1953), The system $MgO-Al_2O_3-H_2O$ and influence of carbonate and nitrate ions on the phase equilibria: *Am. Jour. Sci.*, **251**, 337-361.
- ROY, R., HILL, V. G., AND OSBORN, E. F. (1951), Polymorphism of Ga_2O_3 and the system $Ga_2O_3-H_2O$: *Jour. Am. Chem. Soc.*, **74**, 719-722.
- ROY, R., AND OSBORN, E. F. (1952), Some simple aids in hydrothermal investigation of mineral systems: *Econ. Geol.*, **47**, 717.
- ROY, R., AND OSBORN, E. F. (1954), The system $Al_2O_3-SiO_2-H_2O$, *Am. Mineral.*, **39**, 853-885. See also summary in "Problems of Clay and Laterite Genesis," *AIME*, New York (1952)
- ROY, R., ROY, D. M., AND OSBORN, E. F. (1950), Compositional and stability relationships among the lithium aluminosilicates: eucryptite, spodumene and petalite: *Jour. Am. Ceram. Soc.*, **33**, 152-159.
- TU, K. C. (1950), *Ph.D. Thesis*, University of Minnesota, Department of Geology.
- TURKEVITCH, J., AND HILLIER, J. (1949), Electron microscopy of colloidal systems: *Anal. Chem.*, **21**, 475-485.
- VOORTHUYSEN, J. J. B. VAN EIJK VAN, AND FRANZEN, P. (1950), Synthesis of nickel hydrosilicates: *Trans. Intern. Congress of Soil Sci., Amsterdam, 1950*, vol. III, pp. 34-37.
- (1950b), The influence of SiO_2 on the activity of nickel catalysts: *Rec. Trav. Chim.*, **69**, 666-667.
- (1951), The structure and properties of compounds formed during the preparation of nickel-on-silica catalysts: *Rec. Trav. Chim.*, **70**, 793-812.
- WHITTAKER, E. J. W. (1949), Structure of Bolivian crocidolite: *Acta Cryst.*, **2**, 312.
- (1952), Unit cell of chrysotile: *Acta Cryst.*, **5**, 143.
- YODER, H. S. (1952), The $MgO-Al_2O_3-SiO_2-H_2O$ system and the related metamorphic facies: *Am. Jour. Sci.* (Bowen vol.), 569-627.