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THE *X*-RAY STUDY OF SYNTHETIC Mg-Al SERPENTINES AND CHLORITES*

F. H. GILLERY
(Hydrothermal experimentation by *V. G. Hill*),† *The Pennsylvania State University, University Park, Pennsylvania.*

ABSTRACT

The effect of the hydrothermal conditions of synthesis on the production of the Mg-Al chlorite and the serpentine polytypes has been examined. The results show that temperature has the greatest effect on which mineral is produced and composition the greatest effect on which of three serpentine polytypes is produced.

The stability relations of the serpentines and chlorites are discussed.

INTRODUCTION

This investigation was undertaken in order to determine how the composition and the conditions of hydrothermal synthesis affect the polytypic variety of synthetic serpentines and chlorites. Detailed study of the serpentines and chlorites up to the present time has been concerned largely with natural specimens and several problems concerning the formation of these specimens may be elucidated by a study of the conditions of formation of the synthetic specimens. Roy and Roy (1954) and Yoder (1952) showed that two structures could be synthesized at the clinochlore ($5MgO \cdot Al_2O_3 \cdot 3SiO_2$) composition and that the 14 Å chlorite structure was in all cases the high temperature structure, while the 7 Å kaolin-type mineral variously called a serpentine, antigorite or septechlorite was formed at low temperatures. Nelson and Roy (1954) established that solid solution extended from near chrysotile to amesite ($4MgO \cdot 2Al_2O_3 \cdot 2SiO_2$) but were still unable to establish unequivocally whether or not the serpentines had any true stability range. The synthetic specimens were all made from gels of the general composition $(6-x)MgO$, $(4-x)\ SiO_2$, $x\ Al_2O_3$, which gives the formula $(Si_{4-x}Al_x)(Mg_{6-x}Al_x)O_{10}(OH)_8$ for the serpentines and chlorites produced by complete reaction. x had the values 0, 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.25, 2.50 for this particular investigation.

The temperatures used were between 400° C, and 620° C., hydrothermal pressures between 15,000 p.s.i. and 56,000 p.s.i., and times of treatment from a few minutes to about 30 days.

The procedure for preparing the gels has been described by Roy (1956) and the apparatus for treating the gels described by Roy and Roy (1954)

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* Contribution No. 57-55 from the College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

† At the time of this work V. G. Hill was a Research Associate in Geochemistry, The College of Mineral Industries, The Pennsylvania State University. He is now with the Ghana Geological Survey.

and Nelson and Roy (1954). In the present investigation the gels were reacted both in gold capsules with a buffering envelope, and in sealed gold capsules.

The treated specimens were examined by means of a North American Philips Wide Range Diffractometer, using a scanning speed of 1° (2θ)/min for routine identification, but for more accurate work, such as indexing, a scanning speed of $\frac{1}{4}$° (2θ)/min was used and the results were usually independently checked by means of powder photographs taken with a 114.6 mm diam. Norelco camera. The accurate cell parameters from indexed patterns were derived by a least squares procedure. using all the available reliable reflections and the indexing was finally rechecked using the accurate cell parameters.

The electron micrographs and electron diffraction patterns were taken by Mr. J. J. Comer, using an R.C.A. Model E.M.U.-2D electron microscope.

The conditions of the synthesis and phases produced by the compositions examined are shown in Table 1. Anomalies in the products of some of the treatments are due to incomplete reaction. The percentages of 6-layer serpentine given for some of the specimens are rough estimates and are given with respect to the total serpentine content and not the total of all components present.

THE POLYTYPIC VARIETIES PRODUCED

Chlorites were produced from compositions with $x>0.5$ treated at temperatures above about 500° C. at all the pressures examined, and for times exceeding a few days. Compositions with $x=0$, 0.25 and 0.5 produced a mixed phase of brucite or talc and forsterite with some chlorite. No polytypic varieties were observed within the chlorite species, but many of these varieties can be distinguished only by using single crystal methods, a technique not possible in the present investigation due to the small particle size of the synthetic specimens.

The serpentine-type structure was produced by treating the starting gels at temperatures below about 500° C. and with all the pressures and compositions examined. Three polytypic varieties of serpentines were distinguished and their occurrence was found to depend mainly upon the composition of the gel. One of the polytypes was shown by the electron microscope to be of the fibrous type and was only produced by the composition with $x=0$. This type of serpentine can almost certainly exist with values of $x>0$ but evidently not with x as great at 0.25 which was the next composition examined.*

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* Nagy and Faust (1956), carried out a survey of natural serpentines and stated that natural fibrous serpentines can contain up to about 4% Al_2O_3 in the structure which corresponds to $x=0.2$ in the present nomenclature.

TABLE 1. DATA FOR THE SPECIMENS EXAMINED

Comp.	Temp. ° C.	Pres. p.s.i.	Time days	Phases present	c_0(Å)	% 6-layer
0.25	610	50,000	4	Fors., Bru.	—	—
0.50	610	50,000	4	Fors., Bru.	—	—
0.75	610	50,000	4	Chl., l Serp.	—	—
1.00	610	50,000	4	Chl.	—	—
1.50	610	50,000	4	Chl.	—	—
2.00	610	50,000	4	Serp., Chl., l. Spin.	—	—
2.25	610	50,000	4	Serp., Spin., l. Chl.	—	—
2.50	610	50,000	4	Serp., Spin., l. Chl.	—	—
0.25	445	40,000	18	Fors., Bru., l. Serp.	7.226 Å	—
0.50	445	40,000	18	Serp.	7.258 Å	—
0.75	445	40,000	18	Serp.	7.208 Å	—
1.00	445	40,000	18	Serp.	7.152 Å	—
1.50	445	40,000	18	Serp.	7.096 Å	—
2.00	445	40,000	18	Serp.	7.048 Å	—
0.25	450	15,000	41	Serp., Chl., Bru., Fors.	—	—
0.50	450	15,000	41	Serp., Fors.	7.228 Å	0%
0.75	450	15,000	41	Serp.	7.238 Å	5%
1.00	450	15,000	41	Serp.	7.156 Å	25%
1.50	450	15,000	41	Serp.	7.102 Å	85%
2.00	450	15,000	41	Serp.	7.052 Å	90%
2.25	450	15,000	41	Serp., l. Spin., l. Cor.	7.054 Å	—
2.50	450	15,000	41	Serp., l. Spin., l Cor.	7.054 Å	—
0	450	45,000	15	Serp.	—	—
0.25	450	45,000	15	Serp., l. Fors.	7.162 Å	10%
1.00	450	45,000	15	Serp.	7.140 Å	50%
2.25	450	45,000	15	Serp., Cor.	7.042 Å	—
2.50	450	45,000	15	Serp., Spin., Cor.	7.044 Å	—
0	400	5,000	15	Serp.	—	—
1.00	600	35,000	19	Chl.	—	—
1.50	600	35,000	19	Chl.	—	—
2.00	600	35,000	19	Chl.	—	—
0	620	40,000	0.2	Talc., Fors.	—	—
0.25	620	40,000	0.2	Fors., Bru., Talc, Spin.	—	—
0.50	620	40,000	0.2	Fors., Serp.	7.220 Å	—
0.75	620	40,000	0.2	Serp., Fors., Talc	7.176 Å	10%
1.00	620	40,000	0.2	Serp.	7.140 Å	25%
1.50	620	40,000	0.2	Serp.	7.084 Å	85%
2.00	620	40,000	0.2	Serp., Spin.	7.060 Å	100%
0	620	50,000	0.4	Talc, Fors.	—	—
0.25	620	50,000	0.4	Fors., Bru., Spin.	—	—
0.50	620	50,000	0.4	Fors., Bru.	7.186 Å	0%
0.75	620	50,000	0.4	Serp., Fors.	7.180 Å	5%
1.00	620	50,000	0.4	Serp.	7.134 Å	35%
1.50	620	50,000	0.4	Serp.	7.076 Å	90%
2.00	620	50,000	0.4	Serp., Spin.	7.068 Å	100%

TABLE 1 (*continued*)

Comp.	Temp. ° C.	Pres. p.s.i.	Time days	Phases present	c_0(Å)	% 6-layer
0	400	35,000	16	Serp., Bru.	7.308 Å	—
0.75	400	35,000	16	Serp., Fors.	7.202 Å	5%
1.00	400	35,000	16	Serp.	7.140 Å	25%
1.50	400	35,000	16	Serp.	7.082 Å	95%
2.00	400	35,000	16	Serp., Spin.	7.040 Å	75%
0	400	56,000	19	Serp., Fors., Bru.	—	—
0.75	400	56,000	19	Serp.	—	—
1.00	400	56,000	19	Serp., l. Bru.	—	—
1.50	400	56,000	19	Serp.	—	—
2.00	400	56,000	19	Serp., l. Spin.	—	—
1.00	600	20,000	12 min.	Serp.	—	—
1.00	600	25,000	15 min.	Serp.	—	—
1.00	600	40,000	20 min.	Serp.	—	—
1.00	600	40,000	60 min.	Serp.	—	—
1.00	600	40,000	120 min.	Serp.	—	—
1.00	600	40,000	240 min.	Serp.	—	—
1.00	600	40,000	960 min.	Serp.	—	—
1.00	600	40,000	0.75	Serp.	—	—
1.00	600	40,000	1	Serp.	—	—
1.00	600	40,000	2	Serp., Chl.	—	—
1.00	600	40,000	4	Chl., Serp.	—	—

Chl.—Chlorite, Cor.—Corundum, Bru.—Brucite, Fors.—Forsterite, Serp.—Serpentine, Spin.—Spinel, l.—little.

The other two polytypic varieties are shown by electron micrography to be platy. One which is produced in the low aluminum compositions (x small) can be indexed on the basis of a 1-layer ortho cell (Table 2) and shows much disorder in the b direction. The other is produced in the high aluminum compositions (x large) and can be indexed on the basis of a 6-layer ortho cell (Table 3). The two structures occur together in the medium aluminum compositions.

The cell parameters of the two platy structures show a progressive decrease as x increases (see Table 1). The amount of the 6-layer structure produced increases slightly in relation to the 1-layer as the hydrothermal pressure is increased and further, the basal spacing decreases with increased hydrothermal pressure. The two platy structures must be closely interrelated when they occur together, since despite the different conditions of formation and related change in parameters of the different specimens examined, the x-ray reflections common to the two structures are never resolved into two components or even broadened. The interatomic distances must therefore be almost the same in the two structures. The findings are summarized in Fig. 1.

TABLE 2. LATTICE SPACINGS, INDICES AND INTENSITIES FOR 1-LAYER ORTHO SERPENTINE

d, Å camera	*d*, Å diffractometer	*d*, Å calc.	I/I_0	*hkl*
7.22	7.25	7.25	60	001
4.61	4.61	4.62	20	020
3.89	3.91	3.90	5	021
3.617	3.619	3.624	60	002
2.659	2.655	2.669	5	200
2.504	2.503	2.505	100	201
	2.415	2.416	10	003
2.148	2.148	2.149	35	202
	1.807	1.812	5	004
1.791	1.788	1.791	15	203
1.745	1.744	1.747	5	310
1.543	1.541	1.541	25	060
1.510	1.507	1.507	20	061
1.497	1.496	1.499	15	204
1.447	1.448	1.450	5	005
1.420	1.418	1.418	5	062
1.332	1.329	1.334	5	400
1.313	1.312	1.312	10	401
1.299	1.299	1.299	5	063
1.272	1.274	1.274	5	205
1.253	1.254	1.252	5	402
1.168	1.163		5	

Specimen composition 21 $MgO.3Al_2O_3.13SiO_2$ treated hydrothermally for 41 days at 450° C. and 15,000 psi.

Cell parameters $a=5.338$ Å, $b=9.245$ Å, $c=7.249$ Å, (CuKα radiation 1.54178 Å).

THE PROCESS OF CRYSTALLIZATION OF A GEL

The growth of crystallization of a gel with composition $x=1$, treated at 600° C. and 40,000 p.s.i. for times varying from 10 min to several days has been studied. Under the conditions employed, a gel should produce a chlorite when stability is reached and this is the product after several days treatment. However, after several hours the product is not a chlorite in any state of crystallization but a mixture of 1- and 6-layer serpentines such as would be expected by treating this composition at temperatures less than 500° C. The increase in crystallization is rapid and after about 20 minutes the pattern given by a mixture of 1- and 6-layer serpentines can be recognized although the reflections are broad. After about 50 hours the reflections of a well-crystallized serpentine mixture begin to decrease in intensity and those of a well-crystallized chlorite to appear. From the first appearance of the serpentine reflections

Table 3. Lattice Spacings, Indices and Intensities of 6-Layer Ortho Serpentine

d, Å Camera	*d*, Å Diffractometer	*d*, Å calc.	I/I$_0$	*hkl*
7.08	7.09	7.10	100	006
4.59	4.59	4.597, 4.570	35	020, 021
4.493	4.511	4.493	5	022
4.212	4.236	4.221	5	024
3.842	3.857	3.859	5	026
	3.658	3.669	5	027
3.544	3.551	3.552	100	00, 12
	3.474	3.480	5	028
3.289		3.299	5	029
3.127		3.125	5	02, 10
2.816		2.811	5	02, 12
	2.655	2.654	15	200
2.635	2.635	2.634	55	202
	2.613	2.609	25	203
2.571	2.576	2.575	40	204
2.531	2.534	2.534	15	205
2.486	2.487	2.486	35	206
	2.429	2.433	15	207
2.379	2.377	2.375	80	208
2.315	2.315	2.315	10	209
2.250	2.254	2.253	15	20, 10
2.126	2.125	2.126	5	20, 12
2.001	2.001	2.001	30	20, 14
1.937	1.939	1.940	10	20, 15
1.881	1.881	1.880	5	20, 16
1.769	1.768	1.767	5	20, 18
1.735	1.735	1.737, 1.736, 1.731	5	310, 311, 312
1.661	1.662	1.662	15	20, 20
1.608	1.609	1.611	5	20, 21
1.562	1.561	1.561, 1.565	10	31, 12, 20, 22
1.533	1.534	1.532	65	060
1.500	1.499	1.498	10	066
1.470	1.474	1.472, 1.476	5	068, 20, 24
	1.422	1.421	5	00, 12
1.407	1.408	1.407	10	06, 12
	1.392	1.395	5	20, 26
1.352	1.352		5	
1.321	1.325	1.327	10	400
	1.318		10	
1.287		1.286	10	06, 18
1.269			5	

Specimen of composition 9 MgO.3Al$_2$O$_3$.5SiO$_2$ treated hydrothermally for 41 days at 450° C. and 15,000 psi.

Cell parameters $a = 5.308$ Å; $b = 9.193$ Å; $c = 42.62$ Å (CuKα radiation 1.54178 Å).

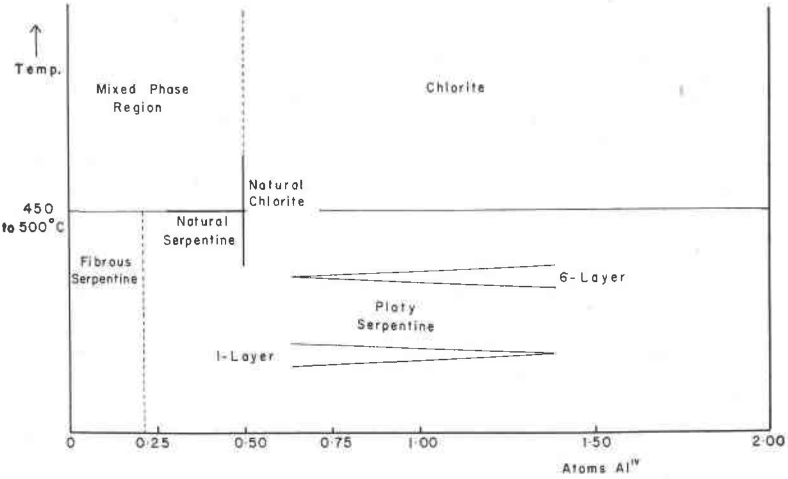

FIG. 1. The relation of the phases found.

to their complete disappearance, the relative amounts of 1- and 6-layer materials remain fixed.

COMPARISON OF THE SYNTHETIC MINERALS WITH THEIR NATURAL EQUIVALENTS

The *x*-ray powder diagrams of the synthetic chlorites appear to be essentially identical with those of natural chlorites. Comparison of careful measurements of the basal spacings of the natural and the synthetic specimens indicate the difference shown in Fig. 2.

The *x*-ray diagrams of the fibrous serpentines appear to be identical with the corresponding natural chrysotiles examined in detail by Whittaker and Zussman (1956). The electron micrographs, however, show the peculiar cone-in-cone effect (Bates, Sand, and Mink, 1950), which has not been noticed in natural specimens.

Several 1-layer specimens of platy serpentines were also described by Whittaker and Zussman (1956) and called lizardites. These appear to be identical with the synthetic 1-layer serpentines. It appears that two types of 6-layer structure exist, one which approximates to a 3-layer cell with *hkl*, $l=2n$ usually more intense than $l=2n\pm1$ (6(3) layer structure), and one which approximates to a 2-layer cell with *hkl*, $l=3n$, usually more intense than $l=3n\pm1$ (6(2) layer structure). The 6(3) layer structure is found in the synthetic specimens investigated. The 6(2) layer structure has been produced hydrothermally in the MgO-GeO_2-H_2O system (Roy and Roy 1954) and has been found naturally (see Brindley and von Knorring, 1954, and Zussman and Brindley, 1957). It approxi-

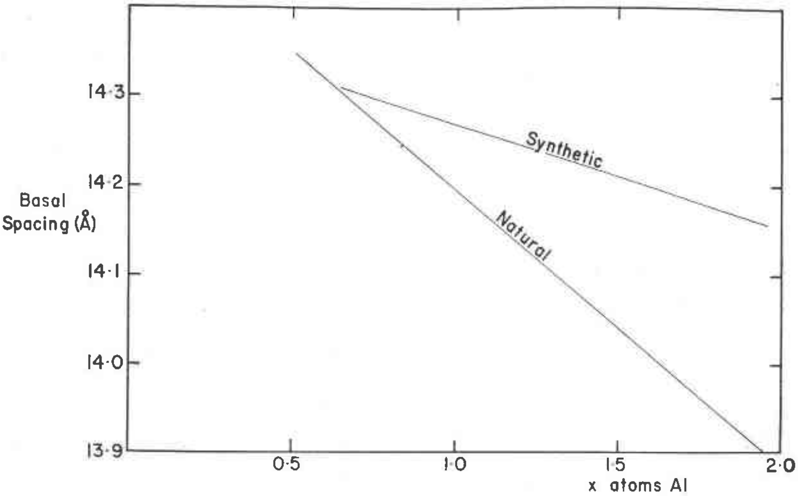

FIG. 2. The variation of the basal spacing of chlorites with composition. (The curve for the natural chlorites is taken from Brindley and Gillery, 1956.)

mates closely the amesite structure reported by Brindley, Oughton and Youell (1951) and by Steinfink and Brunton (1956), amesite having the ideal composition $x=2.0$. S. W. Bailey, Department of Geology, University of Wisconsin kindly supplied films of four natural serpentines found in rock drillings and two of these showed the 6(3)-layer structure and the other two showed the 6(2)-layer structure. Both were mixed with the 1-layer structure.

DISCUSSION

At first sight temperature appears to control whether a chlorite or a serpentine is produced. It may be, however, that serpentines of a possible chlorite composition are metastable. This is suggested by the observations on the crystallization of the gel. Chlorites are formed hydrothermally by way of a serpentine structure and if this process does not reach stability a serpentine will result. Stability takes several days to attain even at 600° C. so that below 500° C. it may take a much longer time than has been allowed in this series of experiments. Hence the serpentines of a possible chlorite composition which appear to be stable below 500° C. may be metastable with respect to chlorite. This point of view may be correlated with the rarity of serpentines with an appreciable aluminum content in nature. An examination of natural chlorite and serpentine analyses indicates that their chemical compositions rarely overlap. The boundary of Al substituted for 4Si atoms is about 0.5 atoms or about 10% Al_2O_3 in the chemical analysis.

The difference in the basal-spacing versus composition curves given by natural and synthetic chlorites could be due to an uneven distribution of cations in the two types of octahedral layer in the latter. If the tetrahedral charge is more than half balanced in the 'talc' octahedral layer, the interlayer charge and the resultant interlayer ionic bonding decrease, hence the basal spacing would increase. This situation existing in the synthetic specimens would explain their generally larger basal spacing. This hypothesis is supported by the tendency of the two curves to converge at the lower Al content where the effect would be expected to be smaller.

It is evident that the amount of Al present in the gel has an overruling effect on the serpentine polytype produced. The formation of fibers rather than plates has been ascribed to the misfit between the octahedral and tetrahedral type layers (See Bates, Hildebrand, and Swineford, 1950, and Roy and Roy, 1954), but the aluminum also controls the amount of 6-layer material present which does not appear to be affected by time or temperature and only slightly by pressure. No explanation can be offered for this observation, though the answer could probably be given if the exact structure of the polytypes were known. The decrease in basal spacing with aluminum content is easily explained by the way the charge on the serpentine layers changes with the substitution of Al. The surplus charge caused by the substitution of Al in the octahedral part of the serpentine layers is balanced by the corresponding substitution of Al for Si in the tetrahedral part. Thus the octahedral part acquires a positive charge and the tetrahedral a negative charge and the layer as a whole is neutral. The layer surfaces which face each other have opposite charges and this provides a force of attraction between them which increases with increasing aluminum content. Hence the basal spacing decreases with increasing aluminum content.

The increased amount of 6-layer structure in relation to the amount of 1-layer structure and the decrease of the basal spacing, both with increase in hydrothermal pressure of formation can be explained by supposing that the 6-layer structure occupies a slightly smaller volume than the 1-layer structure. Increase in the pressure of formation will constrain the system and the equilibrium will move in a direction which will tend to occupy a smaller volume. This can be done by the production of more 6-layer material which will also decrease the basal spacing.

Since the difference in spacing is never noticeable in the mixtures, the difference must be either very small or the mixture must be on almost unit cell scale when the *x*-ray spacing will be a compromise between the two individual spacings.

The important conclusions to be drawn from the study are that:

1. The temperature controls the mineral family produced.
2. The composition is the predominant factor in determining the polytype.

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