Synthesis of Antigorite

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Abstract

Antigorite with a superlattice period of 33 to 38 Å has been synthesized at temperatures of 450° to 550°C, under pressures of 7,500 to 25,000 psi. Its formation depends on the molecular ratio of MgO to SiO_2 and, to a certain extent, on the amount of water present during the reaction but not on the presence of the cations Fe^{2+}, Fe^{3+}, Al^{3+} that are generally found in the natural specimens.

Introduction

Chrysotile, lizardite, and antigorite are the main minerals in the Serpentine Group. The former two have been investigated with various techniques: hydrothermal synthesis (Roy and Roy, 1954; Gillery, 1959; Page, 1966; Chernosky, 1971; Sylla, 1971), systematic chemical analysis of natural specimens (Faust and Fahey, 1962; Tomisaka and Kato, 1963; Page, 1968; Whittaker and Wicks, 1970), and crystal structure analysis of the natural specimens (Whittaker, 1953, 1956abc; Jagodzinski and Kunze, 1954abc; Rucklidge and Zussman, 1965; Krstanović, 1968). Detailed studies of antigorite have hitherto been concerned largely with natural specimens; however, it may be expected that many problems related to the formation of this mineral in nature could be elucidated by discovering the conditions of formation of synthetic antigorite.

Antigorite has an alternating wave structure with a superlattice along the a-axis (Aruja, 1945; Zussman, 1954; Kunze, 1961). According to Kunze (1961), its ideal formula varies systematically with the superlattice period between the theoretical limits $Mg_3Si_4O_{10}(OH)_2$ and $Mg_6Si_4O_{10}(OH)_8$. The most commonly observed compositions occur between $Mg_{5.40}Si_4O_{10}(OH)_{6.80}$ and $Mg_{5.68}Si_4O_{10}(OH)_{7.26}$ (Zussman, Brindley, and Comer, 1957; Kunze, 1961). Hess, Smith, and

Dengo (1952) suggested that its formation may be promoted by shearing. Page (1966) proposed its production by the progressive metamorphism of lizardite and chrysotile under conditions where $P_{H_2O} < P_{total}$. After re-examination of a statistical study by Page (1968), Whittaker and Wicks (1970) concluded that antigorite contains higher SiO_2, lower MgO and H_2O^+, and often a higher abundance of trivalent ions in the octahedral sheet than chrysotile or lizardite. Jasmund and Sylla (1971) reported the synthesis of Mg- and Ni-antigorite in a diluted alkaline suspension held at 320° to 350°C, under 200 to 250 atm for 170 hours, but later (Jasmund and Sylla, 1972) corrected their conclusions and stated that they had synthesized a 6-layer ortho-serpentine without Al and without any trace of an antigorite phase.

The present work has been initiated to determine the effect of variations in chemical composition and temperature and pressure on the formation of antigorite.

Experiments

The procedure for preparing the gels has been reported by Ikeda (1972). The calculated amounts of the standardized ethanolic solutions of magnesium nitrates and tetraethyl orthosilicate were dispensed from a burette and mixed with a magnetic stirrer. The solution was hydrolyzed by addition of NH_4OH and adjusted to a pH value of 12.5. The homogeneous mixtures of the desired compositions were obtained by magnetic stirring of the solution for 1

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TABLE 1. Experimental Results

Run No.	Starting material composition (Mol. ratio) Mg(OH)$_2$: SiO$_2$: H$_2$O			Temp. (°C)	Pres. (psi)	Serpentine varieties synthesized
S01	4.99	4.0	9.46	500	7,500	C
S02	5.36	4.0	5.14	500	7,500	C>>A
S03	5.61	4.0	6.88	500	7,500	C>>A
S04	5.82	4.0	6.48	500	7,500	C>>L
S05	6.16	4.0	13.77	500	7,500	C>>L
S06	5.46	4.0	1.52	500	7,500	C>>L
S07	5.46	4.0	5.61	500	7,500	C>>A,L
S08	5.46	4.0	7.55	500	7,500	C>>A,L
S09	5.46	4.0	14.56	500	7,500	C
S10	5.46	4.0	22.60	500	7,500	C
S11	5.46	4.0	10.92	300	7,500	C
S12	5.46	4.0	10.92	400	7,500	C,L
S13	5.46	4.0	10.92	450	7,500	L>C>>A
S14	5.46	4.0	10.92	500	7,500	C>A
S15	5.46	4.0	10.92	550	7,500	C>>A
S16	5.46	4.0	10.92	500	5,000	C
S17	5.46	4.0	10.92	500	15,000	C,A
S18	5.46	4.0	10.92	500	25,000	A>C

C: chrysotile, A: antigorite, L: lizardite.
>: more than twice, >>: more than ten times.
The relative amounts of the serpentine varieties were roughly estimated under the electron microscope by examining many different areas of the specimen.

hour, aging the precipitate on a water bath for 15 hours, adjusting the pH to the initial value, filtering the precipitate, and drying the precipitate in the air bath at 105°C. The starting materials were analyzed chemically before their use. MgO was determined by EDTA titration, SiO$_2$ by ordinary precipitation method, and H$_2$O through the ignition loss. The data for chemical composition of the starting materials presented in Table 1 are the results obtained from the gravimetric analysis.

Experiments were carried out with approximately 50 mg of gel and varying amounts of water in sealed silver capsules, each enclosed in a pressure vessel (Tuttle, 1949) held at 300° to 550°C ± 5°C, at a total pressure of 5,000 to 25,000 psi ± 500 psi for periods of 5 days.

The materials synthesized were examined with a Rigaku Denki Wide Range Diffractometer equipped with a curved-crystal monochromator and copper tube, operated at 35 kV, 15 mA, at a scan rate of 1/4° (2θ) per min. The transmission electron micrographs and electron diffraction patterns of synthetic materials were examined by using a JOEL JEM T7S type electron microscope operated at 60 kV. A small droplet of distilled water in which synthesized materials were suspended was dried in air on a microgrid reinforced with evaporated car-

bon. The interplanar spacings were determined from the diffraction pattern relative to diffraction rings of aluminum evaporated onto the specimens.

Results

The synthesis of antigorite was investigated by varying four parameters: the ratio of Mg(OH)$_2$ to SiO$_2$, the amount of water present during the reaction, the temperature, and the pressure. Results (Table 1) and typical electron micrographs and a selected area electron diffraction pattern of synthesized serpentine (Figs. 1, 2, and 3) reveal that antigorite, chrysotile, and lizardite were synthesized during the runs. Antigorite occurs as large crystals 0.3 to 1 × 1 to 4 microns in size (Fig. 1a) and
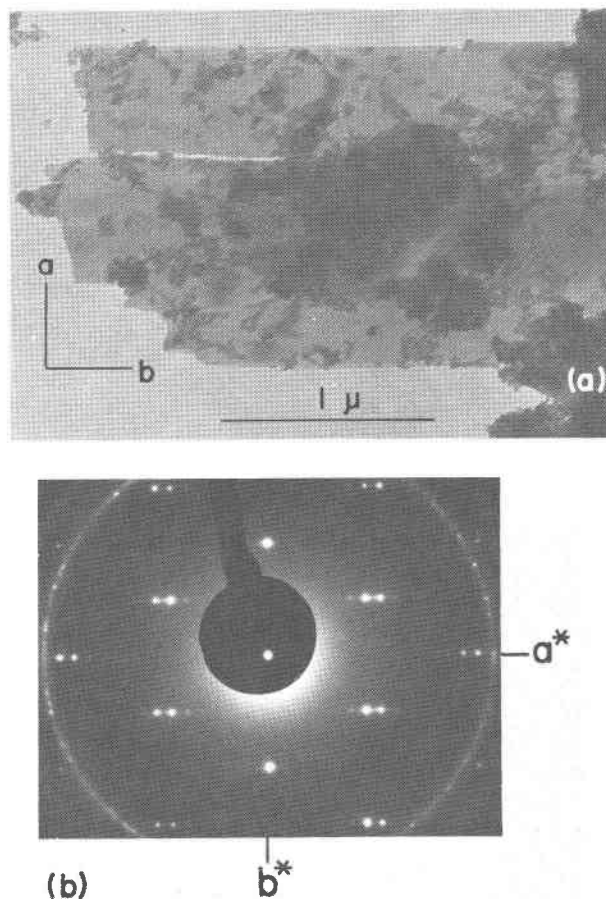

FIG. 1. Synthetic antigorite (S14) formed from a starting material with the composition of 5.46Mg(OH)$_2$·4SO$_2$·10.92H$_2$O held at 500°C, under a pressure of 7,500 psi and for a period of 5 days. (a) Electron micrograph showing large antigorite crystal. (b) Selected area electron diffraction pattern.
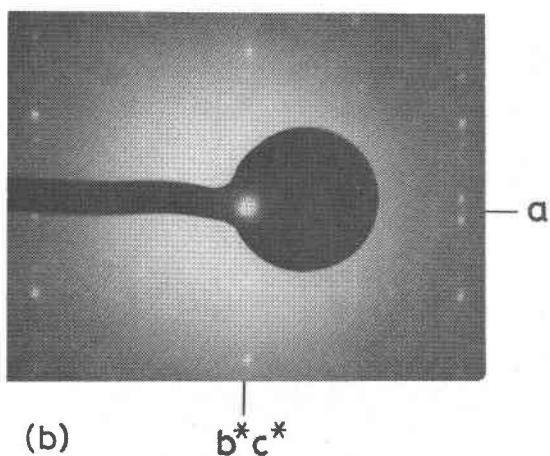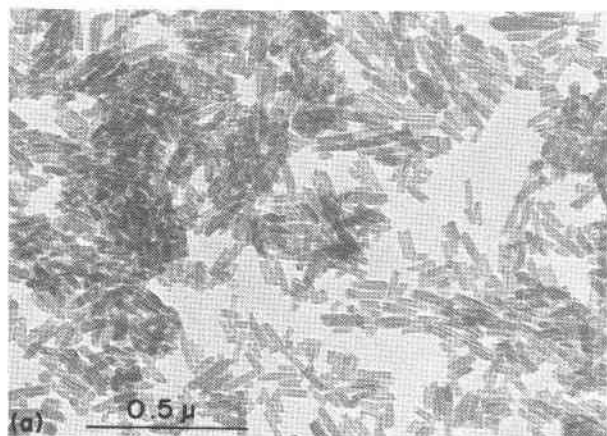
(a) 0.5 μ

(b) b*c*

FIG. 2. Synthetic clinochrysotile (S10) formed from a starting material with the composition of 5.46Mg(OH)₂ · 4SiO₂·22.60H₂O held at 500°C, under a pressure of 7,500 psi and for a period of 5 days. (a) Electron micrograph showing tube-like clinochrysotiles. (b) Selected area electron diffraction pattern.

Forsterite, the only material synthesized other than serpentine minerals, always formed at temperatures of 450° to 550°C. Unfortunately, the 131 and 112 relections of forsterite coincide with serpentine reflections that would distinguish clinochrysotile from orthochrysotile or lizardite. The X-ray diffraction evidence for antigorite, such as superlattice reflections or as the 1.563 and 1.541 Å pair of reflections, is not strong. Therefore the varieties of synthesized serpentine were determined by electron micrographs and electron diffraction patterns.

According to Kunze (1961), the periodicity along the a-axis of the serpentine superlattices varies from 5.09 Å to ∞ with accompanying variations in the molecular ratio of 3.0 to 6.0 MgO to 4 SiO₂. To
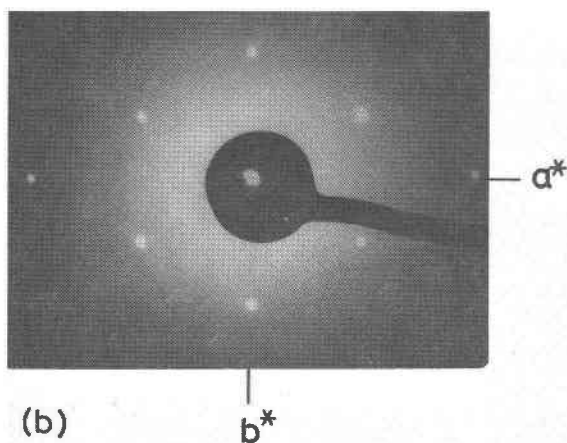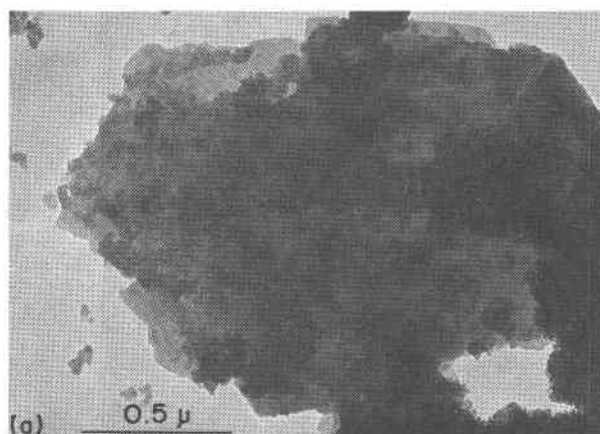

(a) 0.5 μ

(b) b*

FIG. 3. Synthetic lizardite (S13) formed from a starting material with the composition of 5.46Mg(OH)₂·4SiO₂· 10.92H₂ held at 450°C, under a pressure of 7,500 psi and for a period of 5 days. (a) Electron micrograph showing platy lizardites. (b) Selected area electron diffraction pattern.

yields an electron diffraction pattern typical of antigorite (Fig. 1b). The periodicity of its superlattice lies in the approximate range 33 to 38 Å, corresponding to compositions of $Mg_{5.60} \sim _{5.54}Si_4O_{10}$ $(OH)_{7.20} \sim _{7.08}$ (Kunze, 1961, Table 5). Chrysotile occurs as individual tubes, 0.04 to 0.8 microns long and about 0.02 microns in diameter (Fig. 2a), or in aggregates, or on the surface of the antigorite crystals (Fig. 1a), or associated with lizardite crystals (Fig. 3a). It is identified as clinochrysotile from electron diffraction patterns (Fig. 2b). Lizardite occurs as platy crystals 0.1 to 1.0 microns in size (Fig. 3a) which give an electron diffraction pattern like the one shown in Figure 3b. This hexagonal network yields the parameters $a = 5.3$ Å, $b = 9.2$ Å.

examine this relationship a series of 5 day runs (S01 to S05, Table 1) were carried out at 500°C under a pressure of 7,500 psi, with molecular ratios varying for MgO from 4.99 to 6.16 relative to 4.0 SiO_2.

In the range of $MgO:SiO_2 = 5.36$ to $5.61:4.0$, a few fairly large antigorite crystals were synthesized together with an abundance of minute chrysotile crystals. For ratios greater than 5.61:4, abundant chrysotile and a few lizardite crystals were produced. For ratios less than 5.36:4, minute chrysotile tubes and undetermined or unreacted material were observed.

The effect of the water content on the synthesis of antigorite was investigated by varying the water content of a series of runs (S06 to S10, Table 1) with the starting composition, $5.46Mg(OH)_2 \cdot 4SiO_2 \cdot 10.92H_2O$, as these were held at 500° C and 7,500 psi for 5 day periods. Table 1 shows that at a ratio of $14.56H_2O$ to $4SiO_2$ or greater, chrysotile was synthesized, and that at a ratio of 7.55 or $5.61H_2O$ to $4SiO_2$ a few fairly large-sized antigorite crystals formed along with an aggregate of minute chrysotile crystals.

The effect of temperature on the synthesis of antigorite was investigated by holding a material of composition $5.46Mg(OH)_2 \cdot 4SiO_2 \cdot 10.92H_2O$ at various temperatures between 300° and 550° C (S11 to S15, Table 1) at 7,500 psi for 5 day periods. Chrysotile was formed in all runs and large quantities of lizardite were formed in the 400° and 450° C runs. Moderate amounts of antigorite were synthesized at 500° C but only minor amounts at 450° and 550° C.

The effect of pressure on the synthesis of antigorite was investigated with three runs (S16 to S18, Table 1) at 5,000, 15,000 and 25,000 psi, each held at 500° C for 5 day periods, again with a starting composition of $5.46Mg(OH)_2 \cdot 4SiO_2 \cdot 10.92H_2O$. Only chrysotile formed at 5,000 psi, but successively increasing amounts of antigorite formed in the 15,000 and 25,000 psi runs.

Discussion and Conclusions

The runs at varying ratios of $Mg(OH)_2$ to SiO_2 suggest that a Mg : Si ratio below the ideal serpentine ratio is necessary for the synthesis of antigorite. The synthesis of antigorite in a $MgO-SiO_2-H_2O$ system also suggests that the presence of cations such as Fe^{2+}, Fe^{3+}, Al^{3+}, often found in the natural specimens, is not a prerequisite for the formation of the structure of antigorite. The structural reasons why the Mg : Si ratio is lower in antigorite than in the other serpentine minerals have been discussed by Zussman (1954) and Kunze (1956, 1958). The same chemical variation has been noted in natural specimens by Faust and Fahey (1962) and by Whittaker and Wicks (1970). The (OH) contents of these specimens also are slightly lower than that expected from the ideal serpentine composition.

The second series of runs suggests that the amount of water present during synthesis is an important controlling factor. There was always an excess of H_2O over that required for stoichiometry in the runs in the present study, but it was considerably less water than that used by previous researchers. The large amount of water added by previous workers may be the reason why only chrysotile, lizardite, or 6-layer ortho-serpentine were synthesized in their experiments. The reason for control of the synthesis of antigorite by the water content still remains to be discovered, but it may be related to the low OH content of antigorite mentioned above. This problem is now being studied theoretically in our laboratory. It appears clear, however, that the condition of $P_{H_2O} < P_{total}$ proposed by Page (1966) is not a prerequisite for the crystallization of antigorite since the antigorite was produced under the condition of $P_{H_2O} = P_{total}$ as determined from Kennedy's table (1950) relating the density of water to pressure at various temperatures. Also, since the synthesis was carried out under static conditions, it appears that shearing is not a necessary requirement for the formation of antigorite.

The series of runs with increasing temperature and increasing pressure suggests that the formation of antigorite is promoted by higher temperatures and pressures than those required for the formation of chrysotile or lizardite. These results are consistent with the DTA results of Faust and Fahey (1962) and with the fact that antigorite is the serpentine mineral most commonly found in higher grade metamorphic terrains (Jahns, 1967).

The experimental results recorded in this study indicate that antigorite is not a polymorph of chrysotile or lizardite.

References

ARUJA, E. (1945) An X-ray study of the chrysotile structure of antigorite. *Mineral. Mag.* **27**, 65–74.

BRINDLEY, G. W., AND O. VON KNORRING (1954) A new variety of antigorite (ortho-antigorite) from Unst, Shetland Islands. *Amer. Mineral.* **39**, 794–804.

CHERNOSKY, J. V. (1971) Minerals of the serpentine group. *Carnegie Inst. Washington Year Book,* **70**, 153–157.

FAUST, G. T., AND J. J. FAHEY (1962) The serpentine group minerals. *U. S. Geol. Surv. Prof. Pap.* **384A.**

GILLERY, G. H. (1959) X-ray study of synthetic Mg-Al serpentines and chlorites. *Amer. Mineral.* **44**, 143–152.

HESS, H. H., R. J. SMITH, AND G. DENGO (1952) Antigorite from the vicinity of Caracas, Venezuela. *Amer. Mineral.* **37**, 68–75.

IKEDA, K. (1972) Abstract from the report at the annual meeting of Mineralogical Society, June, Tokyo, Japan.

JAGODZINSKI, H., AND G. KUNZE (1954a) Die Röllchenstruktur des Chrysotils. I. Allgemeine Beugungtheorie und Kleinwinkelstreung. *Neues. Jahrb. Mineral., Monatsh.* **10**, 219–240.

———, AND ——— (1954b) Die Röllchenstruktur des Chrysotils. II. Weitwinkleninteferenzen. *Neues Jahrb. Mineral., Monatsh.* **6**, 113–130.

———, AND ——— (1954c) Die Röllchenstruktur des Chrysotils. III. Versetzungswachstum der Röllchen. *Neues Jahrb. Mineral., Monatsh.* **7**, 137–150.

JAHNS, R. H. (1967) Serpentinites of the Roxbury district, Vermont. *In,* P. J. Wyllie, Ed., *Ultramafic and Related Rocks.* John Wiley and Sons, Inc., N. Y., pp. 137–160.

JASMUND, K., AND H. M. SYLLA (1971) Synthesis of Mg- and Ni-antigorite. *Contrib. Mineral. Petrology,* **34**, 84–86.

———, AND ——— (1972) Synthesis of Mg- and Ni-antigorite: A correction. *Contrib. Mineral Petrology,* **34**, 346.

KENNEDY, G. C. (1950) Pressure-volume-temperature relations in water at elevated temperatures and pressures. *Amer. J. Sci.* **248**, 540–564.

KRSTANOVIĆ, I. (1968) Crystal structure of single-layer lizardite. *Z. Kristallogr.* **126**, 163–169.

KUNZE, G. (1956) Die gewellte Struktur des Antigorits, I. *Z. Kristallogr.* **108**, 82–107.

——— (1958) Die gewellte Struktur des Antigoritaes, II. *Z. Kristallogr.* **110**, 282–320.

——— (1961) Antigorit, Strukturtheoretishe Grundlagen und ihre praktishe Bedeutung für die weitere Serpentin-Forschung. *Fortschr. Mineral.* **39**, 206–324.

PAGE, N. J. (1966) *Mineralogy and chemistry of the serpentine group minerals and the serpentinization process.* Ph.D. Thesis, University of California, Berkeley.

——— (1968) Chemical differences among the serpentine "polymorphs." *Amer. Mineral.* **53**, 201–215.

ROY, D. M., AND R. ROY (1954) An experimental study of the formation and properties of synthetic serpentines and related layer silicate minerals. *Amer. Mineral.* **39**, 957–975.

RUCKLIDGE, J. C., AND J. ZUSSMAN (1965) The crystal structure of the serpentine mineral, lizardite $Mg_3Si_2O_5$ $(OH)_4$. *Acta Crystallogr.* **19**, 381–389.

SYLLA, H. M. (1971) *Synthetisierung und Mischkristallbildung von Mineralen aus der Serpentin-gruppe.* Dissertation, Universität zu Köln.

TOMISAKA, T., AND T. KATO (1963) A study on the polymorphs of serpentine minerals. *J. Mineral. Soc. Japan,* **6**, 209–229. (in Japanese).

TUTTLE, O. F. (1949) Two pressure vessels for silicate-water systems. *Geol. Soc. Amer. Bull.* **60**, 1727–1729.

WHITTAKER, E. J. W. (1953) The structure of chrysotile. *Acta Crystallogr.* **6**, 747–748.

——— (1956a) The structure of chrysotile. II. Clinochrysotile. *Acta Crystallogr.* **9**, 855–862.

——— (1956b) The structure of chrysotile. III. Orthochrysotile. *Acta Crystallogr.* **9**, 862–864.

——— (1956c) The structure of chrysotile. IV. Parachrysotile. *Acta Crystallogr.* **9**, 865–867.

———, AND F. J. WICKS (1970) Chemical differences among the serpentine "polymorphs": A discussion. *Amer. Mineral.* **55**, 1025–1047.

ZUSSMAN, J. (1954) Investigation of the crystal structure of antigorite. *Mineral. Mag.* **30**, 498–512.

———, AND G. W. BRINDLEY (1957) Serpentines with 6-layer orthohexagonal cells. *Amer. Mineral.* **42**, 666–670.

———, ———, AND J. J. COMER (1957) Electron diffraction studies of serpentine minerals. *Amer. Mineral.* **42**, 133–153.