NOTES ON THE STRUCTURE OF SERPENTINES

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INTRODUCTION

Warren and Bragg published notes on the structure of chrysotile, $H_4Mg_3Si_2O_9$, in 1930.[2] They were able to show that the fibres possess a double chain structure resembling closely that of the amphiboles. The chains are only loosely joined at right angles to their elongation, probably by residual valencies. Tentative figures for the atomic coordinates along the *a* and *b* axes of the structure were given. No attempt was made by Warren and Bragg to establish the coordinates along the fibre axis (*c* axis), but they concluded from the sharpness of certain reflections that the structure shows little if any variability along the *c* axis. On the other hand variability along the *b* axis is not only conceded but thought likely. The present writer was engaged in the preparation of a manuscript when a paper by Selfridge appeared.[3] He showed that the serpentines may be classified into two main divisions, those which possess a structure like chrysotile, and others which are like antigorite. These findings are in perfect agreement with the present investigation. Therefore, it is unnecessary to repeat Selfridge's conclusions. The present writer went further in the *x*-ray investigation, however, as will be shown.

X-RAY DATA

Iron and copper radiations were used for the powder photographs with the result that the number of lines obtained for the same range of interplanar distances is two to three times as great as those Selfridge recorded with molybdenum radiation. The mineral powders were mounted with collodion on silk thread. The powder rods obtained were 0.8 mm. in diameter. No corrections were applied to the interplanar spacings which are slightly too low for $d > 2.00$ Å. Experience has shown that with minerals like the serpentines, which give many diffuse lines, the probable error in measuring is in the neighborhood of $\frac{3}{4}$ per cent. The antigorite structures give better diffraction patterns than the chrysotiles, in which most lines are very broad and diffuse. But even in antigorite the lines with *h*0*l* indices are unusually wide, indicating some distortion or irregularity parallel to the *c* axis, since the *h*00 reflections are sharp and well defined in both structures.

[1] This study was aided by liberal grants from the Graduate School of the University of Minnesota.

[2] Warren, B. E., and Bragg, W. L.: *Zeit. Krist.*, vol. **76**, pp. 201–210, 1930.

[3] Selfridge, G. C. Jr.: *Am. Mineral.*, vol. **21**, pp. 463–503, 1936.

Tables 1 and 2 record the diffraction lines for chrysotile and antigorite structures. These tables were abridged after the appearance of Selfridge's paper.

TABLE 1. COMPARISON OF POWDER PHOTOGRAPHS OF CHRYSOTILES
Fe Radiation. Radius 57.3 mm.

		Thetford		Saganaga[1]		Chelmsford, Mass.	
No.	*Indices*	*d*	*I*	*d*	*I*	*d*	*I*
1				7.908	2	7.983	2
2	200	7.073	2	7.118	5	7.209	4
3				4.952	0.5	4.930	0.5
4		4.565	2				
5				4.457	2	4.457	3
6		4.380	1 ind.				
7		3.974	2	3.974	1	4.002	2
8	400	3.588	6	3.588	6	3.603	6
9				3.358	0.5		
10						3.013	1
11				2.856	0.5	2.849	1
12		2.706	0.5	2.727	0.5	2.712	0.5
13		2.588	1	2.573	2	2.577	3
14	$20\bar{2}$	2.549	1				
15	202	2.446	3	2.421	3	2.437	3b
16		2.299	0.5				
17	$40\bar{2}$	2.176	ind.				
18	402	2.085	1	2.078	1	2.080	0.5
19				1.903	0.5		
20	800	1.807	1	1.808	1	1.810	1
21		1.736	1	1.732	0.5	1.729	0.5
22		1.680	1	1.672	1	1.679	1
23				1.613	0.5		
24	$80\bar{2}$, 0120	1.519	3	1.519	4	1.520	4
25	802, 1000	1.450	1	1.449	1	1.452	1
26				1.401	0.5		
27	204	1.300	1	1.297	2b	1.299	2b
28	1200	1.209	0.5	1.210	1	1.212	1
29		1.187	ind.	1.189	0.5	1.190	0.5

b = broad.
ind. = indistinct.
[1] Lake Saganaga, Ontario-Minnesota boundary.

TABLE 2. POWDER PHOTOGRAPHS OF ANTIGORITES
Unfiltered Fe Radiation. Radius 57.3 mm.

		Antigorite		"Precious Serpentine"		"Picrolite"	
		Antigorio Valley, Italy		Montville, N. J.		Bohemia	
No.	*Indices*	*d*	*I*	*d*	*I*	*d*	*I*
1	200	7.16	6	7.12	6	7.21	6
2						5.13	0.5
3	040	4.66	0.5	4.61	1	4.68	1
4						4.23	0.5
5	400β	3.96	2	3.95	2	3.99	1
6				3.81	0.5		
7	400	3.588	7	3.592	7	3.603	5
8		3.480	0.5	3.490	0.5	3.483	0.5
9		2.798	1	2.784	1	2.802	1
10	061			2.677	0.5	2.663	0.5 ind.
11	20$\bar{2}$	2.521	4	2.514	4	2.524	4
12	202?			2.450	0.5		
13	600	2.402	1	2.411	2	2.397	1b
14				2.370	0.5		
15				2.210	0.5	2.228	ind.
16	40$\bar{2}$	2.152	1b	2.150	2b	2.152	1b
17				2.012	0.5		
18		1.986	0.5	1.962	0.5		
19				1.880	0.5		
20	60$\bar{2}$	1.848	0.5	1.831	1	1.843	0.5b
21	800	1.808	1	1.808	1	1.810	1
22				1.778	1	1.781	0.5
23	0120β	1.723	0.5	1.722	1	1.727	1
24		1.695	0.5	1.693	0.5	1.697	0.5
25						1.661	0.5
26				1.584	0.5	1.590	0.5
27	0120	1.562	3	1.560	3	1.563	3
28	063	1.538	2	1.536	2	1.538	2
29	80$\bar{2}$	1.529	1	1.522	1	}	1b
30		1.509	1	1.503	1	1.508 }	
31				1.494	1		
32		1.478	0.5	1.472	0.5		
33		1.454	0.5	1.459	0.5		
34	1000	1.442	1	1.446	1	1.446	1
35		1.417	0.5	1.410	0.5	1.415	0.5
36				1.381	0.5	1.383	0.5
37				1.358	0.5		
38		1.342	0.5	1.341	0.5	1.341	0.5
39				1.328	0.5		

TABLE 2 (*Continued*)

		Antigorite		"Precious Serpentine"		"Picrolite"	
		Antigorio Valley, Italy		Montville, N. J.		Bohemia	
No.	*Indices*	*d*	*I*	*d*	*I*	*d*	*I*
40	004?	1.315	1	1.312	2	1.314	1
41		1.298	0.5	1.295	0.5	1.297	0.5
42	204?			1.284	0.5	1.284	0.5
43				1.273	0.5	1.266	0.5
44		1.259	0.5	1.258	0.5		
45				1.244	0.5		
46	1200	1.201	1	1.206	1	1.205	1

b = broad.
ind. = indistinct.

It will be noticed that the values for d for planes with $h00$ indices are very similar in the two structures. Any other apparent similarity may be accidental, however. The indices which have been assigned to certain planes in Tables 1 and 2 are based on the assumption that the dimensions of the unit cell, as given by Warren and Bragg for chrysotile, are essentially correct and apply also to antigorite structures. The most accurate measurement is that of a_0 which varies between 14.40 Å and 14.52 Å for different varieties, b_0 varies between 18.50 Å and 18.74 Å, and c_0 between 5.28 Å and 5.36 Å. β is close to 93°. Making use of the atomic coordinates given by Warren and Bragg for the a and b directions, and of the intensities in the powder photographs, a great deal of time was spent in trying to find the c (or Z) coordinates. By shifting the double chains parallel to the c axis, but preserving the symmetry of space group C_{2h}^3, no very convincing agreement could be found between theoretical and observed intensities. The actual structure of chrysotile must vary therefore to some extent from the ideal one given by Warren and Bragg.

The minerals with antigorite structure give a greater number and better lines than chrysotile. On the assumption that this structure differs from chrysotile only in a shift of the chains parallel to c, no agreement could be found with observed intensities. It appears, therefore, that the structures are only closely similar to each other with respect to the $h00$ planes.

Very interesting observations were made on platy antigorite from

the type locality, the Antigorio Valley. This material evidently possesses a sort of cleavage due to an orientation of submicroscopic fibres or plates. This has been proved by taking x-ray photographs of small plates of the material inclined at different angles to the zero beam. Certain indices were assumed for lines in the powder photographs (Table 2). It was also suspected that the megascopic platy structure of antigorite was parallel to 100. When a plate was inclined to the zero beam in such a way that theoretically a certain plane should have reflected with unusual intensity,

TABLE 3. THEORETICAL AND OBSERVED REFLECTIONS FROM ORIENTED PLATES OF ANTIGORITE

Zero beam at indicated angles to plane of plate

Indices	Θ°	0°		22½°		45°		67½°		90°	
		right	left	right	left	right	left	right	left	right	left
		+	−	−	−	−	−	−	−	−	−
200	7°45′	++	+	−	+	+	+	−	−	−	−
		−	−	−	−	−	−	+	−	−	−
040	11 58	−	−	−	−	−	−	+	−	+	+
		+	−	−	++	−	−	−	−	−	−
400	15 37	++	+	−	+++	+	+	−	−	−	−
		−	−	+	−	+	−	+	−	+++	+++
20$\bar{2}$	22 31	−	+	+	+	++	−	+	+	+++	+++
		−	−	−	+++	−	−	−	−	−	−
600	23 43	−	−	−	+++	−	−	−	−	−	−
		−	+	+	−	+	−	+	+	+	+
40$\bar{2}$	26 40	−	+	+	−	+	−	+	+	+	+
		+	+	−	−	−	−	−	+	−	−
60$\bar{2}$	31 31	−	−	−	−	−	+	−	+	−	−
		−	−	−	++	−	+	−	−	−	−
800	32 18	−	−	−	++	−	++	−	−	−	−
		−	−	+	−	++	−	−	−	−	−
0120	38 12	−	+	+	−	++	−	−	−	+	+
		−	−	−	−	++	−	−	−	−	−
063	38 54	−	−	+?	−	+++	−	−	−	−	−
		+	+	−	−	−	−	+	+	+	+
80$\bar{2}$	39 10	+	+	−	−	−	−	+	+	+	+
		−	−	−	−	−	++	−	−	−	−
1000	42 04	−	−	−	+	−	+++	−	−	−	−
		−	−	+	−	++	−	+	−	−	−
004	47 16	−	+	+	−	++	−	+	−	+?	+?
		+	+	+	−	+	−	−	+	+	+
6120	47 16	−	+	+	−	+	−	−	−	+?	+?
		+	+	+	−	+	−	+	+	−	−
204	48 06	−	+	+	−	+	−	+	+	−	−

the observed reflection agreed as well as could be expected. These observations are tabulated in Table 3. The inclinations of the plates are given at the top of the table. "Right" and "left" refer to the position of the reflection on the film to the right or left of the zero beam, respectively. The sign + means a certain reflection is present, − indicates its absence. The number of + symbols indicate intensity. The upper rows are the theoretical expectations, the lower, the observed reflections.

The data indicate that the indices chosen for the reflections are most probably correct, although there is no way of distinguishing between $20\bar{2}$ and 202, $40\bar{2}$ and 402, $80\bar{2}$ and 802, respectively, as long as the β angle is unknown.

It is certain, however, that in platy antigorite the larger structural units have a parallel or subparallel arrangement with respect to the plane (100), and not with regard to any fibre axis. Whether that means that the antigorite structure is more sheet-like than chain-like is still unknown. This holds true in spite of the fact that some "picrolites" and "baltimorites," which unquestionably appear fibrous in the hand specimen, are identical in structure to antigorite. Massive serpentines like the precious variety from Montville, N. J. also have this structure. On the other hand, massive serpentine from the wall rock of a cross fibre vein of chrysotile shows the chrysotile structure.

Conclusions

The serpentines[4] are divided into two groups, the chrysotiles and antigorites. All other variety names, as already advocated by Selfridge, should be discontinued. The name serpentine should be used where it is impossible to distinguish between the two.

It is believed that dimorphism exists, as chemical analyses show no appreciable differences in the composition of the two structures. Often x-rays will be the only means for identification, since optical properties are very similar in chrysotiles and antigorites. Chrysotile possesses a chain structure as shown by Warren and Bragg. They assigned coordinates to the atoms in these chains for the a and b axes, and computed intensities of reflections for some of the prism and pinacoid planes (exclusive of the basal pinacoid). It is easy to assign atomic coordinates for the c direction on the assumption that the chains are undistorted in this direction. This was done and theoretical intensities for $h0l$ and other planes were calculated. These were in poor agreement with the observed

[4] Ishkyldite described by Syromyatnikov, *Am. Mineral.*, vol. **21,** p. 48, 1936, is excluded from this discussion.

intensities. Therefore, some adjustments in the coordinates of chrysotile, especially in the *a* direction, seem necessary.

The antigorite structure may be chain-or sheet-like. The platy mineral from the type locality shows a definite subparallel to parallel arrangement with respect to (100), and not with regard to any fibre axis.