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The stability of clinochlore + quartz at low pressure

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Abstract

The univariant dehydration reaction which defines the maximum thermal stability of the assemblage clinochlore + quartz,

$$6Mg_5Al_2Si_3O_{10}(OH)_8 + 29SiO_2 = 8Mg_3Si_4O_{10}(OH)_2 + 3Mg_2Si_5Al_4O_{18}\cdot nH_2O + (16 - 3n)H_2O$$

clinochlore — quartz — talc — cordierite — vapor

has been bracketed, with reversed experiments at $P_{H_2O} = P_{total}$. A smooth curve drawn between the brackets passes through the coordinates 0.5 kbar, 482°; 1 kbar, 500°; 2 kbar, 527°; 3 kbar, 551°; 4 kbar, 574°C. The position of the curve is probably within ± 7°C of the stated temperature at each pressure. Synthetic clinochlore, talc, cordierite, and natural quartz mixed in the appropriate proportions with an excess of distilled deionized water were used as starting materials for the bracketing experiments. Reversibility was established by determining the relative growth or diminution (as judged by examining relative intensities of X-ray reflections) of the high with respect to the low temperature assemblage. The established curve lies 55°C below the synthesis point at P_{H_2O} = 2 kbar established by Fawcett and Yoder for Mg-chlorite + quartz and 50°C below the reversed bracket at P_{H_2O} = 1 kbar established by Velde for clinochlore. Phase relations in the water-saturated, silica-rich portion of the system K_2O–MgO–Al_2O_3–SiO_2–H_2O are more complex than had been suspected, due to the intersection of the phase boundary for the reaction above with the phase boundary for the reaction muscovite + clinochlore + quartz = cordierite + phlogopite + H_2O.

Introduction

Despite the widespread occurrence of the assemblage chlorite + quartz in natural rocks, the results of early experiments (Yoder, 1952; Roy and Roy, 1955) suggested that this assemblage was metastable at temperatures between 130° and 1300°C at water pressures to 2 kbar. Later, Turnock (1960) showed that iron-bearing chlorites may coexist with quartz to 600°C at P_{H_2O} = 2 kbar. Fawcett and Yoder (1966), using silica-rich iron-free starting materials along the join anthophyllite–gedrite, demonstrated that chlorite + quartz is stable over a considerable temperature range at water pressures to 5 kbar. The phase diagrams deduced by Fawcett and Yoder were based on synthesis rather than on reversed experiments, although the positions of some phase boundaries were checked with reversed experiments using the natural chlorite leuchtenbergite in the starting material. Fawcett and Yoder determined that compositions of chlorite and talc varied as a function of the pressure of hydrothermal treatment. In light of these two uncertainties, it seemed desirable to reinvestigate the stability of chlorite + quartz. The chlorite composition selected for study is that of clinochlore, $Mg_5Si_3Al_2O_{10}(OH)_8$. The compositions of synthetic chlorite and talc were carefully monitored during the course of the investigation.

The phase boundaries for the reactions

$$6Mg_5Al_2Si_3O_{10}(OH)_8 + 29SiO_2 = 8Mg_3Si_4O_{10}(OH)_2 + 3Mg_2Si_5Al_4O_{18}\cdot nH_2O + (16 - 3n)H_2O$$

clinochlore — quartz — talc — cordierite — vapor

and

$$KAl_2Si_3O_{10}(OH)_2 + Mg_5Al_2Si_3O_{10}(OH)_8 + 2SiO_2 = Mg_2Al_4Si_5O_{18}\cdot nH_2O + KMg_3AlSi_3O_{10}(OH)_2 + (4 - n)H_2O$$

muscovite — clinochlore — quartz — cordierite — phlogopite — vapor

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intersect near 580°C at P_{H_2O} = 4 kbar. Due to the intersection of these two reactions, the petrogenetic grid for the system K_2O–MgO–Al_2O_3–SiO_2–H_2O (KMASH) first proposed by Schreyer and Seifert (1969) and later modified by Bird and Fawcett (1973) has been revised. The results of the present investigation have been reported orally (Chernosky, 1975).

Experimental methods

Starting material

Mixtures with bulk compositions corresponding to $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, $5MgO \cdot Al_2O_3 \cdot 3SiO_2$, and $3MgO \cdot 4SiO_2$ were prepared by weighing and mixing requisite proportions of MgO (Fisher, lot 787699), SiO_2 glass (Corning lump cullet 7940, lot 62221), and γ-Al_2O_3. MgO and SiO_2 glass were fired at 1000°C for two hours to drive off adsorbed water; γ-Al_2O_3 was prepared in three stages by firing $AlCl_3 \cdot 6H_2O$ (Fisher, lot 792733) at 400° for two hours, at 700° for five hours, and at 900°C for one hour. Clinochlore, cordierite, and talc were synthesized hydrothermally from the mixes; examination of the synthetic phases with a petrographic microscope and by X-ray diffraction revealed them to be entirely crystalline with less than 0.5 percent impurities; the impurities will be described in a later section.

Synthetic talc, clinochlore, cordierite, and natural quartz from Brazil, mixed in the appropriate proportions with an excess of distilled deionized water, were used as the starting materials for the bracketing experiments. The high-temperature assemblage constituted 22 percent by weight (excluding H_2O) of the starting material for the reaction.

Procedure

All experiments were conducted at the Massachusetts Institute of Technology in horizontally-mounted, cold-seal hydrothermal vessels. Details concerning the procedure for calibrating the hydrothermal apparatus are described by Chernosky (1973). Temperatures were controlled to within ± 2°C for the duration of each experiment and are judged to be accurate to within ± 5°C of the stated value. Pressures were measured with a 16-inch, factory-calibrated, Bourdon-tube gauge and are believed accurate to ± 2 percent of the stated value.

Unit-cell parameters for each phase used in the starting material were calculated by refining powder patterns obtained with an 11.46 cm Debye-Scherrer camera; FeK_α radiation was used to take the powder pattern for clinochlore, CuK_α radiation was used for all other X-ray work. BaF (a = 6.1971 ± 0.0002A), silicon I (Johnson Matthey Lot Number S 3354, a = 5.43067 ± 0.00018A), and silicon II (a = 5.4301A) were used as internal standards. Silicon I (Huebner and Papike, 1970) and BaF were standardized against gem diamond (a = 3.56703A, Robie *et al.*, 1966); silicon II was obtained from a lot standardized by Peter M. Bell. Least-squares unit-cell refinements were performed with a computer program written by Appleman and Evans (1973).

The products of each bracketing experiment were examined with a petrographic microscope and by X-ray powder diffraction. Because reaction rates at temperatures near the equilibrium curve were sluggish, complete reaction was generally not obtained. Judgement as to which assemblage is stable at a given pressure and temperature was based on an examination of all major reflections for the phases of interest over the interval 5° to 36° 2θ (CuK_α radiation). In order to ascertain the range of intensities which could be obtained from a given reflection within a particular sample, ten smear mounts of the same aliquot (~ 20 mg) of starting material were successively prepared and X-rayed. The range of intensities obtained for a given reflection was remarkably small except for reflections belonging to quartz. Quartz reflections are probably variable due to the small percentage (~ 7.6 weight percent) of this phase present in starting material.[1] Based on observation of these diffraction patterns, a reaction was considered reversed if a 30 percent change (excluding quartz reflections) in intensities of X-ray reflections (relative to a pattern of the starting material) could be observed after the completion of an experiment.

The Δ index of cordierite (Miyashiro, 1957) and the positions of the d_{004} and d_{006} reflections of clinochlore and talc respectively were measured at the conclusion of each experiment. Quartz present in the product of an experiment was used as an internal standard; when quartz was not present among the product phases, it was added. At least two complete oscillations were made with a diffractometer about each reflection of interest at a scanning rate of 1/4° per minute for talc and clinochlore reflections and 1/8° minute for cordierite reflections.

[1] An oral report (Chernosky, 1975) was given prior to discovery of this problem. Subsequent X-ray diffraction studies resulted in the deletion of several low pressure experiments and resulted in a revision of the previously reported position of the equilibrium boundary.

Results

Phase characterization

$Mg_3Si_4O_{10}(OH)_2$: Talc was synthesized hydrothermally at 680°C, P_{H_2O} = 2 kbar in experiments of 5 to 10 days duration. The synthetic product, which contained less than 0.5 percent forsterite as an impurity, typically crystallized in aggregates of fine-grained plates whose powder pattern and unit-cell parameters (Table 1) compare favorably with those of natural talc. The small amount of forsterite impurity could be due to leaching of silica from the starting material by excess water present in the synthesis experiment or to the initial preparation of a starting material deficient in SiO_2. The position of the d_{006} reflection was measured in order to ascertain whether or not talc gained alumina as a result of hydrothermal treatment. The measurements (Table 2) show that the angular position of the d_{006} reflection of hydrothermally treated talc apparently increased (*i.e.*, Al_2O_3 content increases) during experiments in which talc is a stable phase; however, the increase is within the error of measurement and may not be significant. In fact, the measurements fall within the range of values obtained by Fawcett and Yoder (1966) for alumina-free talc synthesized in the pressure range from 2 kbar (2θ = 28.62, CuK_α radiation) to 10 kbar (2θ = 28.64, CuK_α radiation) P_{H_2O}.

Talc synthesized from a mix containing alumina (as in Fawcett and Yoder's experiments) tends to incorporate varying amounts of Al, depending on the pressure of synthesis. On the other hand, the results of the present study suggest that if previously synthesized alumina-free talc is used in the starting material it will not incorporate a measurable amount of alumina, even though alumina is available due to the breakdown of the high temperature assemblage. In other words, the reaction reversed during the present study is not the same reaction which was investigated by Fawcett and Yoder (1966). In the discussion to follow, alumina-free talc is abbreviated Ta and aluminous talc is abbreviated Ta_{ss}.

SiO_2: The natural quartz used in the bracketing experiments is from Minas Gerais, Brazil. The quartz is from a lot obtained by E. Roedder and carefully cleaned at the United States Geological Survey by J. S. Huebner. The unit-cell parameters are given in Table 1.

$Mg_5Al_2Si_3O_{10}(OH)_8$: Clinochlore was synthesized hydrothermally in experiments of 50 days duration at 660°C, P_{H_2O} = 4 kbar. Synthetic clinochlore, which occurs in aggregates of fine-grained plates, was found to be the IIb layer type as defined by Bailey and Brown (1962). The unit-cell parameters of the synthetic product, which contained a trace of forsterite (< 0.5 percent) and up to 5 percent 7A aluminous lizardite as impurities, are given in Table 1. Lizardite did not persist in the products of lengthy bracketing experiments in which clinochlore grew because it is metastable at these P–T conditions. The presence of lizardite in the starting material is not believed to affect the experimental results. The presence of extraneous phases was not detected in any of the bracketing experiments.

Fawcett and Yoder (1966) determined that clinochlore became progressively more aluminous during hydrothermal treatment as water pressure was increased; at P_{H_2O} = 2 kbar chlorite coexisting with

Table 1. Unit-cell parameters of natural quartz and synthetic talc, clinochlore, and cordierite

	Quartz*	Talc	Clinochlore	Cordierite
a	4.9124 (1)	5.27 (4)	5.324 (1)	17.086 (1)
b	---	9.15 (2)	9.224 (3)	9.740 (8)
c	5.4052 (2)	18.66 (10)	14.420 (5)	9.353 (4)
V	112.964 (6)	885 (8)	702.48 (28)	1556.42 (61)
β	---	100°27'	97°6'(1')	----
S	Silicon I	BaF_2	Silicon II	BaF_2
N	13	9	30	42

Figures in parentheses represent the standard deviation in terms of least units cited for the value to their immediate left; these were calculated by the program used to refine the unit cell parameters and represent precision only. All cell parameters are expressed in angstroms. Abbreviations: S = standard used in unit cell refinement; N = number of reflections used in unit cell refinement.
**Determined by J.S. Huebner and K. Shaw*

Table 2. Variation in d_{006} of clinochlore, and Δ of cordierite in experiments defining the thermal stability of clinochlore + quartz

Run No.	P (kbar)	T °C	Talc d_{006}	Clinochlore d_{004}	Cordierite Δ index
Starting Material			28.66 (2)	24.92 (4)	0.24
			Chl + Q = Tc + Co + H_2O		
21	3.7	581	28.64 (8)	--	0.25
5	3	552	28.63 (1)	--	0.24
12	2	540	28.66 (2)	--	0.26
17	1	522	28.63 (4)	--	0.24
18	0.5	495	28.62 (3)	--	0.26
			Tc + Co + H_2O = Chl + Q		
14	4	572	28.61 (2)	25.01 (4)	0.25
6	3	594	28.61 (1)	24.95 (1)	0.27
10	2	504	28.64 (3)	24.92 (6)	--

Figures in parentheses represent the range in measurements for a particular reflection in terms of least units cited for the value to their immediate left. Peak positions are expressed in degrees 2θ, Cu K_α radiation.

quartz at the temperature of the phase boundary contains about 21 weight percent Al_2O_3 and at P_{H_2O} = 5 kbar chlorite contains about 23 weight percent Al_2O_3.

Chernosky (1974) was not able to detect compositional variability in clinochlore in experiments at water pressures to 2 kbar. In order to assess the possibility of variation in clinochlore composition during the bracketing experiments, the position of the d_{004} reflection was determined after each experiment, provided that sufficient clinochlore remained. Unfortunately, the precision with which d_{004} of clinochlore could be measured was only $\pm$ 0.04° 2θ (CuK_α), which corresponds to a compositional variation of about $x = \pm 0.8$ (Shirozu and Momoi, 1972), where x is defined by the relation $(Mg_{4-x}Al_x)(Si_{6-x}Al_x)O_{10}(OH)_8$. There appears to be an upward shift in the angular position of the d_{004} reflection from 24.92 $\pm$ 0.06 to 25.01 $\pm$ 0.04 (Table 2), which suggests that the synthetic product became more aluminous than clinochlore at water pressures above 3 kbar; however, because the variability in 2θ is near the limits of precision with which the d_{004} reflection can be measured it may not be significant. The results suggest that if previously synthesized clinochlore is used in the starting material, it will not incorporate additional alumina for water pressure to at least 2 kbar, even though alumina is available due to the breakdown of the high temperature assemblage. In the discussion to follow, clinochlore is abbreviated Chl and a Mg-chlorite with a different alumina content is abbreviated Chl_{ss}.

Table 3. Experiments bracketing the reaction 6Chl + 29Q = 8Tc + 3Co = $16H_2O$

Experiment	P kbar	T °C	Duration Hours	Comments
22	4	596	1176	Chl(-) Q(-) Tc(+) Co(+)
21	3.7	581	1224	Chl(-) Q(-) Tc(+) Co(+)
14	4	572	1142	Chl(+) Q(+) Tc(-) Co(-)
13	4	557	1142	Chl(+) Q(+) Tc(-) Co(-)
11	4	542	1142	Chl(+) Q(+) Tc(-) Co(-)
1	3	680	864	Chl(-) Q(-) Tc(+) Co(+)
3	3	594	840	Chl(-) Q(-) Tc(+) Co(+)
5	3	552	1128	Chl(-) Q(-) Tc(+) Co(+)
6	3	536	1128	Chl(+) Q(+) Tc(-) Co(-)
7	3	508	1128	Chl(+) Q(+) Tc(-) Co(-)
4	2	580	864	Chl(-) Q(-) Tc(+) Co(+)
8	2	547	1128	Chl(-) Q(-) Tc(+) Co(+)
12	2	540	4320	Chl(-) Q(-) Tc(+) Co(+)
10	2	504	1128	Chl(+) Q(+) Tc(-) Co(-)
15	1	530	1142	Chl(-) Q(-) Tc(+) Co(+)
17	1	522	1176	Chl(-) Q(-) Tc(+) Co(+)
18	0.5	495	2352	Chl(-) Q(-) Tc(+) Co(+)

Abbreviations: Ant = anthophyllite, Chl = clinchlore, Co = cordierite, Q = quartz, Tc = talc. In experiments showing incomplete reaction, growth or diminution of a phase is indicated by a (+) or (-), respectively. All assemblages include H_2O.

$Mg_2Al_4Si_5O_{18}\cdot nH_2O$: Cordierite was synthesized hydrothermally in experiments of 8–10 days duration at 810°C, P_{H_2O} = 1 kbar. X-ray powder patterns of the coarse-grained synthetic product did not contain extraneous reflections; impurities were not detected optically, although numerous inclusions, interpreted as entrapped water, were observed. Unit-cell parameters (Table 1) were calculated from a powder pattern obtained after heat-treating the synthetic cordierite at 900°C for five days.

The "isofract" diagram of Schreyer and Yoder (1964) was used to estimate the water content (0.75 weight percent at P_{H_2O} = 0.5 kbar to 2 weight percent at P_{H_2O} = 4 kbar) of hydrothermally treated cordierite. These estimated water contents are probably high, because the observed water contents of cordierites quenched in test-tube bombs from synthesis at water pressures below 5 kbar are higher than the equilibrium amounts at the synthesis temperature (Newton, 1972).

Hydrothermally synthesized Mg-cordierite can exhibit a continuum of structural states (Schreyer and Yoder, 1964), which are characterized by measuring the distortion index, $\Delta = 2\theta_{131} - 1/2(2\theta_{511} + 2\theta_{421})$ (Miyashiro, 1957). Unfortunately, there is no apparent correlation between Si–Al ordering in the tetrahedral sites and the distortion index (Meagher and Gibbs, 1966; Langer and Schreyer, 1969), so the degree of Si–Al order of the synthetic cordierite and the effect of ordering on the stability relations described in this paper remains unknown. The distortion index, Δ, of cordierite was measured after the completion of each experiment. Results of the measurements (Table 2) show no systematic change in the distortion index as a function of pressure.

The reaction 6 Chl + 29 Qtz = 8 Tc + 3 Co + 16 H_2O

The critical experiments which bracket the position of the univariant equilibrium curve for the dehydration of clinochlore + quartz are given in Table 3 and are plotted on Figure 1. Because the water content of cordierite is a function of the pressure of hydrothermal treatment the reaction should be written:

$$6\,Mg_5Al_2Si_3O_{10}(OH)_8 + 29\,SiO_2 = 8\,Mg_3Si_4O_{10}(OH)_2$$
clinochlore quartz talc
$$+ 3\,Mg_2Si_5Al_4O_{18}\cdot nH_2O + (16 - 3n)H_2O. \quad (1)$$
cordierite vapor

Fawcett and Yoder (1966) located the phase boundary for this reaction at a temperature 55°C (at P_{H_2O} = 2 kbar) higher than the position obtained in the present study (Fig. 1). Two factors may account for the discrepancy: (1) the position of the phase boundary obtained by Fawcett and Yoder is primarily based on synthesis experiments using glass starting materials, and (2) Fawcett and Yoder note that the composition of the synthetic Mg-chlorite coexisting with quartz (21 weight percent Al_2O_3 at 2 kbar; 23 weight percent at 5 kbar) was more aluminous than clinochlore (18.34 weight percent Al_2O_3).

The position of the phase boundary determined by Velde (1973) is some 50° higher (525°C, P_{H_2O} = 1 kbar) than the position obtained by extrapolating the curve from the 4, 3, and 2 kbar brackets obtained in the present study to 1 kbar; no satisfactory explanation for this discrepancy can be given at the present time. Seifert (1970, p. 87) determined that the reaction must occur at a temperature in excess of 670°C at P_{H_2O} = 7 kbar; projection of the phase boundary obtained in the present study to 7 kbar yields an equilibrium temperature of 675°C.

Fleming and Fawcett (1976) have determined that the upper thermal stability of Mg-chlorite (21 weight percent Al_2O_3) + quartz is near 590 ± 10°C at P_{H_2O} = 2.07 kbar, which is 75°C higher than the phase boundary for clinochlore + quartz obtained in the present study. A temperature-composition section (Fig. 2) along the join $Mg_7Si_8O_{22}(OH)_2$–$Mg_5Al_4Si_6O_{22}(OH)_2$ illustrates the problem. Fleming and Fawcett suggest that: (1) the maximum thermal stability of clinochlore + quartz at P_{H_2O} = 2.07 kbar is 565°C—this temperature is read at the point where the phase boundary separating the Tc_{ss} + Chl_{ss} + Q field from the Chl_{ss} + Q field intersects the projection of the clinochlore + quartz tie line (dashed on Fig. 2), (2) Co should not be encountered at a temperature below about 590°C at P_{H_2O} = 2.07 kbar, and (3) Chl + Q react to Tc_{ss} + Chl_{ss} + Q rather than to Tc + Co, as was determined in the present study. The control on the phase boundary separating the Tc_{ss} + Chl_{ss} + Q field from the Chl_{ss} + Q field is not good, because its location is based on synthesis-type experiments. Agreement between the two data sets for the breakdown of Chl + Q can be achieved by modifying the slope of this phase boundary in a manner consistent with the data contained in Table 3.

Although Fleming and Fawcett suggest that Co should not be encountered at temperatures below 590°C at 2 kbar, the data in Table 3 indicates that cordierite grew at 535°C at this pressure. Because

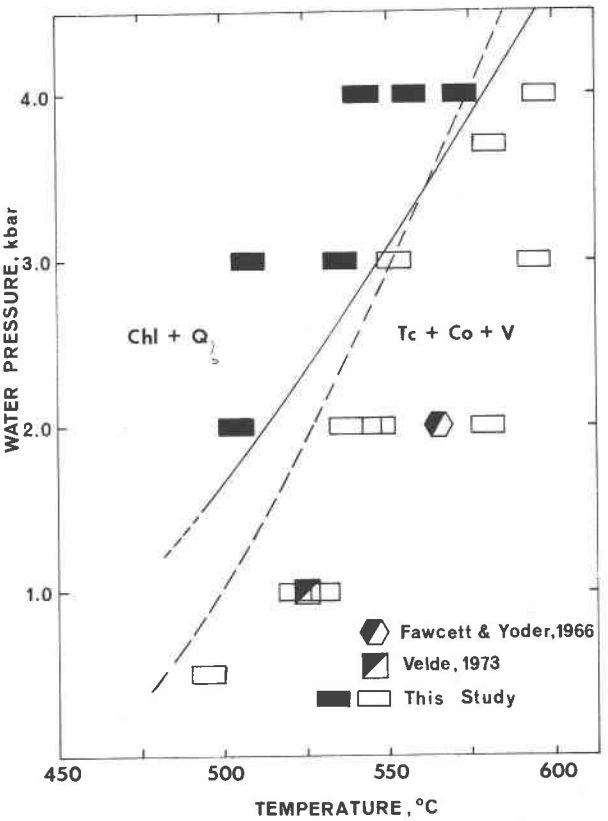

Fig. 1. Dehydration curve for the reaction Chl + Q = Tc + Co + H_2O. Solid symbols represent growth of Chl + Q, and open symbols represent growth of Tc + Co. Rectangles and solid curve represent data obtained during this study. Dashed line represents preliminary phase boundary reported elsewhere (Chernosky, 1975). Size of rectangles represents uncertainty in pressure and temperature. Hexagon represents location of the curve based on synthesis experiments (Fawcett and Yoder, 1966). Square represents location of reversed phase boundary obtained by Velde (1973).

cordierite nuclei were present in the starting material used in this and in the higher-pressure experiments, it could be argued that cordierite grew metastably because nuclei of an assemblage with a lower free energy, hence more stable, were not present. The argument is not convincing because nuclei of clinochlore, one of the presumed low-temperature reaction products, were also present in the starting material and reacted away. In addition, experimental data obtained by Seifert and Schreyer (1970, p. 234) confirm that Mg-cordierite can be a stable phase at 510°C, P_{H_2O} = 2 kbar.

The remaining problem is to ascertain whether Tc_{ss} + Chl_{ss} + Q or Tc + Co is the correct breakdown assemblage of clinochlore + quartz. X-ray diffraction patterns of the high-temperature assemblage (Tables

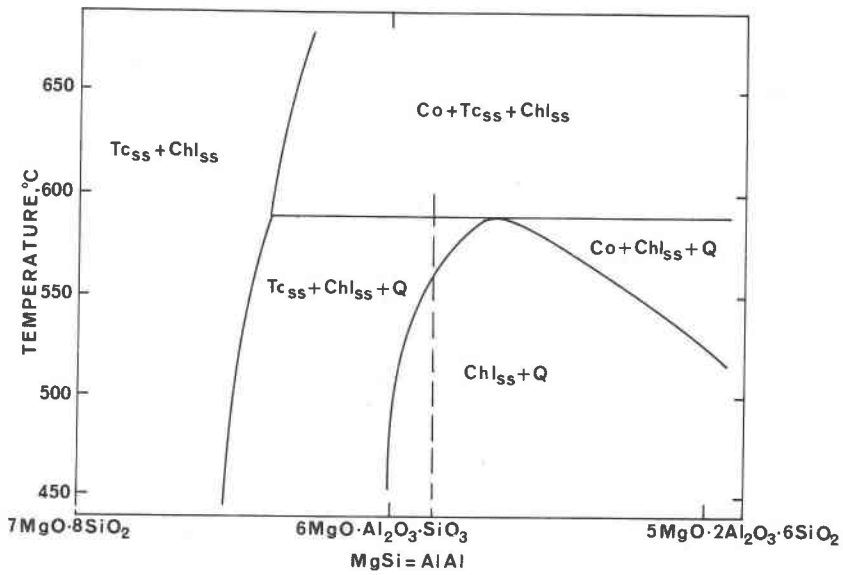

Fig. 2. Temperature-composition section along the join anthophyllite ($7MgO \cdot 8SiO_2 \cdot 2H_2O$)–Mg-gedrite ($5MgO \cdot 2Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$) at P_{H_2O} = 2.07 kbar after Fleming and Fawcett (1976). All assemblages include vapor as a stable phase. Dashed line represents projection of the clinochlore–quartz tie line onto the compositional join.

2 and 3, experiments 5, 12, 17, 18 and 21) clearly show that a starting material containing Chl + Q + Co + Tc has completely reacted to Tc + Co (small amounts of Chl and Q were, however, detected optically in the experimental products). J. J. Fawcett (personal communication, Feb. 1976) suggested that there should be some indication of clinochlore going off composition toward a more Al-rich chlorite at its upper stability, provided that Ta_{ss} + Chl_{ss} + Q is the stable breakdown assemblage. Although the precision with which the d_{006} and d_{004} reflections of talc and clinochlore can be measured is not good, the data in Table 2 indicate little or no departure from end-member compositions as the result of hydrothermal treatment at P_{H_2O} = 2 kbar, and support the inference that Tc + Co is the high-temperature assemblage. Once the chlorite–quartz tie line is cut by the talc–cordierite tie line, the coexistence of chlorite (of any composition) and quartz is prevented. If the tie-line switch occurs at the clinochlore composition, as is suggested by the present experimental data, then clinochlore must be the most stable chlorite, because more aluminous chlorites are prevented from coexisting with quartz. This conclusion is at odds with the data of several investigators (Fleming and Fawcett, 1976; Fawcett and Yoder, 1966; Yoder, 1952), who observe that the most stable chlorite is somewhat more aluminous than clinochlore. However, it is consistent with recent high-pressure data of Standigel and Schreyer (1977), which suggest that clinochlore is the thermally most stable Mg-chlorite. A possible rationale for the conflicting results between this and previous studies is that different starting materials were used. Individually synthesized phases of known composition were used in present experiments, whereas in previous studies an assemblage of crystalline phases was synthesized from a variety of bulk compositions. The compositions of the coexisting phases synthesized in this manner may differ with differing P–T conditions of hydrothermal synthesis and may affect the resulting reversal-type experiments. Clearly, additional experimental work coupled with careful monitoring of chlorite compositions is needed.

The phase diagram and petrologic applications

Figure 3 is a P–T diagram, similar to those constructed by Schreyer and Seifert (1969) and by Bird and Fawcett (1973), showing important phase relations in the water-saturated, silica-rich portion of the system KMASH. Compatibility relations are depicted in AKF diagrams; the aluminosilicate triple point is from Richardson *et al.* (1969). Petrologic applications of the basic phase diagram (Fig. 3) have been discussed at length by Schreyer and Seifert (1969) and by Bird and Fawcett (1973) and will not be repeated here. As shown on Figure 3, the phase boundary for the degenerate reaction Chl + Qtz = Co + Tc + H_2O (1) does not intersect the phase boundary for the reaction Ms + Chl + Qtz = Co +

Phl + H_2O (2) (Bird and Fawcett, 1973) although it does intersect the reaction Co + Ms = Phl + AS + Qtz + H_2O (3) (Bird and Fawcett, 1973) indifferently.

The bracketing data presented in this paper suggest that reaction (1) intersects reaction (2) near 580°C at P_{H_2O} = 4 kbar. As a consequence of this intersection, the phase diagram shown on Figure 3 must be modified. A closed net depicting the chemographic relations among the phases Ms, Tc, AS, Chl, Co, Phl, and H_2O in the water-saturated, silica-rich portion of the system KMASH (Fig. 4) shows the seven new invariant points generated as a result of the intersection of reactions (1) and (2). The [Q] and [V] invariant points and the univariant curves linking these invariant points with the ones shown on Figure 4 were omitted, because only the phase relations in the silica- and water-rich portions of the system are considered. In addition, when the closed net is "opened" it is evident that either the [Ms], [Tc], [AS], and [Phl] invariant points are stable and the [Chl] and [Co] invariant points are metastable or vice versa. Detailed multisystem analysis of the system KMASH (Schreyer and Seifert, 1969) suggests that the invariant point [Tc] (IP_1 of Schreyer and Seifert) is stable, which implies that [Ms], [AS], and [Phl] are also stable and that [Chl] and [Co] are metastable.

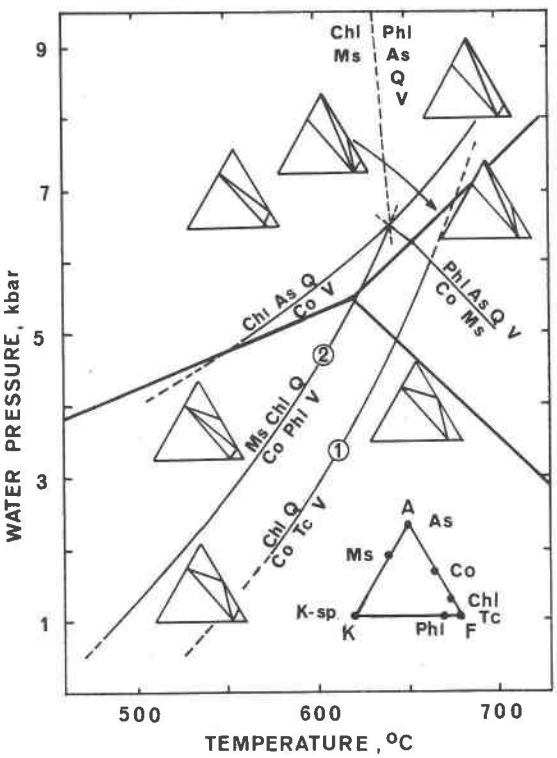

Fig. 3. Pressure–temperature diagram showing some phase relations, as depicted by Schreyer and Seifert (1969) and Bird and Fawcett (1973), in the water-saturated, silica-rich portion of the system K_2O–MgO–Al_2O_3–SiO_2–H_2O. Aluminosilicate triple point is after Richardson *et al.* (1969). Key reactions are numbered as in the text.

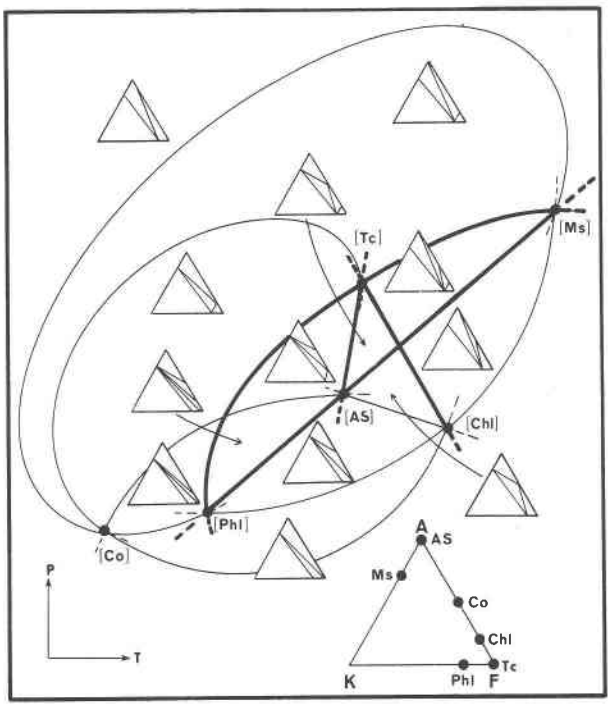

Fig. 4. Closed net depicting phase relations among Ms, Tc, AS, Chl, Co, and Phl in the water-saturated, silica-rich portion of the system KMASH. Key reactions are numbered as in the text. Mineral abbreviations and formulae are listed in Table 4. Heavy lines represent experimentally studied reactions.

The phase relations about the four stable invariant points of Figure 4 are of interest because metamorphic rocks with bulk compositions approaching the system MASH and containing mineral assemblages attributed to high-pressure metamorphism have recently been discovered (McKie, 1959; Chinner and Sweatman, 1969; Vrána and Barr, 1972; Kulke and Schreyer, 1973). Schreyer (1973, 1974) has named schists containing the high-pressure assemblage talc-kyanite "whiteschists."

Reactions and compatibility relations around the [Phl] invariant point (Fig. 4) are of importance because they resemble those observed in natural rocks. To ascertain whether or not the [Phl] invariant point might be stable at geologically reasonable P–T conditions, the experimentally determined reactions were plotted on a P–T diagram (Fig. 5). Additional constraint on the placement of the curves was possible when K-feldspar was included in the multisystem

analysis. Thirty-six invariant points are theoretically possible in a five-component multisystem with nine phases, assuming no compositional degeneracy. Fortunately, the number of invariant points was reduced due to compositional degeneracy and due to the fact that only equilibria in the water-saturated, silica-rich portion of the system were considered. The invariant points and indifferent crossings which appear at the *P–T* conditions of interest are shown in Figure 5. Balanced equations for the phase boundaries shown on Figure 5 are contained in Table 4. Heavy lines represent phase boundaries located experimentally, and dashed lines represent phase boundaries whose positions have been estimated; the aluminosilicate phase boundaries and triple points are after Holdaway (1971) and Richardson *et al.* (1969). The upper thermal stability of pyrophyllite after Kerrick (1968) is also shown on Figure 5. However, pyrophyllite was not included in the multisystem analysis because its upper thermal stability is below that of the reactions and invariant points of interest. The invariant points [Phl], [Tc], and [AS] shown on Figure 4 correspond to invariant points [Phl,K-sp], [Tc,K-sp], and [AS,K-sp] shown on Figure 5. Although the [Ms] invariant point shown on Figure 4 is theoretically stable, the reactions which generate it do not intersect in the *P–T* region shown on Figure 5. The points [Tc-K-sp] and [Chl,Tc] correspond to points [IP_1] and [IP_2] respectively of Schreyer and Seifert (1969).

The *P–T* conditions of the [Chl,Phl] invariant point are probably never attained in nature. However, this invariant point has been included for the sake of completeness. The *P–T* conditions of the [Phl,K-sp] and [AS,Chl] invariant points are possible in natural rocks. Note that both of these invariant points lie in the andalusite field, regardless of which aluminosilicate triple point is considered most reliable, whereas the characteristic assemblage of white schist is talc–kyanite. Kulke and Schreyer (1973) and Chinner and Sweatman (1968) report the alteration of kyanite to sillimanite but not to andalusite. To the writer's knowledge, the assemblage talc–andalusite has not been reported. Several of the assemblages possible around the [Phl,K-sp] invariant point have

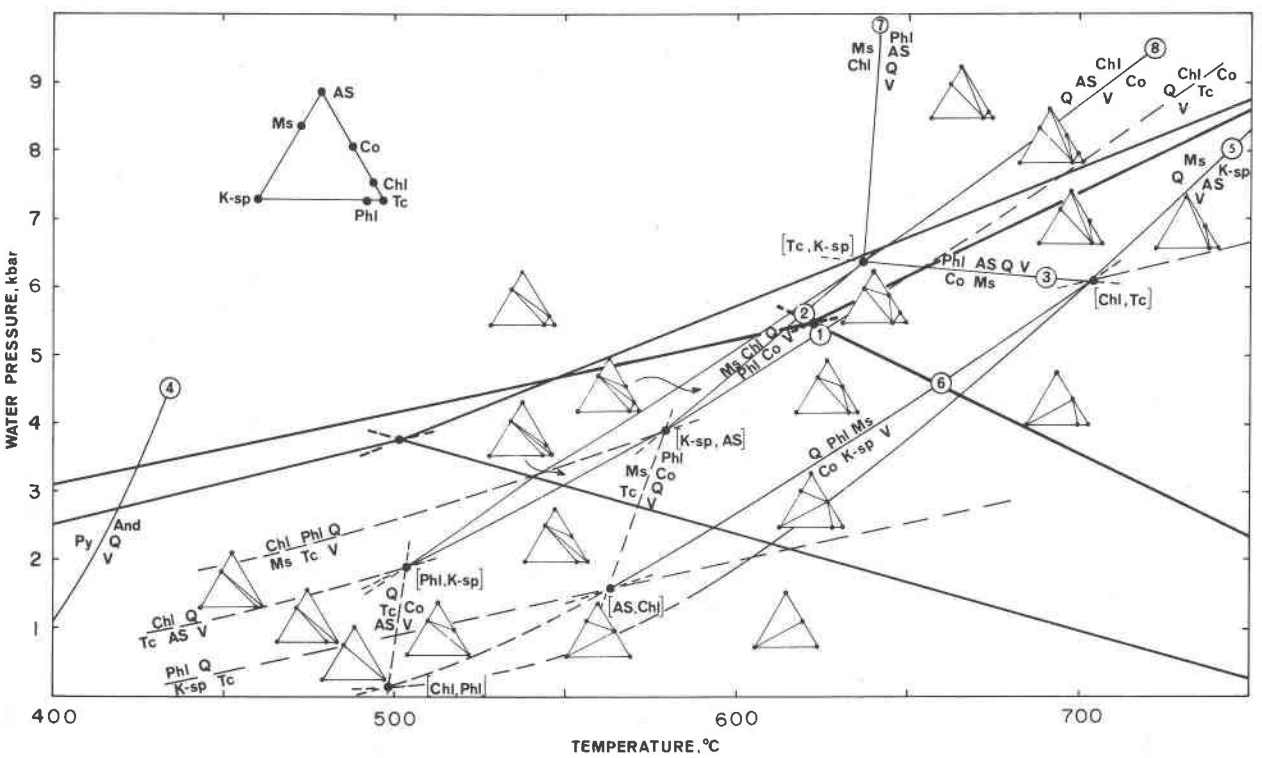

Fig. 5. *P–T* diagram showing the phase relations among Ms, Tc, AS, Chl, Co, Phl, and K-sp in the water-saturated, silica-rich portion of the system KMASH. Solid lines represent experimentally-located phase boundaries; dashed lines represent estimated location of phase boundaries. Compatibility relations are depicted on AKF diagrams. Aluminosilicate triple points after Holdaway (1971) (low pressure) and Richardson *et al.* (1969) (high pressure). Key reactions are numbered as in the text. Mineral abbreviations and formulae are listed in Table 4.

Table 4. Invariant points and reactions for phase boundaries depicted on Fig. 5

Abbreviations and formulae for crystalline phases

Cordierite	Co	$Mg_2Al_4Si_5O_{18}\cdot nH_2O$
Clinochlore	Chl	$Mg_5Al_2Si_3O_{10}(OH)_8$
Muscovite	Ms	$KAl_3Si_3O_{10}(OH)_2$
Phlogopite	Phl	$KMg_3AlSi_3O_{10}(OH)_2$
K feldspar	K-sp	$KAlSi_3O_8$
Aluminum Silicate	AS	Al_2SiO_5
Quartz	Q	SiO_2
Pyrophyllite	Py	$Al_2Si_4O_{10}(OH)_2$
Talc	Tc	$Mg_3Si_4O_{10}(OH)_2$
Vapor	V	H_2O

[Tc,K-sp]	
Ms + Chl + 2Q = Co + Phl + 4V	(2)
5Ms + 3Chl = Q + 5Phl + 8AS + 12V	(7)
2Chl + 11Q + 8AS = 5Co + 8V	(8)
[Chl,Tc]	
Ms + Q = K-sp + AS + V	(5)
2Phl + 6AS + 9Q = 3Co + K-sp + 2V	
6Ms + 2Phl + 15Q = 3Co + 8K-sp + 8V	(6)
[K-sp,AS]	
Ms + Chl + 2Q = Co + Phl + 4V	(2)
3Chl + 23Q + 3Phl = 3Ms + 8Tc + 4V	
6Ms + 8Tc = 17Q + 3Co + 6Phl + 8V	
6Chl + 29Q = 3Co + 8Tc + 16V	(1)
[Phl, K-sp]	
8AS + 11Q + 2Chl = 5Co + 8V	
6Chl + 29Q = 3Co + 8Tc + 16V	(1)
3Chl + 14Q = 5Tc + 3AS + 7V	
Q + Tc + 6AS = 3Co + 2V	
[AS,Chl]	
6Ms + 7Q + 2Tc = 3Co + 6K-sp + 8V	
6Ms + 15Q + 2Phl = 3Co + 8K-sp + 8V	(6)
6Ms + 8Tc = 17Q + 3Co + 6Phl + 8V	
24Ms + 15Tc = 12Co + 7Phl + 17K-sp + 32V	
[Chl,Phl]	
Ms + Q = AS + K-sp + V	(5)
2Tc + Q + 6AS = 3Co + 2V	
6Ms + 7Q + 2Phl = 3Co + 6K-sp + 8V	

Py = AS + Q + V	

Water-rich vapor is present at all invariant points; the quartz- and water-absent reactions have been omitted. The reactions have been balanced assuming cordierite is anhydrous. Key reactions numbered as on Figure 5 and in the text.

been formed by retrogressive metamorphism of talc–kyanite schists due to release of pressure (Vrána and Barr, 1972; Kulke and Schreyer, 1973; Schreyer and Abraham, 1976); however, only talc–andalusite is indicative of low-pressure retrograde reactions.

It must be emphasized that the addition of iron-bearing phases such as staurolite and garnet permit several reactions involving chlorite and muscovite to proceed at temperatures lower than those necessary for reactions in the pure Mg-system to be realized in natural rocks. The reader is referred to Bird and Fawcett (1973) for an excellent discussion of the pitfalls to be avoided in applying the experimental data for the system KMASH to natural rocks.

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