The Upper Stability of Clinochlore at Low Pressure and the Free Energy of Formation of Mg-Cordierite[1]

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Abstract

The univariant reaction governing the upper stability of clinochlore,

$$\underset{\text{clinochlore}}{5Mg_5Al_2Si_3O_{10}(OH)_8} = \underset{\text{forsterite}}{10\,Mg_2SiO_4} + \underset{\text{spinel}}{3MgAl_2O_4} + \underset{\text{cordierite}}{Mg_2Si_5Al_4O_{18} \cdot nH_2O} + \underset{\text{vapor}}{(20-n)H_2O},$$

has been bracketed, with reversed experiments, at: 500 bars, $613 \pm 10°C$; 1000 bars, $651 \pm 10°C$; 2000 bars, $696 \pm 10°C$; and 3000 bars, $732 \pm 10°C$. Reversibility was established by determining the relative growth or diminution of clinochlore in a starting mixture containing equal amounts of the high and low temperature assemblages. The Gibbs free energy of formation of anhydrous Mg-cordierite from the elements ($-2,083$ kcal/mole at 298 K, 1 bar) was calculated from the bracketing data. The isofract diagram of Schreyer and Yoder (1964, Fig. 7) indicates that the maximum water content of the cordierites synthesized in the present experiments was 0.6 moles (1.8 wt percent). Assuming that the entropy contribution of zeolitic water in Mg-cordierite is 14.1 Gb/gf, the free energy of formation of Mg-cordierite containing 0.6 moles of zeolitic water is estimated to be $-2,097$ kcal/mole at 298 K, 1 bar.

Introduction

The occurrence of chlorite group minerals as authigenic crystals in argillaceous sediments, as products of metamorphism and as hydrothermal alterations of pyroxene, amphibole, and biotite implies that chlorites are stable over a wide range of pressures and temperatures. The upper stability of clinochlore was reinvestigated, because relatively little is known about the stability relations and virtually nothing is known about the thermochemical properties of the chlorite group minerals. This investigation was undertaken to provide information on the stability of clinochlore and to re-evaluate the free energies of clinochlore and Mg-cordierite.

A large number of crystalline phases occur in the quaternary system $MgO–Al_2O_3–SiO_2–H_2O$. Those phases pertinent to this investigation are shown in Figure 1.

The chemographic relations among forsterite (Fo), cordierite (Co), enstatite (En), vapor (V), spinel (Sp), and clinochlore (Chl) in the system $MgO–Al_2O_3–SiO_2–H_2O$ are depicted in Figure 2. Note that the

reaction (V), which has been omitted, coincides with the metastable extension of the (Chl) reaction. The chemographic relations for each chlorite composition along the chrysotile-amesite join are identical to those depicted in Figure 2 except for amesite. Because amesite lies on the enstatite-spinel join, compositional degeneracy is introduced and the reactions (Fo) and (Co) become coincident.

Yoder (1952) investigated the maximum thermal stability of clinochlore, which is defined by the reaction (En)

$$\underset{\text{clinochlore}}{5\,Mg_5Al_2Si_3O_{10}(OH)_8} = \underset{\text{forsterite}}{10\,Mg_2SiO_4} + \underset{\text{spinel}}{3\,MgAl_2O_4}$$

$$+ \underset{\text{cordierite}}{Mg_2Si_5Al_4O_{18} \cdot n\,H_2O} + \underset{\text{vapor}}{(20-n)\,H_2O},$$
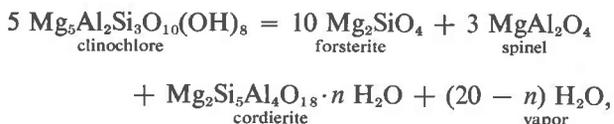
at water pressures between 2,000 and 30,000 psi. Yoder noted that a 7 Å phase, which he called aluminous serpentine, slowly converted to clinochlore above 520°C. Attempts to reverse this reaction were unsuccessful. Similar results were obtained by Roy and Roy (1955) who synthesized clinochlore at temperatures as low as 450°C.

Phase relations along the join

$$Mg_6Si_4O_{10}(OH)_8 – Mg_4Si_2Al_4O_{10}(OH)_8$$

were investigated by Nelson and Roy (1958) who
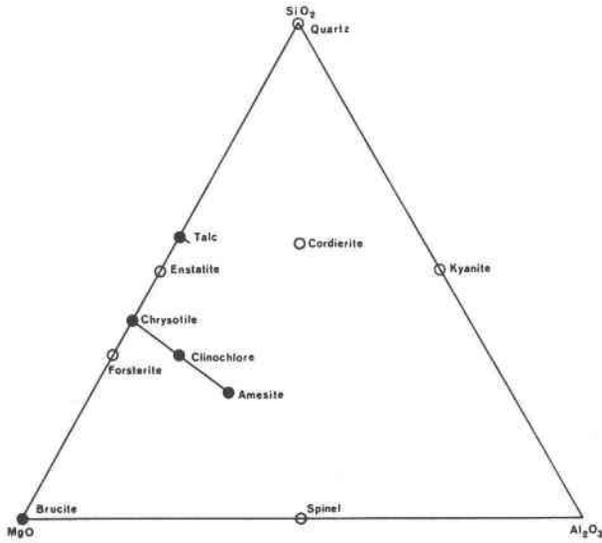
FIG. 1. Crystalline phases in the system MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O pertinent to this investigation. The diagram is a projection, in mole percent, from the H$_2$O apex onto the anhydrous base of a tetrahedron. Solid symbols represent hydrous phases, and open circles represent anhydrous phases.

state "equilibrium maximum stability temperature for the chlorites appears to reach a maximum at the composition of clinochlore" (710°C, $P_{H_2O} \simeq P_{total} = 20,000$ psi).

The maximum thermal stability of clinochlore in the pressure range 6–20 kbar was studied in a piston-anvil apparatus by Segnit (1963) who observed that the reaction,

$$5 \; \underset{\text{clinochlore}}{Mg_5Al_2Si_3O_{10}(OH)_8} = \underset{\text{forsterite}}{7Mg_2SiO_4}$$

$$+ \; 2 \; \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 5 \; \underset{\text{spinel}}{MgAl_2O_4} + 18 \; \underset{\text{vapor}}{H_2O}$$
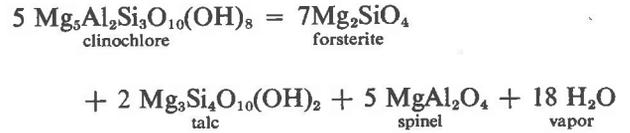
proceeds to the right at 830°C, 15 kbar. Segnit was not able to reverse this reaction. Fawcett and Yoder (1966) studied the maximum thermal stability of clinochlore in the range $P_{H_2O} \simeq P_{total} = 3$–10 kbar. They demonstrated the metastability of the talc — spinel tie line postulated by Segnit (1963) and found that the thermal stability of clinochlore above $P_{H_2O} = 3.5$ kbar was defined by the reaction (Co):
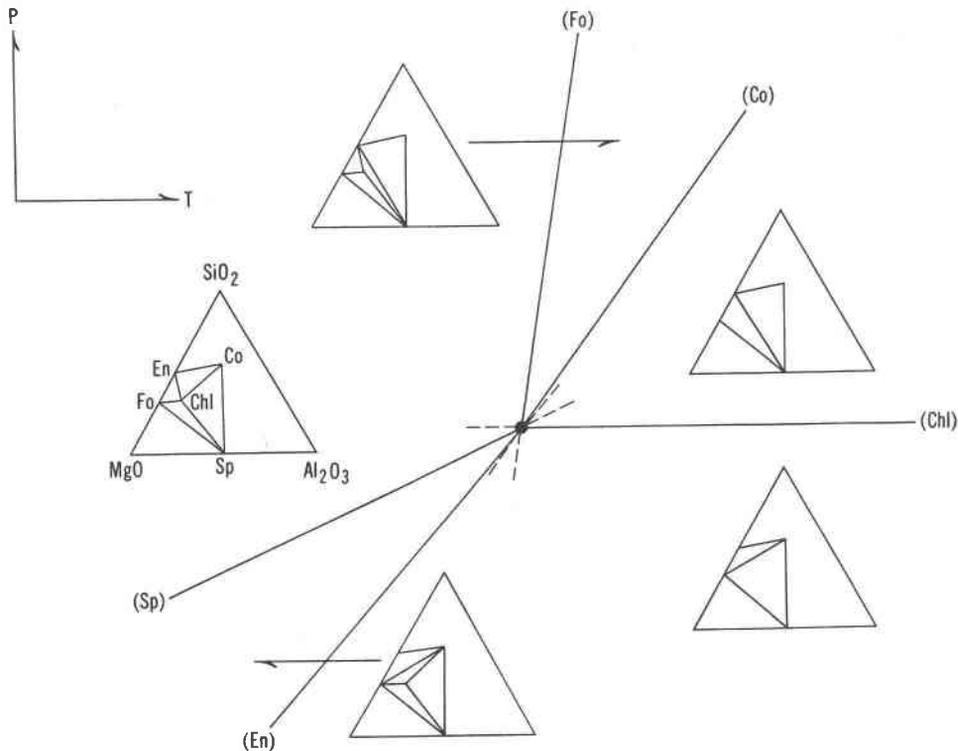
FIG. 2. Chemographic relations among forsterite (Fo), cordierite (Co), enstatite (En), spinel (Sp), clinochlore (Chl), and vapor (V) in the system MgO–Al$_2$O$_3$–SiO$_2$–H$_2$O. The reaction (V) is not shown. The coordinates of the invariant point are 3.25 kbar, 765°C (Fawcett and Yoder, 1966).

$$Mg_5Al_2Si_3O_{10}(OH)_8 = Mg_2SiO_4$$
clinochlore   forsterite

$$+ 2 MgSiO_3 + MgAl_2O_4 + 4H_2O.$$
enstatite   spinel   vapor
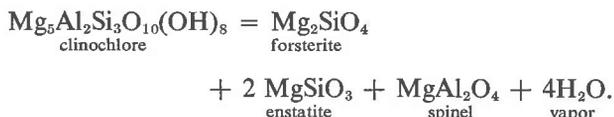
Fawcett and Yoder also showed that the composition of the most stable magnesian chlorite lies about half way between clinochlore and corundophyllite and not at clinochlore as was suggested by Nelson and Roy (1958).

The results of the present investigation have been reported orally (Chernosky, 1973a).

Units, Symbols, and Abbreviations

$G°_f, H°_f, S°_f$ Standard (298 K, 1 bar) gram-formula Gibbs free energy, enthalpy, and entropy of formation of a phase from the elements.

$S°$ Standard (298 K, 1 bar) entropy ("Third Law") of a phase.

T, T_e Temperature in kelvins (K); equilibrium temperature.

P, P_e Pressure in bars (b) or kilobars (kbar); equilibrium pressure.

$\Delta S_{f,s}$ Sum of entropy of formation of product solids minus the sum of entropy of formation of reactant solids.

ΔV_s Sum of total volumes of product solids minus the sum of total volumes of reactant solids.

μ_i The chemical potential of component i.

f_i The fugacity of component i.

$G*_{H_2O}(T_e, P_e) = \Delta G°_f(H_2O)(T_e, 1\ bar)$
         $+ G(H_2O)\ (T_e, P_e) - G(H_2O)(T_e, 1\ bar)$
         (Fisher and Zen, 1971).

n_i The stoichiometric coefficient of constituent i in a reaction.

Gb/gf   Unit of entropy and heat capacity, 1 Gibbs = 1 cal/deg.

gf   Unit gram formula weight of a substance.

cal/bar   Unit of volume, 1 cal/bar = 41.842 cc.

Starting Material

An oxide mix with the bulk composition of clinochlore was 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 previously fired at 1000°C for two hours to drive off adsorbed water; γ–Al_2O_3 was prepared in three stages by firing $AlCl_3 \cdot 6\ H_2O$ (Fisher, lot 792733) at 400°C for two hours, at 700°C for five hours, and at 900°C for one

hour. Clinochlore and the high temperature assemblage (forsterite + cordierite + spinel) were synthesized from the oxide mix. The synthetic products were examined with a microscope and by X-ray diffraction and were found to be devoid of amorphous material. The starting material for the bracketing experiments consisted of synthetic clinochlore mixed with an equal amount of the synthetic high temperature assemblage.

Experimental Procedure

Details concerning the calibration of the conventional hydrothermal apparatus used for the present experiments are described by Chernosky (1973b). 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.

The products of each experiment were examined with a microscope and X-ray diffraction. Reaction rates were sufficient to permit complete or nearly complete reaction of clinochlore to the high temperature assemblage in a reasonable time. However, reaction rates at temperatures close to and below the univariant reaction were sluggish, and complete reaction was generally not obtained. Judgment as to which assemblage was stable at a given pressure and temperature was based on an examination of the complete X-ray diffractometer trace from 5° to 40° 2θ(Cu$K\alpha$ radiation). A reaction was considered reversed if a 30 percent change (relative to a pattern of the starting material) in the intensities of X-ray reflections could be observed after the completion of an experiment.

Results

Phase Characterization

Clinochlore. Clinochlore synthesized in the present experiments is the IIb layer type as defined by Bailey and Brown (1962). A trace of forsterite (<1 percent) and up to 15 percent 7 Å aluminous lizardite were the impurities associated with clinochlore in the starting material. The basal reflections for the 7 Å and 14 Å phases overlap; however, the presence of a 7 Å phase can be detected by examining an X-ray powder photograph or diffractometer trace in the region near $d = 4.65$ Å. A strong clinochlore reflection occurs near $d = 4.75$ Å, whereas a lizardite reflection occurs near $d = 4.59$ Å. An exam-

ination of the X-ray diffraction patterns of bracketing experiments containing clinochlore revealed that the 7 Å serpentine phase had completely reacted during the course of the experiment.

The unit cell parameters of synthetic clinochlore— $a = 5.324(1)$, $b = 9.224(3)$, $c = 14.420(5)$ Å, β 97°6'(1'), $V = 702.48(28)$ Å³, density (calc) = 2.628(1) g/cc, molar volume = 211.535(84) cm³/mole[3] —were obtained by a least squares refinement (Evans, Appleman, and Handwerker, 1963) of a powder pattern taken with a Debye-Scherrer camera (11.46 cm) using FeKα radiation. Silicon ($a = 5.4301$ Å) was used as an internal standard. The powder pattern of synthetic clinochlore (Table 1) compares favorably with the powder pattern of an almost Fe-free natural chlorite from Cobargo, New South Wales (Loughnan and See, 1958) and with a pattern of synthetic clinochlore (Yoder, 1952).

Fawcett and Yoder (1966) noted in experiments conducted at water pressures in excess of 3.5 kbar that the composition of clinochlore drifted away from $Mg_5Al_2Si_3O_{10}(OH)_8$; however, they did not determine the extent of this compositional variability.

The possibility of variation in the composition of clinochlore was investigated by measuring d_{004} before and after each experiment. This spacing is ideally suited to monitor the composition of clinochlore in the bracketing experiments because (1) it is sensitive to the alumina content of chlorite (Fig. 3); (2) it is an intense reflection; and (3) it is not interfered with by reflections from other phases encountered in this study. The precision obtained in measuring the d_{004} peak of clinochlore is within ±0.02° 2θ (CuKα), which corresponds to a compositional variation of ±0.1 in terms of x (Fig. 3). Within the precision of measurement, no evidence for compositional variability of clinochlore in the bracketing experiments was detected for water pressures to 2 kbar. The value of d_{004} for clinochlore synthesized in the present study agrees with the positions obtained by Yoder (1952) and by Nelson and Roy (1958) for synthetic clinochlore (Fig. 3).

Both Yoder (1952) and Segnit (1963) documented the conversion of a 7 Å aluminous serpentine to 14 Å chlorite with diffractometer traces. The present results agree with Yoder's and show a progressive

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TABLE 1. Powder Patterns for Synthetic Clinochlore and a White Chlorite from Cobargo, New South Wales (Loughan and See, 1958)

hKl	Synthetic Clinochlore, This Study*			Loughnan and See (1958)		Synthetic Clinochlore, Yoder (1952)	
	d calc	d obs	I	d obs	I	d obs	I
001	14.305	14.132	s	14.0	9	14.42	32
002	7.152	7.135	s	7.1	10	7.20	100
003	4.768	4.757	s	4.74	10	4.78	52
110	4.584	4.588	m	4.59	1	4.61	13
1̄11	4.509	4.493	w				
021	4.389	4.373	w				
11̄1	4.236	4.242	w	4.26	1		
022	3.876	3.883	w	3.90	1		
112̄	3.684	3.674	w				
004	3.576	3.572	vs	3.55	10	3.58	75
				3.55	·1		
005	2.861	2.864	m	2.85	4	2.87	10
114̄	2.684	2.691	w				
2̄01	2.657	2.656	w			2.67	1
202̄	2.584	2.584	m	2.59	1	2.59	5
201	2.542	2.540	vs	2.55	5	2.55	10
203̄	2.442	2.441	s	2.44	2	2.45	12
202	2.384	2.385	ms	2.38	1	2.391	·4
204̄	2.263	2.260	ms	2.25	1	2.250	
205̄						2.075	1
007	2.044	2.041	w	2.03	1	2.049	4
204	2.009	2.008	vs	2.00	4	2.014	8
206̄	1.890	1.889	m	1.88	1	1.892	3
205	1.831	1.831	m	1.83	1	1.836	3
207̄	1.723	1.724	w			1.722	1
206	1.670	1.671	w			1.684	2
208̄	1.574	1.573	ms	1.57	2	1.583	4
060	1.537	1.539	vs	1.53	4	1.539	8
062	1.503	1.502	ms	1.50	1	1.501	2
063	1.463	1.463	w				
119	1.454	1.455	vw			1.430	2
333	1.412	1.412	w				
208	1.402	1.403	m			1.405	4
402̄	1.329	1.329	vw				
400	1.321	1.321	w				
401̄	1.301	1.301	w				
404̄	1.292	1.292	wm				
406̄	1.221	1.221	w				
404	1.192	1.192	w				
265	1.131	1.131	vw				

*Synthesized at 661°C, 4 kbar, 1368 hours.

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decrease of d_{020} of serpentine with increasing time of hydrothermal treatment. Judging from the appearance of the diffractometer trace, the 7 Å phase synthesized by Segnit at high pressures is assuredly not lizardite or chrysotile. The strong peak at $d = 4.65$, normally present in powder patterns of chrysolite and lizardite, is missing, suggesting that the serpentine phase synthesized by Segnit may be antigorite.

Forsterite. Forsterite typically crystallized as small prismatic or rounded crystals. The position of the 130 reflection at $d = 2.7642$ Å coincides with d_{130} of forsterite synthesized in an alumina free system (Fisher and Medaris, 1969) suggesting that forsterite is "on composition."

Spinel. Spinel typically crystallized as tiny anhedral pinpoints. Schreyer and Schairer (1961) determined that the composition of spinel in equilibrium with cordierite at subsolidus temperatures is $MgAl_2O_4$. Comparison of d_{311} values for spinel synthesized in the present experiments and a high purity spinel synthesized by H. R. Shell of the U. S. Bureau of Mines suggests that spinels synthesized in the bracketing experiments were "on composition."

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[3] Figures in parentheses represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left; these were calculated by the program used to refine the parameters and represent precision only.
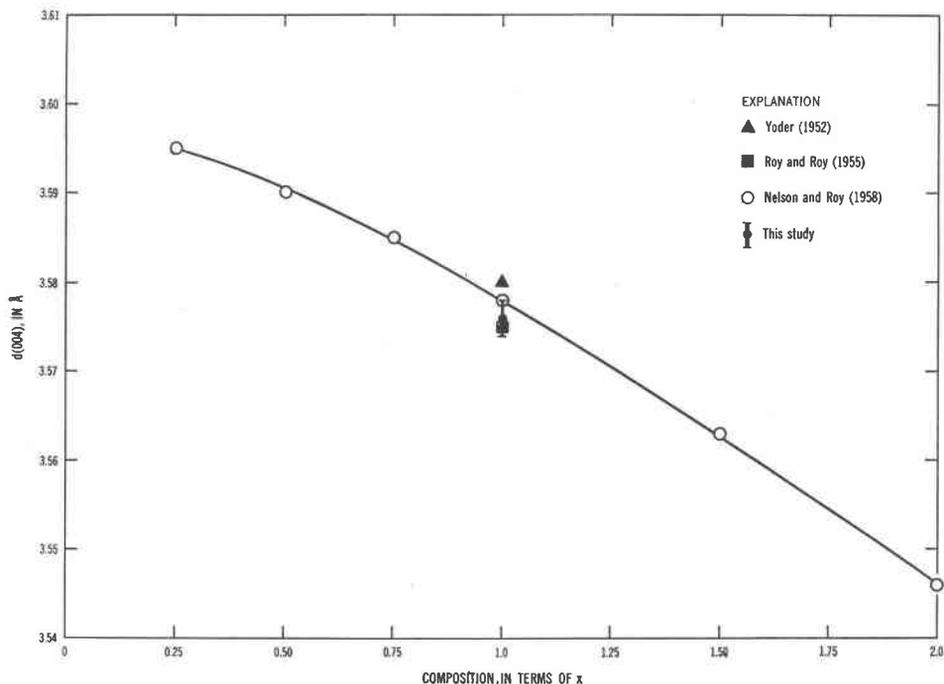
FIG. 3. Plot of $d(004)$ against alumina content of chlorite. Curve is from the data of Nelson and Roy (1958). Numbers along composition axis represent values of x in the formula:

$$(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8.$$

Cordierite. The composition, structural state, and water content of a hydrothermally synthesized cordierite must be specified before it can be considered fully characterized. Schreyer and Schairer (1961) noted that there was no stable solid solution in cordierite within the system MgO–Al_2O_3–SiO_2 below 1300°C; however, they did observe metastable cordierite solid solutions. Cordierite synthesized in the present study was fine grained and had a platy habit. The anhydrous composition of the hydrothermal cordierite in the bracketing experiments could not be determined. It was assumed to be $Mg_2Al_2Si_5O_{18}$.

Schreyer and Yoder (1964) investigated the hydration state of cordierite and constructed an "isofract" diagram relating the degree of hydration to water pressure and temperature. Newton (1972) concluded that the amount of water deduced from Schreyer and Yoder's isofract diagram in the pressure range above 5 kbar P_{H_2O} is stable in the cordierite at the conditions of the experiment. Newton suggested that the observed water contents of cordierites quenched in test-tube bombs from a synthesis in the low-pressure region are almost certainly higher than the equilibrium amounts at the synthesis temperatures.

Schreyer and Yoder's isofract diagram indicates that the water content of the cordierites synthesized in the present study ranges from 1.0 to 1.8 wt percent H_2O which corresponds to 0.33 to 0.6 mole H_2O. Since the maximum pressure attained in the present experiments is 3 kbar, a water content of 1.8 wt percent is certainly an upper limit.

Schreyer and Yoder (1964) showed that it is possible to synthesize hydrothermal Mg-cordierite with a range of structural states. The distortion index $\Delta = 2\theta_{131} - \frac{1}{2}(2\theta_{511} + 2\theta_{421})$ is an X-ray diffraction parameter used to characterize a continuum of cordierite structural states (Miyashiro, 1957). X-ray (Meagher and Gibbs, 1966) and IR absorption data (Langer and Schreyer, 1969) indicate that there is no apparent correlation between Si–Al ordering in tetrahedral sites and the distortion index. The degree of Si–Al ordering of the cordierite used in this study was not determined; hence, the effect of order-disorder on the stability relations of cordierite remains unknown.

Schreyer and Yoder (1964) observed that high cordierite, with $\Delta = 0$, grew first and slowly converted to low cordierite, whose Δ index increased with increasing temperature, pressure, and length of

hydrothermal treatment. In the bracketing experiments performed in this study, the distortion index decreased from a value of $\Delta = 0.28$ in the starting material to a very small or unmeasurable value ($\Delta < 0.10$). The decrease in the distortion index with prolonged hydrothermal treatment may be explained by an hypothesis proposed by Stout (1969), who suggested that the presence of water and other channel constituents is a controlling factor in determining the dimensional symmetry and thus the distortion index of cordierite. Water molecules in the cordierite structure have a preferred orientation parallel to (100). Oxygen coordinated to only Al and Si in the 6-membered rings has a locally unsatisfied charge as well as a distorted position in (100) that may account for the departure of the orthorhombic unit cell from hexagonal dimensions. According to Stout's hypothesis, the addition of water in the structural channels would tend to decrease the distortion index.

Clinochlore Dehydration

The critical experiments which delineate the position of the univariant equilibrium curve for the dehydration of clinochlore to forsterite, cordierite, spinel, and vapor are summarized in Table 2. The dehydration reaction is plotted in Figure 4, where it is compared to the curve obtained by Yoder (1952) and the single point obtained by Nelson and Roy (1958). Reaction rates near the equilibrium boundary were sluggish, especially at low pressure where experiments of 30 days duration did not result in any detectable reaction. For this reason and because the error in individual temperature measurements is

FIG. 4. Dissociation curves for the reaction clinochlore = forsterite + cordierite + spinel + vapor. Solid symbols represent growth of clinochlore, and open symbols represent growth of the high-temperature assemblage. Size of symbols represents uncertainty in pressure and temperature. Solid circle shows the position of the dissociation boundary determined by Nelson and Roy (1958), dashed line is the curve obtained by Yoder (1952). Short-dashed curve is for the reaction involving 1.8 wt percent H_2O in cordierite. Solid curve is for the reaction involving anhydrous cordierite. See text for discussion.

$\pm5°C$, the univariant curve's true position lies within a broad "envelope of uncertainty" (see shaded area, Fig. 5).

Nelson and Roy state that clinochlore dehydration occurs at 710°C, 20,000 psi (1379 bars); however, their Figure 5 (Nelson and Roy, 1958, p. 718) implies that the dehydration occurs at 710°, 1000 atm (1013 bars). In either case, their point lies at too high a temperature and represents a synthesis rather than a reversed boundary (see Fig. 4). Yoder's curve lies at higher temperatures than the curve obtained in this study. An examination of the experimental data (Yoder, 1952, Table 3) indicates only one reversal (700°C, 1034 bars) on the clinochlore bulk composition. The position of the dehydration boundary determined by Yoder was based on synthesis experiments and reversed reactions using natural leuchtenbergite, a synthetic 7 Å aluminous serpentine, or

TABLE 2. Experimental Results for the Dissociation of Clinochlore

Experiment number	P (bars)	T (°C)	Duration (hours)	Condensed Phases
432	500	576	480	Chl (+), Fo(-), Cord (-), Sp(-)
421	500	635	500	Chl (-), Fo (+), Cord (+), Sp (+)
412	500	650	834	Fo, Cord, Sp
407	500	709	141	Fo, Cord, Sp
433	1000	636	500	Chl (+), Fo (-), Cord (-), Sp (-)
417	1000	662	576	Chl (-), Fo (+), Cord (+), Sp (+)
423	1000	672	432	Chl (-), Fo (+), Cord (+), Sp (+)
405	1000	678	141	Chl (-), Fo (+), Cord (+), Sp (+)
411	1000	705	844	Fo, Cord, Sp
408	1000	715	77	Fo, Cord, Sp
381	2000	681	433	Chl (+), Fo (-), Cord (-), Sp (-)
395	2000	694	191	Chl (+), Fo (-), Cord (-), Sp (-)
396	2000	710	190	Chl (-), Fo (+), Cord (+), Sp (+)
410	2000	719	912	Fo, Cord, Sp
397	2000	732	190	Fo, Cord, Sp
388	2000	739	855	Fo, Cord, Sp
404	3000	726	142	Chl (+), Fo (-), Cord (-), Sp (-)
436	3000	750	360	Fo, Cord, Sp
424	3000	766	220	Fo, Cord, Sp

Abbreviations: Chl=clinochlore, Fo=forsterite, Cord=cordierite, Sp=spinel. In experiments showing incomplete reaction, growth or diminution of a phase is indicated by (+) or (-), respectively.

FIG. 5. Log f_{H_2O} against $1/T$ plot for the reaction clinochlore = forsterite + cordierite + spinel + vapor. Open symbols represent growth of the high-temperature assemblage and solid symbols growth of clinochlore. Short-dashed line is for the reaction involving cordierite containing 1.8 wt percent H_2O; long-dashed line is for the reaction involving anhydrous cordierite. Shaded area represents "envelope of uncertainty." Isopleths represent $P_{H_2O} \simeq P_{total}$ in bars. See text for discussion.

phases synthesized on bulk compositions other than $Mg_5Al_2Si_3O_{10}(OH)_8$.

Thermodynamic Considerations

The calculation of thermodynamic parameters from reversed univariant reactions can be used to check the consistency of a set of bracketing experiments and in some cases can lead to thermodynamic values as reliable as those obtained from calorimetric data (see Fisher and Zen, 1971).

The first step in checking the consistency of bracketing data is to plot the data on a log f_{H_2O} against $1/T$ diagram. The variation in the equilibrium constant with temperature is described by van't Hoff's equation:

$$\left(\frac{\partial \ln k}{\partial 1/T}\right)_P = -\frac{\Delta H}{R}.$$

If the activities of the solid phases are unity and if steam is the only volatile species involved in the reaction, van't Hoff's equation reduces to:

$$\left(\frac{\partial \log f_{H_2O}}{\partial 1/T}\right)_P = -\frac{\Delta H}{2.303R}.$$

Provided that ΔH of the reaction remains a constant within the P-T range under consideration, the latter expression indicates that a dehydration boundary will plot as a straight line on a log $f_{H_2O} - 1/T$ diagram. A correction may be necessary to account for the volume change of the solids which contributes to the free energy of the reaction (Eugster and Wones,

1962, p. 91). Provided that the experimental data are internally consistent, an envelope of uncertainty, within which the true position of the dehydration boundary lies, will be defined. Since reaction rates generally decrease substantially in the vicinity of a dehydration boundary, especially at low pressures, the envelope may be quite broad. Consequently, a procedure for locating the true position of a dehydration boundary within the envelope of uncertainty is desirable.

Zen (1971, equation 12) has shown that the entropy of a phase involved in a univariant reaction may be calculated with the relation:

$$-S°_{f, \alpha} = -\sum_{i \neq \alpha} n_i S°_{f, i} + \Delta V_s \frac{P_2 - P_1}{T_2 - T_1}$$
$$+ n_{st} \frac{\mu_{st}(T_2, P_2) - \mu_{st}(T_1, P_1)}{T_2 - T_1}$$

where n_i is the stoichiometric coefficient of constituent i in a reaction ($n_\alpha = 1$), and $\sum_{i \neq \alpha} n_i S°_{f, i}$ is the sum of the entropies of formation of all solid phases except α for which $S°_f$ is to be determined. The change in entropy of reaction for the solid phases, $\Delta S°_{f, s}$ is assumed constant over the temperature and pressure range considered.

If the entropy of the phase in question has been obtained from calorimetric data or estimated by summing the entropies of its component oxides and applying the appropriate volume correction (Fyfe,

Turner, and Verhoogen, 1958), the position of the curve within the envelope of uncertainty can be uniquely determined. The method consists in calculating the entropy of a particular phase from an assumed position for the dehydration curve and comparing it with the calorimetrically measured entropy. The curve is repositioned until the measured entropy and entropy calculated from several pairs of P-T coordinates along the curve agree. The method is successful because relatively small displacements in the position of the curve destroy the consistency between entropy values calculated from several pairs of points along the curve.

Once a thermodynamically consistent curve has been drawn through the bracketing data, the Gibbs free energy of formation of a phase from the elements at 298 K, 1 bar can be calculated from the P-T coordinates of the curve with the relation (Fisher and Zen, 1971, equation 8):

$$\Delta G(T_e, P_e) = 0 = \Delta G°_{f,s}(298, 1)$$

$$- \int_{298}^{T_e} \Delta S°_{f,s}\, dT + \int_1^{P_e} \Delta V_s\, dp + G_{H_2O}{}^*(T_e, P_e).$$

Values for $G_{H_2O}{}^*$, the standard Gibbs free energy of water, have been tabulated by Fisher and Zen (1971). Good estimates of $G°_f$ of a phase can be obtained by approximating the integrals $\int \Delta S°_{f,s}\, dT$ and $\int \Delta V_s\, dp$ by the quantities $\Delta S°_{f,s}\, \Delta T$ and $\Delta V_s\, \Delta P$, respectively

(Zen, 1969). The standard enthalpy of formation is obtained from the relation:

$$G \equiv H - TS.$$

Zen (1969) has shown that calculated free energies are not sensitive to the position of a univariant reaction in P-T space. Errors of 10° to 15°C in the position of a univariant reaction will not result in large differences in the calculated $G°_f$ for a phase. Conversely, accurate free energy data are not sufficient to calculate an accurate position for a univariant reaction.

The suggestions of Zen (1972) regarding the evaluation of the uncertainties involved in the calculations have been followed. The uncertainty in $G°_f$ associated with the input values for the free energy, volume, and entropy of the individual phases has been added to the uncertainty involved in determining the true location of P_e, T_e values. The two–σ convention in reporting uncertainties (Robie and Waldbaum, 1968) has been followed. Table 3 contains the thermochemical values used for the calculations. Fugacity coefficients for water were interpolated from the tables of Burnham, Holloway, and Davis (1969).

Entropy of Clinochlore

The entropy of formation of clinochlore from the elements, obtained by summing the entropies of the individual oxides, varies from -520.27 Gb/gf to

TABLE 3. Thermodynamic Parameters of Phases

	H°$_f$ (298,1) kcal/mole		G°$_f$ (298,1) kcal/mole		S° (298,1) Gb/gf		S°$_f$ (298,1) Gb/gf		V(298,1) cal/bar/gf	
Forsterite Mg$_2$SiO$_4$	+518.980 ±0.460	(3)	-490.55 ±0.5	(3)	22.75 ±0.20	(1)	-95.362 ±0.105	(2)	1.0466 ±0.0007	(1)
Spinel MgAl$_2$O$_4$	-552.800 ±0.500	(1)	-522.961 ±0.510	(1)	19.26 ±0.10	(1)	-100.082 ±0.057	(2)	0.94909 ±0.0007	(1)
Clinochlore Mg$_5$Al$_2$Si$_3$O$_{10}$(OH)$_8$	-2123. ±9.0	(4)	-1968.9 ±8.0	(4)	113.8	(4)	-518. ±3.0	(4)	5.0525 ±0.0020	(4)
Cordierite Mg$_2$Al$_4$Si$_5$O$_{18}$	-2204.5	(4)	-2082.7	(4)	97.33 ±0.90	(1)	-408.834 ±0.458	(2)	5.5636 0.0039	(5)
Clinoenstatite MgSiO$_3$	-370.140 ±0.440	(1)	-349.394 ±0.45	(1)	16.22 ±0.1	(1)	-69.584 ±0.053	(2)	0.75215 ±0.0012	(1)
Quartz SiO$_2$	-217.650 ±0.400	(1)	-204.646 ±0.410	(1)	9.88 ±0.02	(1)	-43.161 ±0.015	(2)	0.54226 ±0.00002	(1)
Kyanite Al$_2$SiO$_5$	-619.930 ±0.540	(1)	-584.000 ±0.550	(1)	20.02 ±0.08	(1)	-120.510 ±0.48	(2)	1.0537 ±0.0017	(1)

Number in parentheses refer to source of the data: (1) Robie and Waldbaum (1968); (2) Zen (1972); (3) King, et al. (1967); (4) this study; and (5) Robie, et al. (1967).

−515.392 Gb/gf depending on whether 9.4 Gb/gf or 10.68 Gb/gf is used for the entropy contribution of H_2O. The value 9.4 Gb/gf is based on an average value for the entropy contribution of water in a number of compounds (Latimer, 1952), and 10.68 Gb/gf is the entropy of ice at 298 K, 1 bar. Zen (1972), using a value of 10 Gb/gf for the entropy contribution of H_2O, calculated the entropy of formation of clinochlore from the dehydration boundary for the reaction: clinochlore = forsterite + 2 enstatite + spinel + 4 vapor. The coordinates for the dehydration boundary, as determined by Fawcett and Yoder (1966), are: 831 ± 6°C, 10 kbar and 785 ± 15°C, 5 kbar. Using the midpoints of these coordinates, Zen obtained a value of −547 Gb/gf. Recognizing that this value was much too negative, Zen adjusted Fawcett and Yoder's 10 kbar temperature to the upper limit (837°C) and the 5 kbar temperature to the lower limit (770°C) and obtained a value of −523 Gb/gf for the entropy of formation of clinochlore. Unfortunately, Fawcett and Yoder's 5 kbar bracket is reversed only on the high temperature side of the boundary; the low temperature point is based on synthesis data.

An independent value for $S°_f$ of clinochlore can be calculated from the bracketing data obtained in this study for the reaction: 5 clinochlore = 10 forsterite + cordierite + 3 spinel + 20 vapor. A log f_{H_2O} − $1/T$ plot of the bracketing data for this reaction (Table 5) is given in Figure 5. The envelope of uncertainty is fairly broad; however, consistent values for the entropy of formation of clinochlore were calculated using the data in Table 3 with the dehydration boundary positioned at the coordinates: (1) 732°C, 3000 bars; (2) 696°C, 2000 bars; (3) 651°C, 1000 bars; and (4) 613°C, 500 bars. From the pairs of points 1, 4; 2, 4; and 1, 3, the respective entropies are −518.0, −521.4, and −514.2 Gb/gf. A value of −518 ± 3 Gb/gf is probably a better estimate of $S°_f$ for clinochlore than −523 Gb/gf because (1) it is consistent with the present experimental results, (2) it agrees with the entropy of formation obtained by the oxide summation procedure, and (3) it is not tied to Fawcett and Yoder's unreversed, 5 kbar bracket for the dehydration of clinochlore.

Gibbs Free Energy and Enthalpy of Clinochlore

Since the dehydration boundary bracketed in the present study involves cordierite for which no reliable $G°_f$ value exists, $G°_f$ of clinochlore was calculated from the 10 kbar bracket of Fawcett and Yoder (1966) for the reaction: clinochlore = forsterite + 2 enstatite + spinel + 4 H_2O. Using a value of −518 Gb/gf for $S°_f$ of clinochlore, a value of −1969 ± 9.0 kcal/mole at 298 K, 1 bar was obtained for $G°_f$ of clinochlore.

The standard state for Al used to obtain $G°_f$ of spinel is that of Al in corundum, for which $G°_f$ is −378.082 ± 0.310 kcal/mole (Robie and Waldbaum, 1968). Since $G°_f$ of spinel was used to obtain $G°_f$ of clinochlore, the standard state for Al in clinochlore is also corundum.

The calculated $G°_f$ of clinochlore presented in this paper differs from previous estimates of −1974 kcal (Zen, 1972) and −1954.8 kcal (Helgeson, 1969, p. 784). Zen (1972) pointed out that since equilibrium was approached only from the super-saturation direction by Mackenzie and Garrels (1965), the free energy value for clinochlore obtained by Helgeson from their data is probably too positive.

On the other hand, the value for the free energy of formation of clinochlore obtained by Zen (1972) is probably too negative because: (1) the value for the entropy of clinochlore used in the calculation was too negative; (2) the high temperature side rather than the midpoint of Fawcett and Yoder's P-T bracket was assumed to be correct; (3) a value of −491.938 kcal rather than −490.55 kcal was used for the free energy of formation of forsterite. The more negative value for $G°_f$ of forsterite (King et al, 1967) was used because it represents a recent determination on a pure synthetic forsterite whereas the more positive value was determined on an impure natural forsterite (Torgeson and Sahama, 1948).

The standard (298, 1) enthalpy of formation of clinochlore from the elements, based on the entropy and free energy values calculated in this paper, is −2123 ± 9.0 kcal.

It must be emphasized that the entropy, free energy, and enthalpy values calculated for clinochlore are only estimates. The values are tenuous because: (1) the free energy and entropy of formation of clinoenstatite rather than enstatite were used; (2) the enstatite in Fawcett and Yoder's experiments contained Al_2O_3; and (3) the clinochlore in their experiments was "off composition."

Gibbs Free Energy and Enthalpy of Mg-Cordierite

Published values for $G°_f$ of cordierite differ by as much as 34 kcal/mole. Compare, for example, the value proposed by Naumov, Ryzhenko, and Khodakovskiy (1971), −2055 kcal/mole, with the

TABLE 4. Gibbs Free Energy and Enthalpy of Formation of "Dry" Mg-Cordierite from the Elements		
P_e bars	T_e °C	$G°_f(298,1)$ kcal/mole
500	613 ±10	-2081.99
1000	651 ±10	-2083.51
2000	696 ±10	-2083.39
3000	732 ±10	-2081.98
	$G°_f$ =	-2082.72
	$H°_f$ =	-2204.61

TABLE 5. Gibbs Free Energy and Enthalpy of Formation of Mg-Cordierite Containing 1.8 Wt Percent (0.06 Mole) H_2O		
P_e bars	T_e °C	$G°_f(298,1)$ kcal/mole
500	618 ±10	-2097.0
1000	652 ±10	-2098.8
2000	694 ±10	-2098.1
3000	729 ±10	-2095.5
	$G°_f$ =	-2097.3
	$H°_f$ =	-2221.7

TABLE 6. Gibbs Free Energy and Enthalpy of Formation of Mg-Cordierite Containing 2.2 Wt Percent (0.07 Mole) H_2O		
P_e bars	T_e °C	$G°_f(298,1)$ kcal/mole
4000	576 ±10	-2100.78
5000	601 ±10	-2100.76
6000	626 ±10	-2100.73
7000	650 ±10	-2100.75
	$G°_f$ =	-2100.75
	$H°_f$ =	-2225.70

value (−2089.9 ± 3.6 kcal/mole) calculated by Bird and Anderson (1973). In a recent compilation of thermodynamic values for minerals, Karpov, Kiselev, and Letnikov (1971) proposed the value −2070.991 kcal/mole. Unfortunately, neither Karpov *et al* nor Naumov *et al* (1971) detail the methods by which the free energies for cordierite tabulated in their respective compilations were calculated.

The coordinates for the dehydration boundary of clinochlore determined in the present study (Fig. 4) were used to calculate $G°_f$ of Mg-cordierite (Table 4). A value of −2082.72 kcal/mole was obtained for "dry" cordierite. The standard state for Al in the $G°_f$ value for Mg-cordierite is tied to the standard state of Al in kyanite which in turn is dependent on the standard state of Al in corundum.

The calculated $G°_f$ for Mg-cordierite shown in Table 4 is based on the assumption that cordierite in the bracketing experiments is anhydrous. However, hydrothermal and natural cordierites are known to contain zeolitic water. Because the entropy of loosely bound, molecular water is greater than the entropy of ice and perhaps greater than the entropy of liquid water, 16.7 Gb/gf (Zen, 1972), it is important to evaluate its effect on the position of the dehydration boundary and on the free energy of Mg-cordierite. The entropy contribution of zeolitic water was assumed to be 14.1 Gb/gf; the assumption is based on the entropy contribution of zeolitic water in analcime. The maximum water content of cordierite synthesized in the present study was previously estimated to be about 0.6 mole (1.8 wt percent). Assuming that this estimate is correct and that the entropy contribution of zeolitic water is 14.1 Gb/gf, the calculated entropy of cordierite containing 0.6 moles H_2O is −417.3 Gb/gf. Using this estimate and constraining the entropy of clinochlore to be −518

Gb/gf, the calculated dehydration boundary is shifted to lower temperatures at high pressures and to higher temperatures at low pressures (see short-dashed lines, Figs. 4 and 5) relative to the boundary for "dry" cordierite.

The P-T coordinates for the dehydration of clinochlore to an assemblage containing cordierite having 0.6 mole H_2O and the calculated value of $G°_f$ of this cordierite are given in Table 5. Note that $G°_f$ for cordierite containing 0.6 mole H_2O (−2097.3 kcal/mole) is considerably more negative than the free energy of anhydrous cordierite (−2082.72 kcal/mole).

The value obtained for $G°_f$ of cordierite in this study can be checked by calculating $G°_f$ of cordierite from the bracketing data of Seifert and Schreyer (1970) for the reaction:

$$2 \text{ Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 8 \text{ Al}_2\text{SiO}_5 + 11 \text{ SiO}_2 =$$
clinochlore   kyanite   quartz

$$5 \text{ Mg}_2\text{Al}_4\text{Si}_5\text{O}_{10} \cdot n \text{ H}_2\text{O} + (8 - n) \text{ H}_2\text{O}.$$
cordierite   vapor
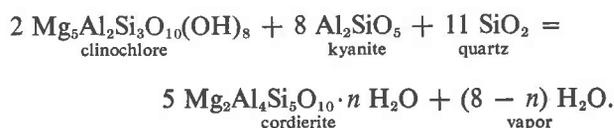
A plot of Seifert and Schreyer's data on a log f_{H_2O} − $1/T$ diagram (Fig. 6) indicates a tight reversal over a 3000 bar interval. The reliability of the data can be checked by using the data to calculate $S°_f$ of clinochlore; as mentioned previously, such a calculation is very sensitive to the position of the dehydration boundary. Assuming that the dehydration boundary passes through the midpoints of the "envelope of uncertainty" (see Fig. 6) and assuming that the cordierite in Seifert and Schreyer's experiments was "dry," the $S°_f$ of clinochlore calculated from several pairs of coordinates along the curve is −563 Gb/gf, a value which is about 45 Gb/gf too negative. A reasonable value for $S°_f$ of clinochlore can be calculated if the entropy contribution of zeolitic water in

cordierite is considered and if the position of the dehydration boundary is shifted somewhat. The isofract diagram of Schreyer and Yoder (1964) suggests that 0.7 mole (2.2 wt percent) is a reasonable estimate for the maximum water content of cordierite synthesized in the 4000 to 7000 bar pressure range. Assuming that the entropy contribution of zeolitic water is 14.1 Gb/gf, the entropy of cordierite containing 0.7 mole H_2O is -419 Gb/gf.

Locating the dehydration boundary at the coordinates: 576°C, 4000 bars; 601°C, 5000 bars; 626°C, 6000 bars; and 650°C, 7000 bars and assuming that -419 Gb/gf is the entropy of cordierite containing 0.7 moles H_2O, a value of -517.3 Gb/gf is obtained for $S°_f$ of clinochlore which is in agreement with the value used in the previous calculations (-518 Gb/gf). The $G°_f$ of Mg-cordierite containing 0.7 moles H_2O, calculated from the above set of coordinates, is -2100.75 kcal/mole (Table 6).

Bird and Anderson (1973) obtained a value of -2088.9 ± 3.6 kcal/mole for $G°_f$ of Mg-cordierite from Seifert and Schreyer's data. The value obtained in this study is probably more accurate because Bird and Anderson (1) assumed a smaller value (0.5 mole H_2O) for the water content of cordierite, (2) did not consider the entropy contribution of zeolitic water in cordierite, (3) used Zen's values for $S°_f$ and $G°_f$ of clinochlore which have been shown in this paper to deviate slightly from best probable values, and (4) used only the midpoints of the 6000 and 7000 bar brackets (Fig. 6) to calculate $G°_f$ of cordierite. A curve drawn through the midpoints of the 6000 and 7000 bar or 4000 and 5000 bar brackets is clearly divergent from the curve constructed on the basis of the entire data set. The three values for $G°_f$ cordierite calculated in the present study indicate that the free energy of Mg-cordierite decreases with increasing water content, i.e., the stability of Mg-cordierite increases as the degree of hydration increases.

The unknown and possibly large uncertainty in the entropy and free energy values for clinochlore and the variable water content of hydrous cordierite prohibits making an accurate estimate of the error associated with the $G°_f$ of cordierite. Thermochemical values calculated for clinochlore and hydrous Mg-cordierite from experimental data depend on the accuracy of the thermochemical data for all other phases involved in a particular reaction. Inaccuracies associated with the thermochemical quantities for these other phases will be propagated throughout
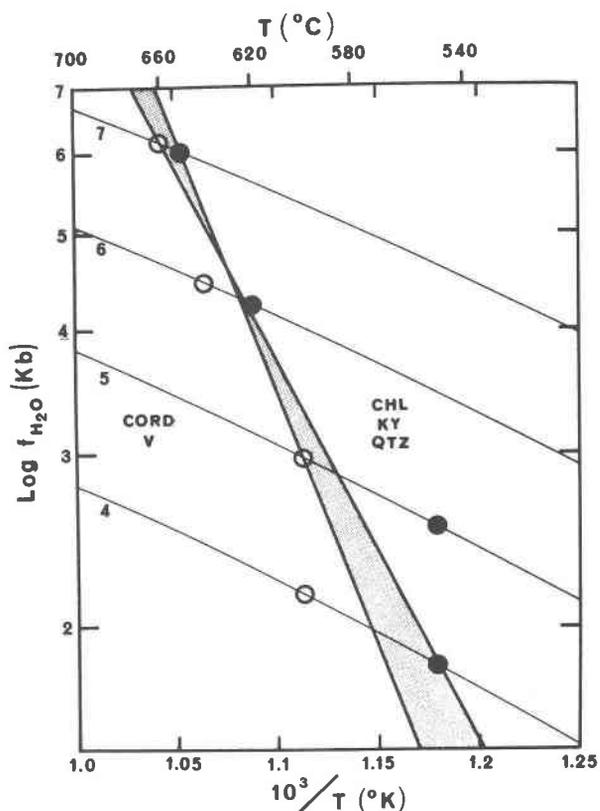
FIG. 6. Log f_{H_2O} against $1/T$ plot for the reaction clinochlore + kyanite + quartz = cordierite + vapor. Data is from Seifert and Schreyer (1970). Open symbols represent growth of the high-temperature assemblage and closed symbols growth of the low-temperature assemblage. Shaded area represents "envelope of uncertainty." Isopleths represent $P_{H_2O} \simeq P_{total}$ in kbars.

the calculations. Potential users of the values presented in this paper are cautioned that they are my "best estimates" (guesses?) and should be treated accordingly.

Acknowledgments

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