

PHASE RELATIONSHIPS OF CHLORITES
IN THE SYSTEM $MgO-Al_2O_3-SiO_2-H_2O$

J. J. FAWCETT¹ AND H. S. YODER, JR., *Geophysical Laboratory,
Carnegie Institution of Washington, Washington, D.C.*

ABSTRACT

The upper stability limits of magnesian chlorites have been determined at pressures up to 10 kb with water pressure equal to total pressure. The breakdown curve passes through the points $768^\circ \pm 7^\circ$ C. at 3.5 kb, $787^\circ \pm 7^\circ$ C. at 5 kb, and $830^\circ \pm 5^\circ$ C. at 10 kb. At the maximum temperature limit of the chlorite stability field the composition of chlorite coexisting with other phases varies with pressure, becoming more aluminous at higher pressures. Above 3.5 kb the magnesian chlorites react to form enstatite+forsterite+spinel+vapor and at lower pressures forsterite+cordierite+spinel+vapor. The invariant point at which forsterite, cordierite, spinel, enstatite, chlorite and vapor can coexist was located at 3.25 ± 0.25 kb and $765^\circ \pm 10^\circ$ C.

In contrast to earlier studies in the system $MgO-Al_2O_3-SiO_2-H_2O$, chlorite and quartz are shown to coexist in equilibrium between 450° and 575° C. at 2 kb P_{H_2O} and between 475° and 600° C. at 5 kb P_{H_2O} . The reaction taking place at the upper limit of the quartz+chlorite field is chlorite+quartz \rightleftharpoons talc+cordierite+vapor. Talc produced during these experiments contains a maximum of 4.00 weight per cent Al_2O_3 (of the hydrous composition) at water pressures of 10 kb. This corresponds to $7.72MgO \cdot 0.28Al_2O_3 \cdot 5.72SiO_2 \cdot 2H_2O$.

INTRODUCTION

The chlorite group of minerals is very widespread in its occurrence in the earth's crust, its environment varying from that of unconsolidated sediments (Carroll, 1963) to both igneous (Lehmann, 1965; Fawcett, 1965) and high-grade metamorphic rocks (Mason, 1962). The great variation in rock types bearing chlorite suggests a very wide range of stability and possibly in chemical composition. It is not surprising, therefore, to find several laboratory studies of the phase relations and stability limits of the chlorites. Yoder (1952) studied the clinocllore ($5MgO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$) composition as part of a wider investigation of the system $MgO-Al_2O_3-SiO_2-H_2O$ and showed that at water pressures up to 2 kb clinocllore breaks down to a mixture of forsterite+cordierite+spinel+vapor. The reaction temperatures at 1 and 2 kb are 680° and 720° C., respectively. This study showed the existence of the tie line between forsterite and cordierite, in agreement with the earlier work of Rankin and Merwin (1918) in the system $MgO-Al_2O_3-SiO_2$. Yoder (1952), in the synthesis of chlorites, encountered the problem of polymorphism discussed earlier by Brindley (1951) and Brindley *et al.* (1951). The most distinctive feature of each type is displayed in the x-ray powder pattern where the chlorite structure (*i.e.* that of the natural chlorites)

¹ Present address: Department of Geology, University of Toronto, Toronto, Ontario, Canada.

displays a 14 Å basal spacing. At low temperatures these compositions form a kaolinite-like structure probably related to the serpentine minerals which have a 7 Å *c* dimension. Roy and Roy (1955) confirmed the existence of the forsterite-cordierite tie line and discussed further the problem of the two structures obtained from chlorite compositions. Nelson and Roy (1954, 1958) made a detailed study of the solid solution in the magnesian chlorites and showed that solid solution of the 14 Å structure extended to the corundophyllite (Hey, 1954) member of the series $(4\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ but not quite to the Al_2O_3 -free composition. The 7 Å structures were produced from the full range of compositions, but there was no unequivocal evidence of the relationship of the two types. Gillery (1959) continued this line of investigation and concluded that in the compositions of the chlorite solid solution series temperature of crystallization controls the mineral family produced (chlorite or serpentine) and chemical composition controls the polytype (one layer, six layer, or mixed layer). There is, however, still no concrete evidence that the 7 Å structure (aluminous serpentine of Yoder or septe-chlorite of Roy and Roy) has a true stability field with respect to the 14 Å chlorites. Both 7 and 14 Å structures have been produced at all pressures investigated in this study, but the problem of their relationship has not been pursued in any detail nor has an attempt been made to study the polytypism outlined by Brown and Bailey (1962, 1963). Segnit (1963) synthesized clinocllore at pressures up to 20 kb in a piston-anvil apparatus, but the products of decomposition at the upper stability limit differ from those in the present investigation and will be discussed more fully below. An additional problem concerns the relationship of the forsterite-cordierite and enstatite-spinel tie lines within the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. This topic was discussed by Tilley (1923) and Roy and Roy (1955) and more recently by Yoder and Chinner (1960) and Chinner and Schairer (1962). New data bearing on the problem are discussed in detail later in this paper.

Phase relations of the magnesian chlorites presented in all experimental studies up to the present time suggest that chlorite and quartz do not coexist in the temperature range 130° to 800° C. at water pressures up to 2 kb. The data of Yoder (1952) and Roy and Roy (1955) consistently suggest that the stable tie lines under these conditions are talc-montmorillonite, talc-pyrophyllite, talc-cordierite, forsterite-cordierite, or enstatite-cordierite, each of which prohibits the existence of a stable quartz+chlorite assemblage. As the most common occurrence of chlorite in nature (low-grade regional metamorphic rocks) is in the presence of excess quartz, there is clearly a discrepancy between the natural occurrences and laboratory data. A series of experiments was designed to in-

investigate this anomaly and test the relationships between the quartz-chlorite tie lines and those of the conflicting assemblages listed above. Results of these studies are presented in the second half of the paper.

The present study was carried out as part of a wider study of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at water pressures up to 10 kb. As the chemical compositions of twenty rock-forming minerals, many of which are of critical importance in metamorphic petrology, can be plotted in this system, a detailed knowledge of its phase relations will assist in the evaluation of metamorphic conditions.

STARTING MATERIALS AND EXPERIMENTAL METHOD

The starting materials for this investigation varied both in bulk composition, plotted in Fig. 1, and physical state. For the determination of the upper stability of the chlorites, oxide mixes of compositions on the chlorite solid solution join were prepared from the purified oxides MgO , SiO_2 and Al_2O_3 supplied by Dr. J. F. Schairer. These compositions were $5.5\text{MgO}\cdot 0.5\text{Al}_2\text{O}_3\cdot 3.5\text{SiO}_2$ (P_2 of Yoder, 1952), $5\text{MgO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$

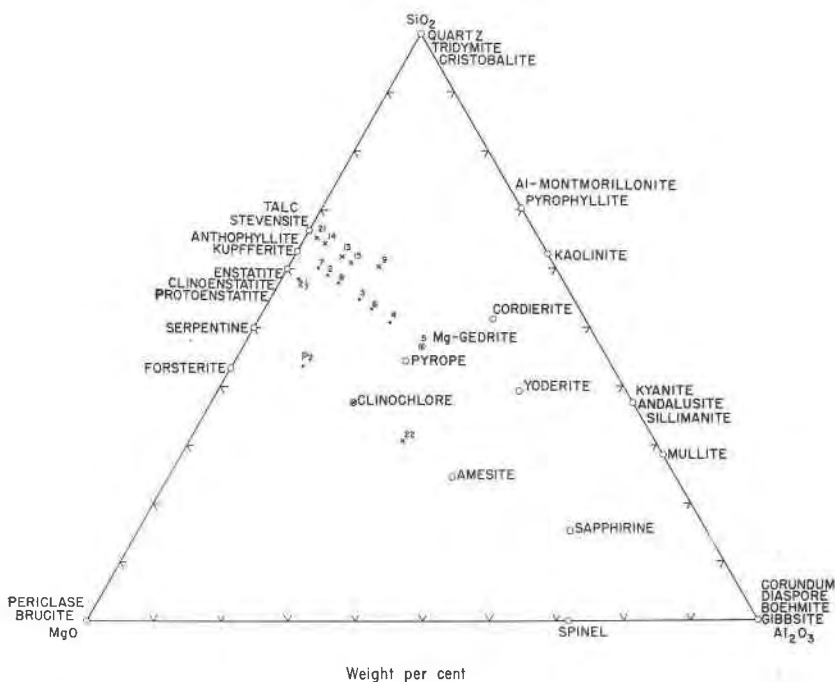


FIG. 1. Composition of phases and starting materials projected onto the anhydrous face of the tetrahedron $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. Solid circles indicate glasses, crosses indicate oxide mixes, and open circles are the mineral phases.

(clinocllore), $4.5\text{MgO} \cdot 1.5\text{Al}_2\text{O}_3 \cdot 2.5\text{SiO}_2$, and $4\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (ame-site composition). For additional starting materials the clinocllore oxide mixture (mix 17) was crystallized under the conditions described below to clinocllore, a mixture of forsterite+cordierite+spinel, or forsterite+enstatite+spinel. A synthetic glass of pyrope composition ($3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) and its crystalline equivalent of cordierite+enstatite+spinel (crystallized at 900°C . and 3.5 kb $P_{\text{H}_2\text{O}}$) were used in several runs and also a natural chlorite (leuchtenbergite) from Gabbs, Nevada (Table 1), the latter kindly supplied by Dr. G. T. Faust (Kerr and Callaghan, 1935).

TABLE 1. ANALYSIS OF NATURAL CHLORITE (LEUCHTENBERGITE) USED AS STARTING MATERIAL (KERR AND CALLAGHAN, 1935)

SiO ₂	31.02
Al ₂ O ₃	20.79
Fe ₂ O ₃	0.04
FeO	1.20
MgO	34.25
CaO	0.02
Na ₂ O	0.51
K ₂ O	0.07
H ₂ O ⁻	0.03
H ₂ O ⁺	12.77
TiO ₂	trace
P ₂ O ₅	0.01
MnO	trace
	100.71

Studies of the quartz-chlorite assemblages were carried out mainly on a series of glasses, prepared under the supervision of Dr. J. F. Schairer, whose compositions may be plotted on the join anthophyllite—Mg-gedrite. The compositions of these glasses and others used in this study are plotted in Fig. 1. In addition to the glasses several oxide mixtures and mixtures of natural and synthetic minerals were used as starting materials. Synthetic minerals used were talc and clinocllore, both prepared for this work; cordierite, supplied by Dr. W. Schreyer; and purified quartz from Lake Toxaway. Natural minerals were a cordierite from Guilford, Connecticut, supplied by Dr. W. Schreyer; the chlorite (leuchtenbergite) already mentioned; a talc from India (not analyzed) supplied by Dr. F. R. Boyd; and quartz from Lisbon, Maryland, supplied by Dr. J. F. Schairer. Oxides and mineral phases were mixed under acetone for 3 to 4 hours in a mechanical mortar and dried at 110°C . for at least

24 hours before use. The mixtures of mineral phases were particularly useful to confirm the results obtained from glasses and also to reverse reactions across the equilibrium curves. Other starting materials such as P_2 and the crystallized amesite composition were available from Yoder's (1952) work in this system.

Charges, together with excess water, were sealed in platinum capsules and held at the required temperature and pressure for periods varying from a few hours to several weeks. Cold-seal pressure vessels (Tuttle, 1949) were employed for runs between 2 and 5 kb P_{H_2O} at temperatures up to 900 and 860° C., respectively. An argon medium, internally heated, pressure vessel (Yoder, 1950) was used for runs under more extreme conditions. The number of successful experiments carried out at pressures up to 5 kb P_{H_2O} has been greatly increased by the use of cold-seal pressure vessels manufactured from Union Carbide Stellite Division's alloy R41. Temperatures up to 860° C. have been imposed on these vessels of $1\frac{1}{4}$ inch outside diameter with $\frac{1}{4}$ inch bore at 5 kb P_{H_2O} and maintained for 6 hours without failure. It should be emphasized, however, that each vessel has its own characteristics on approaching limiting P and T conditions, and explosive failure occurred once during quenching. Similar vessels have been used repeatedly between 775° and 825° C. at 5 kb P_{H_2O} ; however, two have failed during longer runs (3 weeks) in the same temperature range but at lower pressure following successful runs under extreme conditions. The life of the pressure vessels may be lengthened following periodic heat treatment in the manner described by Luth and Tuttle (1963). Fortunately, failure of the R41 alloy is usually similar to that of the more common Union Carbide alloy Stellite 25, *i.e.* by flow rather than by fracture.

Temperatures reported by means of both chromel-alumel and platinum/90 platinum 10 rhodium thermocouples are believed to be accurate to $\pm 5^\circ$. Pressures measured on Bourdon-type gauges up to 5 kb are considered accurate to ± 3 per cent and those by the change in resistance of a manganin coil in the internally heated equipment are considered accurate to ± 1 per cent. All runs were examined under a binocular microscope and also in oil immersion mounts in transmitted light. X-ray diffraction powder patterns of the resulting materials were made for the majority of runs using a Norelco diffractometer.

The more precise measurements of the x-ray patterns from talc and chlorite were made by mixing with the sample Lake Toxaway quartz as an internal standard. The 2θ values recorded are the averages from eight oscillations over a particular pair of peaks.

Optical examination of the run products was often very unsatisfactory, particularly for the runs carried out at lower temperatures (below about

650° C.). Run products are always extremely fine grained under such conditions, and it is often impossible to distinguish even moderate proportions of the various phases under the microscope. The presence of several phases in low-temperature runs is based on their *x*-ray diffraction powder patterns, and there is consequently a larger uncertainty in determining the position of the field boundaries than in the regions where precise optical identification is possible.

THE UPPER STABILITY OF THE MAGNESIAN CHLORITES

Results of the more critical runs which delineate the chlorite stability field are presented in Table 2 and are brought together as a *P-T* diagram in Fig. 2, where the data of Yoder (1952) are shown for the stability limit of clinocllore at pressures up to 2 kb P_{H_2O} . The upper stability limits of magnesian chlorites have been determined at water pressures of $3\frac{1}{2}$, 5, and 10 kb, and the relevant reaction has been reversed at 10 and 5 kb P_{H_2O} . It is important to note, as may be deduced from Table 1, that at water pressures above about $3\frac{1}{2}$ kb clinocllore is not the most stable of the magnesian chlorites. Data presented by Nelson and Roy (1958) showed that at 1000 atmospheres water pressure the magnesian chlorites close to the clinocllore composition are more stable than either the corundophyllite or penninite members of the series (nomenclature of Hey, 1954). Present experiments suggest that the composition of maximum thermal stability varies with pressure and therefore at 5 and 10 kb P_{H_2O} the composition of the most stable of the magnesian chlorites lies about half way between the clinocllore and corundophyllite compositions. The most conclusive evidence for this deduction is the reaction of clinocllore at $3\frac{1}{2}$ kb to produce a mixture of a chlorite+talc+forsterite and at 5 and 10 kb P_{H_2O} to produce forsterite+enstatite+chlorite. The chlorite resulting from each of these runs must be more aluminous than the clinocllore starting material. It is noted in passing that all enstatites reported in this paper are aluminous orthorhombic varieties (Boyd and England, 1960) but there has been no detailed examination of their alumina content. At water pressures up to about $3\frac{1}{4}$ kb magnesian chlorites break down to the assemblage forsterite+cordierite+spinel but above this pressure the forsterite-cordierite tie line is no longer stable and the breakdown assemblage is forsterite+enstatite+spinel. There is no evidence of a stable talc-spinel tie line, as reported by Segnit (1963), under any of the conditions of these experiments. In common with the experience of Yoder (1952) and Roy and Roy (1955) talc+spinel appears in the products of several runs, but it was shown, by increasing the duration of a run, that the talc-spinel tie line is metastable at pressures up to 10 kb P_{H_2O} .

TABLE 2. CRITICAL RUN DATA FOR THE UPPER STABILITY LIMIT OF
MAGNESIAN CHLORITES

<i>T</i> , °C	<i>P</i> , kb	Duration, hours	Result*	Run No.
<i>A. Starting material: Synthetic clinochlore</i>				
1000	2	6	Fo+En+Sp+rare Co	611
1100	2	6	Fo+En+Sp	619
1100	2	96	Fo+Co+Sp	632
1200†	2	97	Fo+Sp+L	636
900	2.5	4	Fo+En+Sp+Co	604
900	2.5	48	Fo+En+Sp+trace Co	537
775†	3	33	Fo+Co+Sp	540
900†	3	96	Fo+En+Sp	562
900†	3.5	24	Fo+En+Sp	537
790	5	138	Fo+Sp+Co+Tc+Chl	639
800	5	24	Chl	395
800†	5	83	Fo+Sp+En+traceChl	704
815	5	40	Tc+Chl+Fo+En+Sp	403
837†	10	11	Fo+En+Sp	578
850†	10	47	Fo+En+Sp	510
<i>B. Starting material: Mix 17, clinochlore composition</i>				
690†	2	230	Chl	522
710†	2	766	Chl+Fo+Tc	529
1000	2	1	Fo+Sp+En	617
1000†	2	6	En+Sp+Fo+Co	610
1100	2	6	Fo+Co+En+Sp	618
1100	2	96	Fo+Co+En+Sp	629
1200	2	97	Fo+Sp+L	633
900	2.5	48	Fo+En+Co+Sp	571
1100	2.5	17.5	Fo+En+Sp	645
765†	2.75	656	Fo+Co+Sp	471
775	3	330	Fo+Co+Sp	538
900	3	96	Fo+En+Sp	559
1100	3	39	Fo+En+Sp	649
1150†	3	4	Fo+Sp+L	664
800	3.1	336	Fo+Co+Sp	661
800†	3.5	486	Fo+Co+En+Sp	437
850†	3.5	264	En+Sp+Fo	454
900	3.5	24	Fo+En+Sp	534
770	5	140	Chl	703
780†	5	131	Fo+Tc+Chl	701
825†	5	116	Fo+En+Sp	433
875†	5	115	Fo+En+Sp	441
825	10	10	Chl+Fo+En	567
837	10	11	Fo+En+Sp	575
850	10	47	Fo+En+Sp	511
<i>C. Starting material: Mix 22 (clinochlore₅₀-amesite₅₀)</i>				
710	2	766	Chl	528
750†	5	164	Chl	546
775	5	195	Chl+Fo+Tc	552
825	10	10	Chl+Fo+En	569

* Am, amesite; And, andalusite; Anth, anthophyllite; Chl, chlorite; Cl, clinochlore; Co, cordierite; Cor, corundum; En, enstatite; Fo, forsterite; L, liquid; M, montmorillonite; P, pyrophyllite; Q, quartz; S, serpentine; Sp, spinel; Tc, talc.

† Runs plotted in Fig. 2.

TABLE 2—(continued)

T, °C	P, kb	Duration, hours	Result*	Run No.
<i>D. Starting material: Leuchtenbergite (natural)</i>				
765	2.75	656	Fo+Co+Chl+Sp	472
765†	3.5	477	Chl	416
775	3.5	212	Fo+Co+Sp+minor Chl	406
800	3.5	118	Fo+En+Sp+Anth+Co+Tc	402
800	3.5	486	Fo+En+Sp+Anth+Co	436
850	3.5	266	Fo+En+Sp+minor Anth+Co	455
787	5	47	Chl	512
800	5	24	Chl	394
825	5	281	Fo+En+Sp+minor Anth	451
875	5	115	Fo+En+Sp	442
850	10	47	Fo+En+Sp	508
<i>E. Starting material: Forsterite+enstatite+spinel, crystallized from mix 17, clinoclone composition</i>				
1000	2	6	Fo+En+Sp	612
1075	2	18	Fo+En+Sp	608
1100	2	6	Fo+En+Sp	620
1100	2	96	Fo+Co+Sp	631
1200	2	97	Fo+Sp+L	634
900	2.5	48	Fo+En+Sp	574
1100†	2.5	17	Fo+En+Sp	643
825†	10	10	Chl+Fo+En+Sp	570
<i>F. Starting Material: Forsterite+cordierite+spinel, crystallized from mix 17, clinoclone composition</i>				
1000	2	6	Fo+Co+Sp	609
1075	2	18	Fo+Co+Sp	607
1100	2	6	Fo+Co+Sp	621
1200	2.5	97	Fo+Sp+L	635
900	2.5	4	Fo+Co+Sp	603
1100	2.5	17	Fo+Co+Sp	644
1100†	2.75	95	Fo+Co+Sp	660
1100†	3	39	Fo+En+Sp	647
800	3.1	336	Fo+Co+Sp	662
780†	3.3	332	Fo+Co+Sp+En	596
<i>G. Starting material: Cordierite+enstatite+spinel, crystallized from glass of pyrope composition at 900°C and 5 kb P_{H₂O}</i>				
1100	2.75	95	Co+En+Sp	659
790†	3.1	336	Fo+Co+Sp	663
<i>H. Starting material: Forsterite+talc+amesitic chlorite (minor)</i>				
770†	5	140	Chl+Tc+Fo (both minor)	702
<i>I. Starting material: Glass, 13MgO·Al₂O₃·15SiO₂</i>				
775†	10	72	Chl+Tc	222

Anthophyllite as well as talc is a metastable breakdown product of chlorite, and the persistence of these two phases lengthens the time required to locate precisely the reaction temperatures. For instance, if synthetic chlorite is used as starting material in a run at 815° C. and 5 kb P_{H₂O}, both talc and anthophyllite persist in the reaction products, together with forsterite+enstatite+spinel, for over 40 hours and traces of anthophyllite are still present after 280 hours. The reaction producing

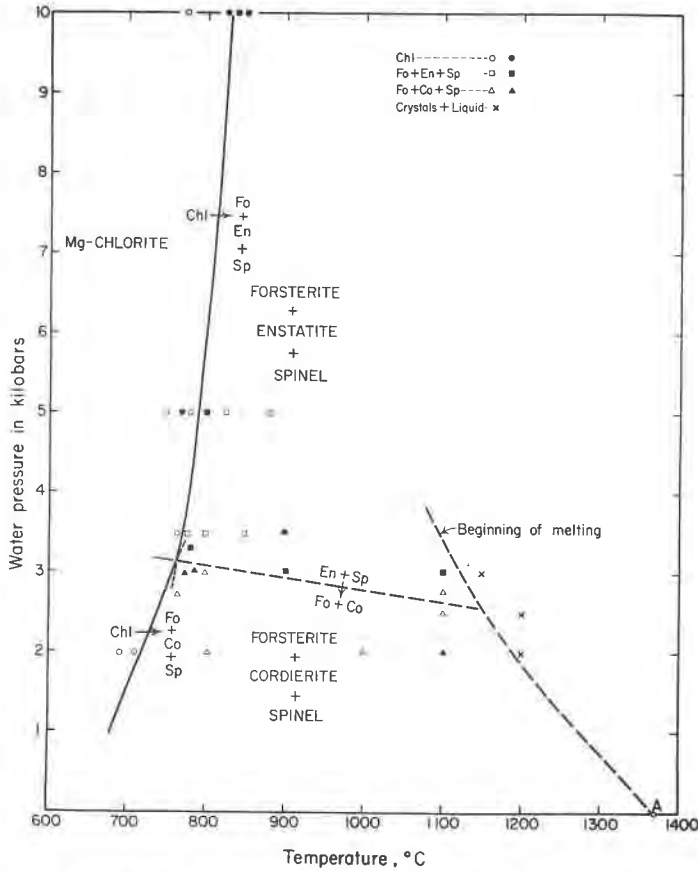


FIG. 2. The upper stability limits of magnesian chlorites. Note that the composition of the chlorite changes with pressure, being approximately of clinocllore composition ($5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) below 3 kb $P_{\text{H}_2\text{O}}$, but at 10 kb $P_{\text{H}_2\text{O}}$ it contains between 1 and 2 moles Al_2O_3 . Below 2 kb $P_{\text{H}_2\text{O}}$ the curve is taken from the data of Yoder (1952), and point A is taken from Rankin and Merwin (1918). Open symbols represent the synthesis of the minerals from glasses or oxide mixtures, and solid symbols represent the conversion from one mineral or mineral assemblage to another, *i.e.*, a reversal of the reaction across a boundary curve.

talc and anthophyllite is probably analogous to that described by Greenwood (1963) for the production of metastable anthophyllite from talc. The chlorite structure consists of interlayered "talc" and "brucite" sheets, and breakdown of the chlorite probably results in the separation of the sheets followed by disintegration of "talc" sheets to anthophyllite + enstatite. Greenwood also reported quartz as a breakdown product of

talc, but it was not detected in the breakdown of chlorite. Forsterite, a major product of the reaction, is not stable in the presence of quartz. Silica released during the disintegration of "talc" layers in the chlorite structure must react immediately with the "brucite" sheets, reaction products depending on temperature and pressure.

Metastability is also a problem in the region of the invariant point on the chlorite reaction curve. The point has not been located very precisely owing to the metastable persistence of all phases involved. Metastable phases are present even after runs of several weeks' duration, regardless of the nature of the starting material. For instance, at 3 kb P_{H_2O} and 775° C., above the chlorite stability and within the forsterite + cordierite field, enstatite crystallizes from a glass of pyrope composition and will persist in a run of 2 weeks' duration. Similarly, at $2\frac{3}{4}$ kb and 765° C. natural leuchtenbergite (clinocllore composition) persists together with its breakdown products forsterite + cordierite + spinel in a run of 656 hours. Even at high temperatures (1100° to 1150° C.) the reaction forsterite + cordierite \rightarrow enstatite + spinel is very slow. At a water pressure of $2\frac{3}{4}$ kb and 1100° C. neither forsterite + cordierite + spinel nor forsterite + enstatite + spinel mixtures (crystalline) show any sign of reaction after 95 hours. This reaction (enstatite + spinel \rightleftharpoons forsterite + cordierite) has been carried to completion in 96 hours at 1100° C. and water pressures of 2 and 3 kb (Table 2, sections E and F). This is interpreted as indicating that the position of the reaction curve is very close to $2\frac{3}{4}$ kb P_{H_2O} at 1100° C. The reaction does not proceed, in the duration of the experiment, unless it is considerably displaced from the reaction curve.

The breakdown products of magnesian chlorites, as established by all work at pressures up to 3 kb P_{H_2O} , are forsterite + cordierite + spinel + vapor. However, several earlier papers (Tilley, 1923; Brindley and Ali, 1950; Roy and Roy, 1955) discuss the possible relationships of the forsterite-cordierite and enstatite-spinel tie lines. Tilley (1923) commented on the relationship of Rankin and Merwin's (1918) work in the system $MgO-Al_2O_3-SiO_2$ to natural assemblages resulting from thermal metamorphism. He noted that the assemblage forsterite + cordierite + spinel is absent in nature and is replaced by enstatite + cordierite + spinel and forsterite + enstatite + spinel. Mineral assemblages containing enstatite + spinel were obtained by Roy and Roy (1955) but were considered by those authors to be metastable. Segnit (1963) reported the breakdown products of clinocllore to be talc + spinel + forsterite at pressures between 6 and 15 kb. Although both Roy and Roy and Yoder found talc + spinel assemblages, the talc-spinel tie line was considered in both papers to be metastable.

Additional experimental evidence bearing on the stability of the enstatite-spinel and talc-spinel tie lines is found in the work of Yoder and

Chinner (1960) and Chinner and Schairer (1962). Yoder and Chinner studied the pyrope composition ($3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) at 10,000 bars $P_{\text{H}_2\text{O}}$ and found that the forsterite-cordierite tie line is cut under those conditions by both the enstatite-spinel and enstatite-sapphirine tie lines. The assemblage talc+sapphirine was also reported in this study but was not investigated in detail. If the talc-spinel tie line is stable at 10 kb $P_{\text{H}_2\text{O}}$ in the temperature range 750° to 1300° C., then it should have been realized in experiments on the pyrope composition. The fact that enstatite+spinel was produced in these experiments suggests that talc+spinel is a metastable assemblage under the conditions investigated.

Chinner and Schairer (1962) restudied the relationships of the forsterite-cordierite and enstatite-spinel tie lines at 1 atmosphere pressure. The starting composition for this work was a glass of pyrope composition. The authors found that the glass crystallized to forsterite+cordierite+spinel at temperatures above 1140° C. but below that temperature orthoenstatite crystallized together with forsterite, cordierite, and spinel. In view of their experience with the same composition under dry and hydrothermal conditions Chinner and Schairer concluded that the orthoenstatite was a metastable phase. Chinner (personal communication, 1963) found that under hydrothermal conditions at 2 kb in the temperature range 750° to 800° C. enstatite crystallizes rapidly from pyrope glass but the assemblage reacts slowly to produce the forsterite-cordierite-spinel assemblage. The relationships of the forsterite-cordierite and enstatite-spinel tie lines have been pursued during the present investigation as both assemblages may be produced from the magnesian chlorite compositions under different physical conditions.

In order to locate the curve for enstatite+spinel→forsterite+cordierite in the region of the invariant point a mixture of all four crystalline phases was used as a starting material. A series of runs of variable duration was made under identical conditions of temperature and pressure, and it was possible to estimate, both by optical and x-ray examination, which of the four phases was disappearing in the longer runs.

It is immediately important to note that the magnesian chlorites are in fact stable at pressures up to 10 kb $P_{\text{H}_2\text{O}}$ and temperatures above 800° C. Indeed, the upper stability range of these minerals, in terms of both temperature and pressure, is surprising in view of their restriction in the regionally metamorphosed rocks to the low- and medium-grade assemblages. However, the probable effects of iron, the most common additional constituent of the natural minerals, in reducing the chlorite stability field, must not be overlooked. Turnock (1960) determined the upper stability of daphnite ($\text{Fe}_{4.8}\text{Al}_{2.4}\text{Si}_{2.8}[\text{O},\text{OH}]_{18}$) and pseudothuringite ($\text{Fe}_{4.2}\text{Al}_{3.6}\text{Si}_{2.2}[\text{O},\text{OH}]_{18}$) and showed that at a water pressure of 2 kb the upper stability of these minerals is from 65° to 160° C. lower than that of

corresponding magnesian chlorites, depending on composition and oxygen pressure. It is still evident, however, that the absence of chlorite from high-grade metamorphic rocks results from the unfavorable bulk composition of the rock and thus reactions with other phases, rather than its instability at higher temperatures and pressures.

The nature of the distribution of univariant curves and their metastable extensions around the invariant point of Fig. 2 was deduced by graphic analysis of the relationships of the five solid phases in equilibrium at that point (Morey, 1957). This analysis shows that, in addition to the three univariant curves shown in Fig. 2, two other curves converge at that invariant point. These are the forsterite-absent curve (chlorite + cordierite \rightarrow enstatite + spinel) and the spinel-absent curve (chlorite + enstatite \rightarrow forsterite + cordierite). As these curves cannot be realized experimentally from the chlorite bulk compositions, they are not shown in Fig. 2. The complete series of curves is shown diagrammatically in Fig. 3.

Experimental data on the upper stability limits of many minerals have been widely used in calculation of heats of reaction (see Orville and Greenwood 1965 for references and discussion of these calculations). The Clapeyron relation was applied to the present data for the upper stability limit of magnesium chlorite but experimental errors are too large to permit a reasonable estimate of ΔH . The calculations do, however, suggest that the stability curve for clinocllore should be at lower temperatures than indicated by Yoder's work. The authors intend to reexamine the upper stability of clinocllore using much longer runs to eliminate the rate of reaction problem encountered in earlier work.

The wide range of stability of the enstatite + spinel assemblage for iron-free minerals removes a considerable anomaly between field and experimental observations. Tilley (1923) first pointed out this irregularity in his discussion of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ and suggested that enstatite + spinel may be a low-temperature tie line and forsterite + cordierite may be its high-temperature equivalent. Friedman (1954) considered the same problem in his study of the emery deposits of Cortland, New York, and considered that the variables pressure and iron content may influence the relationship of the two tie lines. The importance of pressure has been demonstrated in this study but at present there is no information on the influence of iron on the position of the invariant point in terms of temperature and pressure. In the iron-free assemblages, however, it is apparent that pressure is a more significant variable than temperature in governing the relationships of the forsterite + cordierite and enstatite + spinel assemblages. In the analogous system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ the ferrosilite-hercynite assemblage is not found owing to the instability of ferrosilite at low pressures (Lindsley *et al.*, 1964). This difference in

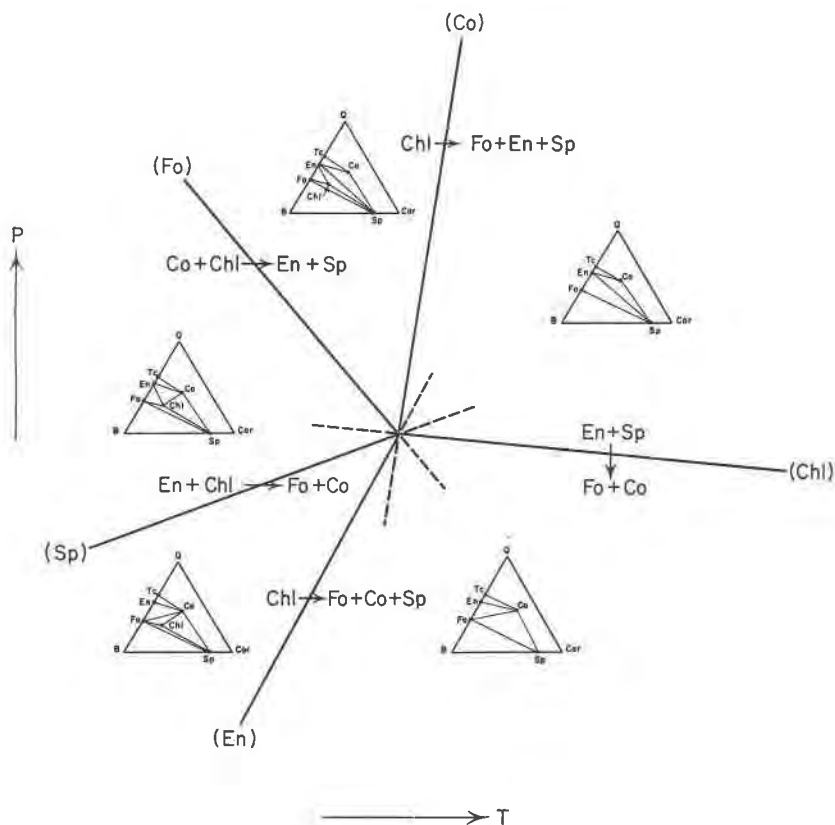


FIG. 3. Distribution of all possible univariant curves around the invariant point involving forsterite (Fo), cordierite (Co), spinel (Sp), enstatite (En), and chlorite (Chl). The abbreviations in parentheses indicate the absent phase for the particular reaction.

phase relations between magnesian and iron end members of the various solid solution series emphasizes the need for investigations of the intermediate compositions.

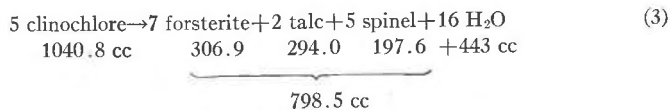
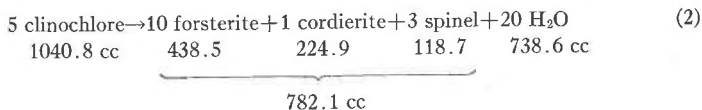
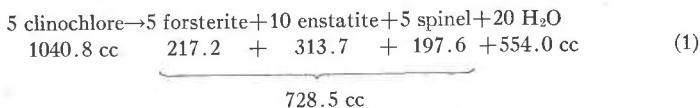
The discrepancy between the results of this study and those reported by Segnit (1963) deserves further discussion and comment. Although the stability limits of clinocllore are not specifically shown in Fig. 2, which shows the upper stability limits of magnesian chlorite, the curve can be inferred from several runs on clinocllore itself. It lies 5° to 10° C. below the curve for the maximum magnesian chlorite stability (Fig. 2). The temperature difference between Segnit's clinocllore synthesis curve and the inferred stability curve is insignificant (Segnit's curve is 15° C. lower at 10 kb and 10° C. lower at 6 kb). The nature of the breakdown assemblage requires clarification. The stable assemblage of forsterite+ensta-

tite+spinel was found at $3\frac{1}{2}$, 5, and 10 kb P_{H_2O} . Talc appeared as a run product in some short disequilibrium runs just above the reaction curve, but it was absent in longer runs under the same conditions. In view of the fact that the present results were obtained from sealed platinum capsules and runs of up to several weeks' duration, the assemblage talc+spinel+forsterite must be considered metastable. Independent evidence of the metastability of the talc-spinel tie line has been discussed above.

In order to consider the possible spatial relationships of the talc+forsterite+spinel assemblage a graphical analysis was made of the six invariant points involved in the relationships of the phases talc, enstatite, forsterite, spinel, cordierite, and chlorite. As the orientation of one of these invariant points has been experimentally determined, the six points may be plotted in their correct orientation on a P - T diagram. Although such a diagram is somewhat complex, it may be inferred from the relationship of the reaction curves that the assemblage talc+forsterite+spinel is not likely to be a stable breakdown assemblage from chlorite.

An additional line of evidence involves the volume relationships of the various assemblages. As Thompson (1955) has emphasized, the change in volume during a dehydration reaction of the type involved in the clinocllore reaction is almost always negative. This is true for each of the three reactions listed below. If the breakdown products of a mineral are not the same at all pressures, then it is to be expected that the high-pressure reaction will result in a greater decrease in volume than that at low pressures.

The molar volumes of the phases involved in the three reactions are also shown below. Molar volumes for water are calculated from the data of Kennedy (1950) at 760° C. and $3\frac{1}{2}$ kb for reaction 1 and 720° C. and 2 kb for reaction 2. The physical conditions required for reaction 3 have not been determined but the molar volume of water is shown for 760° C. at $3\frac{1}{2}$ kb. At 720° C. and 2 kb this would be 591 cc.



Neglecting, for the moment, the volume of the fluid phase produced in these reactions, the greatest decrease in volume is provided by reaction 1. This would thus be anticipated as a high-pressure reaction with respect to reactions 2 and 3. Reaction 3 produces the smallest volume decrease and may therefore be expected as the low-pressure reaction. Experimental work has not substantiated this reaction at low pressure under conditions of $P_{\text{H}_2\text{O}} = \text{total pressure}$. This information adds further weight to the argument that the assemblage forsterite+talc+spinel would not be expected as the stable breakdown product of magnesian chlorite at high pressures. It is obvious from the reactions written above that in a closed system the volume of the fluid phase will have a profound effect on the decomposition reaction if $P_{\text{H}_2\text{O}} = P_{\text{total}}$. The volume relations of the three reactions are changed if the fluid phase is included. For a given temperature and pressure reaction 3 produces a smaller volume than reaction 1 or 2.

Although chlorite is not excluded from regionally metamorphosed rocks by decomposition as shown in the reactions above but rather by reaction with muscovite or biotite, there is still a considerable expulsion of water from the solid phases. If the system is open with respect to water, then the volume of the fluid phase is of little consequence. In a constant volume system, however, if $P_{\text{H}_2\text{O}}$ is equal to or approaches P_{total} , then water released by the reaction may have the effect of increasing $P_{\text{H}_2\text{O}}$ and thus enlarging the stability field of the low-temperature assemblage.

THE ASSEMBLAGE MAGNESIAN CHLORITE+QUARTZ

It is important to note that the chlorites which are stable under the conditions of the limiting curve in Fig. 2 are not in equilibrium with quartz. The chlorite-quartz tie lines are cut, under those conditions, by talc+cordierite or enstatite+cordierite tie lines. Earlier studies in this system (Yoder, 1952; Roy and Roy, 1955) showed that the chlorite compositions are separated from quartz under all conditions of their investigations (130° to 1300° C. and 5000 to 30,000 psi). Turnock (1960) studied the phase relationships of the iron chlorites and showed that they may coexist in equilibrium with quartz throughout their stability field. At a total pressure of 2000 bars iron chlorites are stable up to almost 600° C., the precise temperature depending on the oxygen pressure in the system.

Natural assemblages indicate that chlorite and quartz are two of the most common coexisting minerals in low-grade regionally metamorphosed rocks. Indeed they partially characterize the chlorite zone of progressive metamorphism and often persist into the biotite and even garnet zones

(Barrow, 1893; Tilley, 1925; Mason, 1962). In terms of the facies concept of metamorphism the quartz-chlorite assemblage is most common in the quartz-albite-muscovite-chlorite subfacies of the greenschist facies (Fyfe *et al.*, 1958, p. 218). The large volume and wide distribution of these rocks on the earth's surface suggest that these two minerals may exist together in equilibrium over a certain range of temperature and pressure. Hutton (1940) suggested that the chlorites in low-grade metamorphic rocks are dominantly iron rich but, as a result of the usual fine grain size of the host rocks and the consequent difficulty of obtaining good separations, there is still relatively little information available on the range in chemical composition of chlorites from low-grade metamorphic rocks (see Deer *et al.*, 1962, pp. 138–145).

Starting materials for this study of the quartz-chlorite relations were a series of glasses and oxide mixtures whose compositions lie for the most part on the join anhydrous anthophyllite ($7\text{MgO}\cdot 8\text{SiO}_2$)—Mg-gedrite ($5\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$). It is apparent from Fig. 1 that the compositions of the starting materials plot between the compositions of the chlorite solid solution series and quartz. Determinative runs were made at 2 and 5 kb $P_{\text{H}_2\text{O}}$ with techniques the same as those described earlier in this paper.

The results of critical runs are presented in Table 3, and Fig. 4 shows a projection of the results onto the plane anthophyllite—Mg-gedrite at 2 kb $P_{\text{H}_2\text{O}}$. Although the majority of runs plotted in Fig. 4 represent syntheses of phases from glasses, the positions of boundary curves have been confirmed by reversed reactions involving the phases leuchtenbergite, quartz, talc, and cordierite. It is immediately obvious that the assemblage chlorite+quartz is stable over a considerable range of temperature at both 2 and 5 kb $P_{\text{H}_2\text{O}}$. It is important to remember that this figure is a projection of phase relations and should not be interpreted as a reflection of the upper stability limit of the magnesian chlorites. The diagram has not been completed in the low Al_2O_3 region because of the unknown relationships of the aluminous anthophyllites. Greenwood (1963) has determined the stability of pure magnesian anthophyllite in the presence of excess water, but the problem of nucleation of the aluminous members of the group has not yet been overcome. The presence of a stability field for anthophyllite will undoubtedly complicate the higher temperature phase relations depicted in this paper. At low temperatures (460°C .) a wide range of chlorite compositions is stable in equilibrium with quartz. At higher temperatures the compositional range of chlorite which may coexist only with quartz decreases, and at 2 kb $P_{\text{H}_2\text{O}}$ and the maximum temperature of the quartz-chlorite stability field the chlorite coexisting with quartz contains about 21 weight per

TABLE 3. CRITICAL RUN DATA DELINEATING THE QUARTZ+CHLORITE ASSEMBLAGES

<i>T</i> , °C	<i>P</i> , kb	Duration, hours	Result*	Run No.
<i>A. Starting material: Glass No. 2, 13MgO·Al₂O₃·15SiO₂</i> (34.34 MgO, 6.68 Al ₂ O ₃ , 58.98 SiO ₂ , weight per cent)				
400	2	1584	Tc+M	166
425	2	706	Tc+M	69
450	2	2880	Tc+Q+Chl	300
475	2	665	Tc+Chl	210
500	2	568	Tc+Chl+Q	108
550	2	280	Tc+Chl	65
600	2	648	Tc+Chl	88
650	2	1002	Tc+Chl	126
425	5	431	Tc+Q+M	66
475	5	465	Tc+Chl+Q	338
525	5	1131	Tc+Chl+Q	229
575	5	450	Tc+Chl	88
600	5	258	Tc+Chl	62
650	5	720	Tc+Chl	7
750	5	194	Tc+Chl+(trace Co?)	78
<i>B. Starting material: Glass No. 8, 19MgO·2Al₂O₃·22SiO₂</i> (33.43 MgO, 8.90 Al ₂ O ₃ , 57.67 SiO ₂ , weight per cent)				
400	2	1584	M+Tc+Q	167
450	2	2880	Tc+Q+(Chl?)	301
475	2	1052	Tc+Chl+Q	237
500	2	568	Tc+Chl+Q	107
550	2	1144	Tc+Chl	154
575	2	1246	Tc+Chl	228
600	2	1175	Chl+Tc+trace Co	179
650	2	1002	Tc+Chl	128
475	5	465	Tc+Chl+Q	339
500	5	1384	Tc+Chl+Q	136
525	5	1131	Tc+Chl+Q	230
550	5	1008	Tc+Chl+Q	276
575	5	860	Tc+Chl+Q	159
600	5	926	Tc+Chl+Q	234
625	5	453	Tc+Chl	97
635	5	768	Tc+Chl	281
<i>C. Starting material: Glass No. 3, 6MgO·Al₂O₃·7SiO₂</i> (31.65 MgO, 13.34 Al ₂ O ₃ , 55.01 SiO ₂ , weight per cent)				
400	2	481	M	36
400	2	1003	M	35
425	2	706	M+Q+(trace Chl?)	70
450	2	2880	Chl+Q	302
465	2	1101	Chl+Q	142
500	2	1127	Chl+Tc+Q	139
550	2	1144	Tc+Chl+Q	152
560	2	1008	Tc+Chl+Q	273
567	2	910	Tc+Chl+Q	326
575	2	1246	Tc+Chl+Q	227
600	2	1175	Chl+Tc+Co	180
650	2	647	Chl+Tc+Co	110
425	5	431	Chl+Q+M	67
450	5	861	Chl+Q	31
475	5	1465	Tc+Chl+Q	340

* Abbreviations as in Table 2.

TABLE 3—(continued)

T, °C	P, kb	Duration, hours	Result*	Run No.
500	5	1384	Tc+Chl+Q	137
475	5	1465	Tc+Chl+Q	340
500	5	1384	Tc+Chl+Q	137
525	5	1131	Tc+Chl+Q	231
550	5	741	Chl+Q	29
575	5	450	Tc+Chl+Q	90
600	5	258	Chl+Tc+Q	61
625	5	504	Chl+Tc+Q	124
635	5	768	Chl+Tc+Co	280
650	5	720	Chl+Tc+Co	6
D. Starting material: Glass No. 4, 11MgO·3Al ₂ O ₃ ·13SiO ₂ (28.99 MgO, 19.99 Al ₂ O ₃ , 51.02 SiO ₂ , weight per cent)				
400	2	481	M	37
400	2	1003	M	34
425	2	706	Chl+Q+M	71
450	2	744	Chl+Q	213
465	2	1101	Chl+Q	143
500	2	1127	Chl+Q	140
550	2	454	Chl+Q	120
567	2	910	Chl+Q	327
575	2	1413	Chl+Q+Co	157
600	2	648	Chl+Co+Tc	87
650	2	647	Chl+Co+Tc	111
700	2	1133	Chl+Co+Tc	22
425	5	431	Chl+Q+M	68
450	5	861	Chl+Q	30
562	5	1888	Chl+Q	134
600	5	454	Chl+Q	87
612	5	582	Chl+Q	356
625	5	504	Chl+Q+Co	134
650	5	720	Chl+Tc+Co	5
750	5	194	Chl+Tc+Co	77
E. Starting material: Glass No. 5, 5MgO·2Al ₂ O ₃ ·6SiO ₂ (26.32 MgO, 26.62 Al ₂ O ₃ , 47.06 SiO ₂ , weight per cent)				
350	2	960	M	201
400	2	481	M	38
400	2	1003	M	33
450	2	744	Chl+Q	214
465	2	1101	Chl+Q+M?	144
500	2	568	Tc+Chl+Q	109
525	2	2760	Chl+Q	342
550	2	280	Chl+Q+trace Co	63
575	2	1413	Chl+Q+Co	156
600	2	648	Chl+Tc+Co+Q	86
650	2	1002	Chl+Tc+Co	127
700	2	1133	Chl+Tc+Co	23
400	5	1097	Chl+Q	151
450	5	861	Chl+Q	32
550	5	741	Chl+Q	27
562	5	1888	Chl+Q+trace Co	135
575	5	837	Chl+Q+And	345
600	5	258	Chl+Co+Q	60
625	5	504	Chl+Q+Co+trace Tc	125
650	5	720	Tc+Chl+Co	9

TABLE 3—(continued)

T, °C	P, kb	Duration, hours	Result*	Run No.
<i>F. Starting material: Glass No. 9, 30MgO·6Al₂O₃·47SiO₂</i> (26.05 MgO, 13.17 Al ₂ O ₃ , 60.78 SiO ₂ , weight per cent)				
400	2	1053	M	16
450	2	744	Chl+Q	19
550	2	385	Chl+Q	48
575	2	1246	Tc+Chl+Q+Co	226
650	2	310	Tc+Co	57
400	5	498	M	47
500	5	763	Chl+Q	25
550	5	407	Chl+Q	44
650	5	333	Chl+Q+Tc+trace Co	55
<i>G. Starting material: Mix, talc+cordierite (natural)</i>				
400	2	1053	Chl+Q+Tc+Co	15
450	2	744	Tc+Co+trace Q+trace Chl	20
550	2	335	Tc+Co	50
650	2	333	Tc+Co	54
400	5	498	Chl+Q+trace Tc	46
500	5	763	Chl+Q+trace Tc	24
650	5	310	Tc+Co	58
<i>H. Starting material: Mix, leuchtenbergite+quartz</i>				
400	2	1053	Chl+Q	17
550	2	335	Chl+Q	49
650	2	310	Tc+Co+trace Q	59
400	5	498	Chl+Q	45
550	5	407	Chl+Q	43
650	5	333	Tc+Chl+Q	56
<i>I. Starting material: Glass, 35MgO·7Al₂O₃·41SiO₂</i> (30.76 MgO, 15.56 Al ₂ O ₃ , 53.68 SiO ₂ , weight per cent)				
350	2	960	M	200
450	2	744	Chl+Q	212
500	2	1127	Chl+Q+trace Tc	141
550	2	454	Chl+Q	121
560	2	1008	Chl+Q	274
567	2	910	Chl+Q	325
575	2	1413	Co+Chl+Q	155
600	2	1175	Co+Chl+Tc	181

cent Al₂O₃. The composition of the corresponding chlorite at 5 kb P_{H_2O} is slightly more aluminous, about 23 per cent. These figures are obtained by projecting through the composition of the peak of the quartz-chlorite field on Fig. 4 and its 5 kb analogue, from quartz to the chlorite compositions as shown in Fig. 1. The lower temperature stability limits of the quartz+chlorite field have not been determined with any precision owing to the great length of time required to reach equilibrium. Montmorillonite-bearing assemblages occur at temperatures below 425° C. at 2 kb P_{H_2O} and about 450° C. at 5 kb. For bulk compositions which are both more and less aluminous than that at the maximum of the quartz-

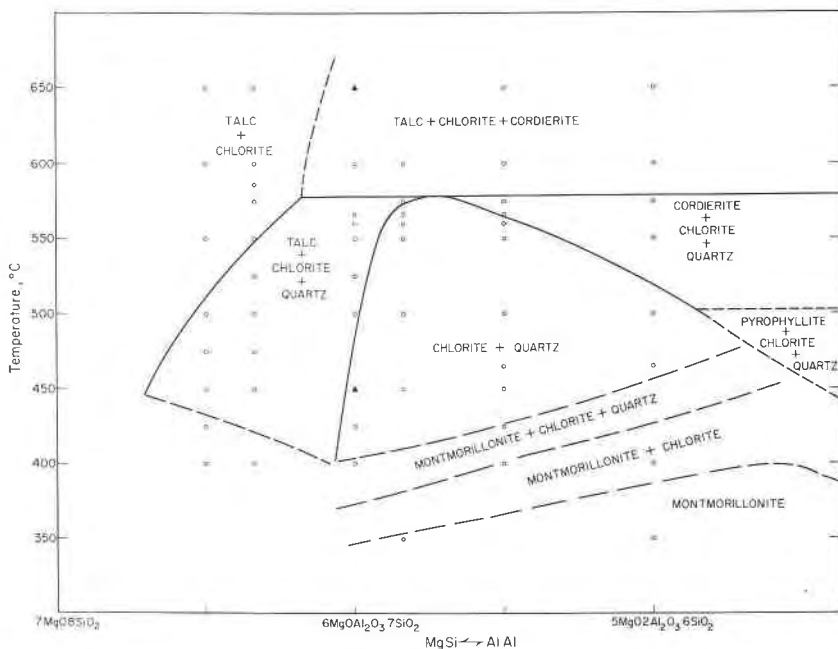
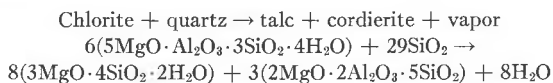


FIG. 4. Temperature-composition section at 2 kb P_{H_2O} along the extended join anthophyllite ($7MgO \cdot 8SiO_2 \cdot 2H_2O$)-magnesian gedrite ($5MgO \cdot 2Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$). The data on the lower stability of cordierite (cordierite \rightarrow pyrophyllite + chlorite) are taken from Schreyer and Yoder (1964).

chlorite field a third crystalline phase joins quartz and chlorite as the temperature is raised above the stability limit of the two-phase assemblage. In less aluminous bulk compositions the assemblage replacing quartz + chlorite, with increasing temperature, is talc + chlorite + quartz and for more aluminous compositions, cordierite + chlorite + quartz.

Above $565^\circ C.$ at 2 kb P_{H_2O} and $625^\circ C.$ at 5 kb all three quartz + chlorite bearing assemblages are replaced by the field of talc + cordierite + chlorite or talc + cordierite + quartz in the more siliceous bulk compositions. The reaction at the upper stability limit of the quartz + chlorite assemblage is:



Several authors have recently commented on the contrasted stability fields of a pure phase and of the same phase in the presence of quartz. On the basis of preliminary experimental data, Yoder and Eugster (1955) suggested that the upper stability limit of the muscovite + quartz as-

semblage is less than 15° C. below that of pure muscovite, and this was later confirmed by Segnit and Kennedy (1957). Ernst's (1961) investigation of glaucophane showed the mineral (a silica saturated species) and the assemblage quartz+glaucophane to have virtually identical stability limits at pressures up to 660 bars. At higher pressures, however, the beginning of melting cuts out the glaucophane-quartz tie line, and the temperature interval between the upper limit of this assemblage and the pure glaucophane upper stability limit increases to about 125° C. at 2 kb P_{H_2O} . Similarly, Eugster and Wones (1962) found that the upper stability limit of the assemblage annite+ $3SiO_2$ is about 120° C. below the upper stability of pure annite at 2 kb and the P_{O_2} of the wustite+magnetite buffer. At 2 and 5 kb P_{H_2O} the upper stability limits of the quartz+chlorite assemblage are about 145° and 170° C. lower than the upper stability limit of pure magnesian chlorite. In direct contrast the work of Turnock (1960) showed that iron chlorites can exist in equilibrium with quartz at their upper stability limits. The critical factor, of course, is the silica saturation of the chlorite breakdown products. Iron chlorites react to form a silica-saturated assemblage, but the magnesian chlorites react to produce assemblages undersaturated with respect to silica. Apparently the Mg/Fe ratio in the chlorite has no appreciable influence on the stability limits of the chlorite+quartz assemblage. It is important, however, that the chlorites of intermediate Mg/Fe ratio be investigated to clarify this conclusion.

Ernst (1961) applied reasoning similar to that set out by Fyfe *et al.* (1958) in a discussion of phase relations of the assemblage glaucophane+quartz. The latter authors (p. 153) considered the influence of excess silica on the stability field of a mineral and concluded that in the case of chlorite the presence of excess silica greatly decreases the stability field of clinocllore. It must be emphasized that the presence of excess quartz can imply a great change in bulk composition compared with pure chlorite. Phase relations determined from such compositions can only reflect the upper temperature limit for the existence of chlorite in that particular bulk composition. Thus the presence of excess quartz together with chlorite is controlled by the limitations of the quartz+chlorite stability fields but has no influence whatsoever on the stability limits of chlorite itself.¹

One of the main problems encountered during the determination of the stability relations of the quartz and chlorite was the rapid but often metastable growth of talc from a wide range of bulk compositions, extending from pure talc to mixtures containing 30 weight per cent Al_2O_3 . In the early stages of the work several anomalous results were obtained

¹ The only proviso for such assemblages is that any heterogeneous reaction can take place only within the stability limits of the reactants and their products.

during the determination of isothermal sections at 2 and 5 kb P_{H_2O} . In order to avoid the intersection of tie lines on the isothermal plane, it was necessary to assume that talc contains a considerable amount of alumina. In several experiments using glasses Nos. 7, 2, and 8 as starting materials the resulting phases were exclusively talc+chlorite. Under the same conditions, however, slightly more aluminous starting materials gave end products of chlorite+quartz. A possible phase diagram can be drawn only if it is assumed that the talc contains an appreciable amount of Al_2O_3 .

Yoder (1952) and Stemple and Brindley (1960) have described the effects of Al_2O_3 on the x -ray powder diffraction pattern of talc, but there are few data available on talc synthesized at pressures above 1 kb P_{H_2O} from bulk compositions containing Al_2O_3 . Yoder noted that talc synthesized in the presence of Al_2O_3 showed a measurable reduction in its c dimension, and Stemple and Brindley interpreted their x -ray studies to indicate that talc may contain up to 3.7 weight per cent Al_2O_3 . Analyses of natural talcs may show Al_2O_3 higher than 3.7 weight per cent (McKie, 1959), but the presence of minor impurities in a mineral which is very difficult to purify may sometimes account for part of the Al_2O_3 . In the present study the nature of the alumina solid solution was assumed to be $AlAl \rightleftharpoons MgSi$, the substitution most frequently invoked for alumina solid solutions in other mineral groups such as amphiboles, chlorites and pyroxenes. The possibilities of an alternative substitution such as $2Al \rightleftharpoons 3Mg$ and the consequent ternary solid solution in talc have not been investigated in this study but should not be dismissed.

A series of compositions (Nos. 10, 21, 14, 13 and 15) corresponding to the $MgSi \rightleftharpoons AlAl$ substitution were used as starting materials for this portion of the work. The Al_2O_3 content of these five mixtures is 0.00, 1.75, 3.53, 7.05, and 8.81 weight per cent, respectively. Of the four aluminous compositions only the 1.75 and 3.53 weight per cent Al_2O_3 mixtures (mixes 21 and 14) have been completely converted to talc at 2, 5, and 10 kb P_{H_2O} . It is interesting to note the reaction times for mixture 14 at 5 kb P_{H_2O} . Reaction products from this mixture held at 5 kb P_{H_2O} and 725° C. for variable periods of time are:

1 hour	talc+chlorite+quartz
65 hours	talc+quartz
768 hours	talc

This same mixture was not completely converted to talc in a run at 525° C. and 2 kb P_{H_2O} after 2760 hours. At 750° C. and 2 kb P_{H_2O} talc was the only product from this mixture after a run of 1104 hours. There are two alternative conclusions which can be drawn from the run at 525° C. and 2 kb P_{H_2O} . The first is that the result emphasizes the drastic reduction in reaction rates at lower temperatures, and the second is that

the Al_2O_3 content of talc is temperature sensitive. There are insufficient data to arrive at a choice between these two alternatives.

X-ray diffraction powder data of talc synthesized during the present study confirm the previous work, which indicated the reduction of the c lattice dimension with increased Al_2O_3 content. Following Stemple and Brindley (1960) the variation of the position of the (006) peak of talc was measured against a quartz standard to estimate variations in the c dimension. The results are illustrated in Fig. 5, which shows the variation in $\Delta 2\theta$ for talc (006) and quartz (131) with changes in the bulk compo-

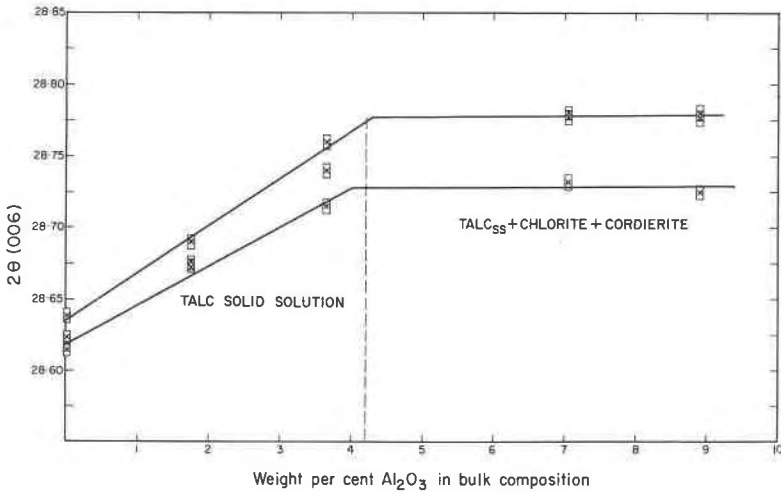


FIG. 5. Variation of the basal spacing of talc with Al_2O_3 content. The size of the box indicates the error in the measurement. The lower line is drawn through points for talc synthesized at 2 kb $P_{\text{H}_2\text{O}}$, and the upper line is for talc synthesized at 10 kb $P_{\text{H}_2\text{O}}$. Values for talc synthesized at 5 kb $P_{\text{H}_2\text{O}}$ are always within the limits set by the 2 and 10 kb samples.

sition of the starting material. Mixtures 13 and 15 (7.05 and 8.81 weight per cent Al_2O_3 , respectively) were never converted to a single phase assemblage. The plot of the data in Fig. 5 suggests that the maximum Al_2O_3 content of talc at water pressures up to 10 kb is 4.0 weight per cent. It is interesting to note that the highest Al_2O_3 content of a natural talc reported in a recent analysis is 3.95 per cent in talc from a talc, yoderite, quartz, kyanite schist (McKie, 1959). Increasing water pressure has an almost negligible effect on the Al_2O_3 content of talc, and the data of Fig. 5 show that the decrease in $\Delta 2\theta$ (006) of talc synthesized at 2 and 10 kb $P_{\text{H}_2\text{O}}$ is on the boundaries of the limits of error in the measurements. This very slight reduction in the c dimension of talcs identical in composition but synthesized at different pressures may represent a genuine contraction of the cell size in response to pressure of

synthesis, but similar data have been interpreted by Crowley and Roy (1960) as a possible indication of Al-Si ordering. Ernst (1963) has suggested that a similar interpretation may account for polymorphism in the alkali amphiboles.

A convenient way of illustrating the phase relations in the $\text{MgO-Al}_2\text{O}_3\text{-}$

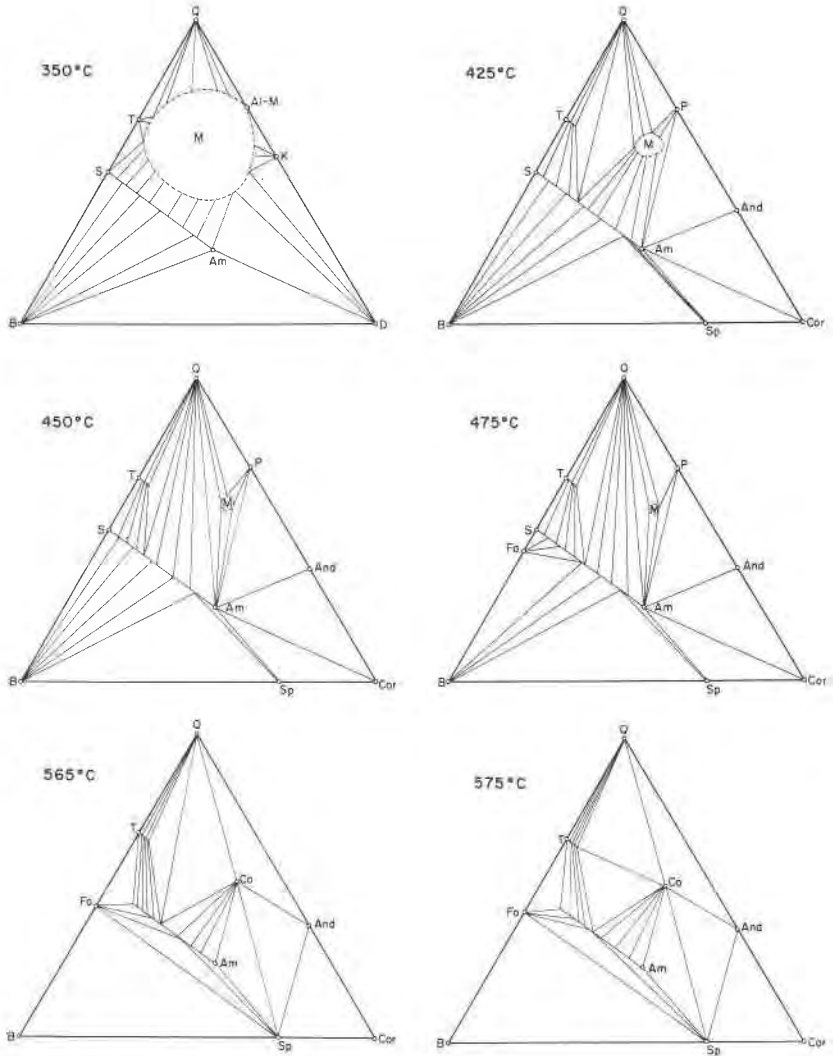


FIG. 6. Isothermal projections in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 2 kb $P_{\text{H}_2\text{O}}$. Data of Yoder (1952), Roy and Roy (1955) and Schreyer and Yoder (1964) have been incorporated to complete the compatibility triangles.

SiO₂-H₂O system to show the extent of the quartz+chlorite assemblages and their relationship to the rest of the system is by means of a series of isothermal sections. Fig. 6 shows a series of such sections through the system at 2 kb P_{H_2O} . The data of Yoder and of Roy and Roy have been used to complete the construction of compatibility triangles, and only those sections which differ appreciably from earlier constructions are shown in this diagram. Stability relations of the montmorillonite phases are modified from those shown by Mumpton and Roy (1956). As further work will be needed to show the precise limits of the montmorillonite stability field in the presence of quartz and chlorite, the field boundary of montmorillonite is indicated only approximately on the figure. Although the sections are in part diagrammatic all relationships have been experimentally verified. A similar series of diagrams can be constructed for the 5 kb P_{H_2O} data with the interesting addition of a very narrow temperature interval in which andalusite or an andalusite-like phase (Aramaki and Roy, 1963) coexists with chlorite and quartz. This assemblage is realized by glass No. 5 at 575° C., just below the lower stability limit of cordierite and above the stability limit of the pyrophyllite-chlorite assemblage. These conditions are very close to the boundary curve for the andalusite-sillimanite reaction (Bell, 1963) and are compatible with the data of Schreyer and Yoder (1964) on the lower stability limit of cordierite. The andalusite x -ray diffraction peaks are small and ill defined, and it is possible that the mineral may be one of the hydrated forms of Al₂SiO₅, recently discussed by Carr and Fyfe (1960) or one of the AS(H) phases of Aramaki and Roy (1963).

APPLICATION TO NATURAL ASSEMBLAGES

In view of the absence of iron and other components such as K₂O, Na₂O, and CO₂ from the system studied, the results can only be applied to natural assemblages with some reservations. However, recognizing both the absence of such components and their probable effect of lowering the upper stability of the assemblages studied, the results can be used to restrict the temperature range of low-grade metamorphism. The temperatures of 625° and 575° C. are the upper limits of the existence of the greenschist facies at 5 and 2 kb P_{H_2O} , respectively. Figure 7 shows the relationship of the upper stability limit of the quartz+chlorite assemblage to the lower stability limit of Mg-cordierite (Schreyer and Yoder, 1964), the Al₂SiO₅ polymorphs (Bell, 1963), and the upper stability of muscovite (Velde, 1964). Yoder and Eugster (1955) and Segnit and Kennedy (1957) determined that the upper stability of the muscovite+quartz assemblage is not more than 15° C. below that of pure muscovite. In view of the absence of any known solid solution between muscovite and chlorite, the upper stability limit of the quartz+chlorite

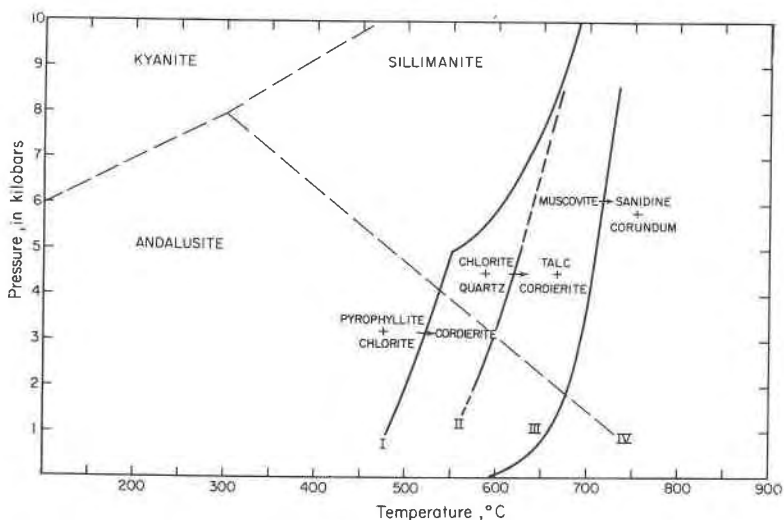


FIG. 7. Relationship of the upper stability limit of the assemblage Mg-chlorite+quartz (curve II) to the lower stability of Mg-cordierite (curve I, Schreyer and Yoder, 1964), the upper stability of muscovite (curve III, Velde, 1964) and the Al_2SiO_5 polymorphs (Bell, 1963).

assemblage sets a maximum temperature for the assemblage chlorite + quartz + muscovite which is characteristic of the greenschist facies. The absence of cordierite from greenschist facies rocks even further—550° C. at 5 kb $P_{\text{H}_2\text{O}}$ and 500° C. at 2 kb $P_{\text{H}_2\text{O}}$. The data of Turnock (1960) suggest that iron does not reduce the maximum temperature of the chlorite + quartz assemblage since it is virtually identical with that of the analogous magnesian assemblage—575° to 600° C. at 2 kb total pressure. It will therefore be extremely interesting to study the phase relations of the intermediate Mg-Fe chlorites.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. F. Schairer for his supervision of the preparation of glasses used in this work. Mineral samples were kindly donated by Drs. G. T. Faust, F. R. Boyd, and W. Schreyer, who also prepared and donated the synthetic cordierite. The manuscript was reviewed by Drs. H. J. Greenwood, B. Velde, and D. R. Wones, and their suggestions led to many improvements in the presentation.

REFERENCES

- ARAMAKI, S. AND R. ROY (1963) A new polymorph of Al_2SiO_5 and further studies in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *Am. Mineral.* 48, 1322-1347.

- BARROW, G. (1893) On an intrusion of muscovite biotite gneiss in the Southeast Highlands of Scotland. *Jour. Geol. Soc. London*, **49**, 330-358.
- BELL, P. M. (1963) Aluminum silicate system: Experimental determination of the triple point. *Science* **139**, 1055-1056.
- BOYD, F. R. AND J. L. ENGLAND (1960) Aluminous enstatites. *Carnegie Inst. Wash. Year Book* **59**, 49-52.
- BRINDLEY, G. W. (1951) Crystal structures of some chamosite minerals. *Mineral. Mag.* **29**, 502-525.
- AND S. Z. ALI (1950) X-ray study of thermal transformation in some magnesium chlorite minerals. *Acta. Cryst.* **3**, 25-30.
- B. M. OUGHTON AND YOUELL (1951) Crystal structure of amesite. *Acta Cryst.* **4**, 552-557.
- BROWN, B. E. AND S. W. BAILEY (1962) Chlorite polytypism: I. Regular and semi-random one-layer structures. *Am. Mineral.* **47**, 819-850.
- (1963) Chlorite polytypism: II. Crystal structure of a one-layer Cr-chlorite. *Am. Mineral.* **48**, 42-61.
- CARR, R. M. AND W. S. FYFE (1960) Synthesis fields of some aluminum silicates. *Geochim. Cosmochim. Acta* **21**, 99-109.
- CARROLL, DOROTHY (1963) Chlorite in sediments off the Atlantic coast of the United States (abstract). *Geol. Soc. Am. Spec. Paper* **76**, 239-240.
- CHINNER, G. A. AND J. F. SCHAIRER (1962) The join $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and its bearing on the system CaO - MgO - Al_2O_3 - SiO_2 at atmospheric pressure. *Am. Jour. Sci.* **260**, 611-634.
- CROWLEY, M. S. AND R. ROY (1960) The effect of formation pressures on sheet structures—a possible case of Al-Si ordering. *Geochim. Cosmochim. Acta* **18**, 94-100.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1962) *Rock-forming Minerals*. Vol. III, *Sheet Silicates*. John Wiley & Sons, Inc., New York.
- ERNST, W. G. (1961) Stability relations of glaucophane. *Am. Jour. Sci.* **259**, 735-765.
- (1963) Polymorphism in alkali amphiboles. *Am. Mineral.* **49**, 241-260.
- EUGSTER, H. P. AND D. R. WONES (1962) Stability relations of the ferruginous biotite, annite. *Jour. Petrol.* **3**, 82-125.
- FAWCETT, J. J. (1965) Alteration products of olivine and pyroxene in flood basalts from the Isle of Mull. *Mineral. Mag.* **35**, 55-68.
- FRIEDMAN, G. M. (1954) The spinel-silica reaction succession: A study of incompatible mineral phases. *Jour. Geol.* **62**, 366-374.
- FYFE, W. S., F. J. TURNER AND J. VERHOOGEN (1958) Metamorphic reactions and metamorphic facies. *Geol. Soc. Am. Mem.* **73**.
- GILLERY, F. H. (1959) X-ray study of synthetic Mg-Al serpentines and chlorites. *Am. Mineral.* **44**, 143-152.
- GREENWOOD, H. J. (1963) The synthesis and stability of anthophyllite. *Jour. Petrol.* **4**, 317-351.
- HEY, M. H. (1954) A new review of the chlorites. *Mineral. Mag.* **30**, 277-292.
- HUTTON, C. O. (1940) Metamorphism in the Lake Wakatipu region. *New Zealand Dept. Sci. Ind. Res. Geol. Mem.* **5**.
- KENNEDY, G. C. (1950) Pressure-volume-temperature relations in water at elevated temperatures and pressures. *Am. Jour. Sci.* **248**, 540-564.
- KERR, P. F. AND E. CALLAGHAN (1935) Scheelite-leuchtenbergite vein in Paradise Range, Nevada. *Bull. Geol. Soc. Am.* **46**, 1957-1974.
- LEHMANN, E. (1965) Non-metasomatic chlorite in igneous rocks. *Geol. Mag.* **102**, 24-35.
- LINDSLEY, D. H., B. T. C. DAVIS AND I. D. MACGREGOR (1964) Ferrosillite (FeSiO_3): Synthesis at high pressures and temperatures. *Science* **144**, 73-74.

- LUTH, W. C. AND O. F. TUTTLE (1963) Externally heated cold-seal pressure vessels for use to 10,000 bars and 750° C. *Am. Mineral.* **48**, 1401-1403.
- MASON, B. (1962) Metamorphism in the southern Alps of New Zealand. *Bull. Am. Mus. Nat. Hist.* **123**, art. 4.
- McKIE, D. (1959) Yoderite, a new hydrous magnesium iron aluminosilicate from Mautia Hill, Tanganyika. *Mineral. Mag.* **32**, 282-307.
- MOREY, G. W. (1957) The system water-nepheline-albite: A theoretical discussion. *Am. Jour. Sci.* **255**, 461-480.
- NELSON, B. W. AND R. ROY (1954) New data on the composition and identification of the chlorites. *Proc. 2nd Nat. Conf. Clays and Clay Minerals, Nat. Res. Council Publ.* **327**, 335-348.
- (1958) Synthesis of the chlorites and their structural and chemical constitution. *Am. Mineral.* **43**, 707-725.
- ORVILLE, P. M. AND H. J. GREENWOOD (1965) Determination of ΔH of reaction from experimental pressure-temperature curves. *Am. Jour. Sci.* **263**, 678-683.
- RANKIN, G. A. AND H. E. MERWIN (1918) The ternary system $MgO-Al_2O_3-SiO_2$. *Am. Jour. Sci.* **45**, 301-325.
- ROY, D. M. (1952) Phase equilibria in the system $MgO-Al_2O_3-SiO_2-H_2O$ and in quaternary systems derived by the addition of SiO_2 , CO_2 and N_2O_5 . Ph.D. Dissertation, The Pennsylvania State University.
- AND R. ROY (1955) Synthesis and stability of minerals in the system $MgO-Al_2O_3-SiO_2-H_2O$. *Am. Mineral.* **40**, 147-178.
- SCHREYER, W. AND H. S. YODER, JR. (1964) The system Mg-cordierite-water. *Neues Jahrb. Mineral., Abhandl.* **101**, 271-342.
- SEGNIT, R. E. (1963) Synthesis of clinocllore at high pressures. *Am. Mineral.* **48**, 1080-1089.
- AND G. C. KENNEDY (1957) Reactions and melting relations in the system muscovite-quartz at high pressures. *Am. Jour. Sci.* **259**, 280-287.
- STEMPLE, I. S. AND G. W. BRINDLEY (1960) A structural study of talc and talc-tremolite relations. *Jour. Am. Ceram. Soc.* **43**, 34-42.
- THOMPSON, J. B., JR. (1955) The thermodynamic basis for the mineral facies concept. *Am. Jour. Sci.* **253**, 65-103.
- TILLEY, C. E. (1923) Paragenesis of minerals of the system $MgO-Al_2O_3-SiO_2$ in thermal metamorphism. *Geol. Mag.* **60**, 101-107.
- (1925) Contact metamorphic assemblages in the system $CaO-MgO-Al_2O_3-SiO_2$. *Geol. Mag.* **62**, 363-367.
- TURNOCK, A. C. (1960) The stability of iron chlorites. *Carnegie Inst. Wash. Year Book* **59**, 98-103.
- TUTTLE, O. F. (1949) Two pressure vessels for silicate-water studies. *Bull. Geol. Soc. Am.* **60**, 1727-1729.
- VELDE, B. (1964) Upper stability of muscovite. *Carnegie Inst. Wash. Year Book* **63**, 141-142.
- YODER, H. S., JR. (1950) High-low quartz inversion up to 10,000 bars. *Trans. Am. Geophys. Union* **31**, 827-835.
- (1952) The $MgO-Al_2O_3-SiO_2-H_2O$ system and the related metamorphic facies. *Am. Jour. Sci.*, Bowen vol., 569-627.
- AND G. A. CHINNER (1960) Grossularite-pyrope-water system at 10,000 bars. *Carnegie Inst. Wash. Year Book* **59**, 78-81.
- AND H. P. EUGSTER (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta* **8**, 225-280.