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SYNTHESIS OF THE CHLORITES AND THEIR STRUCTURAL AND CHEMICAL CONSTITUTION*

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ABSTRACT

Experimental hydrothermal studies on both synthetic and natural phases in a portion of the system MgO-Al_2O_3-SiO_2-H_2O reveal the polymorphic relationship between 7 Å sheet trioctahedral phases and true 14 Å-chlorites. Each polymorphic type allows continuous extensive isomorphous replacement of 2 Al^{3+} for $Si^{4+}+Mg^{2+}$ terminating at the amesite composition. The equilibrium maximum stability temperature for the chlorites appears to reach a maximum at the composition of clinochlore (710° C. at 20,000 psi) and to decrease slightly ($\sim$20° C.) towards both penninite and amesite. The nomenclature and relations among the various chlorites is discussed in the light of this information.

INTRODUCTION

An entirely satisfactory systematization of the chlorite group is difficult primarily because of the discrepancies between chemical and structural data now available for the chlorites. A recent review of the chlorite problem has been given in Hey's excellent paper (1954). The continuous nature of chemical variation between different end member molecules has been shown by chemical analysis of natural chlorites, and Tschermak (1890, 1891) and Winchell (1926) explained the compositional differences between chlorites through isomorphism. Structural investigations reveal that most chlorites contain alternating mica-type and brucite-type layers in their crystal structures (Pauling, 1930). But other chlorites, notably amesite, cronstedtite, many chamosites, and the serpentine or antigorite minerals, and, in fact, all of the end member compositions in Winchell's classification are represented by layer structures consisting of trioctahedral 7 Å units. This lack of isostructural regularity in the chlorite group seems to preclude the existence of isomorphism between the end members. In the course of hydrothermal mineral synthesis studies we have found two isostructural series within the chlorite group which bear a polymorphic relationship to each other. The existence of these two polymorphic isostructural series supplies a significant advance in our understanding of the chlorites.

This paper discusses the magnesian chlorites. A series of trioctahedral

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7 Å phases, herein called septechlorite* structures, extends between the serpentine composition, $6MgO \cdot 4SiO_2 \cdot 4H_2O$, and the amesite composition, $4MgO \cdot 2Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$.† A series of normal chlorite structures extends continuously between the penninite composition, $21MgO \cdot 3Al_2O_3 \cdot 13SiO_2 \cdot 16H_2O$, and the amesite composition. Both synthetic and natural septechlorite structures ranging from penninite to amesite in composition can be converted into normal chlorite structures under proper temperature and pressure conditions. The change from one structural type to the other is a polymorphic transition.

The experimental work described herein was carried out in 1952–53. Since that time much more detailed *x*-ray work has been done in this laboratory, and the reader is referred to forthcoming papers for details.

EXPERIMENTAL METHODS AND PREVIOUS WORK

The magnesian chlorites occur as synthetic phases in the quaternary system MgO-Al_2O_3-SiO_2-H_2O (see Fig. 1). The general phase equilibrium relations in the system were studied by Yoder (1952) and Roy and Roy (1952, 1955). In both investigations two different phases were synthesized at the clinochlore composition, $5MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$. A normal chlorite structure formed under relatively high water vapor pressures and high temperatures. At 1000 atmospheres this structure was said to be stable up to 680° C. Under relatively low water vapor pressures and at lower temperatures a septechlorite structure formed, which above 450° C. and in sufficiently long runs at high water vapor pressures was transformed into the normal chlorite phase. The Roys observed variable unit cell dimensions for septechlorite phases obtained in three phase assemblages from other more aluminous compositions in the system. They reasoned that solid solution must extend beyond clinochlore along the clinochlore-amesite join. Yoder, however, was unable to synthesize a single phase assemblage at the amesite composition, largely because he was unable to prepare a sufficiently reactive mixture. Chrysotile at the serpentine composition had been synthesized previously by Bowen and Tuttle (1949) and was stable up to 500° C. under 1000 atmospheres water vapor pressure.

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* See later for etymology. This trioctahedral unit repeats with a 7 Å periodicity along the *c*-axis. Minerals containing the unit are chlorites in both the mineralogical and chemical sense and are related, as discussed in this paper, to normal chlorites by a polymorphic rearrangement. We have suggested previously (Nelson and Roy, 1954), therefore, that such minerals should be called septechlorites, or 7 Å chlorites. The mineralogical distinctions between these septechlorites and the dioctahedral kaolin minerals is so fundamental that it seems desirable to avoid referring to them as "kaolin-type" minerals.

† This series may, in fact, not be continuous due to the question of tubular magnesium chrysotile and "platy" aluminous members. This is discussed later.

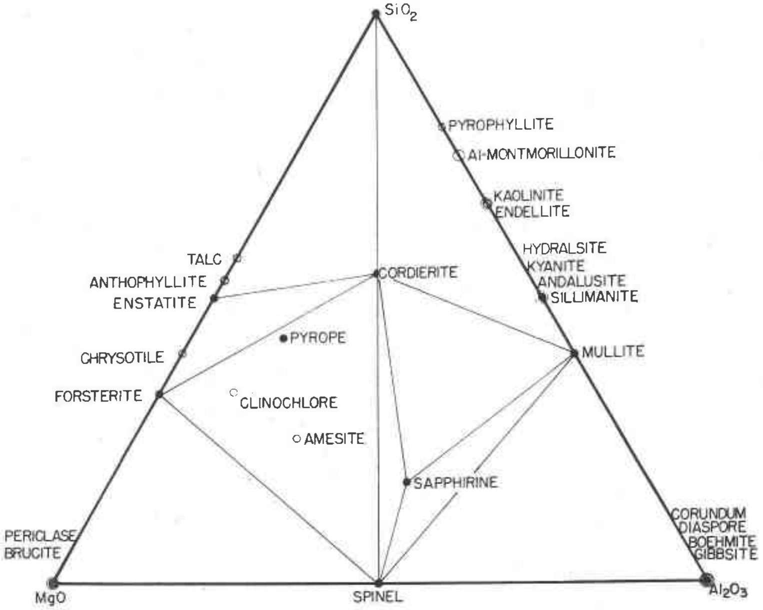

FIG. 1. Mol. per cent composition diagram showing phases in the quaternary system MgO-Al_2O_3-SiO_2-H_2O with compositions projected on to the anhydrous base. Solid dots represent anhydrous phases. Open circles represent hydrated phases actually lying above the plane of the paper. Double open circles indicate more than one phase present at the projected composition point, with the phases differing in water content. Seven compositions studied lie in the join chrysotile-amesite extended. (See Table I for compositions.)

In this investigation a study of compositions lying along the serpentine-amesite join was made in order to determine:

1) whether solid solution extends continuously between the serpentine and amesite compositions,
2) what limits of alumina substitution exist in the magnesian chlorites,
3) whether polymorphic normal chlorite and septechlorite structures extend over the entire range of chlorite composition.

This study was conducted by means of apparatus and techniques that have been described fully in other papers from this laboratory (e.g., Roy and Osborn, 1952, 1954; Roy and Roy, 1952, 1955; Roy, Roy and Osborn, 1953, etc.). The starting compositions, corresponding to those shown in Fig. 1 and Table I, were prepared in the form of amorphous "gels" of alumina, magnesia, and silica (Roy and Roy, 1955; Roy, 1956). The phases were identified in every case by comparing x-ray diffractometer traces of the synthetic products with traces obtained from "standard"

TABLE 1. RESULTS OF REPRESENTATIVE HYDROTHERMAL RUNS

Temperature (° C.)	Pressure (psi)	Duration (days)	Phases Present[1]
a. Composition S-I: $23MgO \cdot Al_2O_3 \cdot 15SiO_2$			
420	10,000	3	SC
440	10,000	17	SC
477	20,000	15	SC
485	30,000	19	SC+tr. For
515	10,000	$2\frac{1}{2}$	SC+For+?
700	18,000	$3\frac{3}{4}$	For+Sp+?
700	10,000	17	For+?
b. Composition S-II: $11MgO \cdot Al_2O_3 \cdot 7SiO_2$			
440	10,000	17	SC
477	20,000	15	SC
515	10,000	$2\frac{1}{2}$	SC+For+?
660	20,000	36	Cl+SC (used for next run)
680	20,000	7	Cl+SC+For
700	18,000	$3\frac{3}{4}$	For+Sp+Talc
700	10,000	17	For+Talc+Sp
c. Composition S-III: $21MgO \cdot 3Al_2O_3 \cdot 13SiO_2$			
440	10,000	17	SC
477	20,000	15	SC
515	10,000	$2\frac{1}{2}$	SC
700	10,000	17	For+Talc+Sp
d. Clinochlore, Composition: $5MgO \cdot Al_2O_3 \cdot 3SiO_2$			
120	5,000	30	SC
160	5,000	55	SC
234	5,000	$9\frac{1}{2}$	SC
266	5,000	11	SC
285	5,000	22	SC
360	15,000	30	SC
410	10,000	19	SC
440	10,000	23	SC
515	10,000	$2\frac{1}{2}$	SC
590	6,000	14	SC
610	15,000	30	Cl
650	10,000	9	SC+tr (For+Talc)
660	20,000	36	Cl (used in next run)
680	20,000	7	Cl
700	18,000	$3\frac{1}{2}$	SC+For+Talc+Sp
720	15,000	$1\frac{1}{2}$	For+Talc+Sp
700	10,000	17	For+Talc+Sp+SC (?)
e. Composition AS-I: $9MgO \cdot 3Al_2O_3 \cdot 5SiO_2$			
120	5,000	30	SC
160	5,000	55	SC
234	5,000	$9\frac{1}{2}$	SC
285	5,000	23	SC
310	5,000	18	SC
350	10,000	30	SC
405	18,000	14	SC

TABLE 1 (*continued*)

Temperature (° C.)	Pressure (psi)	Duration (days)	Phases Present[1]
495	16,000	14	SC+Cl
585	6,000	14	SC
610	18,000	30	Cl
660	20,000	36	Cl (used in next run)
680	20,000	7	Cl+For+?
700	18,000	3½	SC+Cl+Sp
700	10,000	17	SC ? For+Talc+Sp
720	15,000	1½	SC+For+Sp+Talc
f. Amesite Composition A: $4MgO \cdot 2Al_2O \cdot 2SiO_2$			
160	5,000	55	SC
180	5,000	31	SC+Boehm
280	5,000	14	SC+Boehm
265	5,000	10½	SC+Boehm
310	5,000	18	SC
350	10,000	30	SC
400	10,000	26	SC+Sp
415	10,000	7	SC
495	16,000	14	SC
580	5,000	7	SC
610	18,000	30	Cl
650	10,000	9	SC
660	20,000	36	Cl (used in next run)+SC (?)
680	20,000	7	Cl+For+Sp (?)
700	18,000	3½	For+Talc+Sp
700	10,000	17	For+Talc+Sp
g. Composition A-I: $15MgO \cdot 9Al_2O_3 \cdot 7SiO_2$			
360	10,000	30	SC (spacing 7.06)+Boehm
520	18,000	30	Cl+Sp+?
610	18,000	30	Cl+Sp+?
h. Composition A-II: $7MgO \cdot 5Al_2O_3 \cdot 3SiO_2$			
266	5,000	11	SC+Boehm+?
400	10,000	26	SC (spacing 7.06)+Sp+Cor (?)

Mineral	Temperature (° C.)	Pressure (psi)	Duration (days)	Phases Present
i Natural Minerals				
(Antigorite, Antigorio-Frondel)	605	20,000	26	Cl+For+Talc
(Antigorite, Antigorio-Foshag)	605	20,000	26	Cl+For+Talc
(Amesite, Urals)	605	20,000	26	SC+Cl
(Serpentine,* Manchuria-Faust)	605	20,000	26	For+Talc
(Serpentine,* Faust)	605	20,000	26	For+Talc

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[1] Abbreviations used: SC=septechlorite; For.=forsterite; tr.=trace; Sp.=spinel; Cl.=14 Å chlorite; Boehm.=boehmite.

* Analysis shows very low Al_2O_3 content ($\leq 1.0\%$).

Table 2. *X*-Ray Powder Data for Septechlorite of Amesite Composition—Synthesized Hydrothermally at 500° C., 10,000 Psi, 3 Days CuKα, 5 Hrs., Camera Radius: 7 Cm.

d-spacing	Intensity	*d*-spacing	Intensity
7.08	vs	1.704	w
4.62	s	1.664	m, d
3.97	w	1.617	mw
3.55	vs	1.564	w, d
2.65	s	1.540	vs
2.59	m	1.504	mw
2.505	m	1.414	mw, d
2.396	s, d	1.326	w, d
2.270	w	1.294	w
2.110	w	1.130	vw, d
2.013	m, d	1.005	w, d
1.942	w	0.995	w, d
1.886	w		
1.745	w, d		

natural and synthetic materials, supplemented by the usual microscope techniques. In addition to the synthetic compositions, several natural septechlorite minerals were used as starting materials.

Experimental Data

Approximately two hundred hydrothermal runs were made with synthetic compositions and natural minerals as starting materials. Table I summarizes the phases formed at particular temperatures and pressures.

These data show that a septechlorite phase can be synthesized for each composition along the serpentine-amesite join. Solid solution extends to but not beyond amesite, since compositions more aluminous than amesite give three-phase assemblages at all temperatures and pressures. The septechlorite phase in the three-phase assemblages has the same unit cell dimensions as the amesite phase; amesite, therefore, is the maximum limit for alumina substitution in the septechlorite isostructural 2 series.* Table II gives powder diffraction data for a typical member of this series, a septechlorite of amesite composition.

Above about 500° C. and under relatively high water vapor pressures normal chlorite structures form slowly from the septechlorite phases from all compositions more aluminous than that designated

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* In our more recent detailed x-ray studies different polytypes within the septechlorite group have been recognized, but this does not affect the conclusions reported.

S-III. S-III corresponds approximately to the composition of a magnesian penninite. Compositions more aluminous than amesite yield a three phase assemblage, including a normal chlorite structure with the same unit cell dimensions as that forming at the amesite composition. Solid solution in the normal chlorite isostructural series extends continuously from penninite to amesite. Compositions *less* aluminous than penninite form three-phase assemblages above about 500° C., and one phase is always a normal chlorite (or a septechlorite phase in short and low pressure runs) whose unit cell dimensions correspond to phases formed at the penninite composition.

The lowest temperature at which a normal chlorite structure has thus far been synthesized is 450° C., the minimum attained at the clinochlore composition by Roy and Roy (1955). There is a question as to which of the polymorphs is the stable phase below 450° C., and particularly whether or not the septechlorite phases have any true stability range even at low temperatures. The transition from the septechlorite to the normal chlorite structure is extremely sluggish at all temperatures and is favored by higher pressures. Thus, normal 14 Å chlorites are formed in three to four weeks at 1000 atmospheres, but require only a week at 3000 atmospheres and 550° C. It is possible that the 14 Å chlorite structure is the stable one even at low temperatures, an alternative that we tend to favor even though the experimental data allow no unequivocal choice.

There is an experimental limitation on the attempts to resolve this point. When 7 Å phases are converted to 14 Å ones, the powder pattern shows the appearance of new reflections which form the odd orders of the 14 Å series. When, however, we attempt to reverse the process, partial conversion to a 7 Å phase is very difficult to detect since one can only expect minor changes in the relative intensities of the basal reflections. No evidence was found, which would show that the 14 Å phases were less stable than the 7 Å ones under particular conditions. Should the normal chlorite structure be stable at all temperatures one must consider the possibility that the normal chlorite solid solution series could extend from amesite all the way to the serpentine composition. However, we favor the view that a minimum alumina content is necessary to stabilize the normal chlorite structure for reasons discussed later, based both on our experiments and natural occurrences.

In the presence of high water vapor pressures the maximum stability temperature for the normal chlorite structure is about 710° C. at 1000 atmospheres. Normal chlorites of the penninite and amesite compositions appear to have lower maximum stability temperatures than those near the clinochlore composition. However, for a given water vapor pressure there is probably no more than twenty or thirty degrees difference in the maximum equilibrium decomposition temperatures. The usual products of decomposition are forsterite, spinel and cordierite, but naturally these depend on the composition.

The data in Table I obtained from natural minerals that have been used as starting materials are consistent with the data from synthetic compositions. For example, after hydrothermal treatment a normal chlorite structure is formed from the Urals septeamesite. The transition appears to be similar to the polymorphism observed for the synthetic compositions rich in alumina. The Antigorio antigorite contains a relatively small percentage of alumina. After hydrothermal treatment a three-phase assemblage of normal chlorite, forsterite, and talc are formed and this harmonizes with the experimentally derived phase equilibrium relations. The purely magnesian serpentines (chrysotiles) give only the two-phase assemblage forsterite and talc after hydrothermal treatment at high temperatures.

The results of hydrothermal heating should not be confused with the results of "dry" heating experiments with chlorites. Our dry heating experiments have been reported earlier (Nelson and Roy, 1954) and they showed for the first time that the strengthening of a "14 Å" line on heating supposed "chlorites" could not be used as evidence for the presence of the 14 Å chlorite. In each case, both dry and hydrothermal, heating a septechlorite results in the appearance of a "14 Å" line in the powder pattern. In the hydrothermal case this is the first order reflection of the chlorite structure and is sharp and accompanied by all the other reflections of the chlorite structure. The "dry" heating gives only a very diffuse peak nearer 13.5 Å and is accompanied by the partial destruction of the other reflections.

UNIT CELL DIMENSIONS AND STRUCTURAL DATA

Further evidence for the existence of solid solution along the serpentine-amesite join is obtained by observing the regular change in unit cell dimensions that accompanies an increase in alumina content in both the normal chlorite and the septechlorite structures. Figs. 2 and 3 show this change. Values for the basal spacings were determined by slow speed scanning on high angle diffractometers using the (10.1) Lake Toxaway quartz line as a standard. Values for the b_0 parameter were calculated from measurements on the (060) spacing determined in similar fashion using the (21.1) quartz line as a standard. The numerical values represent relative, not absolute, spacings—although they are probably not less accurate than values hitherto reported. The differences recorded are thought to be quite significant since reproducibility to ±0.01° 2θ can

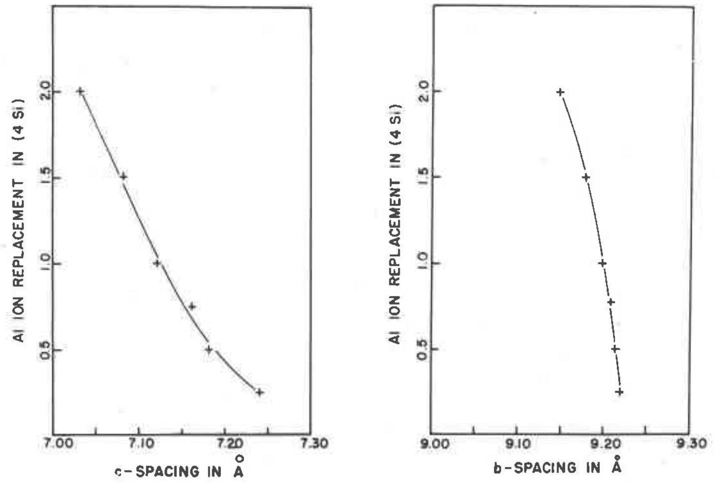


FIG. 2. *a*. Variation in the *c*-spacing of the (7 Å) septechlorite solid solutions up to amesite (Al replacement = 2).

b. Variation in the b_0 parameter of the (7 Å) septechlorite solid solution.

be obtained. The basal spacing of both septechlorite and normal chlorite structures becomes smaller with increasing alumina content, by about 2% in the case of normal chlorites between the clinochlore and amesite compositions. The magnitude of the change is greater in the normal chlorites than in the septechlorites. The septechlorites have a slightly smaller basal spacing than the corresponding normal chlorites. The

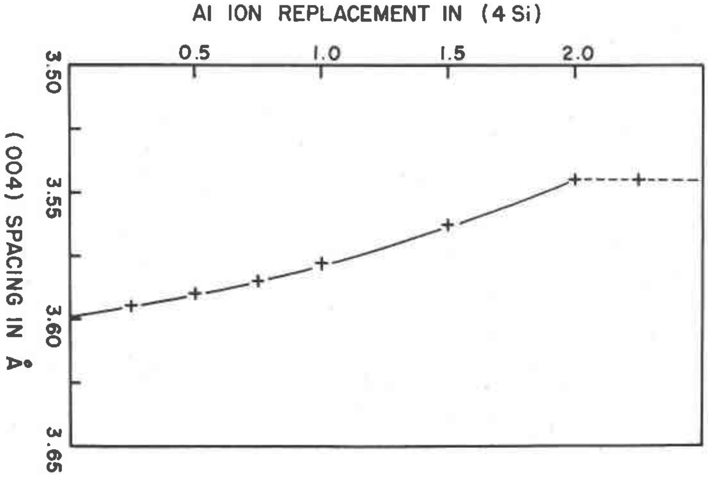


FIG. 3. Variation of the 004 spacing of the (14 Å) normal chlorites.

difference is about 0.16 Å in terms of a first order spacing of approximately 14 Å. The *b* parameter varies in a similar manner decreasing somewhat more slowly than the basal spacing.

PHASE EQUILIBRIUM RELATIONS

From the data obtained (Table I) new conclusions regarding the phase relations in the system MgO-Al_2O_3-SiO_2-H_2O may be drawn. The compatibility triangles in Fig. 4 show the effect of solid solution along the join on phase equilibrium relations in other regions of the quaternary system. The compositions are plotted as projections on the MgO-Al_2O_3-SiO_2 base of a tetrahedron following the usual procedure. The new triangles are revisions of those given by Yoder (1952) and Roy and Roy (1955), and only the critical relations are shown. The triangles show relations ac-

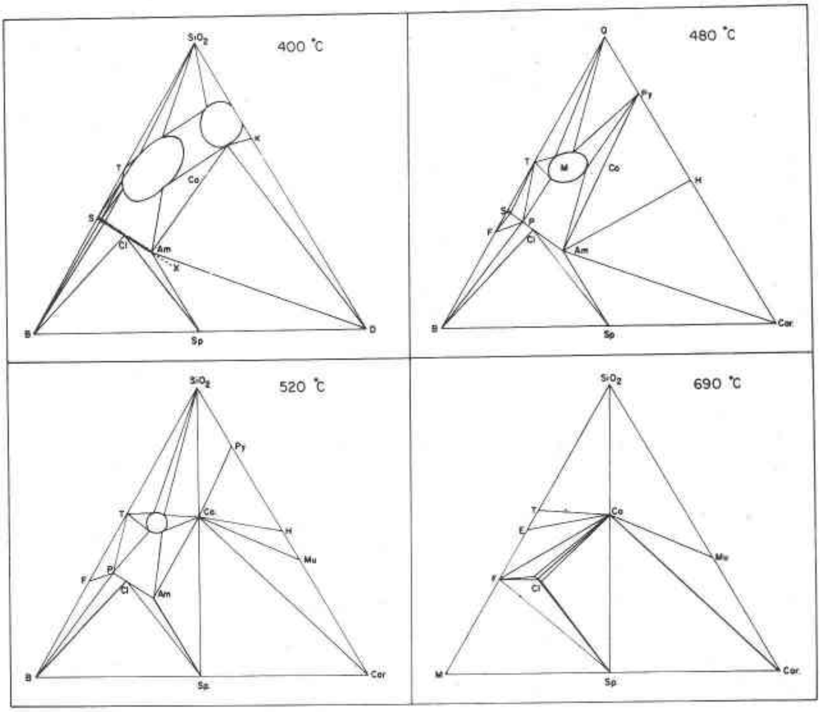
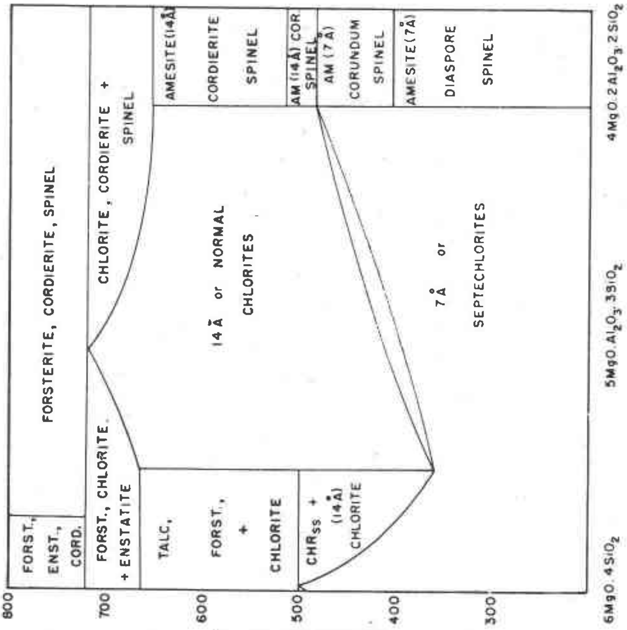


FIG. 4. Four selected isobaric (1000 atm) isothermal (temperature indicated) compatibility triangles for the quaternary system MgO-Al_2O_3-SiO_2-H_2O. Abbreviations can be compared to Fig. 1 where full names are given. The round quaternary solid solution areas are the various montmorillonoids. These revised data are taken from the work of Mumpton and Roy (1955). The precision in such triangles is of a much lower order than for example in isothermal sections of ordinary "dry" equilibrium diagrams.

tually encountered under experimental conditions up to 1500 atmospheres water vapor pressure. Alternative possibilities that could exist at other water vapor pressures (Yoder, 1952) are indicated by dashed lines. Another type of presentation of the results is shown in Fig. 5 which is the partly binary t–x section of greatest interest here. The system becomes quaternary as soon as any solid phase dissociates, e.g., it is binary only at the lower temperatures and the diagram must, therefore, be used with care. Two alternative diagrams are presented, one regarded as more likely than the other. The choice hinges around two incompletely resolved points.

First, chrysotile and synthetic phases of pure serpentine composition have a tubular habit, while the septechlorite phases of more aluminous composition crystallize in very small, well defined, hexagonal plates (see Fig. 6). Solid solution between the tubular and platy habits implies a gradual transition from tube (rolled sheet) to plate. Electron microscope studies of several septechlorites lying between serpentine and penninite in composition failed to reveal any evidence for a gradual change in habit. In general a mixture of tubes and plates was noted, and this suggests the discontinuity shown in Fig. 5*a*. If, on the other hand, high confining pressure or shearing stress produces a flat sheet habit for phases of chrysotile composition, the continuous relations shown in Fig. 5*b* are suggested. The occurrence of tubular chrysotiles and platy antigorites in nature supports Fig. 5*a*. However, most natural antigorites contain some R_2O_3, and previous synthesis work (Roy and Roy, 1954) suggests that a minimum R_2O_3 content is necessary to stabilize the platy habit.

Second, the septechlorites may or may not have a range of thermodynamic stability, a question already discussed. The experimental data do not settle this question. The fact that it is not possible to make 14 Å chlorites with a low alumina content and is more difficult to synthesize normal chlorites from the very high alumina compositions also suggests that if there is a stability range for the septechlorites, this range reaches a maximum temperature near the amesite composition (as shown in Fig. 5*b*). That there may be a true stability range for the least aluminous septechlorites is suggested by the numerous low-R_2O_3 "antigorite" phases in nature *for which no 14 Å polymorph exists*, and for the high-R_2O_3 ones, stability is suggested by the natural occurrences at Chester, Massachusetts and Saranovskoye, Northern Urals. The occurrence of diaspore with amesite at Chester implies a stability range even under moderate temperature ($<\sim$400° C.) and pressure conditions, and the paragenetic relations of amesite and corundophyllite suggest inversion to the septechlorite with lowering temperature. If the Chester association is metastable the relations in Fig. 5*a* apply. The question may be answered by a



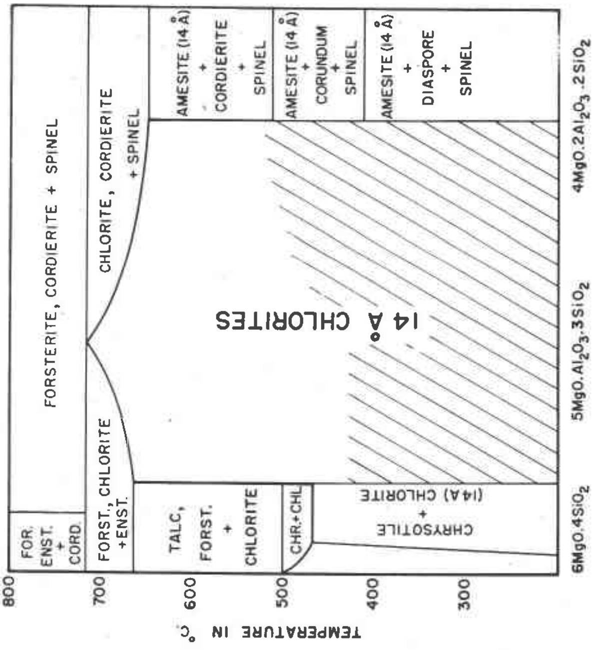


FIG. 5. *a.* Preferred version of a composition-temperature diagram drawn for a pressure of 1000 atmospheres, for the join chrysotile-amesite extended. The lower part of the diagram is a true binary join, above this, however, the equilibrium is quaternary and the diagram shows only the stable solid phases at various compositions as a function of temperature. Precision in such diagrams is poor (±15° C.) especially in the area of solid solutions which decompose to other solid solutions. The preferred version shows as a shaded area the p-t range in which (7 Å) septechlorites form and persist metastably (?) for long periods. Note also the 2-phase region chysotile+chlorite showing a discontinuity in solid solubility along the "chlorite-join."

FIG. 5. *b.* Possible alternative to Fig. 5 *a.* with septechlorites now shown as stable low temperature polymorphic forms of chlorites.

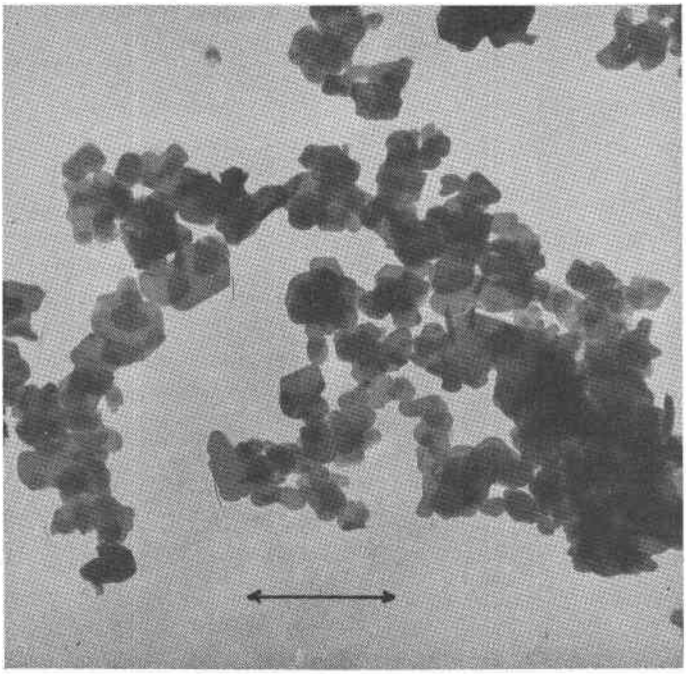
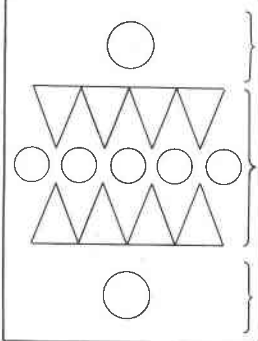


FIG. 6. Electron micrograph showing euhedral well-crystallized septechlorite material (Composition: clinochlore, 450° C., 15,000 psi).

detailed study of the influence of much higher pressures than have been used so far.

In both alternatives of Fig. 5, a minimum alumina content is shown as necessary for formation of the 14 Å normal chlorite structures due to the failure to synthesize normal chlorites containing less alumina than penninite. This is also more easily explained on a structural basis. It should be recalled that changes in composition in the chlorites occur through *simultaneous* substitution of aluminum ions for silicon ions in the tetrahedral layers *and* of aluminum ions for magnesium ions in the octahedral layers. This very important point was first made by Gruner (1944). In Pauling's structural scheme for the layer silicates the chlorites are related to the micas in that a charged brucite-type sheet occupies the interlayer cation position of the micas. A certain minimum charge on this brucite-type sheet may, therefore, be necessary to hold the mica-type layers together. The composition corresponding to a particular brucite layer charge cannot be determined, because different amounts of substitution and charge may occur in the interlayer brucite and the mica-unit octahedral layer. The maximum charge on the interlayer brucite is achieved if all the octahedral substitution occurs in the interlayer brucite. In this case the octahedral layer within the mica-type unit would be uncharged. Substitutions confined to the interlayer brucite would give an interlayer charge equal to the interlayer charge in muscovite with a minimum alumina content corresponding to the clinochlore composition. The possible substitutions are shown schematically in Fig. 7. The normal chlorite isostructural series extends from amesite only as far as penninite, therefore, probably because of the minimum interlayer charge requirements on the brucite-type layer. A detailed structural study of synthetic gallium and nickel analogues of the normal chlorites is being pursued in an attempt to determine the nature of the actual octahedral substitutions and reveal the minimum interlayer charge requirements for mica-type structures.



PHLOGOPITE	HYPOTHETICAL 14 Å CHRYSOTILE	"NEUTRAL" CLINOCHLORE	MAX$^{\underline{M}}$ CHARGE PENNINITE	MAX$^{\underline{M}}$ CHARGE CLINOCHLORE
K +1	$3Mg(OH)_2$ 0	$3Mg(OH)_2$ 0	2.5 Mg 0.5 Al +.5	2Mg.Al +1
3Si.Al	4Si	3Si.Al	3.5 Si 0.5 Al	3Si.Al
6Mg −2	6Mg 0	4Mg.2Al 0	6Mg −1	6Mg −2
3Si.Al	4Si	3Si.Al	3.5 Si 0.5 Al	3Si.Al
K +1	$3Mg(OH)_2$ 0	$3Mg(OH)_2$ 0	2.5 Mg 0.5 Al +.5	2Mg.Al +1

FIG. 7. Schematic illustration of various possibilities in filling the different "layers" of penninite or clinochlore. If the minimum charge required on the layers is the same as in a mica, then the *minimum* Al_2O_3 content with which this can be achieved corresponds to the clinochlore composition.

DISCUSSION OF THE RESULTS

The preceding experimental data allow us to reconsider the problems of chlorite constitution and classification. The following significant points should be borne in mind. A complete sequence of normal chlorite structures with a 14 Å series of basal x-ray reflections can be synthesized for compositions ranging from amesite to penninite. From the same compositions, but generally at lower temperature and water vapor pressure conditions, a second sequence of trioctahedral kaolin-type or "septechlorite" structures with a 7 Å series of basal reflections can be synthesized. For a given composition within this range there exist two polymorphic forms of the chlorite phase. (Each polymorph may, in addition, exist in more than one polytype.) These results were obtained not only for the synthetic compositions but also with the natural minerals studied.

This study did not involve experimental work with chlorites containing large amounts of either ferrous or ferric iron. However, ferrous iron analogues of both the septechlorites and normal chlorites have been described (Brindley, 1951) among the chamosites. Polymorphic relations similar to those described here are almost sure to exist in the iron chlorites.

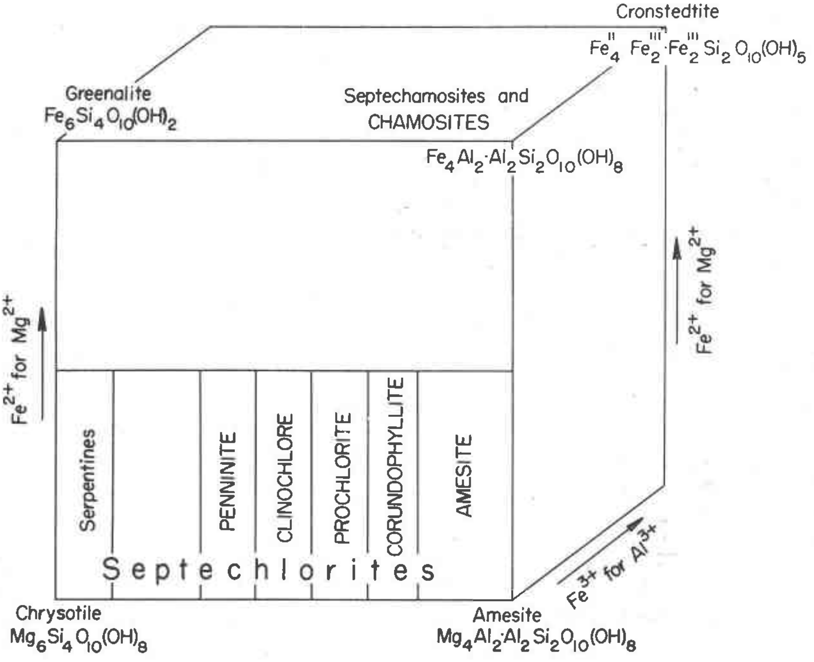


FIG. 8. A revised "Winchell-type" scheme showing compositional relationships among the members of the chlorite group. The septechlorites (roughly equivalent to Winchell's term antigorite) can occur as the low temperature polymorph at any composition which forms a chlorite. In nature Ni^{2+} and Mn^{2+} analogues of the magnesian members are known, and fit directly into the scheme.

The compositions of magnesian and ferroan chlorites can be represented diagrammatically in terms of four end members as has been done in Fig. 8. Chamosite has been used as one end member because both septechlorite and normal chlorite structures are already known from materials described by this name. Most chamosites are rich in alumina and lie close to the end member composition of this diagram. The amesite end member is represented also by both septechlorite and normal chlorite structures. Tschermak's divisions of the orthochlorite series have been used, since they are in common use. Figure 8 is an extension of Winchell's ideas except that we have used molecular proportions as the basis of our subdivisions following Tschermak, instead of weighting the corners. This method of plotting has the double advantage of showing the relative proportions of each end-member in the particular composition under consideration and of indicating the number of substituted aluminum ions in each layer of the structure, a characteristic of particular significance in chlorites. The structural formulae for such chlorite compositions as clinochlore and amesite should, of course, be written: $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$ for clinochlore and $(Mg_4Al_2)(Al_2Si_2)O_{10}(OH)_8$ for amesite. Designations familiar in other mineral groups might also be used. Thus where Sp represents the molecular proportion of the septechlorite end-member and At the molecular proportion of the amesite end-member, penninite might cover the range $Sp_{60}At_{40}$–$Sp_{50}At_{50}$ and clinochlore the range $Sp_{50}At_{50}$–$Sp_{40}At_{60}$, etc. (after Tschermak). If it is remembered that each composition can exist in two polymorphs it is obvious that the one diagram suffices for both the septechlorite and the normal chlorite forms of the same composition, although for plotting optical and other properties two diagrams perhaps will be required.

The introduction of Fe^{3+} for Al^{3+} is another common possibility in nature. This also has been sketched in on Fig. 8 with the Fe^{3+} for Al^{3+} replacement plotted as a third dimension coming out of the plane of the paper. The only important end-member mineral which needs to be considered here is cronstedtite, which is then the amesite analogue with both Fe^{2+} substitution for Mg^{2+} and Fe^{3+} for Al^{3+}.

The ability of synthetic septechlorite structures to accept isomorphous replacements by Mg, Fe^{2+}, Fe^{3+}, Ni, Mn, Cr, Ge and Ga has been studied by Roy and Roy (1954).

Other natural chlorites also show examples of this dimorphism. Thus, in the nickel family one finds both 7 Å and 14 Å material. In the case of the natural samples of schuchardite one cannot be sure whether the 7 Å phase contains much aluminum, or is really an end-member garnierite. In the laboratory both 7 Å and 14 Å members can be prepared, though it has been found to be impossible to convert a sample at the $Ni_5Al \cdot AlSi_3O_{10}(OH)_8$ composition entirely into the 14 Å polymorph.

No synthetic work has as yet been done with the manganese phases but here again it is quite reasonable to presume the existence of the two polymorphs in the "grovesite" sample studied by Hey (1954). Similarly, delessite (= melanolite) and gonyerite correspond then to two isomorphous 14 Å members (with different amounts of substitution of R^{3+})

whereas the 7 Å polymorph is represented by bementite (see Frondel, 1955) and related species.

SUMMARY

In summary, our present concept of the constitution of the chlorites is based on the chemical, structural, and phase equilibrium relations that characterize them. Chlorites as they occur in nature are layer lattice silicates of one of two polymorphic types. The one, typically more perfectly and more coarsely crystalline, is analogous to the mica scheme of crystallization. It is a four-layer structure consisting of mica sheets and substituted brucite sheets. The substituted sheets occupy a position and fill a role analogous to the interlayer cations of the micas. The other, characteristically more fine grained and less perfectly crystallized, (although occasionally giving large well-formed crystals) is a two-layer structure of trioctahedral type. Chemical variations of wide, but not unlimited latitude may occur in both types of structures by a specific type of isomorphous replacement within the lattice. Such substitutions are almost certainly continuous from their maximum to their minimum determined extents, and the characterization of individual chlorite species by narrow and discontinuous ranges of composition is therefore unnatural. The ionic substitutions in the chlorite and septechlorite structures are of the type characterized by simultaneous replacements in tetrahedral and octahedral positions by trivalent ions, particularly aluminum ions. The phase equilibrium studies have shown that there is no *simple* replacement of aluminum by magnesium, or the reverse. The mineral kaolinite and its polymorphs are unique entities characterized by the absence of isomorphous replacements. Such replacements in the septechlorites are exceedingly common. The septechlorite and normal chlorite polymorphs, that may occur singly or together in nature, are not unrelated entities, but under proper conditions the one may undergo transformation to the other. It is unnecessary, therefore, to disassociate from the chlorite family such minerals as antigorite, amesite, and chamosite. The main problem of nomenclature involved is to find a name for the trioctahedral two-layer minerals related to chlorites. We have suggested that it is convenient to call them septechlorites, septechamosites, septeamesites, etc. if and when after *x*-ray examination their structural scheme is found to be based on a 7 Å sequence.

NOTE ON THE ETYMOLOGY OF "SEPTECHLORITE"

As more and more natural assemblages containing chloritic phases with 7 Å series of basal *x*-ray reflections are encountered the problem of naming such minerals and distinguishing them from other chlorites becomes more acute. The problem was recognized by Brindley (1951, p. 65) and by Hey (1954, p. 279) but neither proposed a solution. In our first paper on the data given detailed treatment here (Nelson and Roy, 1954) we suggested that the 7 Å chlorites be designated *septechlorites* in allusion to their most obvious identifying x-ray diffraction characteristics, while the 14 Å chlorites should be designated *normal chlorites*. Such designations are useful only after x-ray examinations have been made. The field worker and the petrographer naturally will refer to all undifferentiated chloritic minerals as *chlorites* in the presently accepted sense. Most such minerals will be normal chlorites.

Some have used the term "kaolin-layer" to refer to all two-layer assemblages. This usage seems to us undesirable because the kaolin minerals are a unique crystallization. They are dioctahedral and triclinic, or perhaps monoclinic. Their crystal chemistry admits no isomorphous substitutions in the ideal formula (Roy and Roy, 1954). No simple substitution of magnesium, nor any other ion, for octahedral aluminum occurs, and there are no germanium, or germanium and gallium substituted analogues of kaolinite. Solid solution between serpentine and kaolinite or "parakaolinite" (Serdyuchenko, 1948, p. 156) almost certainly does not exist. Finally, the kaolin minerals undergo no polymorphic transitions of the type described for septechlorites. The unique crystallization of kaolin minerals is in contrast to septechlorites. Septechlorites are trioctahedral and the resulting higher symmetry gives rise to rhombohedral (cronstedtite) or orthohexagonal (some chamosites) crystallizations. The septechlorite layer admits a great variety of ions through isomorphous substitutions (Roy and Roy, 1954), including germanium and gallium. Al^{3+} entry always involves simultaneous octahedral and tetrahedral substitutions.

Apart from a "synthetic" name such as "femalsite" (ferromagnesian aluminum silicates) the other most likely names are *antigorite* and *serpentine*. We strongly favoured the former for many years, but crystallographic workers more and more tend to restrict this term to the structure type with long ($\sim$42 Å) a-spacing. Serpentine has been associated with a morphological habit and also restricted to the magnesium-rich compositions: no one would, for instance, call euhedral amesite crystals, "serpentine."

The most fundamental and distinguishing characteristic of septechlorites is that under appropriate natural or simulated conditions septechlorites are converted to their normal chlorite polymorphs. This structural and genetic relationship associates normal and septechlorites in nature and in the laboratory. They should be associated in nomenclature, as well.

We hope mineralogists will agree the term "septechlorite" is a happy solution to the problem of naming 7 Å chloritic minerals. It is, of course, not so important what terms are used so long as the fundamental relations between the two types of chlorites are recognized.

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