

# Phase equilibria in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ : chlorites and associated minerals

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**SUMMARY.** Twenty-six compositions in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  were investigated under conditions of 1 and 2 Kb water pressure and temperatures between 300 and 700 °C. The solid solution for 7 Å and 14 Å chlorites has been delimited as well as that of the expanding phases (tri- and dioctahedral montmorillonites and expanding chlorites). Negative slopes were found for the transformation montmorillonite → expanding chlorite, and expanding chlorite → chlorite + quartz and a positive slope for 7 Å → 14 Å transformation. The relative positions of the reactions chlorite + quartz → cordierite + talc, chlorite + andalusite → cordierite + corundum and chlorite + corundum → cordierite + spinel are located between 500 and 650 °C.

Cell dimensions of the synthetic chlorites can be correlated with their chemical composition. Solid solution in synthetic minerals compares well with 325 analysis of natural minerals from the literature, indicating that the chemiographic relations between phases in the simplified synthetic system are applicable to natural mineral assemblages. The phase relations indicate that at low temperature the 7 Å aluminous chlorite is not stable with quartz or another silica phase.

PHASE relations in the system  $\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  have been previously investigated by numerous workers and several studies have dealt with the synthesis and stability of chlorite at medium pressures and temperatures. Initial data (Yoder, 1952; Roy and Roy, 1954) indicated the basic phase relations and reactions in the four-component system. Subsequent work (Nelson and Roy, 1958; Gillery, 1959; Fawcett and Yoder, 1966; Johannes, 1967; Seifert and Schreyer, 1970) in this and adjacent systems permits a more detailed examination of these relations.

However, two major aspects of the chlorite stability and phase relations had not been examined. The limits of chlorite composition as a function of the components  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and of pressure and temperature are not known. Second, the composition and stability of the expanding phases, precursors of the 14 Å chlorite, had not been determined other than at atmospheric pressure and room temperature (Estéoule, 1969). These relations are needed to understand the evolution of sediments undergoing diagenesis and metamorphism.

The aim of the present study is to relate previous work to new information on solid solution and lower thermal stability of chlorites to present a model of chlorite evolution in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ .

## *Methods*

A description of the methods of investigation can be found in Velde (1969). The precision of compositions and temperature and pressure measurement is such that



tions for the  $b$  parameter but not for  $a$  due to the lack of  $hkl$  reflections;  $okl$  and  $ool$  reflections are predominant in chlorites. The  $c$  dimension was estimated by measuring the  $004/002$  reflection. Correlation between  $b$  and  $c \sin \beta$  cell dimensions is very poor, however  $b$  vs. composition is good, as is  $c \sin \beta$  vs. composition. Measurements were made by diffractometer using quartz internal standard, and could be reproduced to  $\pm 0.001$  and  $\pm 0.01 \text{ \AA}$  respectively. Several factors can undoubtedly explain these disappointing results. Of great importance is the poor crystallinity

TABLE I. *Starting materials in ionic percent*

Composition	Mg	Si	Al	Composition	Mg	Si	Al	Composition	Mg	Si	Al
II	50	30	20	XI	38	37	25	XXI	43	22	35
III	40	20	40	XIII	45	38	17	XXII	37	25	38
IV	32	45	23	XIV	49	37	14	XXIII	46	31	23
V	55	35	10	XV	53	39	8	XXIV	50	20	30
VI	45	25	30	XVI	30	30	40	XXV	55	30	15
VII	48	42	10	XVII	30	25	45	XXVI	17	65	18
VIII	35	35	30	XIX	30	40	30	XXVII	20	20	60
X	42	30	28	XX	42	42	16	XXVIII	10	60	30
								XXIX	18	50	32

of the  $14 \text{ \AA}$  phases, which tend at low temperature to retain small quantities of expandable layers, thus making their  $c$  or  $c \sin \beta$  dimension unreliable. This effect is eliminated only at temperatures above  $500 \text{ }^\circ\text{C}$  where the extent of chlorite solid solution is reduced and as a result certain compositions could not be determined with great accuracy. Optical determinations using Cargille index oils (precise to  $\pm 0.002$  units) showed a mean index of refraction of  $1.567$  to  $1.566$  for all chlorites.

Experiments that were used to determine phase field boundaries, reaction boundaries in P-T space, or physical properties of chlorites are given in Table II. A list of the 89 references from which analyses were gathered and used to establish the limits of solid solution in natural chlorites is available from the author upon request.

### Results

The chlorite and trioctahedral expanding phases encountered are defined as follows:

$17 \text{ \AA}$ : denotes expanding phases that formed a  $17 \text{ \AA}$  basal spacing upon saturation in ethylene glycol vapour and  $14.8 \text{ \AA}$  when air-dried. Heating to  $400 \text{ }^\circ\text{C}$  resulted in  $14.2 \text{ \AA}$  spacings. Saturation of interlayer sites with  $\text{K}^+$  ions (KCl solution) did not change the response to glycolation but subsequent heating reduced the basal spacing to  $13.0 \text{ \AA}$ . The cation exchange capacity was found to be  $49 \text{ meq}/100 \text{ g}$  of anhydrous sample (see Velde, 1969, for a description of the method employed).

$15 \text{ \AA}$ : denotes an expanding phase that formed a  $15.2 \text{ \AA}$  basal spacing upon glycolation, in the normal as well as  $\text{K}^+$ -saturated state, air-dried  $14.8 \text{ \AA}$ , and  $14.2 \text{ \AA}$  upon heating to  $400 \text{ }^\circ\text{C}$  for  $\frac{1}{2}$  hour. Cation exchange capacity was  $10 \text{ meq}/100 \text{ g}$ .

$14 \text{ \AA}$ : denotes a non-expanding phase, essentially with a  $14 \text{ \AA}$  basal spacing that does not change upon heating to  $400 \text{ }^\circ\text{C}$ , nor upon potassium saturation.

TABLE II. *Experimental results. P in Kb, T in °C.*

Run	Comp.	P	T	Days	Reactants	Products
<i>17 Å–15 Å</i>						
239	XI	2	373	59	15	16·7+15
145	XX	2	402	62	gel	15+7
211	XIII	2	420	70	17+7	15+7
143	XIII	2	394	62	gel	15+7
183	XIII	2	386	31	gel	17+7
142	XIV	2	394	62	gel	15+7
207	VII	2	412	30	gel	15+7
238	VII	2	373	59	15 ordered+7	16·0+15+7?
307	XIII	1	445	60	15+7	15 ordered+7
20	XIII	1	425	28	gel	16·0+7
60	XX	1	417	40	gel	17+7
306	VII	1	445	60	17+7	15+7?
324	XI	1	389	72	15+7	little change
<i>15 Å–14 Å</i>						
233	XVII	2	421	63	14+Bo	15+17
232	XI	2	421	63	14+Q	15+14+Q(m)
235	VII	2	425	63	14+T	16·1+7+T
228	XVII	2	430	54	gel	14+Bo
229	XI	2	430	54	gel	15+7
187	XI	2	461	45	gel	14+Q?
136	XIII	2	455	42	gel	14
167	VII	2	456	46	gel	14+T
227	VII	2	430	54	gel	15 ordered+7?
323	XXII	1	389	72	7+14(m)	15+7+Bo
276	XIII	1	434	30	14+T	15+7+T
307	XIII	1	445	60	15+7(m)	15 ordered+7
101	XIII	1	464	52	gel	16 ordered+7
46	XIII	1	471	32	gel	14+T(m)
67	VII	1	460	60	gel	16·1+7+T
<i>7 Å–14 Å</i>						
188	X	2	368	34	gel	7
335	X	2	408	7	gel	14
139	X	2	408	55	gel	14
170	XVII	2	396	43	gel	14+Bo+17(m)
69	IX	2	404	62	gel	14+Bo+?
17	XXII	1	357	34	gel	7+Bo
51	X	1	340	79	gel	14
290	X	1	333	70	7	no change
292	X	1	333	70	gel	7+14?
77	XXIII	1	352	46	gel	7
10	XVI	1	376	63	gel	14+Bo
<i>Diact 17 Å–15 Å</i>						
224	XXVIII	2	317	54	gel	17
259	XXVIII	2	357	36	gel	16·4+Q
222	XXVIII	2	383	74	gel	15 ordered+Q?
215	XXVIII	2	437	36	gel	15 ordered+Q?
265	XXVIII	2	452	36	gel	14+Q+Py

TABLE II (cont.)

14-Py-And-Q-Cord						
Run	Comp.	P	T	Days	Reactants	Products
251	XIX	2	480	54	14+Q+Cord	14+Q
266	XIX	2	520	36	14+Q+sill	14+Q
126	XIX	2	525	42	gel	14+Q+Cord
256	XXIX	2	523	36	14+Q+Py	14+Q+Py(m)+Cord(m)
4	XVI	2	525	55	gel	14+And?
280	XIX	1	510	70	14+Q+Py	14+Q+And+Py(m)
82	XIX	1	487	30	gel	14+Q+Cord(m)
288	VIII	1	471	70	14+Cord+Q	14
56	VIII	1	503	32	gel	14+Q+Cord(m)
14+Q $\rightleftharpoons$ T+Cord						
286	XI	1	522	70	14+T+Cord	14+Cord+Q?
283	XI	1	529	70	14+Q	14+Q+T+Cord
14+And $\rightleftharpoons$ Cord+Cor						
325	XXVII	1	558	57	Cord+Cor+14(m)	Cord+Cor+14
321	XVI	1	545	75	14+Cord+Sp	14+Cord+And
14+Cor $\rightleftharpoons$ Cord+Sp						
317	XVI	1	592	75	14+And+Sp	Cor+Sp+14
330	XXVII	1	603	75	gel	14+Cord+Sp
332	XXVII	1	584	93	Cord+Cor+Sp	Cor+Cord+Sp+14
298	XXVII	1	623	48	gel	Cord+Cor+Sp
<i>Amesite-Chlorite</i>						
159	III	2	522	36	gel	7
201	III	2	552	36	gel	7+Sp
57	XXI	2	503	30	gel	7+Sp
278	XXI	2	510	70	7+Sp	no change
157	XXI	2	540	33	gel	14+Sp
65	XXI	2	458	30	gel	7

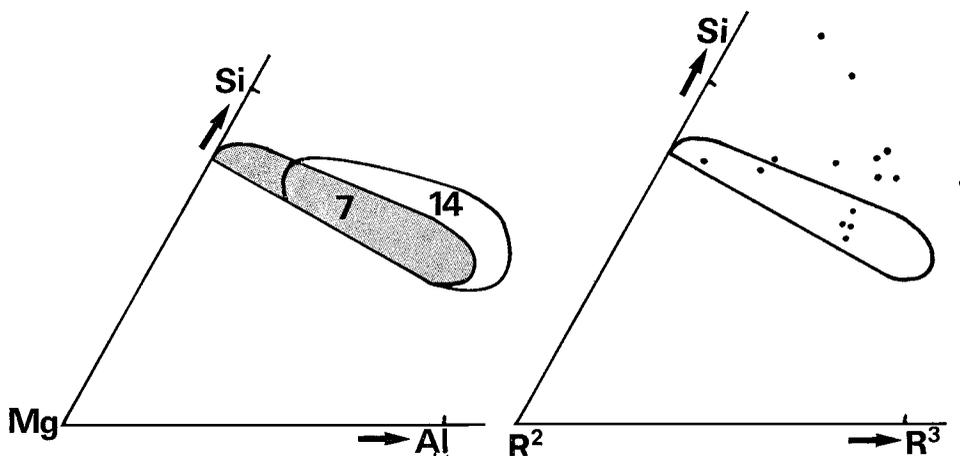
Gel = uncrystallized, coprecipitated and calcined material. 17, 16.7, 15, 7 = approximate basal spacings (in Å) of phyllites after glycolation. Q = quartz, Bo = boehmite, Py = pyrophyllite, Cor = corundum, Cord = cordierite, And = andalusite, Sill = sillimanite, Sp = spinel, Dioc = dioctahedral expandable phase, T = talc, ? = questionable identification, m = minor quantity.

7 Å: denotes a 7 Å chlorite that has no apparent 14 Å reflections.

16.8 Å: An expanding phase with a 16.8 Å expanded basal spacing was encountered between 17 and 15 Å phases when they coexisted or near the 17 Å-15 Å thermal transition. This phase is interpreted as a mixture of the two types.

7 Å and 14 Å solid solution: One can divide the 7 Å chlorites formed in the synthetic system into two groups, those stable below the 320-400 °C range and those found above. In the first group solid solution is more or less restricted to the Al<sup>iv</sup>Al<sup>vi</sup>  $\rightleftharpoons$  SiMg substitution, which has been investigated by Nelson and Roy (1954) and Gillery (1959). These authors have also observed the polymorphic transition 7  $\rightarrow$  14 Å, estimating it to take place between 450 and 500 °C. This is much higher than was found in the present study. It is probable that the longer experimental duration

(months instead of weeks) and wider range of compositions investigated give a better view of the phase relations. For the compositions in the  $Al^{iv}Al^{vi} \rightleftharpoons SiMg$  substitutional series it was observed that the polymorph transition was much slower, i.e. occurred at higher experimental temperatures for comparable run durations than would be deduced from other compositions. This is discussed further in a later section.



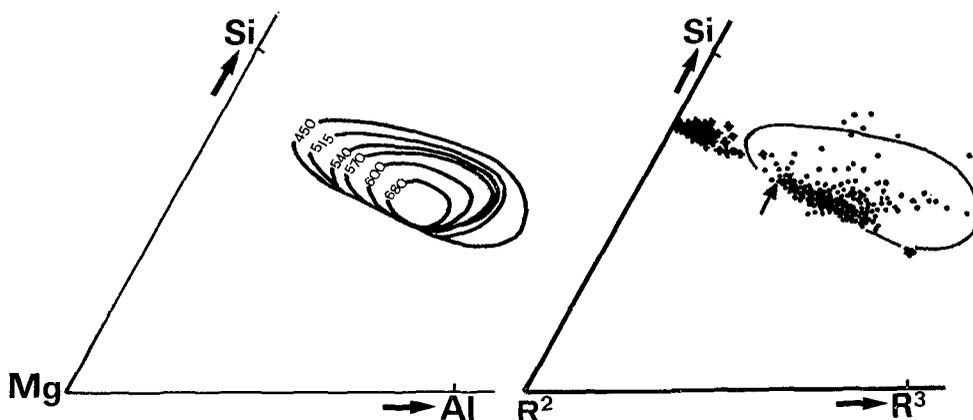
FIGS. 2 and 3: FIG. 2 (left). The maximum extent of solid solution for synthetic 7 Å (shaded area) and 14 Å chlorites at 2 Kb pressure is given. FIG. 3 (right). Compositions of natural aluminous sedimentary 7 Å chlorites plotted in the  $R^{2+}$ - $R^{3+}$ -Si system are compared to synthetic 7 Å forms.

If we consider then the compositional range of the low-temperature 7 Å chlorites, the substitutional possibilities lie largely between  $Mg_3Si_2O_5(OH)_4$  and  $Mg_2Al_2SiO_5(OH)_4$ ; non-aluminous serpentine and amesite (fig. 2). There is some substitution toward a more silica-rich composition. Using 16 analyses of sedimentary 7 Å chlorites (chamosite and berthiérine) we can compare natural and synthetic compositions in the  $Si-R^{2+}-R^{3+}$  coordinates ( $R^{2+} = Mg + Mn + Fe^{2+}$ ;  $R^{3+} = Al + Fe^{3+} + Cr$ ) (fig. 3). It is apparent that the correspondence is poor, but the natural minerals are admitted to be multiphase by most of the authors cited. It is nevertheless instructive to note that sedimentary 7 Å chlorites contain a range of  $R^{2+}/R^{3+}$  ions similar to those synthesized. This is true for iron-rich species (chamosites  $Fe^{2+}/R^{2+} = 0.85$ ) as well as magnesian ones (berthiérine  $Fe^{2+}/R^{2+} = 0.04$ ). The scatter toward high Si compositions could be due to admixture with expanding phases, generally found to contain higher quantities of  $SiO_2$  (see section on expanding minerals). 7 Å chlorite polymorphs found at higher temperatures can be considered along with 14 Å chlorites stable at the same temperatures.

*Amesite.* The relations between co-stable 14 and 7 Å chlorites can be deduced easily from the experiments reported here. However, amesite,  $Mg_2Al_4Si_2O_{10}(OH)_6$ , which is the most aluminous composition in the substitution series  $Al^{vi}Al^{iv} \rightleftharpoons MgSi$  presents a problem. Synthesis and stability of this chlorite was reported previously by Nelson

and Roy (1958). However, natural minerals of this composition are known to be 7 Å polymorphs, although sometimes present as an apparent 14 Å form (Steadman and Nuttall, 1963; Steinfink and Brunton, 1956); this in contradiction with what is known for other aluminous chlorites.

Composition XXI ( $Mg_{45}Al_{35}Si_{25}$ ) between amesite (III in Table I) and  $Mg_{45}Al_{30}Si_{25}$ , the nearest to amesite investigated by Nelson and Roy, was studied to test the continuity of the series of silica-'poor' aluminous chlorites. It was found that a multi-phase product appears near 500 °C at 1 Kb pressure, significantly below the upper



FIGS. 4 and 5: FIG. 4 (left). Solid solution observed at various temperatures and 2 Kb pressure for the 14 Å chlorites. FIG. 5 (right). Natural chlorite and serpentine analyses are plotted as a function of  $R^2-R^3-Si$  content. Dots are 14 Å chlorites, crosses are serpentines. Chemical analyses were not used if they contained  $> 0.10 Ca^{2+}$ ,  $> 6.10$  octahedral ions, or  $> 4.10 Si^{4+}$ . Formulae were calculated on the basis of  $O_{10}(OH)_8$  using the method of Foster (1962). The solid line shows maximum solid solution of coexisting 7 Å and 14 Å chlorites in the Mg-Al-Si synthetic system.

thermal stability of amesite (650 °C, Nelson and Roy). This suggests either that amesite remains metastably present longer than a slightly less aluminous composition or that the solid solution series is broken between composition III and amesite. Experiments done on a composition less silicic than chlorites (XXIV) suggest that amesite is in fact not stable above 500 °C.

This interpretation is all the more plausible since natural mineral compositions (fig. 5) indicate that amesites appear isolated from the main grouping of natural chlorites. Thus the idea of a non-continuous solid solution should be entertained. However, the details of solid solution and possibilities of unmixing or solvus gaps in the series of aluminous chlorites is left to further more detailed investigations.

Fig. 4 illustrates the extent of 14 Å chlorite compositions found in the Mg-Al-Si system at 2 Kb pressure at various temperatures. Compositions more magnesium-rich produce a 7 Å phase, which can coexist with an aluminous 14 Å one below 500 °C. Higher temperatures at constant pressure restrain the range of chlorite solid solution, which centres around the composition  $Mg_{42}Al_{32}Si_{26}$  near 700 °C. Pressure increases the stability of a given chlorite about 25°/Kb. This effect does not, however, appear

to influence the range of solid solution between 1 and 2 Kb, where the only observed change is a slight increase in Al content as pressure increases.

The major difference between the 14 Å chlorite solid solutions deduced previously (Yoder, 1952; Roy and Roy, 1954; Fawcett and Yoder, 1964; Nelson and Roy, 1958) and those of the present study is the silica 'enrichment' due to the substitution  $\frac{1}{2}(\text{MgAl}^{\text{vi}}) \rightleftharpoons \text{Si}_4\Box^{\text{vi}}$ : a vacancy in the octahedral site compensates the increased charge on the structure resulting from the introduction of silica in the tetrahedral site (Foster, 1962).

This substitution allows deviations from the  $\text{Al}^{\text{iv}} + \text{Al}^{\text{vi}}$  substitutional series. The plotted analyses of 198 natural 14 Å chlorites and 110 serpentines from the literature compares well with the range of solid solution for 14 Å chlorite determined in the Mg-Al-Si system (fig. 5).

In the plot of natural mineral analyses,  $\text{Si} = \text{Si}$ ;  $R^{2+} = \text{Mg} + \text{Mn} + \text{Fe}^{2+}$ ;  $R^{3+} = \text{Fe}^{3+} + \text{Al} + \text{Cr}^{3+}$  ions. The analyses were selected according to the method of Foster (1962) after calculation into a mineral chemical formula. For the unit cell of  $\text{O}_{10}(\text{OH})_8$  anions,  $\text{Ca} \leq 0.10$ , octahedrally coordinated ions  $\leq 6.10$ ,  $\text{Si} \leq 4.10$  and total cations  $\leq 10.10$ . Mineral purity could not be assessed in most cases from the data given by the authors. There is a slight tendency for natural 14 Å chlorites to be more siliceous than the synthetic magnesian forms. The mineral analyses lying outside the limits defined for synthetic minerals are not particularly iron-rich so that this deviation cannot be explained by a non-homologous role of  $\text{Fe}^{2+} \rightleftharpoons \text{Mg}^{2+}$  or  $\text{Fe}^{3+} \rightleftharpoons \text{Al}^{3+}$  in the structure. Generally speaking, the natural chlorites conform well with the solid solutions found in synthetic magnesian types.

Fig. 5 also shows the limit of solid solution for 7 Å chlorites stable with 14 Å synthetic chlorites. These limits compare reasonably well with those compositions plotted for natural serpentine minerals. There are, however, several points that fall in the zone between synthetic 7 and 14 Å phases. These might be due to a mixture of serpentine and chlorite in the analysed material, but no evidence can be presented to verify this view. Considering the densities of the points representing natural minerals there seems to be a definite bimodal distribution, which corresponds well with the pattern of solid solution found in the synthetic minerals. It would be necessary to analyse coexisting mineral pairs (serpentine and chlorite) in order to establish the limits of solid solution in natural minerals.

The *cell dimensions* of the various synthetic chlorites change with composition (fig. 6). For the 7 Å polymorphs, which basically follow the  $\text{Al}_2 \rightleftharpoons \text{Si} + \text{Mg}$  substitution (XV is a slight exception) the *o60 vs. composition* plot (fig. 7) shows the *b* dimension to be a function of Al and Si content. The values found are similar to those reported by Nelson and Roy (1958) and Gillery (1956), but slightly larger (0.02 Å for *b*, and 0.05 for *c sin β*). There is no apparent change of *c sin β* dimension due to the change from 7 to 14 Å polymorph, and consequently the values fit closely those given by Nelson and Roy for the 14 Å polymorph. These authors did find a difference between polymorphs.

The totality of single phase chlorite products, in the majority of the 14 Å polymorph, give cell dimensions more variable than the 7 Å series (fig. 6). This is due to the fact that 14 Å phases have variable quantities of Al in octahedral and tetrahedral

sites and a variable octahedral occupancy, which should influence greatly the cell dimensions of the mineral. This also explains why *b* and *c* are not correlated in the more complicated substitutional series. The chlorite structure is obviously deformed by a decrease of ionic occupancy in the octahedral site.

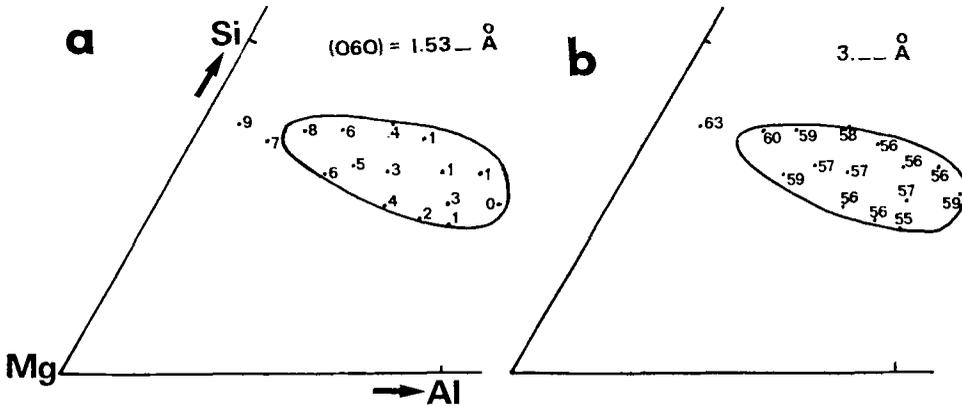
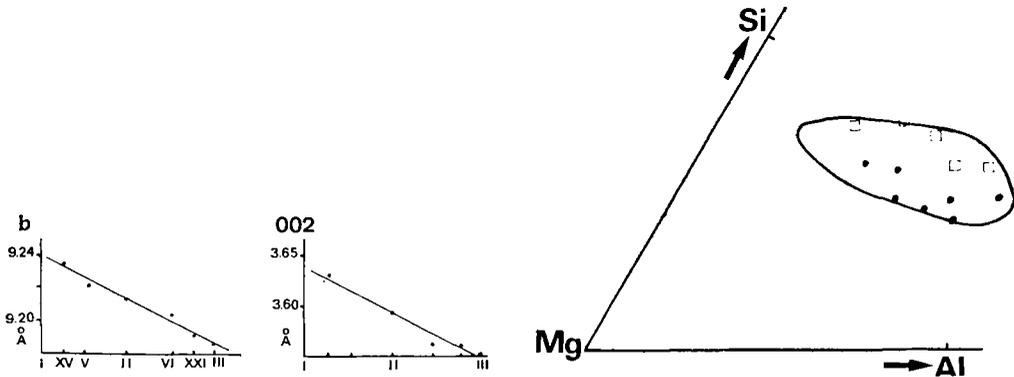


FIG. 6. (a) 060 reflections of single-phase chlorites. (b) 004 reflections of single-phase chlorites.



FIGS. 7 and 8: FIG. 7 (left). Cell parameters *b* and 004 or 002 are plotted as a function of composition in the chlorite series that show principally the MgSi  $\rightleftharpoons$  Al<sub>2</sub> substitution. FIG. 8 (right). Chlorite polytypes are plotted as a function of composition. Type I = dots, types II = squares. Determinations after the method of Brown and Bailey, 1962.

*Polytypes.* The polytypes of the chlorites synthesized have been determined using the criteria of Brown and Bailey (1962) (fig. 8). The monoclinic structure is predominant in aluminous minerals. It appears that the polytype is controlled by polymorph or chemical composition. Type I is typical of low silica compositions where the form Ia is predominant. These compositions also maintain a predominant 7 Å polymorph above 400 °C. More silica-rich (and 14 Å) chlorites are typically type II, of both *a* and *b* forms. These observations are in general agreement with the deductions of relative polytype stability based upon structural information (Brown and Bailey,

1962). The type II is most stable (and most common in nature) while I is less stable and less frequent. This suggests that the type I found in synthetic chlorites with a persistent dominant 7 Å structure indicates the metastable persistence of this 7 Å polytype even though a small 14 Å peak is present in the X-ray diffraction pattern. Hayes (1970) has found a similar polytype distribution pattern for authigenic 7 Å and metamorphic 14 Å chlorites.

*Expandable phases.* There are apparently three distinct types of stable expandable minerals in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  at high pressures. A trioctahedral series, with a possible general formula  $[(\text{Mg}_{2-x}\text{Al}_x)_3(\text{Si}_{4-(x+0.34)}\text{Al}_{(x+0.34)})_4](\text{Mg}_{0.17})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , which is parallel to the  $\text{Al}^{\text{VI}}\text{-Al}^{\text{IV}}$  substitutional series of the chlorites. The net charge on the 2:1 structure is about  $-0.34$  per  $\text{O}_{10}(\text{OH})_2$ . This compositional series is divided into two parts: one predominantly fully expandable at low temperatures (17 in tables and figures) and an aluminous form, which increases its compositional range with temperature. This latter phase is expandable to 15.2 Å upon a glycolation (15 in tables and figures). Both types contract to about 14 Å spacings when heated to 400 °C at 1 atmosphere.

These typical properties of the expanding phases correspond to those of swelling chlorite (17 Å phase) and vermiculite or expandable chlorite (15 Å phase), see Brown (1961). Natural random interlayering of montmorillonite+chlorite may possibly occur (Seifert, 1970). However, this is unlikely since the 15 Å phase has the same bulk composition as the 17 Å series. Since chlorites contain less silica than the expanding phases a third mineral, quartz, would have to be produced to allow montmorillonite-chlorite interlayering. Quartz was not evident in run products that contained a 15 Å phase.

A dioctahedral expandable mineral was observed that seems to be centred around the composition  $\text{Mg}_{10}\text{Al}_{30}\text{Si}_{60}$  giving an approximate formula  $[(\text{Al}_{1.66}\text{Mg}_{0.34})^{-0.34}(\text{Si}_{3.77}\text{Al}_{0.23})^{-0.23}](\text{Mg}_{0.29})^{+0.58}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . This composition gives a structure expandable to 17 Å below 370 °C at 2 Kb and 15.2 Å above this temperature. Its upper stability limit is similar to that of the trioctahedral magnesian series. Conversion between the two expandabilities, 15 and 17, and compositions between two forms of different compositions give a 16.2 Å expandable structure, which sometimes shows an ordering peak at low angles (30 Å). Also, the 15 Å structure is frequently ordered near its upper thermal-stability limit. Cation exchange-capacity determinations and response to potassium saturation are different from those for the trioctahedral phases. However, further work is needed to delimit the entire substitutional series before such measurements will be meaningful.

It is assumed that no fully expandable mineral exists in the system  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  at high P-T conditions. Experiments to determine the lower stability of talc in this study and in that of Johannes (1969) produced serpentine plus quartz. However, a Mg-Si montmorillonite (stevensite) has been synthesized at 80 °C and 1 atmosphere (Esquevin, 1960).

It is instructive to compare the physical characteristics of the different trioctahedral minerals as a function of the interlayer ion present. Aluminous minerals prepared

either at low or high temperature (Estéoule, 1969; Iiyama and Roy, 1963) that contain calcium or sodium ions respond to polar liquids in the same fashion as dioctahedral montmorillonites, i.e. 12.5 Å upon heating to 100 to 150 °C, 14 Å under air-drying, 17 Å upon water or glycol saturation. Apparently the non-aluminous forms (stevensite) containing Na<sup>+</sup> or Ca<sup>2+</sup> interlayer ions respond in a like manner. These characteristics contrast with the trioctahedral expanding phases studied here, which can be supposed to contain magnesium interlayer ions, and which are more closely comparable, in physical properties, to an expanding chlorite or a vermiculite.

It is possible to attribute the difference in physical behaviour to the presence of a hydrated alumina-magnesium complex in the interlayer position, which prevents complete collapse of the layers to a mica-like structure. If the interlayer ion were fully exchangeable, potassium saturation would produce a collapsible structure, which would reduce to an approximate 10 Å basal spacing upon heating. This is not the case for the expanding phases observed here. The exact quantity and position of aluminium ions in the octahedral sites and interlayer sites cannot be assessed at present. A somewhat similar problem arises for the chlorites themselves. At present we can only say that these expanding trioctahedral minerals are not simply trioctahedral montmorillonites.

#### *Phase relations in P-T space*

One of the most fundamental points in phase equilibria involving chlorites is the relationship between 7 and 14 Å polymorphs. In nature, 7 Å phases identified as serpentines have a limited compositional range (fig. 5), but when the environment of their formation indicates low-temperature conditions, that of sediments, the solid solution is expanded toward trivalent ionic forms. Nelson and Roy (1958) suggested the name septechlorite for aluminous low-temperature polymorphs. The experimental data of their study suggests an apparent temperature of 450 to 500° for the 7 Å-14 Å transformation, which contrasts sharply with the information available for natural minerals such as chamosite and berthierine.

The simple polymorph transition for single-phase chlorite products was not accomplished in the experiments reported here. However, compositions outside the boundaries of 7 Å chlorite solid solution indicate the limits of chlorite polymorph stability. Silica-rich compositions (XIII, XI) and one more aluminous than 14 Å chlorite (XXII) indicate that the 14 Å chlorites are stable above 300 °C at 1 Kb and 400 °C at 2 Kb (fig. 9). The transition 7 Å → 14 Å was observed in the presence of other phases because there is a larger solid solution range in the 14 Å chlorite than in 7 Å chlorites. The slope of the polymorphic transition is rather great (~ 100 °C/Kb), an observation that should lead to caution about the determinations since the cell volumes, based on *b* and *c* cell dimensions, appear to change little during the transformation. Little information can be gathered from natural examples. Sedimentary chlorites found on ocean and estuary bottoms are 7 Å whereas those in sedimentary rocks are usually 14 Å. However, the physical conditions of polymorphic stability cannot be deduced from available information for natural iron-bearing species.

The association quartz+chlorite is limited both in P-T and compositional space.

The reaction chlorite+quartz = cordierite+talc, established at 2 Kb by Fawcett and Yoder (1964) has been determined at 1 Kb in the present study (525 °C). The compositional limit of the most magnesian chlorite in the quartz-chlorite field is at  $Mg/Al = 85/15$ , exactly that of this association found in natural rocks (see figs. 5 and 1). This suggests a close parallel between the iron-bearing system and that studied

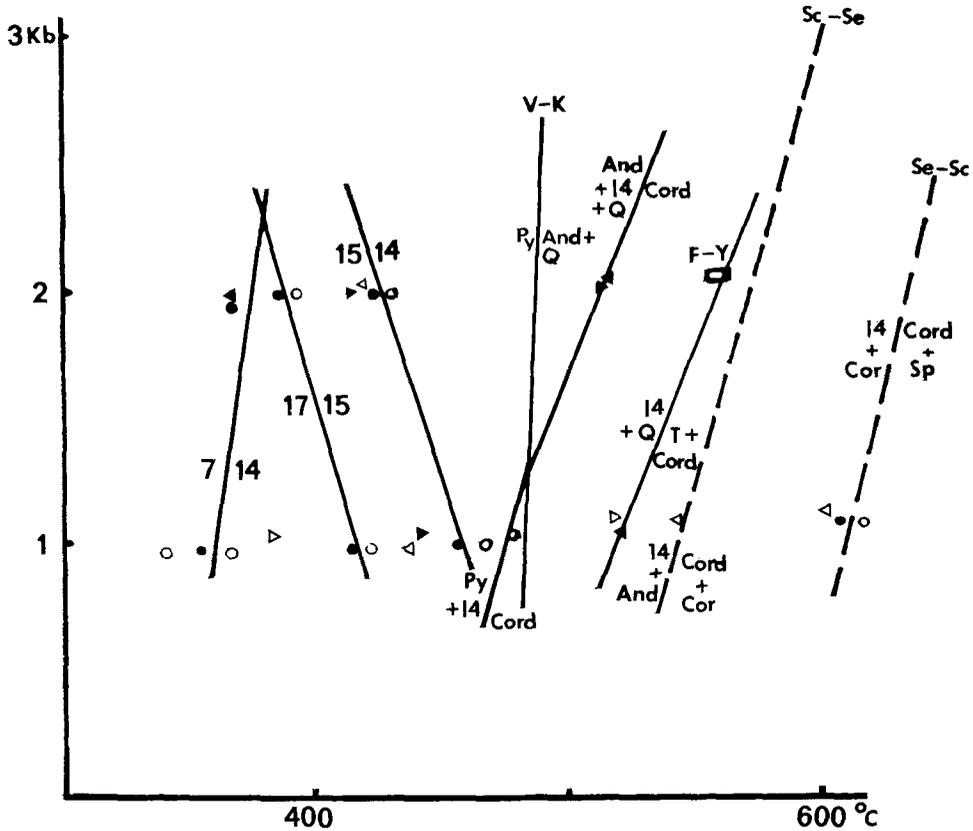


FIG. 9. Determined boundaries for the reactions critical to chlorite stabilities are given as a function of pressure and temperature. The points marked F-Y = data from Fawcett and Yoder (1969); Se-Sc = Seifert and Schreyer (1970); Sc-Se = Schreyer and Seifert (1969). V-K = Velde and Kornprobst (1969). Triangles indicate the direction of reaction observed in the products. Circles represent synthetic products from gels.

experimentally. The lower temperature limit for the association is that of the upper stability of the 15 Å expandable phase, near 450 °C in the magnesian system.

Phase relations in P-T space for chlorite, andalusite, pyrophyllite, quartz, and cordierite have been determined, or redetermined, at 1 and 2 Kb (fig. 9). The reaction pyrophyllite = andalusite+quartz joins the chlorite+pyrophyllite = cordierite and chlorite+andalusite+quartz = cordierite curves near 1.4 Kb at 490 °C. This is in



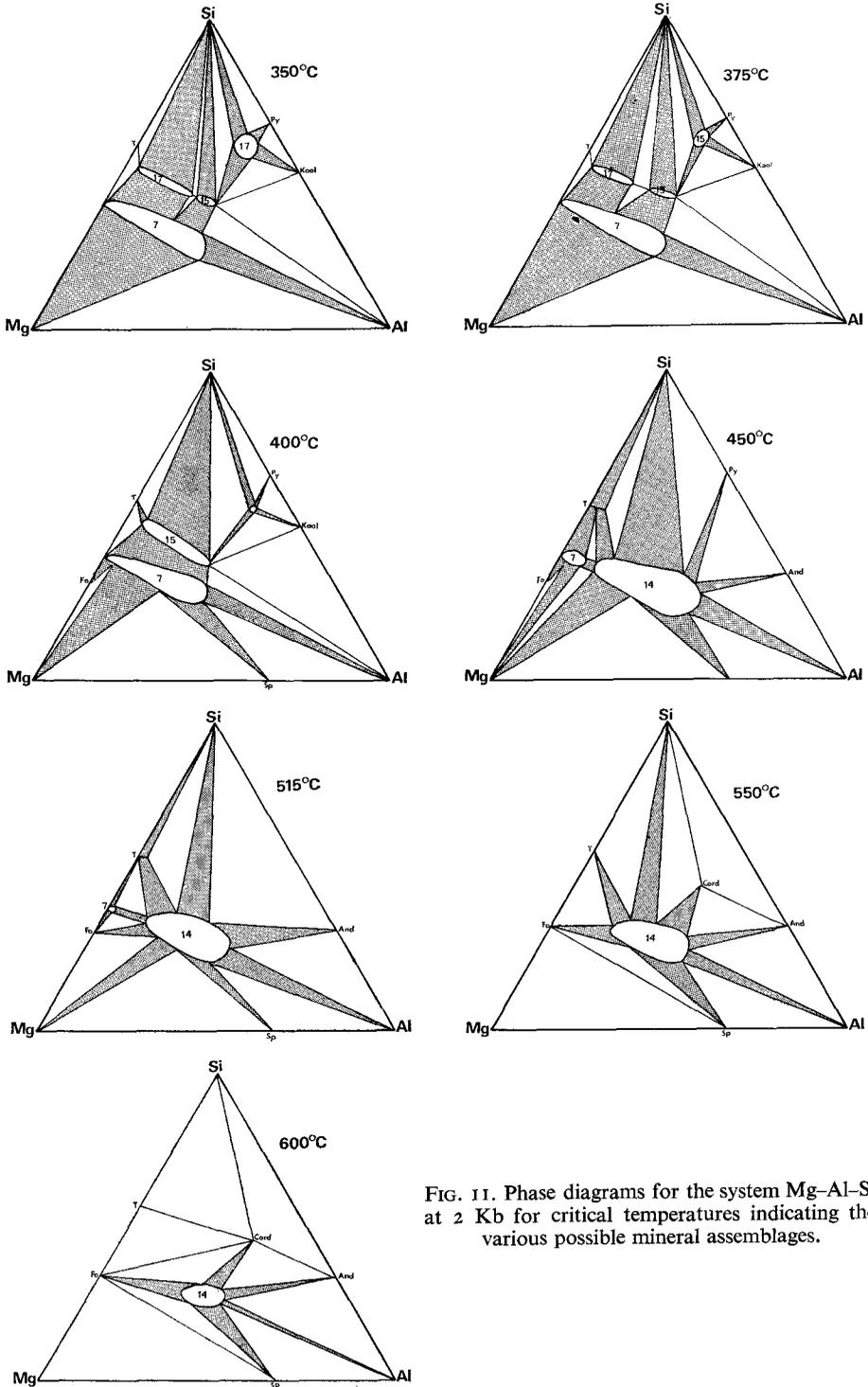


FIG. 11. Phase diagrams for the system Mg-Al-Si at 2 Kb for critical temperatures indicating the various possible mineral assemblages.

of other minerals. It is thus probable that these chlorite analyses do not represent single phase material, but instead, sediments in the course of transformation to a chlorite. This is apparent in the study of Porrenga (1967) where the chlorites are just beginning to form, and where the analysis plots closest to montmorillonoids. Rohrllich *et al.* (1969) also indicate the presence of montmorillonoids in the material they have analysed as chlorite.

If the compositional series of single phase Mg and Fe<sup>2+</sup> 7 Å chlorites are parallel, the common occurrence of quartz with these chlorites is difficult to understand since the phase relations deduced in the magnesian system would seem to preclude such a stable association (fig. 11). Solubility data for quartz and other forms of silica indicate that quartz is the stable phase at 25 °C, 1 atmosphere pressure (Krauskopf, 1959). But in many natural waters the silica concentration exceeds that which is controlled by quartz solubility. In nature as in the laboratory, the form of silica precipitated from solution is non-crystalline. Thus the effective reactions observed in nature at low temperature will be governed by amorphous silica and not quartz, even though the latter might be physically present. As a result, 7 Å chlorite can form in the presence of quartz, but not amorphous silica. In cases of silica saturation, an expandable phase will be present instead of 7 Å chlorite.

*Conclusion.* Probably the most important aspect of this study is the inference that synthetic and natural minerals have nearly the same phase relations and compositional limits. This permits a reasonably liberal use of the experimental data in interpreting natural mineral assemblages. It should be recalled, however, that the addition of iron will undoubtedly lower the thermal stability of the chlorite phases relative to other silicates.

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