

ANTIGORITE FROM THE VICINITY OF CARACAS, VENEZUELA*

H. H. HESS, R. J. SMITH, *Princeton University, Princeton, N. J.*,

AND

G. DENGO, *Dirección de Minería y Geología, Caracas, Venezuela.*

ABSTRACT

A chemical analysis of antigorite from Venezuela indicates the formula $Mg_7Si_5O_{13}(OH)_8 \cdot n H_2O$, rather than the formula for serpentine commonly given. *X*-ray diffraction data, thermal analysis data, optical and physical properties of the antigorite are given.

Field evidence indicates that the chrysotile type of serpentine goes to antigorite under dynamothermal conditions slightly higher than the chlorite-biotite subfacies of the greenschist facies. In the process chromite and magnetite are gradually resorbed and disappear leaving a rock composed entirely of antigorite.

INTRODUCTION

A monomineralic antigorite rock was found by Dengo in the course of making a geological map of the Federal District of Venezuela (Dengo, 1949). Inasmuch as antigorite has been the subject of considerable debate in petrological and mineralogical literature it was thought worth while to describe this specimen in some detail.

CHEMICAL COMPOSITION

Though much has been written on antigorite there are no superior chemical analyses of the mineral available in the literature so far as the writers are aware. An analysis by Peck is given in Table 1. The material analyzed is a rock consisting almost entirely of antigorite, the only impurity noted being a fraction of a per cent of unidentified dusty inclusions of fibrous character and having much lower indices of refraction than antigorite.

An attempt to recalculate the analysis into the usual serpentine formula, $Mg_6Si_4O_{10}(OH)_8$ shows a poor fit (columns 7 and 8, Table 1). It is evident that the Mg:Si ratio is close to 7:5. A number of trial calculations to determine the probable relationship of (OH) and H_2O in the mineral assuming Mg:Si = 7:5 resulted in arriving at columns 5 and 6 of Table 1 as the most likely solution. The formula deduced indicates 21 O(OH) of which 8 are (OH) and leaves a remainder of H_2O . What information is available in the literature indicates a rather wide range of variation in H_2O content—from slightly less than 12 weight per cent to somewhat over 14 per cent. This suggests that the number of molecules

* Princeton Investigations of Rock Forming Minerals, number 6.

TABLE 1. CHEMICAL COMPOSITION

	1	2	3	4	5	6	7	8
			Ion Ratios		Cations to 21 O(OH)	Theoretical	Cations to 18 O(OH)	Theoretical
SiO ₂	43.60	Si ⁺⁴	726 15½	741½	4.97	5	4.16	4
Al ₂ O ₃	1.03	Al ⁺³	20 4½					
Cr ₂ O ₃	.02	Cr ⁺³	—					
Fe ₂ O ₃	.90	Fe ⁺³	11					
FeO	.81	Fe ⁺²	11					
MnO	.04	Mn ⁺²	½					
MgO	41.00	Mg ⁺²	1017					
NiO	.16	Ni ⁺²	2					
CaO	.05	Ca ⁺²	1					
Na ₂ O	.01	Na ⁺¹	—					
K ₂ O	.03	K ⁺¹	1					
H ₂ O+	12.18	Ti ⁺⁴	—	1201	8.05	8	7.57	8
H ₂ O-	.08	H	1201					
TiO ₂	.01	O	3131					
	99.92	H ₂ O	78	78	1.40	1 to 3		

Analyst Lee C. Peck, Rock Analysis Laboratory, University of Minnesota.

Density 24° C/4° C = 2.607.

Approximate general formula: Mg₇Si₃O₁₈(OH)₈ · nH₂O, Ni⁺², Fe⁺², Mn⁺², etc., may substitute for Mg⁺² in part.

Al⁺³Al⁺³, Fe⁺³Al⁺³, Cr⁺³Al⁺³, etc., may substitute for Mg⁺²Si⁺⁴ to a limited extent.

of H₂O in the formula (represented by "n" in Table 1) might vary from n = 1 to n = 3. In the present analysis n is near the lower value, n = 1.4.

X-RAY DIFFRACTION DATA

The powdered antigorite was examined with a low powered Philips x-ray spectrometer. Three records were made using an iron target with a manganese filter and three with a copper target and nickel filter. The averaged values for three runs on each sample are given in Table 2, columns 2 and 3. In the conversion of 2θ to d spacings the tables made by Switzer, Axelrod, Lindberg and Larsen (1948) were used. In these K_α Cu is 1.5418 Å. and K_α Fe is 1.9373 Å. The estimated relative intensities are given in columns adjacent to the d spacings of columns 2 and 3 but are not directly comparable to the intensities of column 1.

Dr. H. S. Yoder of the Carnegie Geophysical Laboratory very kindly offered to run the same powder on a Philips x-ray spectrometer having greater accuracy with respect to 2θ and higher resolving power. His results are given in Table 2 column 1. The following pertinent data with

TABLE 2. X-RAY DIFFRACTION PATTERN

1		2		3	
Copper Target (Yoder)		Iron Target (aver. 3)		Copper Target (aver. 3)	
d_{hkl} Å	I	d_{hkl} Å	I	d_{hkl} Å	I
8.05	10	7.97	$\frac{1}{2}$	—	—
7.30	<400	7.23	8	7.34*	8
6.95	24	—	—	—	—
6.51	16	—	—	—	—
6.10	6	—	—	—	—
5.78	8	—	—	—	—
4.67	6	—	—	—	—
4.62	7	4.62	1	4.64	1
4.27	4	4.27	1	—	—
4.01	6	3.99	2	—	—
3.63	<300	3.612	10	3.625	10
3.51	24	—	—	—	—
2.88	2	—	—	—	—
—	—	2.777?	$\frac{1}{2}$	—	—
—	—	2.686?	$\frac{1}{4}$	2.685	$\frac{1}{4}$
2.59	4	—	—	—	—
2.57	8	2.554	$\frac{1}{2}$	—	—
2.52	70	2.522	5	2.531	6
2.46	9	2.443	$\frac{1}{2}$	2.462	$\frac{1}{4}$
2.42	38	2.419	6	2.429	1
2.39	9	2.392	$\frac{1}{2}$	2.399	2
2.35	5	2.286	$\frac{1}{2}$	—	—
2.237	6	2.239	$\frac{1}{2}$	2.243	$\frac{1}{4}$
2.208	7	2.199	$\frac{1}{4}$	2.209	1
2.167	22	2.163	6	2.167	3
2.150	20	—	—	—	—
2.126	4	2.119	$\frac{1}{2}$	—	—
2.035	4	2.032	$\frac{1}{2}$	—	—
1.886	3	1.884	$\frac{1}{2}$	—	—
1.830	12	1.833	$\frac{1}{2}$	1.833	$\frac{1}{2}$
1.815	23	1.813	4	1.820	2
1.781	14	1.779	2	1.784	1
1.755	4	—	—	—	—
1.736	10	1.733	2	1.738	$\frac{1}{4}$
1.688	2	—	—	—	—
1.640	2	—	—	—	—
1.584	3	—	—	—	—
1.560	12	1.559	$\frac{1}{2}$	1.559	1
1.540	9	—	—	—	—

* = 7.28 compared to Muscovite standard.

TABLE 2—(continued)

1		2		3	
Copper Target (Yoder)		Iron Target (aver. 3)		Copper Target (aver. 3)	
d_{hkl} Å	I	d_{hkl} Å	I	d_{hkl} Å	I
1.535	9	1.532	$\frac{1}{2}$	1.537	$\frac{1}{4}$
1.524	13	1.520	$\frac{1}{2}$	1.523	2
1.509	8	—	—	—	—
1.497	10	1.497	$\frac{1}{2}$	1.496	1
1.479	7	1.477	$\frac{1}{2}$	1.480	$\frac{1}{2}$
1.466	6	—	—	—	—
1.462	6	—	—	1.460	$\frac{1}{2}$
1.451	10	1.451	2	1.452	$\frac{1}{2}$
1.448	9	—	—	—	—
1.443	5	—	—	—	—
1.438	3	1.440	$\frac{1}{2}$	—	—
—	—	—	—	1.339	$\frac{1}{2}$
1.328	3	—	—	—	—
—	—	—	—	1.314	1
—	—	—	—	1.279	2
—	—	—	—	1.261	1
—	—	—	—	1.209	1

regard to the measurements were supplied by Yoder:

Dry powder, $-150 +250$ mesh x -rayed in shallow cell mount using Philips Geiger counter spectrometer. Copper radiation, nickel filter 25 Kv, 20 Ma, scan speed $\frac{1}{2}$ ° per minute, time constant 4 seconds, angular aperture 1°, receiving slit 0.006 inch, goniometer radius 170 mm. Calibrated with silicon using:

Plane	2θ (Cu K)
111 β	=25.654
220 α_1	=47.302
311 α_1	=56.122
400 α_1	=69.130
331 α_1	=76.376
422 α_1	=88.030

Error is approximately 0.01° 2θ over region investigated, intensities subject to error as probable result of preferred orientations in sample. Scale intensity arbitrary. Spacings based on Cu K_{α} =1.5418 Å in range 10°–40° 2θ and on Cu K_{α_1} =1.54050 for 40°–70° 2θ .

THERMAL ANALYSIS DATA

Thermal curves of the antigorite from room temperature to 1000° C. are given in Fig. 1. They show a strong endothermal peak at $782^{\circ} \pm 5^{\circ}$ C.

and a broad shallow endothermal peak starting a little above 100° C. The exothermal peak at 810° to 830° C. commonly reported for antigorite is absent. The broad shallow low temperature endothermal effect probably represents the loss of H₂O while the larger peak at 782° C. represents dissociation of the antigorite structure probably with loss of its (OH).

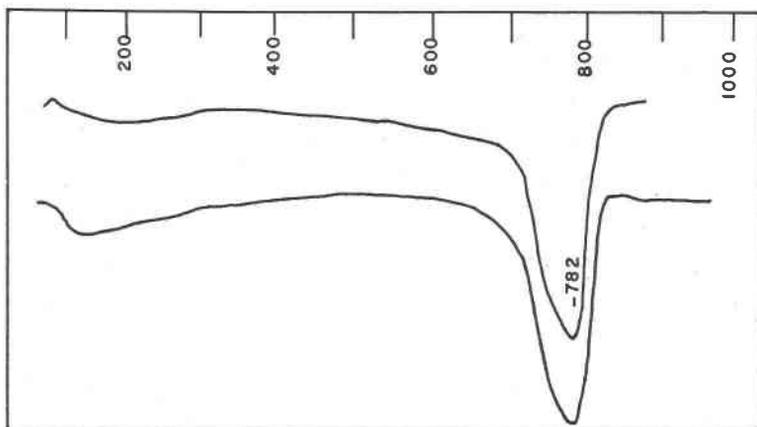


FIG. 1. Thermal curves for antigorite DF180. Scale along top of diagram is in degrees C.

PHYSICAL PROPERTIES

The antigorite rock is pale green in color, massive rather than foliated and has a dull luster rather than the resinous or the waxy luster common for serpentines. It is comparatively hard, approximately 3½ on Mohs scale.

The density determined on seven 20 milligram fragments with a Berman balance using toluene averaged 2.603, 23° C/4° C. A seven gram cube weighed in air and toluene gave a density of 2.609, 24° C/4° C.

Examination in thin section and in powders shows a well developed {001} cleavage. The presence of a {100} parting is indicated in the powders but is rarely seen in the thin sections.

The antigorite occurs in bladed aggregates. The crystals reach as much as a millimeter in length and are generally elongated parallel to *a*. There is considerable variation in grain size, some portions of the rock being exceedingly fine-grained aggregates.

OPTICAL PROPERTIES

The indices of refraction were determined by immersion methods using a temperature control cell on the microscope stage and sodium light. Taking advantage of the {100} parting and {001} cleavage the three principal indices of refraction were determined as follows with an accuracy of ±0.0005:

$$N_z = 1.5670$$

$$N_y = 1.5660$$

$$N_x = 1.5615$$

$$N_z - N_x = 0.0055$$

The optic angle was measured on the universal stage and found to be $47\frac{1}{2} \pm 1/2^\circ$ with dispersion $r > v$ moderate and sign negative.

Z is in the plane of the {001} cleavage and X is perpendicular to this cleavage so far as it was possible to determine. A very slight departure from parallel or perpendicular might be overlooked inasmuch as the cleavage traces are not quite straight as a rule and many of the antigorite blades have been slightly bent. The same difficulty arises in trying to measure the crystallographic angle β which is close to 90° . Y is parallel to the *b* crystallographic axis, assuming the cleavage represents {001} and the parting {100}.

Under crossed nicols the antigorite shows anomalous interference colors. This is one of the most distinctive features of most antigorite as compared to chrysotile. Grains oriented so that they show moderate to low path difference—in the grays—have a distinctly bluish tint.

PETROLOGICAL DATA AND CONCLUSIONS

Antigorite has not been found in laboratory investigations of the MgO-SiO₂-H₂O system, hence its field of stability is not known (Bowen and Tuttle, 1949). Two natural modes of occurrence have often been described: (1) in dynamothermally metamorphosed ultramafic igneous rocks; and (2) as bastite, a replacement of magnesian orthopyroxene in serpentinized periodotites. In the latter the bulk of the rock has been serpentinized to form chrysotile serpentine or serpophite, probably a variety of the same mineral.

Thus far the grade of metamorphism at which chrysotile serpentine goes to antigorite has not been determined. Smith, however, has found chrysotile serpentinites intruded into a sedimentary sequence in the Los Teques area, south of Caracas, Venezuela, which have suffered low grade metamorphism without alteration to antigorite. The sediments were originally tuffs, silicified tuffs, cherts, shales and a minor amount of limestone. Metamorphism altered them to phyllites with the following minerals characteristic: fine flakes of sericite and chlorite, recrystallized chert now fine-grained quartz aggregates, chloritoid, minor amounts of fine biotite locally and epidote. This assemblage represents the chlorite-biotite subfacies of the greenschist facies. Inasmuch as the serpentinite has been subjected to this metamorphism and has not developed antigorite, a higher degree of metamorphism must be required to produce the

change. In the northern portion of the area mapped by Smith metamorphic rocks belonging to the albite-epidote amphibolite facies are found. In these the serpentinites have been antigoritized. The rocks containing these serpentinites have probably suffered two episodes of metamorphism, one preceding and the other subsequent to the intrusion of the ultramafics. Whether the second stage of metamorphism was equivalent to the albite-epidote amphibolite facies, or slightly lower in grade, cannot be exactly determined. This places the grade at which antigoritization takes place as above the chlorite-biotite subfacies of the greenschist facies, but equal to or slightly less than the albite-epidote amphibole facies.

Antigorite develops generally in rocks which have been subjected to strong shearing stress, so far as the writers are aware. Pure thermal metamorphism such as where basaltic magmas intrude serpentinites does not generally result in the development of antigorite, even up to temperatures where regenerated olivine is being developed in the ultramafic (Leech 1949). This suggests that the reaction chrysotile→antigorite occurs at rather low temperature but is so sluggish that ordinarily it does not occur unless assisted by the catalytic action of shearing. Shearing alone, however, is evidently not enough to produce antigoritization or it would be found in the greenschists mentioned above. Both shearing and a temperature higher than that at which the greenschist facies develops must generally be necessary to promote this reaction even though antigorite may well be the stable phase at the temperature of formation of the greenschist facies. A favorable chemical environment may result in crystallization of antigorite without shearing as indicated below in the discussion of bastite.

THE FORMATION OF BASTITE

Bates and Mink (1950) postulate that chrysotile and antigorite are morphologically analogous to endellite and kaolinite crystallizing as tubes and plates, respectively. All of these are layered structures. In the case of chrysotile the silicon-oxygen layer of the unit cell is slightly smaller than the $\text{Mg}(\text{OH})_2$ layer thus resulting in curvature and the formation of tubes. Bates and Mink point out that antigorite commonly contains more Al_2O_3 than chrysotile. The substitution of 4Al for 6Mg in a small percentage of the structure would be sufficient to make the layers equal in size, thus eliminating the curvature. Inasmuch as olivine is virtually devoid of Al_2O_3 and magnesian orthopyroxene normally contains 1.5% of Al_2O_3 , the replacement of olivine by chrysotile and enstatite by bastite (antigorite) might thus be explained. If, however, the conclusion presented in the present paper that antigorite does not have the same Mg:Si

ratio as chrysotile, then the formation of the antigorite plates also may be explained on other grounds. The relative increase in Si^{+4} ions with respect to Mg^{+2} ions in the structure could also account for the lack of curvature of the antigorite plates. In this case the replacement of olivine by chrysotile and enstatite by bastite might be related to the higher silica content of pyroxene and antigorite relative to olivine and chrysotile.

ACKNOWLEDGMENTS

The field work during which the antigorite was discovered was carried out under the sponsorship of the Dirección de Minería y Geología of the Estados Unidos de Venezuela, A. Schwarck, Director. The laboratory work was a detail in a broad investigation of the Caribbean region being carried on under a contract between the Office of Naval Research and Princeton University (N6onr-27008).

The work of Aruja, Brandenberger, Epprecht and Niggli, Caillere, Gruner, Hargraves and Taylor, Hey and Bannister, Selfridge, Warren and Bragg and others on serpentines have formed much of the background for this paper but have not been particularly cited in the text.

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Manuscript received June 29, 1951.