# THE STABILITY OF MG-CHLORITE

by

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#### Abstract

The equilibrium Chlorite = Cordierite + Forsterite + Spinel +  $H_2O$  has been experimentally determined with a chlorite of composition Mg4,75Al2.5Si2,75O10(OH)8. Brackets have been obtained between 605 and 640°C at 0.5 kb, 644 and 670°C at 1.0 kb and 690 and 704°C at 2.0 kb. These data are not notably displaced from Chernosky's (1974) data for the same equilibrium with a chlorite of clinochlore composition  $(Mg_{3}Al_{2}Si_{3}O_{10}(OH)_{8})$ , however they are more constraining. A thermodynamic analysis of the above data and data on related equilibria included ideal solution models describing compositional variability in cordierite. orthopyroxene and chlorite. The  $H_2O$  content of cordierite was described using a model based on that of Newton and Wood (1979). The hydrous end-member has two moles of H<sub>2</sub>O and the volumes of the end-members are different; this allows the full range of data to be described with one function. Al-content of orthopyroxene was calculated with Gasparik and Newton's (1984) model. Solid solution in chlorite was modelled by choosing the end-members,  $Mg_6Si_4O_{10}(OH)_{\delta}$  and  $Mg_4Al_4Si_2O_{10}(OH)_{\delta}$ , and using ideal configurational entropy to describe the free energy of mixing. Disordering phenomena in cordierite and spinel were accounted for by adding small entropies of disorder to the third law entropies. Linear programming was used to calculate consistent thermochemical properties for all phases considered. Experimental results indicate that the upper thermal stability of Mg-chlorite is affected by only a few degrees for the composition used here. The thermochemical properties derived allow more complete modelling of systems that include chlorite.

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#### INTRODUCTION

The upper thermal stability of chlorite in the system  $MgO-Al_2O_3-SiO_2-H_2O$  has been experimentally investigated in a number of studies. The equilibria limiting this stability are, with increasing pressure,

$$5 \text{ Chlorite} = 1 \text{ Cordierite} + 10 \text{ Forsterite} + 3 \text{ Spinel} + 20 \text{ H}_2\text{O}$$
 (1)

(Fawcett and Yoder, 1966; Chernosky, 1974; this study),

$$1 \text{ Chlorite} = 1 \text{ Orthopyroxene} + 1 \text{ Forsterite} + 1 \text{ Spinel} + 4 \text{ H}_2 \text{O}$$
(2)

(Fawcett and Yoder, 1966; Staudigel and Schreyer, 1977; Jenkins, 1981) and

2 Chlorite = 1 Pyrope + 3 Forsterite + 1 Spinel +  $8 H_2O$ 

(Staudigel and Schreyer, 1977). Invariant points are generated by the intersections of equilibria (1) and (2) and by (2) and (3). Of the equilibria generated from these invariant points two have been experimentally determined,

$$1 \text{ Cordierite} + 5 \text{ Forsterite} = 5 \text{ Orthopyroxene} + 2 \text{ Spinel}$$
(4)

(Fawcett and Yoder, 1966; Seifert, 1974; Herzberg, 1983) and

2 Orthopyroxene + 1 Spinel = 1 Pyrope + 1 Forsterite(5)

(Danckwerth and Newton, 1978; Perkins et al., 1981; Gasparik and Newton, 1984). The stoichiometric coefficients in the above equilibria are for chlorite of clinochlore composition, orthopyroxene of enstatite composition (6 oxygen formula unit) and anhydrous cordierite.

Both solid solution and/or site and stacking disorder affect some of the phases involved. Chlorite has a variable aluminum content (Fawcett and Yoder, 1966) and stacking disorder (Spinnler et al., 1984). There is also the possibility of disorder on the tetrahedral and octahedral sites. Cordierite has a variable volatile content that is a function of pressure, temperature and coexisting fluid phase (Schreyer and Yoder, 1964; Johannes and Schreyer, 1981) and possible disordering on the tetrahedral sites (Gibbs, 1966). There is also the possibility of disordering the volatile channel-site species. The aluminum content of orthopyroxene varies as a function of pressure, temperature and stable assemblage (Wood, 1974) and ordering of octahedral aluminum in Mg-orthopyroxenes has been described (Ganguly and Ghose, 1979). Solid solution in spinel between MgAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> has been documented (Roy et al., 1953; Navrotsky and

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(3)

Kleppa, 1967) and spinel can exhibit significant disorder between the normal and inverse structures (Navrotsky and Kleppa, 1967). Non-stoichiometric behaviour in forsterite and pyrope has not been documented, at least for the range of conditions considered here, and for the purposes of this study  $H_2O$  is considered to be pure.

Many of the above problems have been addressed experimentally and theoretically, however the effect of variable aluminum content in chlorite has not been determined. One of the purposes of this study was to experimentally determine this effect on equilibrium (1), the low pressure, high temperature breakdown of chlorite. The other purpose was to combine the new data with existing data on equilibria (1) through (5) and activity models for non-stoichiometric behaviour to calculate internally consistent thermochemical properties for the phases involved. The derived properties will allow more precise calculation of the upper thermal stability of chlorite as well as other equilibria involving chlorite.

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Table I	[
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Symbols, abbreviations and com	positions		
$\Delta G_{r}(P,T)$	Free energy change for a reaction at pressure and temperature.		
$\Delta G_{r}^{0}(P,T)$	Free energy change of a reaction for the phases in their standard state at pressure and temperature.		
$\Delta G_{\text{H}_2\text{O}}(\text{P},\text{T})$	Free energy of formation from the elements of $H_2O$ at pressure and temperature.		
$\Delta_{f} H^{0}(P_{r},T_{r})$	Enthalpy of formation from the elements of a phase at 1 bar and 298.15 K.		
$\Delta H_r(P_r, T_r)$	Enthalpy of reaction at 1 bar and 298.15 K.		
$\Delta H_{s}(P_{r},T_{r})$	Enthalpy of reaction for the solid phases in a reaction at 1 bar and 298.15 K.		
S°	Third law entropy for a phase.		
$\Delta S^{o}_{S}(P_{r},T_{r})$	Third law entropy change of reaction for the solid phases.		
V	Molar volume of a phase.		
$\Delta V_{s}$	Volume change of reaction for the solid phases in a reaction.		
$\Delta Cp_r$	Heat capacity change of reaction.		
ΔCp <sub>s</sub>	Heat capacity change of reaction for the solid phases in a reaction.		
xchl coph	Mole fraction of corundophyllite $(Mg_4Al_4Si_2O_{10}(OH)_8)$ in chlorite.		
x <sup>cord</sup> hcrd	Mole fraction of hydrous cordierite ( $Mg_2Al_4Si_5O_{18}{\cdot}2H_2O$ ) in cordierite.		
xOpx En	Mole fraction of enstatite $(Mg_2Si_2O_6)$ in orthopyroxene.		
Chlorite (Chl) Clinochlore (Clin) Chls (Chls) Corundophyllite (Coph) Cordierite (Cord,Cd) Enstatite (En) Forsterite (Fo) Orthopyroxene (Opx) Pyrope (Py) Spinel (Sp)	$ \begin{array}{l} Mg_{6}Si_{4}O_{10}(OH)_{\epsilon} - Mg_{4}Al_{4}Si_{2}O_{10}(OH)_{\epsilon} \\ Mg_{5}Al_{2}Si_{3}O_{10}(OH)_{\epsilon} \\ Mg_{6}Si_{4}O_{10}(OH)_{\epsilon} \\ Mg_{4}Al_{4}Si_{2}O_{10}(OH)_{\epsilon} \\ Mg_{2}Al_{4}Si_{5}O_{10} \cdot nH_{2}O \\ Mg_{2}Si_{2}O_{6} \\ Mg_{2}SiO_{4} \\ Mg_{2}Si_{2}O_{6} - MgAl_{2}SiO_{6} \\ Mg_{3}Al_{2}Si_{3}O_{12} \\ MgAl_{2}O_{4} \end{array} $		

#### **EXPERIMENTAL METHOD**

### **Starting Materials**

An oxide mix was prepared from reagent grade chemicals in the molar proportions 4.75MgO: 1.25Al<sub>2</sub>O<sub>3</sub> : 2.75SiO<sub>2</sub>. Periclase (MgO) was prepared by baking MgO (Fisher Certified Reagent-Lot #741694) for approximately 24 hours at  $1300^{\circ}$ C and cristobalite (SiO<sub>2</sub>) by baking silicic acid (Fisher Certified Reagent - Lot #730944) for approximately 24 hours at  $1300^{\circ}$ C. K-Al<sub>2</sub>O<sub>3</sub> was prepared from Al(OH)<sub>3</sub> nH<sub>2</sub>O (Fisher Certified Reagent - Lot #745229) by baking at 400° C for four hours, 700° C for one hour and  $1000^{\circ}$ C for one hour. The oxides were ground under alcohol and dried in a vacuum furnace for approximately 24 hours at  $120^{\circ}$ C before use. Appropriate proportions were carefully weighed out and the mix was ground for approximately two hours under distilled water in an agate mortar. To ensure homogeneity the mix was periodically dried and collected into the bottom of the mortar. The resulting mix was then dried and stored in a dessicator.

Chlorite was synthesized from the oxide mix plus approximately 25 wt% distilled water in two steps - 4kb,  $400^{\circ}$  C, 7 to 10 days and 4kb,  $700^{\circ}$  C, 14 to 18 days. The first step helped prevent extraneous phases such as spinel and forsterite from nucleating and the second annealed the structure to the 14ÅIIb (Bailey and Brown, 1962) polytype. A trace of spinel was identified optically but not in amounts large enough to significantly affect the composition of the chlorite. The amount of spinel was estimated to be less than 0.1 volume percent from the Comparison Charts for Visual Estimation of Percentage Composition (Terry and Chilingar, 1955). If spinel is the only extraneous aluminous phase and the volumes of spinel and chlorite are taken to be 40 cm<sup>3</sup> and 210 cm<sup>3</sup> respectively then the change in the chlorite composition is calculated to be less than 0.01 atoms of aluminum per formula unit.

The high temperature assemblage (cordierite, forsterite and spinel) was synthesized from slightly impure chlorite obtained in earlier, less successful, chlorite syntheses. The synthesis conditions were 2 kb,  $740^{\circ}$  C and 14 days. No impurities were detected by either x-ray diffraction or optical methods.

#### Technique

All experiments were conducted in standard cold seal pressure vessels of either Stellite K-25 or Rene 41 alloys. The furnaces are horizontally mounted and wound with coiled nichrome wire.

Temperatures were measured with sheathed chromel-alumel thermocouples mounted in an external well designed to hold the thermocouple tip close to the sample. The configuration was calibrated at one atmosphere between  $300^{\circ}$  C and  $800^{\circ}$  C and the temperature gradients were found to be less than  $\pm 1^{\circ}$  C over the three centimetre length of the sample capsule. Temperature was controlled by fully

proportional controllers that normally control to less than  $\pm 1^{\circ}$  C. Precise daily measurements were made using either a temperature compensated digital thermometer with a resolution of  $1^{\circ}$  C or a potentiometer with an estimated resolution of  $0.1^{\circ}$  C. Temperature was not monitored continuously so an effort was made to make measurements at different times of day to avoid any possible systematic differences. No systematic differences were noted. Quoted temperatures are the means of the daily measurements (corrected by the calibration determinations) and the associated errors are sums of two standard deviations, gradient uncertainties and an estimated  $3^{\circ}$  C for thermocouple calibration uncertainties.

The pressure media were either methane or distilled  $H_2O$ . Measurements were made every one to three days, usually daily, with either an Ashcroft Maxisafe gauge with a resolution 15 bars or a Heise Bourdon tube gauge with a resolution of 5 bars. Experiments with pressure drops of more than 3% were not considered successful. The quoted pressures are the means of the measurements and the associated errors are sums of two standard deviations plus an estimated 20 bars for gauge accuracy.

The starting materials for reversal experiments were made of two mixtures of reactants and products: 15-20 wt% of the reactants plus 80-85 wt% of the products; and 80-85 wt% of the reactants plus 15-20 wt% of the products. Each run consisted of two experiments in a single pressure vessel, one capsule with the first mixture and the other with the second mixture. Gold capsules were loaded with 10 to 20 mg of mix plus approximately 25 wt% distilled H<sub>3</sub>O, then sealed, weighed and loaded into the pressure vessel. Runs were brought to temperature in about one half hour and stabilized within two hours. Quenching was accomplished by placing the vessel into a cooling jacket and blowing compressed air around the vessel. The temperature dropped more than  $250^{\circ}$  C within the first minute and to less than  $100^{\circ}$  C after five minutes. The remaining pressure was released and the capsules were removed, weighed, punctured, dried, reweighed and then opened for examination. Only runs that showed no weight loss during the experiment were used. Results were examined optically and by x-ray diffraction and if complete reaction had not occurred the reaction direction was determined by examining x-ray diffractograms and analyzing peak height ratios. Estimated changes in peak heights of at least 30% for chlorite and lesser but opposite amounts for cordierite, forsterite and spinel were taken as unequivocal indication of reaction. Experiments that resulted in lesser changes were considered indeterminate.

#### Phase Characterization

All solid phases were identified by optical properties, x-ray diffractograms and morphology. Chlorite was characterized by a bulk refractive index and by a cell refinement from powder diffractograms. Precise characterizations of cordierite, forsterite and spinel were not considered necessary as their x-ray patterns and optical properties agreed with published data. Also, the non-stoichiometric behaviour of

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cordierite has been well studied elsewhere and the disorder in spinel was not determined in this study.

Chlorite occurred as fine grained aggregates of crystals ranging in size from less than one micron to two microns. The small grain size and the aggregate habit precluded an accurate measurement of the refractive indices and therefore only a bulk index was measured. The refractive index was bracketed between 1.572 and 1.580 in white light. This compares well with indices of 1.581 to 1.586 quoted for clinochlore and approximately 1.576 for a chlorite of the composition studied here (Troger, 1979, pages 116-118). A representative x-ray powder diffraction pattern is shown in Figure 1 to demonstrate the crystallinity of the chlorite starting material. The structure is the IIb polytype (notation of Bailey and Brown, 1962). In order to refine the cell parameters of the chlorite used here, four scans (two with increasing 2 $\Theta$  and two with decreasing 2 $\Theta$ ) were made using silicon metal (a=5.4305 Å) as an internal standard, CuKa radiation and a scan rate of  $1/4^{\circ}$  2 $\Theta$ /minute. The means of the peak positions were calculated and the corresponding d-spacings were used in the program of Evans et al. (1963) to calculate refined cell parameters. Observed and calculated d-spacings and the refined cell parameters are presented in Table II. Also shown are data from Chernosky (1974) for synthetic clinochlore. The a, b and c cell parameters all somewhat smaller than those determined by Chernosky and  $\beta$  is the same within one standard deviation. The d-spacing of (001) as a function of aluminum content has been calibrated in a number of studies: Brindley and Gillery (1956) - naturals, Nelson and Roy (1958) - synthetics, Gillery (1959) - synthetics, Albee (1962) - naturals, Shirozu (1972) - synthetics. The curves determined in these studies are shown in Figure 2. Natural chlorites appear to show a greater dependence of d(001) on Al-content but the chlorites used in those calibrations contain impurities, mainly iron. It is not clear if the impurities have an effect on the basal repeats. Also shown in Figure 2 is the value of d(001) for the chlorite synthesized in this study. The calculated value of d(001) agrees well with the curves derived from synthetics and is slightly larger than those of the naturals. No evidence was found to indicate the presence of a 7Å phase noted by Chernosky (1974). He quotes the intensities for the basal repeats (001), (002), (003) and (004) to be all of equal intensity (based on estimates from a Debye-Scherrer film pattern). The intensities of the basal repeats for the chlorite in this study have ratios of (001)/(002) and (003)/(004)equalling 0.42 and 0.84 respectively and these ratios appear to remain constant over the length of the experiments. This might represent some sort of stacking disorder but without independent evidence or more study no conclusions can be made.

Cordierite was identified as hexagonal prisms as large as 100 microns in length. Miyashiro (1957) proposed the  $\Delta$  index to measure the degree of Al/Si disorder in cordierite. More recent evidence shows this index to be also a function of composition (Selkregg and Bloss, 1980) and long range versus short range order (Putnis, 1980). As a result the  $\Delta$  index has not been used in this study.



Figure 1. Representative x-ray powder diffraction pattern for a synthetic chlorite with composition  $Mg_{4.75}Al_{2.5}Si_{2.75}O_{10}(OH)_{9}$ . The scan was made at 2' 20/min with nickel filtered copper radiation and the scale is approximately 400 counts per second. The first five orders of the basal repeat are not shown completely in order to show other peaks more clearly.

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Table II

		631 H25H3 010(011)8		
	Synthetic chlorite Mg4.75Al25Si27	sO10(OH)		Clinochlore Chernosky (1974) Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>
h k l	d(calc) <sup>1</sup>	d(obs)	I(/100) <sup>2</sup>	d(obs)
$\begin{array}{c} 0 & 0 & 1 \\ 0 & 0 & 2 \\ 0 & 0 & 3 \\ 0 & 2 & 0 \\ 1 & 1 & 0 \\ \hline 1 & 1 & 0 \\ \hline 1 & 1 & 1 \\ 0 & 2 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \\ \hline 1 & 1 & 1 \\ \hline 2 & 0 \\ 2 & 1 & 1 \\ \hline 2 & 0 & 2 \\ \hline 2 & 0 & 2 \\ \hline 1 & 1 & 2 \\ 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 2 & 2 \\ \hline 1 & 1 & 2 \\ \hline 0 & 0 & 5 \\ \hline 1 & 1 & 2 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 4 \\ \hline 2 & 0 & 5 \\ \hline 0 & 0 & 6 \\ \hline 2 & 0 & 8 \\ \hline 0 & 0 & 0 \\ \hline 0 & 6 & 2(?) \\ \hline 0 & 6 & 3 \\ \hline 1 & 1 & 9 \\ \hline 0 & 0 & 10 \\ \hline 3 & 3 & 3 \\ \hline 2 & 0 & 8 \\ \hline \end{array}$	14.234 7.117 4.745 4.596 5.576 4.500 4.374 4.226 4.053 3.861 3.674 3.558 2.847 2.673 2.654 2.580 2.539 2.438 2.380 2.257 2.258 2.033 2.004 1.884 1.826 1.779 1.717 1.665 1.568 1.532 1.498 1.458 1.448 1.424 1.409 1.397	4.752 4.592 4.501 4.384 4.238 4.055 3.862 3.560 2.846  2.653 2.579 2.538 2.437 2.376 2.258 2.258 2.034 2.004 1.885 1.826 1.781  1.568 1.532 1.501  1.423  1.423	$\begin{array}{c} xx \\ xx \\ 40 \\ \hline 30 \\ 25 \\ \hline 20 \\ 20 \\ 15 \\ 20 \\ xx \\ xx \\ xx \\ \hline 15 \\ 35 \\ 100 \\ 80 \\ 40 \\ 35 \\ 20 \\ 35 \\ 85 \\ 35 \\ 35 \\ 10 \\ \hline 15 \\ 55 \\ 70 \\ 20 \\ \hline - \\ 20 \\ \hline - \\ 50 \end{array}$	$ \begin{array}{c} 14.132\\ 7.135\\ 4.757\\\\ 4.588\\ 4.493\\ 4.373\\ 4.242\\\\ 3.883\\ 3.674\\ 3.572\\ 2.864\\ 2.691\\ 2.656\\ 2.584\\ 2.540\\ 2.441\\ 2.385\\ 2.260\\\\ 2.041\\ 2.008\\ 1.889\\ 1.831\\\\ 1.724\\ 1.671\\ 1.573\\ 1.539\\ 1.502\\ 1.463\\ 1.455\\\\ 1.412\\ 1.402\\ 5.224(1) \end{array} $
a(A) b(Å) c(Å) β V(cm <sup>3</sup> /mole)	5.317(1) 9.192(2) 14.349(2) 97° 8'(1') 209.515(51)			5.324(1) 9.224(3) 14.420(5) 97° 6'(1') 211.535(84)

D-spacings and refined cell parameters for synthetic chlorites,  $Mg_{4,75}Al_{2,5}Si_{2,75}O_{10}(OH)_8$  and  $Mg_5Al_2Si_3O_{10}(OH)_8$ 

<sup>1</sup>All d-spacings are given in Å. <sup>2</sup>Intensities are given relative to (201) (see Figure 1). The intensities of the peaks for the first five orders of the basal repeat are discussed in text. ? Assumed Miller indices.



Figure 2. Mg-chlorite volumes as a function of Al-content.

- A. Brindley and Gillery (1956) calibrated from natural Fe-Mg chlorites (data range from 0.4-0.8x<sup>chl</sup><sub>coph</sub>).
- B. Nelson and Roy (1958) synthetic Mg-chlorites (data range from 0.5-1.0x<sup>chl</sup><sub>coph</sub>).
- C. Gillery (1959) synthetic Mg-chlorites (data range from 0.25-1.0x<sup>chl</sup><sub>coph</sub>).
- D. Albee (1962) natural Fe-Mg chlorites (data range from 0.3-0.8x<sup>chl</sup><sub>coph</sub>).
- E. Shirozu and Momoi (1972) synthetic Mg-chlorites (data range from 0.3-1.0x<sup>chl</sup><sub>coph</sub>).
- F. This study synthetic Mg-chlorite, box represents approximately two standard deviations in d-spacing. The error in composition was a maximum of  $\pm .01x_{coph}^{chl}$ .

Spinel usually occurred as euhedral grains of less than 1 micron in size although a few octahedral grains up to 2 microns were noted. Forsterite was identified as anhedral to euhedral grains of platy habit with a range in size from 1 to 20 microns. No evidence of non-stoichiometric behaviour was observed in either forsterite or spinel. This is consistent with the findings of Chernosky (1974) in his study of clinochlore stability.

#### Results

Experimental reversals of equilibrium (1)  $(Chl = Cd + Fo + Sp + H_2O)$  were made at pressures of 0.5, 1.0 and 2.0 kilobars. The conditions and results of the experiments are listed in Table III. Fawcett and Yoder (1966) note shifts in the chlorite composition and therefore care was taken to monitor any such shifts. This was done by measuring (004) and higher order basal peaks against forsterite and spinel peaks before and after the experiments. Within the precision of measurement no shift in the peaks was noted. The precision corresponds to approximately 0.1 atoms of aluminum per formula unit. Chernosky (1974), in his study of the same equilibrium using clinochlore, also finds no shift in peak positions. The composition of chlorite is therefore considered to remain constant during the course of the experiments.

Non-stoichiometric behaviours in cordierite and spinel were not measured for the following reasons. The variable water content of cordierite was not measured as the quench rates were not sufficient to prevent rehydration. In addition, pressures and temperatures were outside the 'quenchable' region shown by Medenbach et al. (1980). The degree of order in spinel could not be measured because of small grain size. There are powder diffraction techniques available to measure order in spinels (eg. Furuhashi et al., 1973) but they are not suitable for the Mg-Al spinel considered here. These techniques measure the difference between the theoretical and observed intensities of the diffraction patterns. The theoretical intensities are calculated based on the scattering factors of the elements involved. Magnesium and aluminum have similar scattering factors and therefore the calculated intensities are not very sensitive to ordering in the structure.

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Table III

Experimental data on the equilibrium: Chlorite = Cordierite + Forsterite + Spinel + $H_2O_1$ Chlorite composition: $Mg_{4,75}Al_{2,5}Si_{2,75}O_{10}(OH)_8$				
Run #	P(bars)	T(° C)	Duration	Results
Chl-124b1	500(20) <sup>2</sup>	594(7)	487(hrs)	b-80% reaction to Chl <sup>3</sup> (chl peaks diffuse)
Chl-130a,b <sup>1</sup>	500(25)	605(5)	884	a-80% to Chl b-80% to Chl
Chl-131a,b	500(25)	629(5)	884	a-no apparent reaction b-no apparent reaction
Chl-120a,b	500(25)	633(6)	480	a-no apparent reaction b-no apparent reaction
Chl-128a	500(20)	640(5)	516	10% to $Cd + Fo + Sp$
Chl-125b	1000(25)	644(5)	487	80% to Chl (chl peaks diffuse)
Chl-129a	1000(30)	670(4)	520	30% to $Cd + Fo + Sp$
Chl-112a,b	1000(20)	673(5)	480	a-10% to Cd+Fo+Sp b-100% to Cd+Fo+Sp
Chl-121a,b	1000(20)	679(7)	482	a-no reaction⁴ b-100% to Cd+Fo+Sp
Chl-113a,b	1000(50)	692(5)	480	a-100% to Cd+Fo+Sp b-100% to Cd+Fo+Sp
Chl-101	2000(50)	690(10)	480	appearance of Chl (St. mat. – Cd+Fo+Sp)
Chl-132a,b	2000(30)	704(5)	759	a-20% to $Cd+Fo+Spb-100% to Cd+Fo+Sp$
Chl-114a,b	2000(50)	705(5)	480	a−no reaction⁴ b−100% to Cd+Fo+Sp
Chl-133a,b	2000(50)	719(5)	742	a-100% to Cd+Fo+Sp b-100% to Cd+Fo+Sp
Chl-115a,b	2000(50)	729(5)	480	a-100% to $Cd + Fo + Sp$ b-100% to $Cd + Fo + Sp$

<sup>1</sup> a represents 4:1 mixture of reactants and products, b represents 4:1 mixture of products and reactants.

<sup>2</sup> Numbers in brackets represent errors in the last significant digit(s) of the quoted values. <sup>3</sup> x% represents the estimated percentage change in ratios of reactants to products. <sup>4</sup> The starting material is pure chlorite.

#### THERMODYNAMIC ANALYSIS

A thermodynamic analysis of the experimental data was used to test for internal consistency, both within the data itself, and with other related experimental data. Thermochemical properties (heat capacities, enthalpies, entropies and volumes) for all the phases considered in this study were either adopted from existing sources or derived to be consistent with existing phase equilibria and calorimetric data.

The heat capacity function and the coefficients used in this study are from Berman and Brown (1985):

$$Cp = k_0 + k_1/T^{0.5} + k_2/T^2 + k_3/T^3.$$
(6)

Table IV lists the coefficients for the phases considered here. Compressibilities and expansivities were not considered in this study. The enthalpies, entropies and volumes of the phases involved were constrained, where data exists, to be consistent with that data. If constraining data did not exist then estimates were made.

The free energy of  $H_2O$  was calculated using a combination of the routines of Haar et al. (1979) and Delany and Helgeson (1978). Below 10 kilobars the Haar et al. routine was used and above 10 kilobars the Delany and Helgeson routine was used (see Berman, 1985). The reference states of enthalpy and entropy for  $H_2O$  were those of water from CODATA (1978). Forsterite and pyrope were treated as stoichiometric phases and therefore the calculation of their free energy is straightforward. The other phases (cordierite, orthopyroxene, spinel and chlorite) are affected by non-stoichiometric behaviour and the calculation of the resulting free energy contributions for each is outlined below.

#### Cordierite

The thermodynamic characterization of cordierite is complicated by its variable composition and by possible disordering on the tetrahedral sites. Cordierite contains varying amounts of  $H_2O$  (in the chemical system studied here) which is a function of pressure and temperature. Several comprehensive models have been presented to describe this behaviour (Newton and Wood, 1979; Lonker, 1981; Martignole and Sisi, 1981) but none of them reproduces the existing hydration data adequately. A new model is presented here to provide a single function to describe the  $H_2O$  content over the full range of existing P-T data.

#### Crystal chemistry

The crystal chemistry of cordierite has been well studied and is discussed in detail by Wallace and Wenk (1980), Hochella et al. (1979), Cohen et al. (1977), Meagher and Gibbs (1977) and Gibbs (1966).

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Table IV

Phase (species)	k.	<b>k</b> <sub>1</sub>	<u>k</u> 2 .	k,
Clinochlore Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	1213.28439	0.	- 11217.1299	-1256253287.
Chls Mg <sub>6</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	1200.38715	- 306475.	-10925.2168	-1167926773.
Coph Mg₄Al₄Si₂O₁₀(OH)₅	1228.18163	306475.	-11509.0430	-1344579801.
Cordierite Mg₂Al₄Si₅O₁₅·nH₂O	937.62415	-11023143.	-7166.2532	1425736441.
Enstatite Mg <sub>2</sub> Si <sub>2</sub> O <sub>6</sub>	333.15900	-4541120.	-2401.1760	558300800.
Forsterite Mg₁SiO₄	238.64137	0.	- 2001.2607	-116243280.
Pyrope Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	640.72000	- 4701900.	- 4542.0690	0.
Spinel MgAl₂O₄	235.89993	- 1710415.	-1766.5781	40616926.

Heat capacity coefficients for phases and species considered in this study:  $Cp = k_0 + k_1/T^{\sigma_5} + k_2/T^2 + k_3/T^3$  (J/mol K).

Briefly, cordierite ( $Mg_2Al_4Si_5O_{15} nH_2O$ ) is a framework silicate made of six-membered rings of silicon and aluminum tetrahedra stacked along the c-axis. The rings are connected by three alumina and silica tetrahedra and form channels that allow constituents to pass through the structure. In the channels and between the rings are cavities where ions and molecules may reside.  $H_2O$  molecules were the only species considered in this study.

Two naturally occurring 'polymorphs' have been recognized, cordierite (orthorhombic) and indialite (hexagonal). They have been thought to be related through a process of continuous tetrahedral aluminum disordering with indialite being completely disordered (Miyashiro, 1957). However, Meagher and Gibbs (1977), in a single crystal refinement of indialite from the type locality, find a significant degree of order in the structure. They estimated the Bragg–Williams long range order parameter, z, to be 0.38 (z=0 for full disorder). Putnis and Bish (1983) synthesized cordierites with a range of structural states by annealing stoichiometric Mg–cordierite glass in air. The conditions of synthesis were temperatures of between

 $1000^{\circ}$  C and  $1400^{\circ}$  C for periods of 15 minutes and 3 hours respectively. The resulting synthetic cordierites were studied by high resolution transmission electron microscopy and showed local ordering. They found by using longer synthesis times orthorhombic cordierite resulted. Schreyer and Schairer (1961a) estimated the transition temperature between the two 'polymorphs' to be greater than  $1440^{\circ}$  C at one atmosphere. These lines of evidence indicate that at temperatures below at least  $1400^{\circ}$  C (one atmosphere) ordered, orthorhombic cordierite is stable. Gibbs (1966), in a single crystal refinement of natural cordierite, found a small amount of disorder on the tetrahedral sites but for the puposes of this model cordierite will be considered to be in the fully ordered state.

Mirwald (1982) presented evidence of a non-quenchable phase transition in anhydrous cordierite. Dynamic experiments were conducted in a piston cylinder apparatus and discontinuities were found in piston-pressure versus displacement curves, which he interpreted to be the result of a phase transition. He predicted the transition to be at 2.2 kilobars, room temperature and at 8.8 kilobars, 900° C and estimated the volume change of the transition to be  $\Delta V/V^{\circ} = 0.0025$  (from an experiment at room temperature).

The occurrence, position and orientation of  $H_2O$  in cordierite has been studied by a number of different authors and methods: Aines and Rossman (1984) - high temperature infrared spectroscopy, Carson et al. (1982) - nuclear magnetic resonance, Armbruster and Bloss (1982) - infrared spectroscopy, Hochella et al. (1979) - high temperature single crystal x-ray diffraction, Goldman et al. (1977) infrared spectroscopy, Cohen et al. (1977) - x-ray and neutron diffraction and Tsang and Ghose (1972) nuclear magnetic resonance. All evidence indicates that  $H_2O$  occurs as molecular  $H_2O$  and is positioned in the channel cavities. However, it is likely that their is more than one position in the structure. Natural and synthetic cordierites have been found to have more than one mole  $H_2O$  per unit formula (Leake, 1960; Mirwald et al., 1979) and if the only position is at the centre of the channel cavities (0,0,1/4) then the limit of water content would be one mole per formula. Another possible position for the  $H_2O$  molecule could be in the middle of the six-membered rings (0,0,1/2). There is no evidence for hydrogen substitution for silicon (Cohen et al., 1977). Most of the above studies conclude that  $H_2O$  exists in two orientations: Type I, in which the H-H vector is parallel to the c crystallographic axis and Type II, in which the H-H vector is perpendicular to c (notation of Wood and Nassau, 1967). In both types the H-O-H plane is in the bc crystallographic plane. There are some suggestions that the  $H_2O$  molecule is present in other orientations. Hochella et al. (1979) suggest from neutron  $\Delta \rho$  maps that H<sub>2</sub>O exists in only one orientation and that Type I and II orientations are vector components of that orientation (H-O-H plane inclined 29° from (100) and the H-H vector 19° from c). Cohen et al. (1977) also calculate neutron  $\Delta \rho$  maps but interpret the results to represent a space average of four orientations. High temperature infrared spectroscopy at one atmosphere by Aines and Rossman (1984) show that below 200° C H<sub>2</sub>O is structurally bound and at 400° C  $H_2O$  begins to exhibit gas-like characteristics. The spectra obtained indicate that both Types I and II  $H_2O$  exist to temperatures of 600° C.

#### Thermodynamic model

The existing models of Newton and Wood (1979) and Lonker (1981) assume ideal mixing of the anhydrous and hydrous end-members and equal molar volumes for the solid phase. Newton and Wood use a hydrous end-member with 1.2 moles H<sub>2</sub>O and calibrate their model by regressing to the data of Mirwald and Schreyer (1977). Above water contents of about two weight percent (5 kilobars at  $600^{\circ}$  C) the data are reproduced but at lower contents the model underestimates the data. Lonker uses one mole of H<sub>2</sub>O in the hydrous end-member and regresses to data from different pressures. A pressure dependence of cordierite water content was demonstrated and he allowed that this effect could be accounted for by a difference in the end-member volumes, however, he disregards this effect on the basis of published cell volumes of cordierite. They show a negligible volume dependence on  $H_2O$  content (Holdaway and Lee, 1977; Dasgupta et al., 1974; Newton, 1972). Lonker presented two models, one regressed from cold seal data (lower pressures) and one from the higher pressure piston cylinder data. Neither model is consistent with all the data and he does not choose between them. Martignole and Sisi (1981) consider H<sub>2</sub>O in cordierite to be similar to that in zeolites. They presented a model based on Raoult's law and derived an activity expression for anhydrous cordierite. The data they used to calibrate the model are the low pressure data of Schreyer and Yoder (1964), many of which are suspect due to the pressures and temperatures being outside the "quenchable region" (Medenbach et al., 1980).

In order to resolve the inconsistencies of the above models, a new model was developed. The crystal chemical evidence allows for complex models to be considered but the existing data are inadequate over a large enough pressure and temperature range to warrant a model more complex than ideal solid solution. Mirwald et al. (1979) reported water contents of synthetic cordierites of up to 1.3 moles  $H_2O$  and Leake (1960) reported contents of natural cordierites of up to 1.6 moles  $H_2O$ . The hydrous end-member was chosen to have two moles of  $H_2O$  in order to cover the possible range of water contents. The equilibrium used to describe  $H_2O$  in cordierite is:

$$Mg_{2}Al_{4}Si_{5}O_{18} + 2H_{2}O = Mg_{2}Al_{4}Si_{5}O_{18} \cdot 2H_{2}O.$$
(7)

The free energy change of this equilibrium can be expressed as,

$$\Delta G_r(P,T) = \Delta G^o_r(P,T) + RT \ln k$$

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(8)

where  $\Delta G_{r}^{0}(\mathbf{P},\mathbf{T})$  is the standard state free energy change of the reaction and k is the equilibrium constant. If ideal site mixing in a binary system and a pure vapour phase are assumed then,

$$RTln k = 2RTln[x_{hcrd}^{cord} / (1 - x_{hcrd}^{cord})].$$
(9)

Combining equations (8) and (9) and expanding  $\Delta G_r^0(P,T)$ ,

$$\Delta G_{r}(P,T) = \Delta H_{s}(P_{r},T_{r}) + \int_{T_{r}}^{T} \Delta C p_{s} dT + (P-P_{r}) \Delta V_{s} - T \Delta S_{s}^{\circ} - T \int_{T_{r}}^{T} \Delta C p_{s} / T dT$$
$$- 2 \Delta G_{H_{2}O}(P,T) + 2RT \ln \left[ x_{hcrd}^{cord} / (1-x_{hcrd}^{cord}) \right].$$
(10)

Now setting  $\Delta G_r(P,T) = 0$ , and rearranging to gather unknowns on the left hand side, we have

$$\Delta H_{s}(P_{r},T_{r}) - T\Delta S_{s}^{\circ} + (P-P_{r})\Delta V_{s} = -\int_{T_{r}}^{T} \Delta Cp_{s} dT + T\int_{T_{r}}^{T} \Delta Cp_{s}/T dT + 2\Delta G_{H_{2}O}(P,T) - 2RT\ln\left[x_{hcrd}^{cord}/(1-x_{hcrd}^{cord})\right].$$
(11)

The experimental data below provide pressures, temperatures and compositions that allow calculation of the right hand side of the equation. When the data are considered as reversed brackets each data point generates a linear inequality ( $\Delta G_{T}(P,T) < or > 0$ ) that provides a constraint on the values of  $\Delta H_{s}(P_{T},T_{r})$ ,  $\Delta S_{s}^{o}$  and  $\Delta V_{s}$ . To define a finite region of feasible solutions there must be a minimum of one more datum than there are unknowns, more data can potentially provide additional constraints on this region.

#### Experimental data

Several sets of data exist which give the  $H_2O$  content of Mg-cordierite in equilibrium with  $H_2O$  as a function of pressure and temperature. The studies and their methods are:

- 1. Duncan (1982).
  - a. Cold seal apparatus.
  - b. Gravimetric determination of  $H_2O$  content.
  - c. 1 and 2 kilobars, 550 to  $750^{\circ}$  C.
  - d. Experiments are reversed.
- 2. Mirwald et al. (1979).
  - a. Cold seal and piston cylinder apparatus.
  - b. Coulometric determination.
  - c. Cold seal 0.5 to 5 kilobars, 500 to 600° C.
    Piston cylinder 3 to 11 kilobars, 500 to 800° C.

- 3. Mirwald and Schreyer (1977).
  - a. Cold seal and piston cylinder apparatus.
  - b. Coulometric determination.
  - c. Cold seal 0.5 to 3 kilobars, 500 to  $600^{\circ}$  C.

Piston cylinder – 3 to 10.5 kilobars, 500 to  $800^{\circ}$  C.

- 4. Duncan and Greenwood (1977).
  - a. Cold seal apparatus.
  - b. Gravimetric determination.
  - c. 1 and 2 kilobars, 550 to  $750^{\circ}$  C
  - d. Reversed experiments.
- 5. Gunter (1977a).
  - a. Apparatus not reported cold seal (personal communication, Greenwood, 1984).
  - b. H<sub>2</sub>O determination technique not reported gravimetric determination (personal communication, Greenwood, 1984).
  - c. 1 kilobar, 500 and  $600^{\circ}$  C.
- 6. Holdaway (1976).
  - a. Cold seal apparatus.
  - b.  $H_2O$  determination technique not reported.
  - c. 3 kilobars, 800° C.
- 7. Newton (1972).
  - a. Piston cylinder and opposed anvil apparatus.
  - b. Estimated from refractive index calibration from Schreyer and Yoder (1964).
  - c. Piston cylinder 8 kilobars, 500 and  $750^{\circ}$  C.
    - Opposed anvil 10 kilobars,  $750^{\circ}$  C.
- 8. Schreyer and Yoder (1964).
  - a. Cold seal piston cylinder apparatus.
  - b. Wet chemistry determination.
  - c. 0.5 to 10.0 kilobars, 500 to 1100° C.

There are problems with the experimental and analytical techniques such as rehydration on quench and analytical uncertainty, Lonker (1981) discussed the problems in some detail.

The data of Mirwald et al. (1979) and the 2 kilobar data of Duncan (1982) were chosen to calibrate the model. Mirwald et al. provided enough experimental detail to allow some confidence in the results and Duncan (1982) used isobaric and isothermal quenching techniques to demonstrate reversal of equilibrium

water contents. Table V lists the data used in the calibration of the model. The other available data were eliminated for the following reasons:

- 1. Duncan (1982) 1 kilobar data.
  - a. Talc formation is reported although not for specific experiments. Experience in the same chemical system and under similar experimental conditions suggests that talc formation is more likely at 1 kilobar.
- 2. Mirwald and Schreyer (1977).
  - a. These data are considered to be superceded by Mirwald et al. (1979).
  - b. The data must be estimated by interpolating from a graphic representation. Compositions are not given directly but must be estimated from the given isopleths.
- 3. Duncan and Greenwood (1977).
  - a. These data are superceded by Duncan (1982).
  - b. The data are presented without full experimental detail.
- 4. Gunter (1977a).
  - a. The experimental and analytical techniques are not detailed.
  - b. The experimental conditions are outside the quenchable region given by Medenbach et al. (1980).
- 5. Holdaway (1976).
  - a. The datum is outside the quenchable region of Medenbach et al. (1980).

6. Newton (1972).

- a. He does not consider the data from the piston cylinder apparatus to be trustworthy.
- b. It is not clear that H<sub>2</sub>O was present as a vapour phase in the opposed anvil experiments.
- c. The refractive indices quoted are too imprecise to provide precise estimates of  $H_2O$  content.
- 7. Schreyer and Yoder (1964).
  - a. The 1 and 2 kilobar experiments are outside the quenchable P-T region.
  - b. The 5 kilobar datum is superceded by Mirwald et al. (1979).
  - c. Other data are not presented in a format useful here.

Constraints on the enthalpy, entropy and volume of anhydrous cordierite are available from calorimetric and crystal chemical data. Charlu et al. (1975) present calorimetric data that allows calculation of  $\Delta_f H^o(P_r, T_r)$ , the enthalpy of formation from the elements, to be -9174.406± 3.0 kJ/mol. The entropy for fully ordered cordierite is constrained to lie between 403.338 and 410.869 J/mol·K (Kelley, 1960) and the volume is constrained to lie between 233.09 and 233.35 cm<sup>3</sup>/mol (Robie et al., 1967).

Table	V
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P(kilobars) <sup>1</sup>	$\frac{T(^{\circ}C)^{i}}{\cdots}$	$nH_2O(moles)^2$
Mirwald et al $(1979)^3$		
	500	0.42
1.0	500	0.48
1.0	600	0.42
2.0	500	0.58
2.0	600	0.54
3.0	500	0.64
3.0	600	0.62
4.0	500	0.76
4.0	600	0.64
4.0	700	0.62
5.0	500	0.78
5.0	600	0.68
6.0	. 600	0.80
6.0	800	0.60
7.0	500	0.84
7.0	600	0.84
7.0	700	0.64
8.0	500	1.08
8.0	600	0.82
8.0	800	0.62
9.0	500	1.20
9.0	600	0.90
9.0	650	0.86
9.0	700	0.74
9.0	800	0.68
10.0	550	1.08
10.0	600	0.92
10.0	750	0.80
10.5	800	0.78
11.0	500	1.32
11.0	700	0.92
11.0	800	0.82
Duncan (1982)⁴ – 2kb data		
2.0	500	0.68
2.0	600	0.52-0.63
2.0	650	0.47-0.57
2.0	700	0.33-0.44
2.0	· 750	0.18-0.35

Cordierite hydration data used in the calibration of the cordierite model.

<sup>1</sup>Errors are  $\pm 3\%$  (pressure),  $\pm 10^{\circ}$  C (temperature) and  $\pm 10\%$  (composition) for all data. <sup>2</sup>The compositions are given as numbers of moles H<sub>2</sub>O per formula unit of cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>13</sub> nH<sub>2</sub>O).

<sup>3</sup>Mirwald et al.'s data are given as 'equilibrium' compositions and pressures and temperatures are estimated from the graphical representation.

<sup>4</sup>Duncan's data are given as bracketed compositions for the conditions quoted.

# Fitting procedure

The data of Duncan (1982) were reversed and therefore directly represent inequalities. The inequalities can be quantified in terms of free energy where  $\Delta G_{r}(P,T) > 0$  for reactants stable and  $\Delta G_r(P,T) < 0$  for products stable. Equilibrium (7) (acrd + 2H<sub>2</sub>O = hcrd) is considered and equation (11) shows the form of the inequalities, with the equal sign being replaced by the appropriate inequality sign. The data of Mirwald et al. (1979) were given as "equilibrium" points although they inherently represent bracketing compositions. Brackets were generated about the given data points in the following manner. Pressures and temperatures were estimated from their graphic representation and adjusted by assuming errors of  $\pm$  3% and  $\pm$  10° C respectively. Compositions were adjusted by the quoted error of  $\pm$  6% and recalculated to mole fractions of the hydrous end-member. The directions of adjustment are dictated by the sign of the slope of the equilibrium and by the relative stability of the assemblages. Figure 3 shows diagrammatically the direction of the pressure, temperature and composition adjustments. The slope of the equilibrium is positive and hydrous cordierite is stable at high pressure in P-T space and in T-x space the slope is negative and hydrous cordierite is stable at low temperature. If the reactants (anhydrous cordierite  $+ 2H_2O$  are stable then the pressure is decreased, the temperature is increased and the H<sub>2</sub>O content is increased (see Figure 3). The opposite adjustments are made for products stable. The data of Duncan (1982) are quoted as reversed brackets and therefore generation of brackets was not required, however, similar adjustments were made to the quoted data with assumed errors of  $\pm 20$  bars,  $\pm 10^{\circ}$  C and  $\pm 10\%$  in composition.

The adjusted experimental data were first tested for internal consistency and then used to calculate internally consistent enthalpies, entropies and volumes for the two end-members. Linear programming techniques were used to solve the systems of linear inequalities represented by equation (11) (see discussion in the Linear Programming Analysis below). The data of Mirwald et al. (1979) were found to be inconsistent if the above errors were used. By relaxing the brackets to  $\pm 10\%$  in composition (pressure and temperature errors remaining the same) internal consistency was achieved. They quoted errors of  $\pm 6\%$  in composition, however this was given as a relative error and errors for individual determinations could have been greater. Several modifications of the model were investigated and are discussed below.

The heat capacity of the hydrous end-member was estimated in two ways. First by adding the heat capacity of two zeolitic water (Berman and Brown, 1985) to that of anhydrous cordierite and second by adding two steam. An example of the differences between calculations is shown in Figure 4. The curves shown exhibit minimums at low temperatures and steep negative slopes at lower temperatures. This behaviour is not interpreted to be real but merely to be a numerical artifact of the model, resulting from the



Figure 3. Diagrammatic representation of the generation of brackets from the cordierite hydration data. Perr, Terr and Xerr are the errors in pressure, temperature and composition. Note the change in slope between the two diagrams: Both demonstrate hydrous cordierite dehydrating at higher temperatures.



Figure 4. Isopleths of cordierite,  $n_{H_2O}$  represents the number of moles  $H_2O$  per unit formula. The fine lines are calculated from properties derived from a fit where the heat capacity of the hydrous cordierite end-member was estimated with zeolitic water. The bold lines are calculated from properties derived from another fit where the heat capacity of the end-member was estimated with steam. Also shown are the range of P-T data (dotted line) and the approximate stability field of hydrous cordierite (dashed line), taken from Schreyer and Yoder (1964).

change in entropy along the equilibrium. The stability field of cordierite lies above the region where this behaviour is evident (see Figure 4) and the data are reproduced adequately by the model. This behaviour is thus not considered to affect calculations involving stable cordierite.

Both models are consistent with the data but they diverge outside the data, especially at lower temperatures. The model using the heat capacity estimated with steam is preferable for the following reasons. Evidence from the high temperature infrared study of Aines and Rossman (1984) indicates that  $H_2O$  exists in cordierite, at least partially, in a gas-like state at temperatures above  $400^{\circ}C$  (at one atmosphere). The heat capacity of zeolitic water is calculated from calorimetric data for analcime to temperatures of  $400^{\circ}C$ , whereas the cordierite hydration data starts at  $500^{\circ}C$ . In addition, calculations with the heat capacity estimate using steam appear to extrapolate more reasonably to lower temperatures.

The phase transition suggested by Mirwald (1982) was also tested in the model. The transition was calculated by linearly regressing to the points given in Table 1 of Mirwald (1982); this implies a zero  $\Delta Cp$  of reaction. A phase transition in hydrous cordierite was assumed to be superimposed on the anhydrous transition and therefore the model was expanded to have two hydration equilibria, one at low pressure and one at high pressure. Volume constraints on the high pressure anhydrous phase were calculated from the low pressure volume constraints using the 0.0025 value for  $\Delta V/V^{\circ}$  given by Mirwald. The entropy of the low temperature phase was constrained to be less than that of the high temperature phase as, in general, the high temperature assemblage of an equilibrium has a greater entropy than that of the low temperature one. With these constraints the compositional errors for Mirwald et al. had to be relaxed to  $\pm 8\%$  to obtain internal consistency, but the resultant volume difference between the two hydrous polymorphs was approximately 8 cm<sup>3</sup>/mol (approximately 4% difference). This is much larger than the volume changes in other polymorphic phase transitions and is not considered reasonable. In addition, the differences between isopleths of H<sub>2</sub>O content calculated for the two stability fields were small and, for simplicity, the transition was ignored.

#### Results

The final stages of modelling included testing the data for internal consistency and also the calculation of the final set of thermochemical properties for the phases. The errors in the data of both Duncan (1982) and Mirwald et al. (1979) were  $\pm 3\%$  in pressure,  $\pm 10^{\circ}$  C in temperature and  $\pm 10\%$  in composition. These errors were necessary to obtain internal consistency using the model with a single hydration equilibrium and no high pressure polymorphs. The entropy and volume of anhydrous cordierite were fixed at the midpoints of the crystal chemical and calorimetric constraints and different objective functions were used first to minimize then to maximize the P-T slope of the equilibrium. The entropy and

volume of the hydrous end-member were then fixed at the midpoints of the ranges calculated and the final fit was made to determine  $\Delta H_r(P_r, T_r)$ .

The resulting changes in enthalpy, entropy and volume for the end-members are given in Table VI. The heat capacity coefficients for anhydrous cordierite are listed in Table IV and those for the hydrous end-member may be calculated by adding the coefficients for two steam (also in Table IV) to those of anhydrous cordierite. Isopleths calculated from equation (10) with the data in Table VI E shown in Figure 5. Also shown, for comparison, are isopleths calculated using the model of Newton and Wood (1979). At pressures above 6 kilobars the two models are in fair agreement but at low pressures Newton and Wood predict  $H_2O$  contents that are approximately half the values predicted with this model.

#### Table VI

Changes in enthalpy, entropy and volume for anhydrous and hydrous cordierite end-members. Hydrous cordierite ( $Mg_2Al_4Si_5O_{18} \cdot 2H_2O$ ) minus anhydrous cordierite ( $Mg_2Al_4Si_5O_{18}$ ).

$\frac{\Delta H_{s}(P_{r},T_{r})}{(J/mol)}$	ΔS <sup>₀</sup> <sub>S</sub> (J/mol·K)	$\Delta V_{s}$ (cm <sup>3</sup> /mol)
- 563493.8	156.665	23.066

#### Orthopyroxene

The solid solution behavior in orthopyroxene in the chemical system MASH has been described recently by Gasparik and Newton (1984) where they used a Tschermak's exchange between enstatite ( $Mg_2Si_2O_6$ ) and Mg-Tschermaks ( $MgAl_2SiO_6$ ). The aluminum content is a function of pressure, temperature and stable assemblage defined by the two equilibria,

1  Enstatite  + 1  Spinel = 1  Mg-Tschermaks  + 1  Forsterite	(12)
1 Enstatite $+ 1$ Mg-Tschermaks $= 1$ Pyrope.	(13)

Gasparik and Newton (1984) used their data plus data from Perkins et al. (1981) and Danckwerth and Newton (1978) to calibrate their model. They assumed constant heat capacities, a linear volume of solution and also included expansivities and compressibilities. Disordering phenomena in spinel or orthopyroxene were not explicitly included in their model. Gasparik and Newton regressed the data from each stability field to obtain  $\Delta H_{970}^{0}$ ,  $\Delta S_{970}^{0}$  and  $\Delta V_{298}^{0}$  for equilibria (12) and (13). The functions obtained give the equilibrium aluminum content of orthopyroxene as a function of pressure, temperature and stable



Figure 5. Water content of Mg-cordierite in equilibrium with  $H_2O$  as a function of pressure and temperature. The isopleths are labelled with the number of moles of  $H_2O$  (n) per unit formula. Bold lines are the isopleths calculated from the data in Table VI and the fine lines are isopleths calculated using the model of Newton and Wood (1979).

assemblage. The free energy of orthopyroxene was calculated by,

 $\Delta G_{Opx}(P,T) = \Delta G_{Opx}^{\circ}(P,T) + RTInx_{En}^{Opx}.$ 

Ordering of aluminum in orthopyroxene has been investigated by Ganguly and Ghose (1979) in a crystallographic study of synthetic and natural orthopyroxenes. They found the tetrahedral aluminum to be almost completely ordered into one of the tetrahedral sites and the octahedral aluminum to be partially ordered into the M1 site. This allows more complex modelling but was not considered in the calculation of orthopyroxene free energy.

## Spinel

Solid solution towards  $Al_2O_3$  is known (Roy et al., 1953; Navrotsky and Kleppa, 1967), however, Roy et al. and Seifert (1974) found no evidence of solid solution below  $1100^{\circ}$  C. In addition, Chernosky (1974), in his related study, found no evidence of solid solution. The same chemical system, phases and conditions were analyzed here and therefore spinel was considered to be on composition.

The effect of variable disorder in spinel was not considered in the analysis for the following reasons:

1. The degree of disorder is not known accurately as a function of pressure and temperature.

2. The phase equilibria data used here were not constraining enough to warrant the use of a disordering model.

The calculations below estimate a possible contribution of variable disorder to the free energy of spinel.

O'Neill and Navrotsky (1984) used the relation,

$$\Delta G_{c.d.} = \Delta G_d - TS_c \tag{14}$$

to describe the free energy of disorder.  $\Delta G_{c.d.}$  is the free energy of cation disorder,  $\Delta G_d$  is the non-configurational free energy and S<sub>c</sub> is the configurational entropy. Equation (14) may be expanded to,

$$\Delta G_{c.d.} = \Delta H_d - T(S_c + S_d), \qquad (15)$$

where  $\Delta H_d$  and  $S_d$  are the enthalpy and entropy of disorder. If the functions for  $\Delta H_d$  and  $S_d$  from O'Neill and Navrotsky (1984) and  $S_c$  from O'Neill and Navrotsky (1983) are used (15) expands to,

$$\Delta G_{c.d.} = (a_A - a_B)x + \beta x^2 T \{ -R[x \ln x + (1 - x)\ln(1 - x) + x\ln(x/2) + (2 - x)\ln(1 - (x/2)) ] + (a_A - a_B)x \}$$
(16)

The parameters  $a_{A,B}$  are empirically determined "site preference enthalpies" for cations corresponding to the general formula AB<sub>2</sub>O<sub>4</sub>,  $\beta$  is a constant for the type of spinel considered (2-3 here, notation of Navrotsky and Kleppa, 1967) and  $\sigma_{A,B}$  are "site entropies" analogous to the site preference enthalpies (see Navrotsky and Kleppa, 1967). Values for these parameters were given in O'Neill and Navrotsky (1984). The variable x is the degree of disorder indicated in the formula  $A_{1-x}B_x(A_xB_{2-x})O_4$ , where A and B represent the octahedral and tetrahedral sites.

Unfortunately the degree of disorder, x, is not known as a function of pressure and temperature and could not be measured in the products of the experiments due to small grain size. Wood and Holloway (1984) estimated x as a function of temperature by assuming a constant enthalpy of disorder ( $\Delta H_{c.d.}$ ) of 83.68 kJ/mol in the relation,

$$-\Delta H_{cd} / RT = \ln \left[ x^2 / ((1-x)(2-x)) \right].$$
(17)

The free energy contribution from disorder was calculated, from equations (16) and (17), to be -246 J/mol at  $600^{\circ}$  C and -4868 J/mol at  $1600^{\circ}$  C, the approximate range of temperatures considered in this analysis. If the spinel in the experiments reached equilibrium states of disorder then the free energy effects can be significant. Wood and Holloway (1984) showed that the phase equilibria data cannot be fit using this model.

#### Chlorite

Mg-chlorite has a variable content of aluminum and evidence from natural chlorites suggest that the range of solution is between  $Mg_{5.4}Al_{1.2}Si_{3.4}O_{10}(OH)_8$  and  $Mg_{4.4}Al_{3.2}Si_{2.4}O_{10}(OH)_8$  (Foster, 1962). In order to encompass the range of composition, the end-members  $Mg_6Si_4O_{10}(OH)_8$  (Chls) and  $Mg_4Al_4Si_2O_{10}(OH)_8$  (Coph) were chosen. Crystal chemical evidence so far obtained is not sufficient to define rigorously the solution characteristics so a Tschermak's exchange was assumed. If ideal solution is assumed the free energy of chlorite can be expressed as,

$$G_{chl}(P,T) = (1 - x_{coph}^{chl}) G_{chls}(P,T) + x_{coph}^{chl} G_{coph}(P,T) + 2RT[x_{coph}^{chl} lnx_{coph}^{chl} + (1 - x_{coph}^{chl})ln(1 - x_{coph}^{chl})].$$
(18)

 $G_{chls}(P,T)$  and  $G_{coph}(P,T)$  are the free energies of the end-members at pressure and temperature and  $x_{coph}^{chl}$  is the mole fraction of corundophyllite in chlorite. For the clinochlore composition  $x_{coph}^{chl}$  is 0.5 and for the composition considered here  $(Mg_{4.75}Al_{2.5}Si_{2.75}O_{10}(OH)_8)$ ,  $x_{coph}^{chl}$  is 0.625. The reason for doubling the configurational entropy term is that there are two atoms of aluminum substituting on the

tetrahedral sites (coupled substitution with octahedral aluminum).

The heat capacities of the end-members were estimated by adding or subtracting the heat capacities of the appropriate oxides to or from the heat capacity of clinochlore. Berman and Brown (1985) used the calorimetric data of Henderson et al. (1983), for a natural chlorite close to the clinochlore compositiont, to calculate the heat capacity coefficients for clinochlore (adjustments were made for the compositional differences).

There is possible disordering on the tetrahedral and octahedral sites in the 2:1 layer and also on the octahedral sites of the interlayer. Stacking disorder is also possible. Bailey and Brown (1962) discussed the crystal chemistry of chlorite and gave a geometric basis for twelve polytypes. They indicated that only three of these polytypes have been found naturally with the IIb polytype being the most common. Mixing of polytypes will result in stacking disorder and this has been investigated by Spinnler et al. (1984). They used single crystal x-ray methods, high resolution transmission electron microscopy and electron diffraction in a study of a natural chlorite close to the clinochlore composition. The stacking order observed was nearly completely ordered although some disorder was noted. None of the disordering phenomena in chlorite are well understood nor were they measured in the synthetic chlorite used in this study and so were not considered in the modelling done here.

#### Linear Programming Analysis

Linear programming was chosen as the mathematical technique to analyze the data, as opposed to the more widely used regression analysis, because it is compatible with the nature of phase equilibria data. Phase equilibria data provide information about the relative stability of assemblages ( $\Delta G_r <>0$ ) but give little statistical information about the distance from the equilibrium. Linear programming was introduced into the geologic literature by Gordon (1973; 1977) and since then a number of studies have utilized this technique (for example: Day and Halbach, 1979; Day and Kumin, 1980; Halbach and Chatterjee, 1982; 1984; Berman and Brown, 1984; Day et al., 1985).

#### Phase equilibria data

The data retrieved from the literature for equilibria (1) through (5) are listed in Table VII, only experiments that demonstrated reversal are included. The nominal pressures and temperatures were adjusted to the limits allowed by the quoted or estimated errors in the manner described in the cordierite analysis above. These constraints were further relaxed using estimates for the bracketing compositions of orthopyroxene and chlorite. For orthopyroxene the minimum and maximum aluminum contents were

Table VII

Phase equilibria data for equilibria (1) through (5)				
Study	P(kbars)	T(°C)	Stable assemblage	
(1) $\underline{Chl = Cd + Fo + Sp + H_2O}$				
This study Mg <sub>4,75</sub> Al <sub>2,5</sub> Si <sub>2,75</sub> O <sub>10</sub> (OH) <sub>8</sub>	0.50(.025) <sup>1</sup> 0.50(.020) 1.00(.025) 1.00(.030) 2.00(.040) 2.00(.030)	605(5) <sup>1</sup> 640(5) 644(5) 670(4) 690(10) 704(5)	Chl Cd + Fo + Sp Chl Cd + Fo + Sp Chl Cd + Fo + Sp	
Chernosky (1974) Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	$\begin{array}{c} 0.500(.020) \\ 0.500(.020) \\ 1.000(.020) \\ 1.000(.020) \\ 2.000(.040) \\ 2.000(.040) \\ 3.000(.060) \\ 3.000(.060) \end{array}$	576(5) 635(5) 636(5) 662(5) 694(5) 710(5) 726(5) 750(5)	Chl Cd + Fo + Sp Chl Cd + Fo + Sp Chl Cd + Fo + Sp Chl Cd + Fo + Sp	
(2) $\underline{Chl = Opx + Fo + Sp + H_2O}$	5.000(.000)	, 30(3)	Currorbp	
Jenkins (1981)	10.000(.300) 10.000(.300) 14.000(.420) 14.000(.420)	815(10) 825(10) 850(10) 860(10)	Chl Op $x + Fo + Sp$ Chl Op $x + Fo + Sp$	
Staudigel and Schreyer (1977)	$11.000(^{2})$ $11.000()$ $15.000()$ $15.000()$ $18.000()$ $18.000()$	825(20) 840(20) 845(20) 850(20) 875(20) 890(20)	Chl Opx + Fo + Sp Chl Opx + Fo + Sp Chl Opx + Fo + Sp	
Fawcett and Yoder (1966) (3) $Chl = Py + Fo + Sp + H_2O$	5.000(.150) 10.000(.100) 10.000(.100)	800(5) 825(10) 837(10)	Opx + Fo + Sp Chl Opx + Fo + Sp	
Staudigel and Schreyer (1977)	$22.000()^{2})$ $22.000()$ $25.000()$ $30.000()$ $30.000()$ $35.000()$	890(20) 900(20) 890(20) 900(20) 875(20) 880(20) 880(20) 880(20)	Chl Py + Fo + Sp Chl Py + Fo + Sp Chl Py + Fo + Sp Chl Py + Fo + Sp Chl	
(4) $Cd + Fo = Opx + Sp$	40.000()	800(20)	. Chi	
Herzberg (1983)	1.750(.100) 2.200(.100) 1.500(.100)	1150(25) 1150(25) 1200(25)	Fo+Cd Opx+Sp Fo+Cd	

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Table VII (continued)

Study	P(kbars)	T(°C)	Stable assemblage
Herzberg (1983) (continued)	2.200(.100) 1.200(.100) 1.500(.100)	1200(25) 1300(25) 1300(25)	Opx + Sp Fo + Cd Opx + Sp
Seifert (1974)	3.000(.200) 3.025(.200) 2.800(.200) 3.000(.200) 2.500(.200) 2.800(.100)	850(15) 905(15) 1000(15) 1000(15) 1100(15) 1100(15)	Fo + Cd $Opx + Sp$ $Fo + Cd$ $Opx + Sp$ $Fo + Cd$ $Opx + Sp$
Fawcett and Yoder (1966)	3.100(.063) 3.300(.069)	790(5) 780(5)	Fo+Cd Opx+Sp
$(5)  \underline{Opx + Sp = Py + Fo}$			
Gasparik and Newton (1984)	21.960(2%) <sup>3</sup> 21.340(2%) 29.700(2%) 29.250(2%)	1200(15) 1200(15) 1600(15) 1600(15)	Py + Fo Opx + Sp Py + Fo Opx + Sp
Perkins et al. (1981)	26.440(2%) <sup>4</sup> 25.620(2%) 24.570(2%) 21.840(2%) 20.020(2%) 22.890(2%) 20.380(2%) 20.500(2%) 25.160(2%) 20.000(2%) 21.480(2%)	1465(15) 1435(15) 1405(15) 1240(15) 1100(15) 1260(15) 1110(15) 1100(15) 1425(15) 1085(15) 1145(15)	Pv + Fo $Py + Fo$ $Opx + Sp$ $Opx + Sp$ $Py + Fo$ $Opx + Sp$ $Py + Fo$ $Py + Fo$ $Py + Fo$ $Opx + Sp$ $Py + Fo$
Danckwerth and Newton (1978)	18.800(2%) 18.200(2%) 19.050(2%) 19.500(2%) 19.000(2%) 20.000(2%) 19.500(2%) 20.500(2%) 20.000(2%)	900(10) 900(10) 950(10) 950(10) 1000(10) 1000(10) 1050(10) 1100(10) 1100(10)	Py + Fo Opx + Sp Py + Fo

<sup>1</sup>Numbers in brackets represent errors used to adjust the pressures and temperatures for the linear programming analysis. <sup>2</sup>Pressures given by Staudigel and Schreyer (1977) – corrections and adjustments are explained in the text. <sup>3</sup>Pressures have been corrected for friction using the functions of Gasparik and Newton (1984). <sup>4</sup>Pressures have been corrected for friction using the function of Perkins et al. (1981). assumed to be that of the pyroxene used in the starting materials (usually enstatite) and that calculated by the model of Gasparik and Newton (1984). The chlorite compositions for equilibria (2) and (3) were bracketed by the composition of the starting material (clinochlore) and the composition given by Jenkins (1981),  $Mg_{4.88}Al_{2.24}Si_{2.88}O_{10}(OH)_8$ . This was given as the approximate composition of chlorite at the breakdown to orthopyroxene, forsterite and spinel at 14 kilobars (850° C). Specific adjustments to the data for each equilibrium are outlined below:

Equilibrium (1):  $Chl = Cd + Fo + Sp + H_2O$ 

- 1. Fawcett and Yoder (1966), Chernosky (1974). Quoted pressure and temperature errors were used and the chorite composition was assumed to be clinochlore.
- 2. This study. Quoted pressure and temperature errors were used and the chlorite composition was  $x_{coph}^{chl} = 0.625$ .

Equilibrium (2):  $Chl = Opx + Fo + Sp + H_2O$ 

- 1. Fawcett and Yoder (1966). Quoted pressure and temperature errors were used. The orthopyroxene composition was bracketed between enstatite and the calculated equilibrium composition and chlorite between clinochlore and that of Jenkins.
- 2. Staudigel and Schreyer (1977). Temperature errors of  $\pm 20^{\circ}$ C were used as the quoted temperatures were not adjusted for the pressure effect on the emf of the thermocouple. The quoted temperature error was  $\pm 10^{\circ}$ C. Pressures were corrected using the function of Gasparik and Newton (1984) for a talc plus soft glass assembly. Quoted pressures are nominal and the pressure medium used was talc plus boron nitride (W. Schreyer, personal communication). An error of  $\pm 5$  percent was assumed after the correction. The orthopyroxene composition was bracketed between enstatite and the calculated equilibrium composition and the chlorite composition between clinochlore and that of Jenkins.
- 3. Jenkins (1981). Quoted pressure and temperature errors were used. The orthopyroxene composition was assumed to be the calculated equilibrium composition. The composition of the orthopyroxene in the starting materials was 10 mole percent Mg-Tschermaks which is close to the calculated compositions. Chlorite composition was bracketed between clinochlore (starting material) and that of Jenkins.

Equilibrium (3):  $Chl = Py + Fo + Sp + H_2O$ 

1. Staudigel and Schreyer (1977). See above.

Equilibrium (4): Cd + Fo = Opx + Sp

- 1. Fawcett and Yoder (1966), Seifert (1971). Quoted pressure and temperature errors were used. The orthopyroxene composition was bracketed between enstatite, the starting material, and the calculated equilibrium composition. Hydrated cordierite was assumed.
- Herzberg (1983). Quoted pressure and temperature errors were used. The orthopyroxene composition was bracketed between 20 mole percent Mg-Tschermaks (starting material) and the calculated equilibrium composition. Anhydrous cordierite was assumed as the experiments were run in the absence of H<sub>2</sub>O.

Equilibrium (5): Opx + Sp = Py + Fo

1. Danckwerth and Newton (1979), Perkins et al. (1981) and Gasparik and Newton (1984). Quoted pressure and temperature errors were used. The orthopyroxene compositions were assumed to be the calculated equilibrium compositions as the compositions of the pyroxenes used in the starting materials were close to the calculated ones.

### *Constraints*

The entropies and volumes for phases other than chlorite were constrained to the properties derived by Berman (1985). The properties he derived are consistent with phase equilibria and calorimetric data in the larger chemical system  $K_2O-Na_2O-MgO-FeO-Fe_2O_3-CaO-Al_2O_3-SiO_2-H_2O-CO_2$ . There are two points to note: The entropies of cordierite and spinel include small contributions for disorder, approximately 8 J/mol and 3 J/mol respectively. These adjustments allow the calculated enthalpies of cordierite and spinel to agree more closely with calorimetric determinations. Disorder in natural cordierite has been documented by Gibbs (1966). The contribution for disorder in spinel was estimated by Gasparik and Newton (1984) and has been successfully used by Harris and Holland (1984) and Berman (1985).

The properties of chlorite were constrained in two ways. At the clinochlore composition ( $x_{coph}^{chl} = 0.5$ ) the solution was constrained to the properties derived for clinochlore by Berman (1985). Constraints were also estimated for the volumes and entropies of the two end-members. There are some data for the volumes of Mg-chlorite as a function of Al-content and they are listed in Table VIII. Most of the volume data are for synthetic chlorites of the clinochlore composition. There are data for cell parameters of natural chlorites (eg. Albee, 1962; Foster, 1962; Brindley and Gillery, 1956) but only for the variation of d(001) with Al-content (see Figure 2) in Fe-Mg chlorites, and of d(060) with Fe-Mg ratio. These data suggest a larger dependence of volume on Al-content than the limited data on synthetic chlorites indicate (see Figure

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Volumes of Mg-chlorites		
Study	xchl coph	V(cm <sup>3</sup> /mol)
Forward Loder (1066)	0.5	208.16
Pird and Faucett (1973)	0.5	208.10
Charporky $(1974)$	0.5	211.74
$M_{c}Onie et al (1975)$	0.5	211.555
Standigel and Schrever (1977)	0.5	209.59
Chemosky (1978)	0.5	210.49
Henderson et al (1983)	0.5	209.8
Jenkins and Chernosky (1985)	0.5	210.98
Johand and Chemosky (1985)	0.5	210.82
	0.5	210.76
	0.6	210.43
	0.7	210.32
This study	0.625	209.515

2), but the effect cannot be fully evaluated due to the lack of volume data. A range of end-member volumes were calculated as follows. All of the data in Table VIII were linearly regressed to determine a slope of -2.68 for the volume of solution. This is considered to represent the minimum difference of the end-member volumes if ideal solution is assumed. A maximum difference was estimated by using the two volumes that give the steepest slope: Bird and Fawcett (1975),  $x_{coph}^{chl} = 0.5$ ,  $V = 211.74 \text{ cm}^3/\text{mol}$  and this study,  $x_{coph}^{chl} = 0.625$ ,  $V = 209.52 \text{ cm}^3/\text{mol}$ . The slope calculated was -17.80. If a volume of clinochlore of 209.818 (Berman, 1985) was assumed, then the volume ranges of the end-members are: 210.5-216.0 cm<sup>3</sup>/mol for the aluminum free end-member and 203.0-209.0 cm<sup>3</sup>/mol for the other end-member. The entropies of the end-members were estimated using the method of Helgeson et al. (1978). When the minimum  $\Delta V$  (2.68 cm<sup>3</sup>/mol) of the two end-members and a clinochlore entropy of 429.77 J/mol·K were used then the entropies of the two end-members were calculated to be 439.94 J/mol·K (chls) and 419.60 J/mol·K (coph) ( $\Delta S = 20.34 \text{ J/mol·K}$ ). If the maximum  $\Delta V$  (17.80 cm<sup>3</sup>/mol) was assumed then the entropies were calculated to be 447.68 J/mol·K (chls) and 411.86 J/mol·K (coph) ( $\Delta S = 35.82 \text{ J/mol·K}$ ).

#### Fitting procedure

The above data and constraints were used to calculate possible ranges of values for the thermochemical properties of the chlorite solution allowed by the phase equilibria data included in this study. This was accomplished, after fixing the volume of clinochlore to be that of Berman (1985) (209.818

cm<sup>3</sup>/mol), by using different objective functions in the linear programming routines. The enthalpies of enstatite, forsterite, pyrope and H<sub>2</sub>O were fixed to the values calculated by Berman (1985). The range of entropy for clinochlore was calculated to be between approximately 420 J/mol·K and 480 J/mol·K. An entropy of clinochlore of 429.77 J/mol·K is preferred as this is the value calculated from a much larger data set (Berman 1985). Henderson et al. (1983) calorimetrically determined the entropy of clinochlore to be 397.3 J/mol·K, a difference of 32.5 J/mol·K. Disorder on the tetrahedral and octahedral sites can account for the apparent discrepancy. At the clinochlore composition one of four tetrahedral sites and one of six octahedral sites can be assumed to be occupied with aluminum. If stacking disorder and excess entropy are ignored then the maximum configurational entropy of clinochlore is -6R[(1/6)ln(1/6) + (5/6)ln(5/6)] - 4R[(1/4)ln(1/4) + (3/4)ln(3/4)] = 41.18 J/mol·K. This would appear to indicate that the difference between the calculated entropy from the phase equilibria data and the calorimetrically determined entropy are for a nearly fully disordered phase and a nearly fully ordered phase respectively.

In order to see if the phase equilibria data constrained the properties of the chlorite end-members the volume and entropy constraints on the end-members were removed and several calculations were made. The entropy and volume of clinochlore were fixed at the values shown above (429.77 J/mol·K and 209.818 cm<sup>3</sup>/mol) and the ranges of the entropies and volumes of the end-members were determined. No significant bounds were found. The entropies of the end-members ranged from 0.0 to twice that of clinochlore (860 J/mol·K) and the volumes were only loosely constrained to within approximately 60 cm<sup>3</sup>/mol. This is not surprising as the free energy constraints on the solution are at or near the middle of the compositional range considered.

The enthalpies of cordierite, spinel and chlorite were then determined by first constraining the enthalpies of cordierite and spinel to those derived by Berman (1985). When these constraints were added the system of inequalities became inconsistent. By increasing the enthalpy of spinel by approximately 400 J/mol to -2303.32 kJ/mol all constraints were satisfied. There are two reasons that explain why this was necessary: The bracketing composition of the higher aluminum chlorite used in Berman's study was  $Mg_{4.8}Al_{2.4}Si_{2.8}O_{10}(OH)_8(x_{coph}^{chl} = 0.6)$ , higher than the composition used here; he used a different activity model for describing the variable chlorite composition – clinochlore was used as the standard state and the activity of clinochlore in the higher aluminum chlorite was assumed to be 0.8. The adjustment in the enthalpy of spinel allowed better agreement with the measured values of  $-2302.00\pm 2.70$  kJ/mol (Shearer and Kleppa, 1973) and  $-2299.71\pm 1.53$  kJ/mol (Charlu et al., 1975).

#### Results

The resulting enthalpies, entropies and volumes of the phases determined here are listed in Table IX. Included are the estimated properties for the two end-members of the chlorite solution. The entropies of the end-members were taken to be the midpoints of the ranges estimated above. This allowed the calculated volumes to be close to the midpoints of the estimated ranges. Figure 6 shows equilibrium (1) calculated from the data in Tables IV and IX for the clinochlore composition and for the chlorite composition used in the experiments in this study. Also shown are the most constraining data from Chernosky (1974) and this study, all data have been adjusted by quoted errors in pressure and temperature. The displacement for this difference in composition is approximately  $8^{\circ}$  C at 2 kilobars.

The set of all five equilibria considered in this study are shown in Figure 7. The equilibria are calculated assuming excess  $H_2O$  and with variable compositions of cordierite and orthopyroxene. The chlorite composition used in the calculation was  $x_{coph}^{chl} = 0.6$ , the composition indicated in Frost (1975). He studied the contact metamorphism of an ultramafic package in the Paddy-Go-Easy Pass area of Washington. This allowed him to track the composition of Mg-rich chlorite to their breakdown to orthopyroxene, forsterite and spinel. He found the aluminum content of chlorite to increase as breakdown was approached and the final composition to be  $x_{coph}^{chl} = 0.6$ . This might represent the equilibrium composition of Mg-chlorite at breakdown more accurately than clinochlore. There are other equilibria generated from the two invariant points but for clarity they are not shown.

Table IX

for phases and species used in this study.				
Phase	$\Delta_{f} H^{0}(P_{r}, T_{r})$ (J/mol)	$\frac{S^{\circ}(P_{I},T_{I})}{(J/mol \cdot K)}$	V (cm³/mol)	
Clinochlore Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	- 8921085.4	429.77	209.82	
Chls Mg₅Si₄O₁₀(OH)₅	- 8890543.1	432.28	216.08	
Corundophyllite Mg <sub>4</sub> Al <sub>4</sub> Si <sub>2</sub> O <sub>10</sub> (OH) <sub>8</sub>	-8951627.7	404.20	203.56	
Cordierite $Mg_{4}Al_{4}Si_{2}O_{10}(OH)_{8}$	-9162360.3	418.50	233.09	
Enstatite $Mg_2Si_2O_6$	- 3092948.5	132.34	62.68	
Forsterite Mg <sub>2</sub> SiO <sub>4</sub>	-2176634.6	94.01	43.80	
Pyrope Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	-6290010.0	267.27	113.18	
Spinel MgAl <sub>2</sub> O <sub>4</sub>	-2303323.8	83.67	39.74	
Water H2O(liq)	-285830.0	69.92		

Calculated enthalpies of formation from the elements, third law entropies and molar volumes for phases and species used in this study.



Figure 6. The equilibrium Chlorite = Cordierite + Forsterite + Spinel +  $H_2O$ . The curves are labelled with  $x_{coph}^{chl}$ , 0.5 represents the clinochlore composition and 0.625 is the composition used in the experiments of this study. Solid symbols are reversals for the low temperature side of the equilibria and the open symbols are for the high temperature side. The triangles are data from Chernosky (1974) and the squares are data from this study.



Figure 7. The upper thermal stability of Mg-chlorite. Equilibrium compositions of cordierite and orthopyroxene are calculated as a function of pressure, temperature and coexisting assemblage by the models of this study (cordierite) and Gasparik and Newton (1984) (orthopyroxene). The composition of chlorite used is  $x_{coph}^{chl} = 0.6$ . Other equilibria generated from the two invariant points are not shown.

#### CONCLUSIONS

The upper thermal stability of Mg-chlorite at a given pressure is dependent on the breakdown assemblage and the composition of chlorite. With increasing pressure the breakdown assemblage changes to include cordierite, orthopyroxene and then pyrope (all present with forsterite, spinel and H<sub>2</sub>O). Some of these phases exhibit compositional variations and/or ordering phenomena. The variable H<sub>2</sub>O content in cordierite was described with a model using ideal solution between the end-members Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub> and Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>·2H<sub>2</sub>O. Orthopyroxene aluminum content was also described by a model employing ideal solution between the end-members Mg<sub>2</sub>Al<sub>4</sub>Si<sub>2</sub>O<sub>10</sub>(OH)<sub>8</sub>. The variable composition of chlorite was modelled assuming ideal solution between the end-members Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and MgAl<sub>2</sub>Si<sub>6</sub>O<sub>10</sub>(OH)<sub>8</sub> and Mg<sub>4</sub>Al<sub>4</sub>Si<sub>2</sub>O<sub>10</sub>(OH)<sub>8</sub>. Disordering phenomena in cordierite and spinel were accounted for by adding small entropies of disorder to the third law entropies and ordering of Al on the octahedral sites in orthopyroxene was not accounted for. Differences between the calorimetrically determined entropy for clinochlore and that calculated from phase equilibria data can be accounted for by entropies of disorder on the tetrahedral and octahedral sites.

The above assumptions and estimations were combined with new and existing data to derive internally consistent thermochemical properties for the phases considered. The results indicated a small displacement of high entropy reactions such as the breakdown equilibria of chlorite as a result of variable aluminum contents of Mg-chlorite. Displacement of the low pressure breakdown of chlorite due to variable Al-content of chlorite was not resolved experimentally. There are not enough data available to be able to define the solution mechanisms operating in Mg-chlorites and the data were able to be fit assuming ideal solution and a Tschermak's exchange. Evidence from natural systems indicates the composition of Mg-chlorite at the breakdown to orthopyroxene, forsterite and spinel is  $x_{conh}^{chl} = 0.6$ .

The accumulation of more crystal chemical, calorimetric, spectroscopic and phase equilibria data will allow more precise modelling of the solid solution and disordering behaviours in chlorite. Crystal chemical data will help constrain the volume of solution and provide information on the substitution mechanisms that occur, as well as determination of long range stacking orders. Studies utilizing high resolution transmission electron microscopy might allow determination of short range stacking disorder. Calorimetric studies can provide direct measurements of the thermochemical effects of solid solution and also of disorder and spectroscopic data might indicate the distribution of cations in both the octahedral and tetrahedral sites. Phase equilibrium studies could provide data useful in deriving end-member properties and possibly solution effects in chlorite. Equilibria having small entropies of reaction would be useful in measuring the effects of not only solid solution but also of disordering. The displacement of such equilibria might be significant enough to resolve some of these effects.

#### REFERENCES

- Aines, R.D. and Rossman, G.R. (1984) The high temperature behavior of water and carbon dioxide in cordierite and beryl. American Mineralogist, 69, 319-327.
- Albee, A.L. (1962) Relationships between the mineral association, chemical composition and physical properties of the chlorite series. American Mineralogist, 47, 851-870.
- Armbruster, T. and Bloss, F.D. (1981) Mg-Cordierite: Si/Al ordering, optical properties, and distortion. Contributions to Mineralogy and Petrology, 77, 332-336.
- Armbruster, T. and Bloss, F.D. (1982) Orientation and effects of channel H<sub>2</sub>O and CO<sub>2</sub> in cordierite. American Mineralogist, 67, 284–291.
- Berman, R.G. and Brown, T.H. (1984) A thermocynamic model for multicomponent melts, with application to the system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Geochimica et Cosmochimica Acta, 45, 661-678.
- Berman, R.G. and Brown, T.H. (1985) Heat capacity of minerals in the system Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>: Representations, estimation and high temperature extrapolation. Contributions to Mineralogy and Petrology (in press).
- Berman, R.G. (1985) A thermodynamic data base for the system Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>. AECL Technical Report (in review).
- Bird, G.W. and Fawcett, J.J. (1973) Stability relations of Mg-chlorite-muscovite and quartz between 5 and 10 kb water pressure. Journal of Petrology, 14, 415-428.
- Brindley, G.W. and Gillery, F.H. (1956) X-ray identification of chlorite species. American Mineralogist, 41, 169-186.
- Brown, B.E., and Bailey, S.W. (1962) Chlorite polytypism: I. Regular and semi-random one-layer structures. American Mineralogist, 47, 819-850.
- Carpenter, M.A., Putnis, A., Navrotsky, A., and McConnell, J.D.C. (1983) Enthalpy effects associated with A1/Si ordering in anhydrous Mg-cordierite. Geochimica et Cosmochimica Acta, 47, 899-906.
- Carson, D.G., Rossman, G.R., and Vaughan, R.W. (1982) Orientation and motion of water molecules in cordierite: A proton nuclear magnetic resonance study. Physics and Chemistry of Minerals, 8, 14-19.
- Charlu, T.V., Newton, R.C., and Kleppa, O.J. (1975) Enthalpies of formation at 970 K of compounds in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> from high temperature solution calorimetry. Geochimica et Cosmochimica Acta, 39, 1487-1497.
- Chernosky, J.V. (1974) The upper stability of clinochlore at low pressure and the free energy of formation of Mg-cordierite. American Mineralogist, 59, 496-507.

CODATA (1978) CODATA Task Group on Key Values for Thermodynamics 1977, 28,1-17.

Cohen, J.P., Ross, F.K., and Gibbs, G.V. (1977) An x-ray and neutron diffraction study of hydrous low cordierite. American Mineralogist, 62, 67-78.

- Danckwerth, A., and Newton, R.C. (1978) Experimental determination of the spinel peridotite to garnet peridotite reaction in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> in the range 900°-1100°C and Al<sub>2</sub>O<sub>3</sub> isopleths of enstatite in the spinel field. Contributions to Mineralogy and Petrology, 66, 189-201.
- Dasgupta, H.C., Seifert, F., and Schreyer, W. (1974) Stability of mangano-cordierite and related phase equilibria in part of the system MnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Contributions to Mineralogy and Petrology, 43, 275-294.
- Day, H.W. and Halbach, H. (1979) The stability field of anthophyllite: The effect of experimental uncertainty on permissible phase diagram topologies. American Mineralogist, 64, 809-823.
- Day, H.W. and Kumin, H.J. (1980) Thermodynamic analysis of the aluminum silicate triple point. American Journal of Science, 280, 265-287.
- Day, H.W., Chernosky, J.V. and Kumin, H.J. (1985) Equilibria in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O: A thermodynamic analysis. American Mineralogist, 70, 237-248.
- Duncan, I.J. (1982) The evolution of the Thor-Odin gneiss dome and related geochronological studies. Unpublished PhD. Thesis, University of British Columbia.
- Duncan, I.J. and Greenwood, H.J. (1977) The effect of molecular water on the thermodynamic properties and stability relations of Mg-cordierite. Geological Society of Canada Annual Meeting Abstracts, 2, 17.
- Evans, H.T., Jr., Appleman, D.E., and Handwerker, D.S. (1963) The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method. American Crystallographic Association Annual Meeting, Programs with Abstracts, 42p.
- Farrell, E.F. and Newnham, R.E. (1967) Electronic and vibrational absorption spectra in cordierite. American Mineralogist, 52, 380-388.
- Fawcett, J.J. and Yoder, H.S. Jr. (1966) Phase relationships of the chlorites in the system  $MgO-Al_2O_3-SiO_2-H_2O$ . American Mineralogist, 51, 353-380.
- Foster, M.D. (1962) Interpretation of the composition and a classification of the chlorites. United States Geological Survey Professional Paper, 414-A.
- Frost, B.R. (1975) Contact metamorphism of serpentinite, chloritic blackwall, and rodingite at Paddy-Go-Easy Pass, Central Cascades, Washington. Journal of Petrology, 16, 272-313.
- Furuhashi, H., Inagaki, M., and Naka, S. (1973) Determination of cation distribution in spinels by x-ray diffraction method. Journal of Inorganic Chemistry, 35, 3009-3014.
- Ganguly, J. and Ghose, S. (1979) Aluminous orthopyroxene: Order-disorder, thermodynamic properties, and petrologic implications. Contributions to Mineralogy and Petrology, 69, 375-385.
- Gasparik, T. and Newton, R.C. (1984) The reversed alumina contents of orthopyroxene in equilibrium with spinel and forsterite in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Contributions to Mineralogy and Petrology, 85, 186-196.
- Gibbs, G.V. (1966) The polymorphism of cordierite I: The crystal structure of low cordierite. American Mineralogist, 51, 1068-1087.

- Gillery, F.H. (1959) The x-ray study of synthetic Mg-Al serpentines and chlorites. American Mineralogist, 44, 143-152.
- Goldman, D.S. and Rossman, G.R. (1977) Channel constituents in cordierite. American Mineralogist, 62, 1144-1157.
- Gordon, T.M. (1973) Determination of internally consistent thermodynamic data from phase equilibrium experiments. Journal of Geology, 81, 199-208.
- Gordon, T.M. (1977) Derivation of internally consistent thermochemical data from phase equilibrium experiments using linear programming. In: Short Course in Applications of Thermodynamics to Petrology and Ore-deposits (H.J. Greenwood, ed.), Mineralogical Association of Canada, 231p.
- Gunter, A.E. (1977a) Water in synthetic cordierites and its significance in the experimental reaction: Aluminous-biotite + sillimanite + quartz = iron-cordierite + sanidine + water. Geological Society of Canada Annual Meeting Abstracts, 2, 22.
- Haar, L., Gallagher, J. and Kell, G.S. (1979) Thermodynamic properties for fluid water: Water and steam
   their properties and current industrial applications. Proceedings of the 9th International Conference on the Properties of Steam, 69-82.
- Halbach, H. and Chatterjee, N.D. (1982) The use of linear parametric programming for determining internally consistent thermodynamic data for minerals. In: High Pressure Researches in Geoscience (W. Schreyer, ed.) E. Schweizerbartsche Verlagsbuchhadlung, 475-491.
- Halbach, H. and Chatterjee, N.D. (1984) An internally consistent set of thermodynamic data for twenty-one CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> -H<sub>2</sub>O phases by linear parametric programming. Contributions to Mineralogy and Petrology, 88, 14-23.
- Harris, N.B.W. and Holland, T.J.B. (1984) The significance of cordierite-hypersthene assemblages from the Beitbridge refion of the Central Limpopo Belt: Evidence for rapid decompression in the Archaen? American Mineralogist, 69, 1036-1049.
- Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278A, 229p.
- Henderson, C.E., Essene, E.J., Anovitz, L.M., Westrum, E.F., Jr., Hemingway, B.S., and Bowman, J.R. (1983) Thermodynamics and phase equilibria of clinochlore, (Mg<sub>5</sub>Al)(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>8</sub>. EOS, 64, 466.
- Herzberg, C.T. (1983) The reaction forsterite + cordierite = aluminous orthopyroxene + spinel in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Contributions to Mineralogy, and Petrology, 84, 84-90.
- Hochella, M.F., Jr., Brown, G.E., Jr., Ross, F.K., and Gibbs, G.V. (1979) High-temperature crystal chemistry of hydrous Mg- and Fe-cordierites. American Mineralogist, 64, 337-351.
- Holdaway, M.J. (1976) Mutual compatibility relations of the Fe<sup>2+</sup>-Mg-Al silicates at 800° C and 3 kb. American Journal of Science, 276, 285-308.
- Holdaway, M.J., and Lee, S.M. (1977) Fe-Mg cordierite stability in high grade pelitic rocks based on experimental, theoretical, and natural observations. Contributions to Mineralogy and Petrology, 63, 175-198.
- Jenkins, D.M. (1981) Experimental phase relations of hydrous peridotites modelled in the system  $H_2O-CaO-MgO-Al_2O_3-SiO_2$ . Contributions to Mineralogy and Petrology, 77, 166-176.

- Jenkins, D.M. and Chernosky, J.V. (1985) Phase equilibria and crystallographic properties of Mg-chlorites. American Mineralogist, in press.
- Johannes, W. and Schreyer, W. (1981) Experimental introduction of CO<sub>2</sub> and H<sub>2</sub>O into Mg-cordierite. American Journal of Science, 281, 299-317.
- Kawasaki, T. and Matsui, Y. (1983) Thermodynamic analysis of equilibria involving olivine, orthopyroxene and garnet. Geochimica et Cosmochimica Acta, 47, 1661-1679.
- Kelley, K.K. (1960) Contributions to the data on theoretical metallurgy. XIII. High temperature heat-content, heat-capacity, and entropy data for the elements and inorganic compounds. United States Bureau of Mines Bulletin, 584, 232p.
- Lane, D.L. and Ganguly, J. (1980) Al<sub>2</sub>O<sub>3</sub> solubility in orthopyroxene in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: A reevaluation, and mantle geotherm. Journal of Geophysical Research, 85, 6963-6972.
- Langer, K. and Schreyer, W. (1969) Infrared and powder x-ray diffraction studies on the polymorphism of cordierite. American Mineralogist, 54, 1442-1459.
- Langer, K. and Schreyer, W. (1976) Apparent effects of molecular water on the lattice geometry of cordierite: A discussion. American Mineralogist, 61, 1036-1040.
- Leake, B.E. (1960) Compilation of chemical analyses and physical constants of natural cordierites. American Mineralogist, 45, 282-298.
- Lonker, S.W. (1981) The P-T-X relations of the cordierite-garnet-sillimanite-quartz equilibrium. American Journal of Science, 281, 1056-1090.
- Martignole, J. and Sisi, J. (1981) Cordierite-garnet-H<sub>2</sub>O equilibrium: A geological thermometer, barometer and water fugacity indicator. Contributions to Mineralogy and Petrology, 77, 38-46.
- McOnie, A.W., Fawcett, J.J. and James, R.S. (1975) The stability of intermediate chlorites of the clinochlore-daphnite series at a 2kbar P<sub>H2O</sub>. American Mineralogist, 60, 1047-1062.
- Meagher, E.P. (1967) The crystal structure and polymorphism of cordierite. Unpublished PhD Thesis, Pennsylvania State University.
- Meagher, E.P. and Gibbs, G.V. (1977) The polymorphism of cordierite: II. The crystal structure of indialite. Canadian Mineralogist, 15, 43-49.
- Medenbach, O., Maresch, W.V., Mirwald, P.W., and Schreyer, W. (1980) Variation of refractive index of synthetic Mg-cordierite with H<sub>2</sub>O content. American Mineralogist, 65, 367-373.
- Mirwald, P.W. and Schreyer, W. (1977) Die stabile und metastabile abbaureaktion von Mg-cordierit in talk, disthen und quarz und ihre abhängigkeit vom gleichgewichtswassergehalt des cordierits. Fortschritte der Mineralogie und Petrologie, 55, 97-99.
- Mirwald, P.W., Maresch, W.V., and Schreyer, W. (1979) Der wassergehalt von Mg-cordierit zwischen 500° und 800° C sowie 0.5 und 11 kbar. Fortschritte der Mineralogie und Petrologie, 57, 101-102.

Mirwald, P.W. (1982) A high-pressure phase transition in cordierite. American Mineralogist, 67, 277-283.

Miyashiro, A. (1957) Cordierite-indialite relations. American Journal of Science, 255, 43-62.

- Navrotsky, A. and Kleppa, O.J. (1967) The thermodynamics of cation distribution in simple spinels. Journal of Inorganic Nuclear Chemistry, 29, 2701-2714.
- Navrotsky, A. and Kleppa, O.J. (1973) Estimate of enthalpies of formation and fusion of cordierite. Journal of the American Ceramics Society, 56, 198-199.
- Nelson, B.W. and Roy, R. (1958) Synthesis of the chlorites and their structural and chemical constitution. American Mineralogist, 43, 707-725.
- Newton, R.C. (1972) An experimental determination of the high pressure stability limits of magnesian cordierite under wet and dry conditions. Journal of Geology, 80, 398-420.
- Newton, R.C. and Wood, B.J. (1979) Thermodynamics of water in cordierite and some petrologic consequences of cordierite as a hydrous phase. Contributions to Mineralogy and Petrology, 68, 391-405.
- O'Neill, H.St.C., and Navrotsky, A. (1983) Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. American Mineralogist, 68, 181-194.
- O'Neill, H.St.C., and Navrotsky, A. (1984) Cation distributions and thermodynamic properties of binary spinel solid solutions. American Mineralogist, 69, 733-753.
- Perkins-III, D., Holland, T.J.B., and Newton, R.C. (1981) The Al<sub>2</sub>O<sub>3</sub> contents of enstatite in equilibrium with garnet in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at 15-40 kbar and 900°-1600°C. Contributions to Mineralogy and Petrology, 78, 99-109.
- Putnis, A. (1980a) The distortion index in anhydrous Mg-cordierite. Contributions to Mineralogy and Petrology, 74, 135-141.
- Putnis, A. (1980b) Order-modulated structures and the thermodynamics of cordierite reactions. Nature, 287, 128-131.
- Putnis, A. and Bish, D.L. (1983) The mechanism and kinetics of Al, Si ordering in Mg-cordierite. American Mineralogist, 68, 60-65.
- Robie, R.A., Bethke, P.M., and Beardsley, K.M. (1967) Selected x-ray crystallographic data, molar volumes, and densities of minerals and related substances. United States Geological Survey Bulletin 1248, 87p.
- Roy, D.M. and Roy, R. (1955) Synthesis and stability of minerals in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. American Mineralogist, 40, 147-178.
- Roy, D.M., Roy, R. and Osborn, E.F. (1953) The system MgO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O and the influence of carbonate and nitrate ions on the phase equilibria. American Journal of Science, 251,337-361.
- Schreyer, W., and Schairer, J.F. (1961a) Compositions and structural states of anhydrous Mg-cordierites: A re-investigation of the central part of the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Journal of Petrology, 2, 324-406.
- Schreyer, W. and Yoder, H.S., Jr. (1964) The system Mg-cordierite-H<sub>2</sub>O and related rocks. Neues Jahrbuch fur Mineralogie und Petrologie, 101, 271-342.

Segnit, E.R. (1963) Synthesis of clinochlore at high pressures. American Mineralogist, 48, 1080–1089.

- Seifert, F. (1974) Stability of sapphirine: A study of the aluminous part of the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Journal of Geology, 82, 173-204.
- Seifert, F., and Schreyer, W. (1970) Lower temperature stability limit of Mg cordierite in the range 1-7 kb water pressure: A redetermination. Contributions to Mineralogy and Petrology, 27, 225-238.
- Selkregg, K.R. and Bloss, F.D. (1980) Cordierites: Compositional controls of Δ, cell parameters, and optical properties. American Mineralogist, 65, 522-533.
- Shearer, J.S. and Kleppa, O.J. (1973) The enthalpies of formation of MgAl<sub>2</sub>O<sub>4</sub>, MgSiO<sub>3</sub>, Mg<sub>2</sub>SiO<sub>4</sub> and Al<sub>2</sub>SiO<sub>5</sub> by oxide melt solution calorimetry. Journal of Inorganic Nuclear Chemistry, 35, 1073–1078.
- Shirozu, H. and Momoi, H. (1972) Synthetic Mg-chlorite in relation to natural chlorite. Mineralogical Journal, 6, 464-476.
- Spinnler, G.E., Self, P.G., Iijima, S., and Buseck, P.R. (1984) Stacking disorder in clinochlore chlorite. American Mineralogist, 69, 252-263.
- Staudigel, H. and Schreyer, W. (1977) The upper thermal stability of clinochlore, Mg<sub>5</sub>Al[AlSi<sub>3</sub>O<sub>10</sub>](OH)<sub>8</sub>, at 10–35 kb P(H<sub>2</sub>O). Contributions to Mineralogy and Petrology, 61, 187–198.
- Stout, J.H. (1975) Apparent effects of molecular water on the lattice geometry of cordierite. American Mineralogist, 60, 229-234.
- Stout, J.H. (1976) Apparent effects of molecular water on the lattice geometry of cordierite: A reply. American Mineralogist, 61, 1041-1044.
- Terry, R.D., and Chilingar, G.V. (1955) Comparison charts for visual estimation of percentage composition. Journal of Sedimentary Petrology, 25, 229-234.
- Tsang, T., and Ghose, S. (1972) Nuclear magnetic resonance of <sup>1</sup>H and <sup>27</sup>Al and Al-Si order in low cordierite Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub> nH<sub>2</sub>O. Journal of Chemical Physics, 56, 3329-3332.
- Wallace, J.H., and Wenk, H. (1980) Structure variation in low cordierites. American Mineralogist, 65, 96-111.
- Wood, B.J. (1974) The solubility of alumina in orthopyroxene coexisting with garnet. Contributions to Mineralogy and Petrology, 46, 1-15.
- Wood, B.J. and Holloway, J.R. (1984) A thermodynamic model for subsolidus equilibria in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Geochimica et Cosmochimica Acta, 48, 159-176.
- Wood, D.L., and Nassau, K. (1967) Infrared spectra of foreign molecules in beryl. Journal of Chemical Physics, 47, 2220-2228.
- Yoder, H.S. (1952) The MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system and the related metamorphic facies. American Journal of Science, Bowen Volume, 569-627.

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