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**LA THÈSE A ÉTÉ
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AN EXPERIMENTAL STUDY OF
SYNTHETIC CORDIERITES

by

Avril Ellis Gunter, BSc, MSc.

A thesis submitted to the Faculty of Graduate
Studies in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Carleton University

Ottawa

September, 1977

(C)

Avril Ellis Gunter

1977

The undersigned hereby recommend to
the Faculty of Graduate Studies acceptance of
this thesis, submitted by Avril Ellis Gunter,
BSc. MSc, in partial fulfillment of the require-
ments for the degree of Doctor of Philosophy.

Chairman, Department of Geology

Supervisor

External Examiner

September 1977

ABSTRACT

This experimental study of synthetic cordierites was undertaken to evaluate the effect of the variable water content of this mineral on metamorphic reactions.

Cordierites of $\text{Fe}/(\text{Fe} + \text{Mg})$, 0.00, 0.25, 0.50, 0.65 and 1.00 have been hydrothermally synthesised at pressures of 1 to 3 kilobars and temperatures between 550°C and 750°C . Cell constants for an Mg-cordierite, containing 0.32 mols H_2O are: $a = 17.010$, $b = 9.839$, $c = 9.343\text{\AA}$. For an Fe-cordierite, containing 0.41 mols H_2O , the cell constants are: $a = 17.207$, $b = 9.854$, $c = 9.289\text{\AA}$. Infrared spectra indicated that all water present in cordierite is in molecular form.

The H_2O content in mols of end-member cordierites may be correlated with their mean refractive index by the following equations:

$$W_{\text{Mg}} = -43.6543 + 28.638 \text{ RI}_{\text{Mg}}$$

$$W_{\text{Fe}} = -45.293 + 29.146 \text{ RI}_{\text{Fe}}$$

Using a knowledge of the H_2O content of Mg-cordierites (from thermogravimetric analysis) and Fe-cordierites (from mean refractive index measurements), at known conditions of temperature and water fugacity, equilibrium constants for the reactions:

derived as, $\ln K = 10893/T - 18.47$ and $\ln K = 17802/T - 24.66$ respectively.

At temperatures below 800°C Fe-cordierites contain more water than Mg-cordierites.

Cordierite reactions have been considered as combinations of simultaneous equilibria involving anhydrous and hydrous (monohydrate) cordierite species. This approach has been illustrated by calculations in the systems, $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-H}_2$ and $\text{K}_2\text{O-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-H}_2$. In the latter system, the reactions aluminous-biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + sanidine $\pm$ vapour and Fe-cordierite + muscovite $\rightleftharpoons$ aluminous-biotite + sillimanite + quartz were determined experimentally. The Fe-cordierite-sanidine reaction was reversed on the graphite-methane buffer, at 1 kilobar between 626° and $631^\circ \pm 5^\circ\text{C}$, at 1.5 kilobars between 634° and $644^\circ \pm 5^\circ\text{C}$ and at 2 kilobars between 639° and $645^\circ \pm 5^\circ\text{C}$. An additional reversal occurred on the NNO,OH(GX,COH) buffer at 1 kilobar between 603° and $613^\circ \pm 5^\circ\text{C}$. One reversal was obtained on the Fe-cordierite-muscovite reaction on the graphite-methane buffer at 2 kilobars between 575° and $580^\circ \pm 5^\circ\text{C}$.

The data of the Fe-cordierite-sanidine reaction and calculation of the reaction Fe-cordierite $\rightleftharpoons$ almandine + sillimanite + quartz, indicate the position of the invariant point [Mus] where Fe-cordierite, almandine, aluminous-biotite, sanidine, sillimanite and quartz coexist. (685°C , 3.35 kilobars where $P_{\text{H}_2\text{O}} = P_{\text{TOTAL}}$, and 640°C , 1.6 kilobars where $P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}$ of the QFI buffer).

Application of the experimental results to natural systems has the following implications. In the present state of knowledge, the assemblage; garnet, cordierite, sillimanite and quartz should not be used as a geothermometer and geobarometer. Also, due to the

difference in H_2O content of the Fe and Mg components in natural cordierites, distribution of iron and magnesium between coexisting garnet and cordierite is not a reliable indicator of the temperatures of metamorphism.

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LIST OF SYMBOLS AND ABBREVIATIONS

P	pressure in bars
f_i	fugacity of gas i
ϕ_i	fugacity coefficient of gas i
T	temperature in degrees Kelvin
$T^{\circ}\text{C}$	temperature in degrees Centigrade
R	gas constant
S	entropy
H	enthalpy
G	Gibbs' free energy
ΔG°	Standard Gibbs' free energy change of reaction
a_i	activity of component i in solution
γ_i	activity coefficient of component i in solution
μ_i	chemical potential of component i in solution
K	equilibrium constant
ln	natural logarithm
log	logarithm to the base 10

$$R^2 = 1 - \frac{\sum_1^N (Y_{\text{obs}} - Y_{\text{calc}})^2}{\sum (Y_{\text{obs}})^2 - \frac{(\sum Y_{\text{obs}})^2}{\text{diff. of } N \text{ and } D + 1}}$$

where Y = dependent variable

N = number of points

D = degree of polynomial in fit.

GENERAL INTRODUCTION

Metamorphic rocks formed from shale (sediments rich in aluminum and potassium) have been used since the beginnings of metamorphic-petrology (Barrow 1893) to indicate the conditions of metamorphism. Since then, there have been innumerable field and laboratory studies on pelitic rocks to investigate the sequence of mineral reactions occurring in an area or to determine the stability limits of minerals or reactions. Much effort has been devoted towards the construction of a petrogenetic grid to show the changes in phase relations between the major rock-forming minerals with variation in temperature, pressure, composition of the phases and the metamorphic fluid. Many rock forming minerals of pelites have variable composition but may be considered as solid solution series between iron and magnesium end-members. (Biotites, chlorites, garnets, cordierites, orthopyroxenes). Several petrogenetic grids have been developed based on average compositions of these ferro-magnesium silicates. (In terms of increasing $(Fe/Fe + Mg)$ the usual sequence is cordierite < chlorite < biotite < staurolite < garnet). Examples of this approach are seen in Albee (1965), Hess (1969), Thompson and Norton (1968) and Grant (1973).

Iron has a variable valency and the stability of rock forming minerals with an iron end-member component is sensitive to the hydrogen fugacity of metamorphic fluids. Experimental studies involving iron silicates require that

the fugacity of hydrogen be controlled in some manner.

Solid-solid buffers first described by Eugster (1957) have been used extensively in this manner. Another method is

the hydrogen membrane technique described by Shaw (1967).

A significant development has been the graphite-methane buffer, first described by Eugster and Skippen (1967)

which allows long runs to be made without loss of buffering capacity. Using all available information on iron end-member rock forming silicates augmented by new experimental work using the graphite-methane buffer, it was originally hoped that a quantitative iron end-member grid could be developed.

The stability of almandine garnet has been investigated by Hsu (1968); Richardson (1968), Hoschek (1968) and Ganguly (1968, 1972) studied staurolite; Hoschek (1968), Grieve and Fawcett (1974) and Ganguly (1968) all did experimental work involving chloritoid and Fawcett and James (1976) investigated chlorite.

Rutherford developed phase relations in the system $\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{O}_2$ at 2 kb pressure. In spite of this wealth of information it became apparent that there were many difficulties in developing an iron end-member grid. The composition of chlorites allows for extensive substitution of Al-Al for Fe^{2+} -Si and Fe^{3+} can also be a major component. The structure of staurolite and its water content are a matter for debate. Without major studies on the chlorite group and staurolite a grid for low temperature metamorphism did not appear feasible.

A high temperature grid would involve among others the phases garnet, cordierite, orthopyroxene, sillimanite and muscovite-K spar. Discussion and calculation of reactions involving cordierite are complicated by what has become popularly known as "the water problem in cordierite". Cordierite, which has the general formula $(\text{FeMg})_2 \text{Al}_4 \text{Si}_5 \text{O}_{18}$, can be synthesised under anhydrous conditions (Schreyer and Schairer 1961) but always occurs naturally with up to three weight percent water. In all petrogenetic grids cordierite has been treated as an anhydrous phase and any contribution of water to cordierite reactions ignored. (Hess, Albee, and A.B. Thompson (1976)). Another approach has been to assume a mean water content for the cordierites used in an experimental reaction. Chernosky (1973) and Bird and Anderson (1973) used this method to determine thermochemical data for magnesium cordierite. (These authors studied the breakdown of clinocllore to give cordierite. This reaction involves the production of large quantities of water which minimises the water problem in cordierite). Schreyer and Yoder (1964) showed that water content of cordierites is not a fixed value but is instead a function of temperature, pressure and the fugacity of water. Any study of cordierite reactions must consider the simultaneous reaction of the mineral with water. Before any attempt at developing even a partial quantitative petrogenetic grid for pelitic minerals can be made, the water problem in cordierite must be solved.

A thorough understanding of the structure, polymorphism and compositional variation in cordierite is needed before the nature and amount of water in cordierite can be studied. Part one of this thesis is devoted to an examination of the structural state, physical properties and water content of five synthetic cordierites of $(\text{Fe}/\text{Fe} + \text{Mg})$ 0.00, 0.25, 0.50, 0.65 and 1.00.

Cordierite can exist both as hexagonal high-cordierite and as orthorhombic low-cordierite. X-ray studies have provided information on the distortion index (which is an empirical measure of the deviation of the orthorhombic polymorph from hexagonal symmetry) and cell parameters of eighteen samples which include examples of both hydrous and anhydrous cordierites of all compositions. Infrared spectra were prepared to study the nature of water in cordierite. Mossbauer spectra provide a means of studying both the oxidation state of iron and also the number and structural state of the sites in which iron exists. Data obtained from X-ray, infrared and Mossbauer studies are presented in Chapter I.

Chapter II is devoted to the measurement of water content of synthetic cordierites (prepared under a variety of conditions) and to the relationship between the water content and refractive indices of a particular sample. Also considered are the possible compositional dependence of water content, and quench problems.

Chapters I and II make up Part I of this thesis which is concerned with synthetic cordierites across the

entire Mg-Fe join

The second part of the study considers the phase relations of iron cordierite in two systems, $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-H}_2$ and $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-H}_2$. Of particular interest in the potassium free system is the relationship between cordierite and garnet and in particular the reaction; cordierite $\rightleftharpoons$ garnet, sillimanite and quartz. This has been studied experimentally by Richardson (1968) and Weisbrod (1973) and theoretically by Froese (1973). This reaction is particularly sensitive to the amount of water in cordierite and is used as an example of the way cordierite reactions should be approached.

The system $\text{K}_2\text{O-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-H}_2$ has been used as a model for the iron end-member reactions of pelitic rocks. It is an especially good approximation for cordierite bearing rocks as these are typically low in calcium and sodium. Two reactions in this system have been studied experimentally; biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + sanidine + vapour and biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + Muscovite + vapour. This enables us to determine the phase relations of Fe-cordierite with the potassium bearing phases, muscovite, biotite and sanidine and sillimanite.

Chapter III examines the application of the experimental results to natural systems. Metamorphic petrologists have often encountered problems in interpreting cordierite occurrences in rocks. For example, attempts to use the distribution of iron and magnesium

between coexisting garnet and cordierite, as an indicator of the temperatures and pressures of metamorphism have resulted in confusion and dissention. A knowledge of the effect of the water in cordierite on that mineral's reactions, has indicated the magnitude of the problem and provided a theoretical basis for solving it.

7

PART I

STRUCTURE, PHYSICAL PROPERTIES,
AND WATER CONTENT OF CORDIERITES

ON THE JOIN $Mg_2 Al_4 Si_5 O_{18}$
- $Fe_2 Al_4 Si_5 O_{18}$

CHAPTER I STRUCTURE, CELL CONSTANTS, INFRARED AND
MOSSBAUER SPECTRA OF SYNTHETIC CORDIERITES

1. CORDIERITE COMPOSITION AND STRUCTURE

The idealised composition of cordierite is $(\text{Me})_2\text{Al}_2\text{Si}_2\text{O}_{10}$, where Me is almost exclusively magnesium and iron. Cordierites are richer in magnesium than any of the other ferro-magnesium minerals of metamorphosed pelites and it is rare to find natural cordierites with an $(\text{Fe}/\text{Fe} + \text{Mg})$ greater than 0.5. An iron-rich cordierite found in a zoned pegmatite near Dolni Bory, Czechoslovakia has been given the species name of sekaninaite. The synthetic minerals can be produced over the entire Mg-Fe join.

The mineral contains variable amounts of water; the maximum observed value is 4.8 wt% (Leake, 1960) although few cordierites contain more than 3 wt% water. There are also small but significant amounts of alkali metals and beryllium.

Cordierite may occur in either a hexagonal or orthorhombic form. The hexagonal form commonly known as high-cordierite or indialite has been found only from fused sediments but is the stable form synthesised at temperatures greater than 830°C . The space group of high cordierite is $P6_3/\text{Mcc}$. The orthorhombic polymorph of cordierite, known as low-cordierite, is the form commonly found naturally and produced when cordierites are synthesised at temperatures less than 830°C . Throughout this study the term Mg-cordierite applies to a composition

<u>Mineral Name</u>	<u>Distortion Index</u>	<u>Structural State</u>	<u>Refractive Indices</u>	<u>Occurrence</u>
High Indialite	$\Delta = 0$	Disordered	el.524	In fused sediments produced synthesised above 830°C
			wl.528	
Low Indialite	$\Delta = 0$	Disordered	el.537	Products synthesised below 830°C
			wl.541	
High Subdistortional Cordierite	$0.29 > \Delta > 0$	Intermediate Order	el.53-1.54	Volcanic rocks fused sediments and synthetic cordierite
			wl.54-1.55	
Low Subdistortional Cordierite	$\Delta = 0.29 - 0.31$	Ordered	el.52-1.56	Metamorphic rocks, pegmatites, and quartz veins
			wl.53-1.57	
High Peridistortional Cordierite	$\Delta = 0.29 - 0.31$	Ordered	el.53-1.54	Blast furnace linings; xenoliths in volcanic rocks
			wl.54-1.55	
Low Peridistortional Cordierite	$\Delta = 0.29 - 0.31$	Ordered	el.52-1.56	Not yet found in nature
			wl.53-1.57	

Table 1 Nomenclature of the structural state of cordierite

(Modified after Miyashiro (1955) and Miyashiro et al (1957)).

of $\text{Mg}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18}$ and Fe-Cordierite to the composition $\text{Fe}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18}$. Intermediate cordierites of compositions $\text{Mg}_{1.5} \text{Fe}_{0.5} \text{Al}_4 \text{Si}_5 \text{O}_{18}$, $\text{Mg} \text{Fe} \text{Al}_4 \text{Si}_5 \text{O}_{18}$, and $\text{Mg}_{0.7} \text{Fe}_{1.3} \text{Al}_4 \text{Si}_5 \text{O}_{18}$ were also synthesised.

In their early structural studies, Takane and Takeuchi (1936) concluded that cordierite was isotypic with beryl $\text{Be}_3 \text{Al}_2^{\text{IV}} \text{Si}_6^{\text{VI}} \text{O}_{18}$ and had the general formula $\text{Al}_3^{\text{IV}} \text{Me}_2^{\text{VI}} (\text{AlSi}_5)^{\text{IV}} \text{O}_{18}$ where Me is iron and magnesium.

Cordierite was classed as a ring silicate, both polymorphs consisting of six membered hexagonal rings of linked $(\text{Si-Al})^{\text{IV}} \text{O}_4$ tetrahedra joined by Al^{IV} and Me^{VI} . Takane and Takeuchi assigned random distribution of one Al and five Si atoms to the six-membered ring. Miyashiro et al (1955) suggested that ordering is possible in the tetrahedral sites within the ring and assumed that the lattice constants, refractive indices and optic axial angle are a function of this ordering. They suggested a classification of cordierites (Table 1) based on a measure of the deviation from hexagonal geometry. The distortion index is defined as $\Delta = 2\theta_{131} - (2\theta_{511} + 2\theta_{421})/2$ where the 2θ angles are measured using Cu K α radiation. The three reflections 131, 511 and 421 are coincident if the geometry is hexagonal. The distortion indices of natural cordierites are in the range 0 to .29 with the majority of natural cordierites having distortion indices close to 0.20. Most early workers on cordierite have used the orientation $a > b > c$ for the orthorhombic cell and in the present study the same orientation is adopted to facilitate comparison.

Figure 1 Al-Si ordering sequences in low cordierite (Gibbs 1966)

The detailed structure of low cordierite was determined by Gibbs (1966) on the Guildford cordierite $\Delta = 0.24^\circ$. He found that it is more proper to consider the ordering of Si and Al in a framework structure of four Al and five Si atoms rather than a ring structure of one Al and five Si atoms. The framework consists of four-membered rings of alternating AlO_4 and SiO_4 tetrahedra cross-linked with six membered rings of $\text{Al}_2\text{Si}_4\text{O}_{18}$ composition. Gibbs showed that apart from the two adjacent Si atoms in the six-membered ring there is perfect alternation (Figure 1) of Al and Si atoms both laterally and vertically. There are five distinct tetrahedral sites in cordierite (Figure 2) and T_3 , T_4 and T_5 tetrahedra make up the six-membered ring. T_3 has a mean T-O bond length of $1.611\text{\AA}$ and T_4 a mean T-O bond length of $1.61\text{\AA}$. Both are fully occupied with Si. T_5 is considerably larger with a mean T-O bond length of $1.744\text{\AA}$ and is 96% filled with Al. T_1 has a mean T-O bond length of $1.753\text{\AA}$ and is completely filled with Al and T_2 with a mean bond length of $1.621\text{\AA}$ is 92% filled with Si. The octahedral site is slightly flattened and shares two edges with AlO_4 tetrahedra and one edge with a SiO_4 tetrahedra (Figure 2). The mean Me-O bond length is $2.119\text{\AA}$ (range $2.113\text{\AA} - 2.124\text{\AA}$).

It became apparent that the distortion index is not solely a measure of Al-Si order when Meagher (1967) showed that the Haddam cordierite which had $\Delta = 0.12^\circ$ is

as fully ordered in Al and Si as Gibbs' Guildford cordierite with $\Delta = 0.24^\circ$. Even a high cordierite $\Delta = 0^\circ$ was found to be 35% ordered. All the octahedral sites in low cordierite have the same shape and Fe-Mg order caused by site preference is not likely.

Two more studies on the structure of cordierite have recently been published: one a low cordierite containing water from White Well, Australia (Cohen et al 1977) and another on indialite from the type locality of Bokano, India (Meagher and Gibbs, 1977). The latter authors found considerable disorder of Al and Si in indialite. The Al contents of tetrahedra within and without the ring are 0.30 and 0.72 respectively, corresponding to a Bragg-Williams (1934) long range ordering parameter of 0.38 in comparison with the theoretical maximum of 0.75 within the constraints of $P6/Mcc$ symmetry. It is also possible (as suggested by Langer and Schreyer (1969)) that short-range ordered domains exist in indialite. No evidence of cations in the channels nor evidence of vacancies in octahedral sites was found. The work of Cohen et al on the White Well cordierite with a distortion index of 0.24° confirmed the structure determined by Gibbs and the fully ordered arrangement of Al and Si.

Analyses of natural cordierite always showed the presence of water and the nature and amount of this water has been a matter of controversy for many years. Farrington (1892) considered that water is an integral part of cordierite whereas Doelter (1917), who knew that

cordierites could be synthesised under anhydrous conditions suggested that all water in cordierite analyses is due to alteration products. Working in the system $MgO - Al_2O_3 - SiO_2$ Schreyer and Schairer (1961) confirmed that completely anhydrous cordierite could be synthesised, thus proving that water is not an essential part of the mineral structure. Although water may not be a necessary part of the structure, it is directly incorporated into the mineral in some way, as Schreyer and Yoder (1960) showed in their study of the system cordierite-water. They also found that the amount of water in a cordierite depended on the conditions of synthesis, decreasing with increase in temperature and increasing with increase in pressure. Throughout this study the term "anhydrous cordierite" refers either to material synthesised under anhydrous conditions or from which the water has been removed, and "hydrous cordierite" refers to material containing water.

Water in natural cordierites has been studied by Sigiura (1959) and Iiyama (1960) and they suggested that two types of water are possible in cordierites; molecular water, present in the ring channels parallel to c, and bonded water present as $(OH)^-$ groups. Schreyer and Yoder (1964) concluded from infrared studies of synthetic hydrous cordierites that there was no evidence for bonded water. The structural studies of Gibbs (1966) and Cohen et al (1977) confirmed the presence of molecular water and determined that it occurred within the large cavities

Two-Coordinated Oxygen		Three-Coordinated Oxygen	
Atoms	rms amplitude of vibration	Atoms	rms amplitude of vibration
04	0.056 Å	01	0.058 Å
05	0.091 Å	02	0.055 Å
06	0.082 Å	03	0.062 Å

TABLE 2 RMS OF AMPLITUDE OF VIBRATION FOR OXYGEN ATOMS
IN LOW CORDIERITE (GIBBS 1966)

formed by two adjacent six-membered rings. However, there is disagreement over the orientation of the water molecules within the ring cavities. Based on a study of electronic and vibrational spectra, Farrell and Newman (1967) decided that the water molecules were oriented parallel to (100), whereas Cohen et al have stated that the water molecules are oriented parallel to (001). The latter authors from X-ray neutron diffraction conclude that the water molecules are disordered in four directions parallel to (001).

The possible effect on the structure of cordierite of the presence or absence of water in the channels has been considered by Stout (1975). Gibbs had measured the RMS of amplitude of vibration of the oxygen atoms in low cordierite (Table 2) and found that O_4 had more than the expected two coordination. Stout suggested that hydrogen bonding between O_4 and the water molecule was responsible for the additional coordination. He suggested a model (Figure 3) whereby O_4 is "kinked" into the open channels due to its coordination with molecular water causing a shortening of the cell parameter a with respect to b , with a corresponding decrease in the distortion index. The effect of dehydration in his model is to increase the O_4-O_4 distance across the channel, forcing T_5 and T_4 apart and lengthening a with respect to b . In other words, for low cordierite (fully ordered in Al and Si) the distortion index should be inversely proportional to the water content of the mineral.

Figure 3 Proposed model for the change in the structure of low cordierite on dehydration. (After Stout 1975).

In addition to Al-Si order-disorder and the structural effect of water, the cordierite problem is further complicated by the distribution and oxidation state of Fe in the structure. Mossbauer studies by Duncan and Johnson (1973, 1974) on oriented sections of a natural cordierite containing 1.85 wt% iron showed that 80% of Fe is present as Fe^{2+} in the octahedral site, 18% as Fe^{2+} in a second non-octahedral site (presumably the ring channels) and 2% as Fe^{3+} in T_1 . On dehydration the Fe^{2+} attributable to the second site is removed and replaced by an additional 18% Fe^{3+} with high spin resonance. In disagreement with Duncan and Johnson, Rossman (1976) found that only a small fraction of the iron occurred in the channels and on the basis of optical absorption spectroscopy and powder Mossbauer spectra of natural cordierites concluded that this iron was non-structural.

The structural problems of cordierites are complex and not yet resolved. For synthetic cordierites only the magnesium end-member has been studied in any detail. The present study is concerned with synthetic cordierites across the entire Fe-Mg join, both hydrous and anhydrous. An attempt will be made to assess the structural state of these cordierites.

2. PREPARATION OF SYNTHETIC CORDIERITES

(a) Preparation of Gels

The cordierites used in this study ((Fe/Fe + Mg) 0.0, 0.25, 0.50, 0.65 and 1.00) were synthesised hydrothermally from 'gels' of appropriate compositions. The gels were produced from 'Analar' grade reagents which had been previously standardised. The sources of material were aluminum wire for Al, iron sponge for Fe, magnesium oxalate for Mg and tetraethyl orthosilicate (T.E.O.S.) for Si. The calculated quantities of aluminum wire, iron sponge and magnesium oxalate were dissolved in nitric acid and this solution was heated on a water bath until most of the nitrates were driven off. After cooling the T.E.O.S. was added to solution and the hydroxides were precipitated immediately by the addition of 10ml ethyl alcohol and concentrated ammonium hydroxide. After drying on a water bath the gels produced were heated until all the nitrates were removed, ground under acetone, heated overnight in a muffle furnace at 1000°C and finally reground under acetone. All compositions containing iron were reduced by heating at 600°C in a stream of hydrogen for several hours. The iron end-member cordierite was also prepared from a mixture of kaolinite and synthetic fayalite. The kaolinite was kindly provided by Dr. R.S. Dean, Mines Branch, Department of Energy Mines and Resources. Full details of reagent standardisation, details of gel preparation and an analysis of the kaolinite used are given in Appendix 1.

(b) Hydrothermal Synthesis

All cordierites were synthesised at temperatures between 500°C - 800°C at pressures of 1000 or 2000 bars in standard "Tuttle" type pressure vessels. Temperatures were measured by a chromel-alumel thermocouple inserted into a wall in the pressure vessel closely adjacent to the sample chamber. The temperature was monitored continuously during the experiments with a Leeds Northrup strip chart potentiometer (readability $\pm 2^{\circ}\text{C}$) (and was checked periodically by a Leeds Northrup K3 potentiometer with a readability of $\pm 0.5^{\circ}\text{C}$.) The temperatures are believed accurate to $\pm 5^{\circ}\text{C}$. Pressures were measured by a Bourdon tube pressure gauge and are believed accurate to $\pm 5\%$ of the stated value.

All cordierites were prepared with controlled activity of water and hydrogen. The two methods of controlling these activities were the graphite-methane buffer G,CH,(X,OH) and NNO,OH(GX,COH) . The buffer notations are those of Eugster and Skippen (1967). The charges consisted of gel (or fayalite-kaolinite mix) plus approximately 20-25% water. The capsules were silver-palladium (Ag Pd) for the G,CH(X,OH) buffer and three concentric capsules; silver, silver-palladium and gold for the NNO,OH(GX,COH) buffer as described by Eugster and Skippen. In the latter case the charge was contained in a crimped silver tube within a welded silver-palladium tube containing graphite, water and oxalic acid-benzoic acid mix. The outer gold capsule contained nickel-

bunsenite mix and water. Runs were quenched under isobaric conditions in a stream of compressed air and were cooled below 150°C in less than two minutes. Fe-cordierite runs required seeding with 5-10% of previously synthesised material to obtain high yields.

(c) Purity of Synthetic Cordierites.

The run products were checked for identity and impurity by X-ray and optical microscopy. A total of 107 cordierite samples were prepared: 24 of the Mg-cordierite, 60 of the Fe-cordierite, 4 of (Fe/Fe + Mg) 0.25, 15 of (Fe/Fe + Mg) 0.50, and 4 of (Fe/Fe + Mg) 0.65. The material synthesised was fine grained and rarely well crystallised with an average grain size of 2μ . (Plate 1 & 2). Birefringence was weakly developed and twinning was seen only occasionally in crystals of Mg-rich cordierite. Refractive index was the only optical property measured on the material. The purity of Mg-cordierite and cordierite of (Fe/Fe + Mg) 0.25 samples was better than 95%.

Quartz was observed in the X-ray diffraction patterns of cordierites with (Fe/Fe + Mg) 0.50, 0.65 and 1.00. It occurred as minute inclusions within the cordierite grains and was commonly associated with a greenish inclusion of an isotropic mineral of high refractive index (approximately 1.8). In the Fe-cordierite synthesis runs this impurity was identified as hercynite ($\text{Fe Al}_2 \text{O}_4$) on the basis of refractive index (approximately 1.8) and its isotropism.

Plate I Scanning electron micrograph of a synthetic
hydrous Fe-cordierite.

10 μ

I

Plate 2 Scanning electron micrograph of an intermediate
synthetic hydrous cordierite, (Fe/Fe + Mg), 0.50

10 μ

II

When the iron-rich cordierite is dehydrated, in vacuum a colour change from grey to pale, reddish brown is observed. This colour change is not associated with the cordierite but with the spinel impurity which changes in colour to reddish brown with an increase in refractive index. The refractive index of the cordierite is lowered on dehydration. The amount of impurity in the iron-cordierite runs was as high as 15-20%.

3. X-RAY STUDIES

(a) Measurement of Distortion Index

The distortion index is traditionally measured for all natural and synthetic cordierites. (Natural cordierites from metamorphic rocks have distortion indices of 0.10 - 0.29). As has been previously noted the distortion index is not a measure of Al-Si ordering in the six-membered ring of tetrahedra. Its main use is to indicate if a cordierite is hexagonal or orthorhombic. The 131, 511 and 421 peaks of these synthetic cordierites were not resolvable in X-ray diffraction patterns even at scanning speeds of $1/8^\circ/\text{min}$ and it was not possible to determine the distortion index directly. However, Langer and Schreyer (1969) developed another parameter, the width index, which can be correlated with the distortion index and this parameter could be measured. An X-ray diffraction pattern is made using Cu $k\alpha$ radiation between $30-29^\circ$ at a scanning speed of $1/8^\circ/\text{min}$ and a chart speed of $2\text{cm}/\text{min}$. A representative pattern which is produced by this procedure is shown in Figure 4(a). Vertical lines are drawn from the baseline to the maximum height and to the height plateau between 29.5° and 30° 2θ Cu $k\alpha$. (The plateau represents the incipient appearance of the 131 peak. The width index is measured across the pattern at a height which is the mean of the one third heights of the two vertical lines as is shown in Figure 4(a). Langer and Schreyer were able to measure both distortion index and width index for samples used in their heating

Figure 4(a) Measurement of Width-index (after Langer and Schreyer, 1969)

Figure 4(b) Correlation of 'width-index' with distortion-index (after Langer and Schreyer 1969)

experiments and provide a correlation between the two empirical parameters (Figure 4(b)). The synthetic cordierites in the present study showed width indices around 0.40 which correlates with a distortion index of 0.15. This indicates that the synthetic cordierites are orthorhombic and not hexagonal. (There was no increase in width index observed after water had been removed from the cordierite structure).

(b) Measurement of Cell Parameters of 18 Synthetic Cordierites

(i) Method

Powder diffraction films were prepared of four magnesium cordierites, eight intermediate cordierites and six iron-cordierites from both hydrous and anhydrous material. A Debye-Scherrer camera (diameter 114.59mm) and filtered Cobalt $K\alpha$ radiation (1.30kv. and 16mA) were used. The exposure times were 24-36 hours, and silicon (NBS SRM640) was used as an internal standard. (The 111 reflection of silicon interferes with the cordierites 402, 222 doublet and this line was measured from a film lacking an internal standard. Cordierite reflections adjacent to 402, 222 were accurately measured relative to Si and subsequently used to measure 402, 222 on the Si free film.) Attempts were made to fit the observed lines to both hexagonal and orthorhombic cells. Refinement based on a hexagonal cell resulted in poor convergence. Width index and infrared studies had indicated that the synthetic material is orthorhombic. The cordierite diffraction

hkl	1 Co-S-2		1 Co-S-1		Visually Estimated Intensities	1 Co-S-12 TGA 750		1 Co-S-12 TGA 1100		hkl
	(Fe/Fe + Mg) 0.0 Observed	Calculated	(Fe/Fe + Mg) 0.0 Observed	Calculated		(Fe/Fe + Mg) 0.0 Observed	Calculated	(Fe/Fe + Mg) 0.0 Observed	Calculated	
200	8.4928	8.5049	8.4928	8.5015	90	8.4963	8.5160	8.5173	8.5029	200
110	8.4928	8.4502	8.4928	8.4480	90	8.4963	8.4674	8.5173	8.4842	110
310	4.8911	4.8997	4.8911	4.8980	8	4.9083	4.9073	4.8957	4.9055	310
002	4.6701	4.6713	4.6701	4.6740	5	4.6848	4.6658	4.6681	4.6674	002
400					VW	4.2667	4.2580			400
112	4.0905	4.0882	4.0873	4.0898	20	4.0969	4.0864	4.1033	4.0894	112
312	3.3771	3.3810	3.3746	3.3814	20	3.3877	3.3816	3.3793	3.3814	312
402	3.1341	3.1408	3.1341	3.1447	40	3.1405	3.1451	3.1451	3.1430	402
222	3.1341	3.1335	3.1341	3.1339	40	3.1405	3.1353	3.1451	3.1392	222
511	3.0330	3.0371	3.0313	3.0367	70	3.0364	3.0406	3.0373	3.0379	511
421	3.0330	3.0296	3.0313	3.0289	70	3.0364	3.0339	3.0373	3.0353	421
512	2.6450	2.6415	2.6447	2.6414	20	2.6489	2.6436	2.6447	2.6450	512
422	2.6450	2.6465	2.6447	2.6463	20	2.6489	2.6486	2.6447	2.6464	422
004	2.3380	2.3402	2.3371	2.3370	15	2.3390	2.3379	2.3358	2.3377	004
711	2.2857	2.2860	2.2857	2.2852	5	2.8852	2.8887	2.2876	2.2861	711
531										531
622	2.1705	2.1696	2.1684	2.1693	10					622
532					3	2.1042	2.1006	2.1023	2.1023	532
224					2			2.0452	2.0447	224
404										404
640										640
533	1.8759	1.8750	1.8756	1.8750	5	1.8771	1.8763	1.8768	1.8777	533
351	1.8074	1.8070			5					351
604	1.8074	1.8030			5	1.8014	1.8022	1.8016	1.8016	604
550	1.6902	1.6900	1.6903	1.6896	5	1.6907	1.6905	1.6903	1.6907	550
624	1.6902	1.6905	1.6903	1.6907	25					624
552	1.5884	1.5892	1.5884	1.5890	10					552
643	1.5884	1.5885	1.5884	1.5890	10					643

Table 3(a) Observed and calculated d values and visually

estimated intensities for Mg-cordierites reflections.

hkl	2 Co-S-1 (Fe/Fe + Mg) 0.25		2 Co-S-2 TGA (Fe/Fe + Mg) 0.25		Visually Estimated Intensities	3 Co-S-5 (Fe/Fe + Mg) 0.50		hkl
	Observed	Calculated	Observed	Calculated		Observed	Calculated	
200	8.5208	8.5125	8.5075	8.5121	90	8.4858	8.5295	200
110	8.5208	8.4522	8.5075	8.4740	90	8.4858	8.5295	110
310	4.9164	4.9037	4.9188	4.9071	8	4.9304	4.9201	310
002	4.6701	4.6695	4.6689	4.6646	5	4.6618	4.6565	002
400					VW	4.2667	4.2647	400
112	4.0921	4.0876	4.0867	4.0864	30	4.0873	4.0846	112
312	3.3879	3.3816	3.3911	3.3808	100	3.3710	3.3820	312
402	3.1405	3.1456	3.1396	3.1440	40	3.1391	3.1450	402
222	3.1405	3.1341	3.1396	3.1363	40	3.1391	3.1404	222
511	3.0390	3.0393	3.0419	3.0398	70	3.0442	3.0454	511
421	3.0390	3.0315	3.0419	3.0345	70	3.0447	3.0423	421
512	2.6495	2.6477	2.6508	2.6473	20	2.6502	2.6499	512
422	2.6495	2.6426	2.6508	2.6438	20	2.6502	2.6499	422
004	2.2336	2.3347	2.3307	2.3323	15	2.3292	2.3282	004
711	2.2869	2.2878	2.2876	2.2880	3			711
531					15	2.2363	2.2357	531
622			2.1740	2.1761	10	2.1772	2.1752	622
532			2.1007	2.1012	5			532
224					5	2.0437	2.0423	224
533					5	2.0437	2.0435	533
351	1.8756	1.8756			3			351
604			1.6908	1.6904	3	1.8008	1.8013	604
624	1.6906	1.6908			25	1.6909	1.6910	624
552	1.5898	1.5900			10			552
643	1.5898	1.5891	1.5904	1.5907	10			643

Table 3(b) Observed and calculated d values and visually

estimated intensities for some intermediate

synthetic cordierite reflections.

hkl	3 Co-S-12Q1A (Fe/Fe + Mg) 0.50		3 Co-S-12Q1B (Fe/Fe + Mg) 0.50		Visually Estimated Intensities	3 Co-S-2 TGA Fe/Fe + Mg (0.50)		hkl
	Observed	Calculated	Observed	Calculated		Observed	Calculated	
200	8.5068	8.5300	8.5420	8.5245	90	8.4858	8.5501	200
110	8.5068	8.4945	8.5420	8.5054	90	8.4858	8.4954	110
310	4.9219	4.9179	4.9281	4.9179	8	4.9199	4.9258	310
002	4.6587	4.6534	4.6518	4.6584	5			002
400	4.2615	4.2650	4.2693	4.2623	vw	4.2632	4.2750	400
112	4.0905	4.0812	4.0905	4.0858	30	4.0873	4.0835	112
312	3.3782	3.3801	3.3771		100	3.3750	3.3840	312
402	3.1387	3.1442	3.1387	3.1468	40			402
222	3.1387	3.1371	3.1387	3.1408	40			222
511	3.0416	3.0448	3.0424	3.0442	70	3.0443	3.0506	511
421	3.0416	3.0399	3.0424	3.0415	70	3.0433	3.0431	421
512	2.6473	2.6490	2.6489	2.6493	20	2.6515	2.6533	512
422	2.6473	2.6457	2.6489	2.6493	20	2.6515	2.6505	422
004	2.3260	2.3267	2.3297	2.3292	15	2.3287	2.3284	004
711	2.2899	2.2922			3			711
513					15	2.2369	2.2378	513
622	2.1745	2.1741	2.1752	2.1746	10	2.1794	2.1772	622
532	2.1038	2.1041	2.1048	2.1057	5			532
224	2.0397	2.0406			5	2.0448	2.0418	224
404					5	2.0448	2.0448	404
533	1.8786	1.8778				1.8799	1.8792	533
641						1.8204	1.8208	641
604			1.8012	1.8014				604
624	1.6903	1.6901	1.6910	1.6910				624
643						1.6917	1.6920	643

Table 3(c) Observed and calculated d-values and visually

estimated intensities for some intermediate and

Fe-cordierite reflections.

hkl	4 Co-S-1 (Fe/Fe + Mg) 0.65		4 Co-S-2 TGA (Fe/Fe + Mg) 0.65		Visually Estimated Intensities	Co-S-10 (Fe/Fe + Mg) 1.00		Co-S-20 (Fe/Fe + Mg) 1.00		hkl
	Observed	Calculated	Observed	Calculated		Observed	Calculated	Observed	Calculated	
200	8.5279	8.5521	8.5739	8.5569	90	8.5704	8.6035	8.5633	8.5973	200
110	8.5279	8.4936	8.5739	8.5023	90	8.5704	8.5508	8.5633	8.5471	110
310	4.9241	4.9267	4.9585	4.9298	5	4.9585	4.9570	4.9585	4.9585	310
002					VW					002
400	4.2771	4.2760	4.2615	4.2784	3	4.2754	4.3017	4.2684		400
112	4.0778	4.0832	4.0881	4.0822	35	4.0872	4.0812	4.0842	4.0815	112
312	3.3857	3.3841	3.3814	3.3837	100	3.3922	3.3892	3.3889	3.3886	312
402	3.1433	3.1496	3.1456	3.1496	40	3.1544	3.1560	1.1477	3.1558	402
222	3.1433	3.1379	3.1456	3.1387	40	3.1544	3.1455	3.1477	3.1444	222
511	3.0442	3.0510	3.0489	3.0525	70	3.0668	3.0676	3.0637	3.0648	511
421	3.0442	3.0467	3.0489	3.0451	70	3.0668	3.0596	3.0637	3.0373	421
512	2.6476	2.6536	2.6544	2.6542	20	2.6605	2.6622	2.6573	2.6612	512
422	2.6476	2.6483	2.6544	2.6493	20	2.6605	2.6575	2.6573	2.6562	422
004	2.3307	2.3283	2.3287	2.3268	15	2.3229	2.3222	2.3229	2.3231	004
531	2.2899	2.2883			5					531
623	2.1779	2.1773								513
532			2.1064	2.1068		2.1853	2.1866	2.1875	2.1854	622
224			2.0455	2.0411	3	2.1168	2.1153	2.1148	2.1139	532
404			2.0455	2.0408	5	2.0393	2.0406	2.0412	2.0408	224
533	1.8789	1.8791			5	2.0393	2.0434	2.0412	2.0438	404
604			1.7985	1.7984	5			1.8847	1.8842	533
334	1.7980	1.7983						1.8004	1.8000	604
624	1.6920	1.6920	1.6914	1.6941	25	1.6948	1.6946	1.6939	1.6943	334
643			1.5943	1.5941	10	1.5999	1.5999	1.5986	1.5989	624

Table 3(d) Observed and calculated values and visually

estimated intensities for some Fe-cordierite

reflections.

hkl	Co-S-28		Co-S-34		Visually Estimated Intensities	Co-S-36		Co-S-36 TGA		hkl
	Observed	(Fe/Fe + Mg) 1.00 Calculated	Observed	(Fe/Fe + Mg) 1.00 Calculated		Observed	(Fe/Fe + Mg) 1.00 Calculated	Observed	Calculated	
200	8.6061	8.5974	8.5632	8.5939	90	8.5467	8.6073	8.5880	8.5989	200
110	8.6061	8.5406	8.5632	8.5464	90	8.5467	8.5423	8.5880	8.5552	110
310			4.9552	8.9552	5	4.9279	4.9568			310
400			4.2806	4.2969	5					400
112	4.0857	4.0827	4.0823	4.0827	45	4.0860	4.0810	4.0804	4.0828	112
312	3.3965	3.3893	3.3872	3.3889	100	3.3949	3.3900	3.3910	3.3895	312
402										402
222	3.1370	3.1447	3.1480	3.1457	30	3.1404	3.1445	3.1436	3.1469	222
511	3.0572	3.0649	3.0624	3.0642	70	3.0685	3.0676	3.0613	3.0658	511
421	3.0572	3.0571	3.0624	3.0577	70	3.0685	3.0587	3.0613	3.0599	421
512	2.6592	2.6604	2.6587	2.6609	20	2.6595	2.6631	2.6594	2.6618	512
422	2.0592	2.6564	2.6587	2.6567	20	2.6595	2.6572	2.6594	2.6579	422
040	2.4613	2.4601			15	2.4603	2.4598			040
004	2.3258	2.3241	2.3237	2.3237	10	2.3220	2.3233	2.3220	2.3229	004
573								2.1151	2.1158	513
622	2.1866	2.1855			5					622
532			2.0407	2.0407	5	2.0416	2.0409			532
224	2.0404	2.0413			5					224
404	2.0404	2.0443			5					204
533	1.8838	1.8843			5	1.8842	1.8847	1.8853	1.8854	533
351	1.8251	1.8252			5					351
604					5					604
334	1.8006	1.8003	1.8009	1.8006	7			1.8015	1.8011	334
624	1.6946	1.6947	1.6946	1.6946	23	1.6951	1.6950	1.6951	1.6948	624
823	1.6623	1.6623			3					823
643					3					643

Table 3(e) Observed and calculated values and visually estimated intensities for some Fe-cordierite reflections.

patterns were indexed using XRPDF card 12-303.

(ii) Reflections observed

The following reflections were found in all the cordierite films measured; (200, 110), 310, 112, 312, 222, (511, 421), (512, 422), 004, 622, 624, and 643. The 002 and 711 lines decreased in intensity with increase in (Fe/Fe + Mg) and were not measurable for iron end-member cordierites. Treatment of the line at $d = 3.14$ as the doublet (402, 222) worked well for magnesium cordierites but for iron cordierites refinement of the cell constants only proved possible when this line was treated as 222 only. For d values between 1.75 and 2.3 there are many lines which were often unresolvable due to line fusion or uncertainty over indexing. For these d values the lines given in Tables 3a-e represent those which are clear and sharp and can be assigned unambiguously to a particular reflection. A list of reflections measured, observed and calculated d values and visually estimated intensities are given in Tables 3a-e. Samples with the suffix TGA refer to anhydrous material.

(iii) Cell parameters.

Cell constants for synthetic Mg-cordierite are available from Schreyer and Schairer (1961) and Schreyer and Yoder (1964) among others. The cell constants of Schreyer and Yoder for an Mg-cordierite of distortion index $\Delta = 0.25$ is included in Table 4. Hsu (1968) reported cell constants of Fe-cordierite based on a refinement of only 6 lines and these are given in Table 6.

Sample (Fe/Fe + Mg)	a	b	c	V(A ³)	a-√3b	Water Content in mols from	
						TGA Measurements	
1Co-S-2	0.0 17.010 (.007)	9.737 (.002)	9.343 (.003)	1547.3 (.4)	.145	0.32	
1Co-S-1	0.0 17.003 (.005)	9.735 (.001)	9.348 (.003)	1547.3 (.4)	.142	0.32	
1Co-S-12Q1 TGA 1150°C	0.0 17.032 (.007)	9.789 (.007)	9.332 (.004)	1551.0 (.7)	.129	0.0	
1Co-S-12Q1 TGA 7500C	0.0 17.025 (.008)	9.770 (.005)	9.335 (.003)	1554.0 (.9)	.05	0.00	
Schreyer & Yoder(1964)	0.0 17.06 (.02)	9.72 (.01)	9.33 (.09)	1547.0 (.4)	-	unknown	
2Co-S-1	0.25 17.025 (.007)	9.742 (.003)	9.339 (.003)	1548.9 (.5)	.152	0.40	
2Co-S-2	0.25 17.025 (.008)	9.770 (.005)	9.329 (.004)	1551.8 (.5)	.101	0.0	

Table 4 Cell constants of magnesium-rich cordierites.

Sample (Fe/Fe + Mg)	a	b	c	$\frac{V(A^3)}{V(A^3)}$	a- $\sqrt{3}b$	Water Content from TGA Measurements
3Co-S-5	0.50 17.059 (.008)	9.814 (.004)	9.313 (.002)	1556.1 (.5)	.06	0.44
3Co-S-12-1	0.50 17.060 (.005)	9.795 (.004)	9.307 (.002)	1552.2 (.5)	.094	0.61
3Co-S-12-2	0.50 17.049 (.005)	9.814 (.003)	9.317 (.002)	1559.9 (.3)	.05	0.61
3Co-S-2 TGA 350°C	0.50 17.100 (.013)	9.789 (.007)	9.314 (.003)	1559.0 (.6)	.145	0.0
4Co-S-1	0.65 17.104 (.007)	9.785 (.004)	9.313 (.002)	1558.8 (.5)	.155	0.40
4Co-S-2 TGA 300°C	0.65 17.114 (.009)	9.797 (.005)	9.307 (.003)	1560.5 (.5)	.144	0.0

Table 5 Cell constants of intermediate cordierites.

Sample (Fe/Fe + Mg)	a	b	c	VA ³	a-√3b	Water Content Measured from TGA
Co-S-10	1.00	17.207 (.007)	9.854 (.004)	9.289 (.002)	1574.9 (.4)	.14
Co-S-20	1.00	17.195 (.008)	9.842 (.005)	9.292 (.002)	1572.6 (.4)	.147
Co-S-28	1.00	17.195 (.004)	9.840 (.002)	9.296 (.002)	1573.0 (.3)	.151
Co-S-34	1.00	17.188 (.004)	9.850 (.003)	9.295 (.002)	1573.6 (.5)	.126
Co-S-36	1.00	17.215 (.010)	9.839 (.004)	9.293 (.003)	1574.0 (.7)	.173
Hsu(1968)	1.00	17.17 (.07)	9.86 (.05)	9.28 (.03)	1574.1 (5.4)	unknown
Co-S-36 TGA 900°C	1.00	17.198 (.009)	9.862 (.007)	9.292 (.003)	1576.0 (.7)	.116
						0.00

Table 6 Cell constants of iron-cordierites

Cell constants of the intermediate cordierites have not previously been reported.

The cell parameters of the eighteen cordierites are given in Tables 4, 5 and 6 with their estimated standard deviations. Also given is the parameter $a - \sqrt{3}b$ which gives an indication of the deviation of the cell from orthohexagonality.

There is an increase in a with increase in $(Fe/Fe + Mg)$ but no clear trend is discernable on dehydration.

There is an increase in b with an increase in $(Fe/Fe + Mg)$ and for all compositions except 0.50, there is an increase in b when the material is dehydrated. Heating a magnesium cordierite to $1150^{\circ}C$ instead of only $750^{\circ}C$ produces a further increase in b .

In contrast to a and b , c decreases with increase in $(Fe/Fe + Mg)$ and for any particular composition there is a further decrease in c for material dehydrated below $900^{\circ}C$. However for a magnesium cordierite heated to over $1150^{\circ}C$, c was larger than for material heated to $750^{\circ}C$.

Cell volume increases with increase in $(Fe/Fe + Mg)$ and for any composition there is a small increase in cell volume on dehydration. The hydrous cordierites of $(Fe/Fe + Mg)$ 0.0, 0.25, 0.50 and 0.65 were synthesised under similar conditions of temperature, pressure and buffer used and should be comparable with

Figure 5(a) Variation of b cell parameter with $(\text{Fe}/\text{Fe} + \text{Mg})$ in hydrous cordierites.

Figure 5(b) Variation of a cell parameter with $(\text{Fe}/\text{Fe} + \text{Mg})$ in hydrous cordierites.

Figure 5(c) Variation of c-cell parameter with (Fe/Fe + Mg) in hydrous cordierites.

Figure 5(d) Variation of V cell parameter with (Fe/Fe + Mg) in hydrous cordierites.

Figure 6(a) Variation of b cell parameter with (Fe/Fe + Mg) in anhydrous cordierites.

Figure 6(b) Variation of a cell parameter with (Fe/Fe + Mg) in anhydrous cordierites.

Figure 6(c) Variation of c cell parameter with (Fe/Fe + Mg) in anhydrous cordierites.

Figure 6 (d) Variation of V cell parameter with (Fe/Fe + Mg) in anhydrous cordierites.

respect to water content. The five Fe-cordierites, the cell constants of which were refined, have a range of water content. The variation of the cell parameters, a , b , c and V , of the hydrous cordierites with respect to composition is given in Figure 5(a),(b),(c),(d) and a similar plot for the anhydrous cordierites in Figure 6(a),(b),(c),(d).

As pointed out by Stout (1975) the distortion index is a measure of the deviation of the cell from hexagonal geometry. As the distortion index increases so does the parameter $a - \sqrt{3}b$. (For ideal orthohexagonality $a - \sqrt{3}b = 0$). Stout suggested that the effect of removing water from the cordierite structure would be to increase the O_4-O_4 distance across the ring channel forcing T_5 and T_4 apart and lengthening a with respect to b thus increasing both the distortion index and $a - \sqrt{3}b$. Except for the composition $(Fe/Fe + Mg) \sim 0.50$, $a - \sqrt{3}b$ decreases on dehydration. Therefore the synthetic cordierites do not follow Stout's suggested model.

4. INFRARED ABSORPTION SPECTROSCOPY

(a) Introduction

When molecules or groups of atoms are excited by infrared radiation, vibrational and rotational modes are caused. Each absorption band is characteristic for a particular movement of the molecule or group of atoms. Water may be present in minerals as adsorbed water, water of crystallisation, molecular within cavities in the structure or as hydroxyl (OH^-) ions. These may be distinguished on the basis of infrared spectra as differing degrees of hydrogen bonding give rise to different absorption bands. Infrared spectra were run on iron and magnesium end-members hydrous cordierites to determine the nature of water in the structures. Molecular water can be removed by heating to only a few hundred degrees whereas the removal of structural (OH^-) normally requires temperatures in excess of 1000°C . Infrared spectra were also run on two dehydrated samples of magnesium cordierite, one heated to 750°C and the other heated to 1150°C .

Infrared spectra are sensitive to short range order, which may be defined as those arrangements and disarrangements that take place entirely within the unit cell and are associated with rotational symmetry. These spectra are useful for studying glasses and the onset of crystallisation. For example, the crystallisation of magnesium cordierite from glass of composition $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ was studied by Langer and Schreyer (1969). The main bands of the cordierite spectra are present in

the glass but the spectra become gradually more complex as crystallisation first to high-cordierite and then low cordierite takes place. While a corresponding change in distortion index from $\Delta = 0.0$ for high cordierite through intermediate cordierite $\Delta = 0.10$ to a maximum distortion index = 0.21 occurs. The published spectra from the work of Langer and Schreyer provide a basis for comparison with infrared spectra for both iron and magnesium cordierites from the present study.

(b) Experimental Details

The spectra were obtained by Dr. B. Chang of Department of Chemistry, Carleton University. Two instruments were used; most of the spectra were run on a Perkin-Elmer grating infrared spectrophotometer model 237B and for better resolution the hydrous cordierites were run on a Perkin-Elmer grating infrared spectrophotometer Model 225. The spectra were recorded between 200cm^{-1} - 4000cm^{-1} and polystyrene was used for calibration.

The finely ground samples were dried in an oven at 110°C and mixed with KBr, and were pelleted in an evacuable die. All but two of the spectra were prepared using KBr pellets. Halide pellets absorb moisture easily which may lead to spurious molecular water bands. To guard against this problem the spectra of the two dehydrated samples (magnesium cordierite heated to either 750°C or 1150°C) were re-run using nujol mulls on polyethylene.

Figure 7(a) Infrared spectra of Mg and Fe-cordierites between 1600-4000cm⁻¹

Figure 7 (b) Principal H₂O vibration modes.

<u>Vibration State</u>			<u>Water Vapour</u>	<u>Cordierite</u> <u>Farrell & Newman</u>	<u>This</u> <u>Study</u>
<u>V₁</u>	<u>V₂</u>	<u>V₃</u>	<u>cm⁻¹</u>	<u>cm⁻¹</u>	<u>cm⁻¹</u>
0	1	0	1595	1650	1650
0	2	0	3151	3240	Broad peak
1	0	0	3652	3580	
0	0	1	3756	3680	3680
0	1	1	5332	5260	
0	2	1	6874	6800	
1	0	1	7252	7110	
1	1	1	8807	8620	
2	0	1	10613	10380	

Table 7 Comparison of H₂O vibration bands in the gaseous state with those observed in cordierites.

(c) Experimental Results

(i) Water in cordierite

Initial infrared spectra of both iron and magnesium hydrous cordierites in the region 1200cm^{-1} - 4000cm^{-1} indicated a broad band between 3200 - 3600cm^{-1} and additional bands at 1650cm^{-1} , 2930cm^{-1} and 3690cm^{-1} . (See Figure 7a). These bands are similar to those found in this region by Schreyer and Yoder (1964) on both a synthetic hydrous magnesium cordierite and on a natural cordierite containing 1.62 wt% water.

Molecular water has three fundamental vibration modes; v_1 and v_3 are the symmetric and antisymmetric stretching modes and v_2 is a bending mode of lower frequency. (See Figure 7b). Farrell and Newman (1969) assigned vibrational transformations to various bands of the cordierite spectra in the region 1500cm^{-1} - 11000cm^{-1} by comparison with the spectrum of water vapour. These are shown in Table 7. The bending mode (v_2) has increased in frequency while the stretching modes (v_1 and v_3) have decreased in frequency from the gaseous to the solid state. According to Farrell and Newman, the observation of transitions of the bending mode is conclusive evidence of molecular H_2O .

The peak at 3690cm^{-1} may be indicative either of absorbed water or of the presence of tetrahedral $(\text{OH})^-$ in the cordierite structure. It was for this reason that spectra were run on the two dehydrated samples. (Heating to 750°C would be insufficient to remove structural $(\text{OH})^-$.)

Figure 8(a) Infrared spectrum of Mg-cordierite, heated to 750°C, as a KBr pellet.

Figure 8(b) Infrared spectrum of Mg-cordierite, heated to 1100°C, as a KBr pellet.

Figure 8(c) Infrared spectrum of a sample of nujol on polyethylene.

Figure 8(d) Infrared spectrum of Mg-cordierite, heated to 750°C, with nujol on polyethylene.

Spectra using KBr pellets were run on samples heated to 750°C and 1150°C and these spectra are shown in Figures 8(a) and 8(b). The peak at 3690cm^{-1} is missing, indicating that in the hydrous samples it represented water adsorbed onto the surface of the cordierite grains and not structural (OH)⁻. However the KBr spectra show a small broad peak in the region $3300\text{--}3600\text{cm}^{-1}$. KBr adsorbs water very readily so the spectra were rerun using samples mulled with nujol. The nujol on polyethylene spectrum is shown in Figure 8(c) and the spectrum of the sample heated to 750 in Figure 8(d). These spectra demonstrate that all water has been removed from the cordierite structure by heating to only 750°C which is additional evidence that all the water in cordierite is present as molecular H₂O only. This conclusion is similar to that reported by Schreyer and Yoder (1964), Gibbs (1966), Farrell and Newman (1969) and Cohen et al (1977).

(ii) Infrared spectra of cordierite between wave numbers $300\text{--}1200\text{cm}^{-1}$

The infrared spectrum of cordierite in the region $300\text{--}1300\text{cm}^{-1}$ is due to the silicate framework. The spectrum is divided into six bands, A, B, C, D, E and F. (See Figures 9 and 10), three of which A, E and F are already discernable in glass of composition $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ as shown by Langer and Schreyer. The transition from high to low cordierite is characterised by increased splitting of bands A, B, D, E and F and increasing intensity of B and C. Table 8 shows the band splitting obtained by

Figure 9 Infrared spectrum of Fe-cordierite synthesised at 700°C,
2 kilobars pressure on the graphite-methane buffer between
300-1200cm⁻¹.

Figure 10 Infrared spectrum of Mg-cordierite synthesised at 700°C.
 • 2 kilobars pressure on the graphite-methane buffer between
 300-1200 cm⁻¹.

Band System	1. High Cordierite $\Delta = 0.0$		2. Intermediate Cordierite $\Delta = 0.09$		3. Low Cordierite $\Delta = 0.21$		4. Iron Cordierite $\Delta = 0.104$	
A			297		295		300	
			344		340		355	
	387		386		386		390	
	429		426		425		430	
B			449		446		455	
			486		486		475	
	576		569		568		565	
			582		582		580	
C					598svw			
	638		621		620		670	
			679		655svw			
	677		705svw		677		690	
D					708 vw			
	768		752		751		750	
			771		771		785	
E			911		830svw		895	
	957		958		908		960	
			1029		958		1020	
					975s			
F					1010s			
					1030			
	1090				1080svw			
F			1145s		1148		1140	
	1175		1165s		1160s		1170	
			1182		1180			

Table 8 Position of band maxima in spectra of high, intermediate and low cordierite by Langer and Schreyer (1969) and of a synthetic Fe-cordierite synthesised at 700°C, 2 kilobars on the graphite-methane buffer.

Langer and Schreyer for high cordierite, an intermediate cordierite $\Delta = 0.9$ and low cordierite $\Delta = 0.21$, and for comparison the approximate values for the spectrum of an iron end-member cordierite synthesised at 700°C and 2kb on the graphite-methane buffer. The spectrum for the iron end-member cordierite is shown in Figure 9 and for a magnesium cordierite synthesised under the same conditions in Figure 10. These two spectra appear closest to the spectra of intermediate cordierites. (This agrees with the value of distortion index obtained by X-ray diffraction). Langer and Schreyer tentatively assign band F to a SiO_4 stretching mode, band E to an AlO_4 stretching mode and band A to both SiO_4 and AlO_4 bending modes. Band D is often characteristic of silicates containing six-membered rings. Bands B and C are both tentatively assigned to octahedral vibrations. The gradual appearance of G and the increased complexity of both bands represent an increasing degree of order in the mineral.

(d) Conclusions

Infrared spectra on magnesium and iron end-member synthetic cordierites have shown that all water in the cordierite can be removed by heating to 750°C and have confirmed the findings of previous workers (Schreyer and Yoder, Farrell and Newman, Cohen et al) that all the water in cordierite is present as molecular H_2O . There is no evidence for any structural water (OH^-).

Spectra of the two end-members between 300cm^{-1} and 1200cm^{-1} are similar both to each other and to spectra by Langer and Schreyer of intermediate cordierites $\Delta = 0.10$.

5. MOSSBAUER SPECTROSCOPY

(a) Introduction

Mössbauer spectra of minerals have been used to characterize the oxidation state of iron (Fe^{2+} or Fe^{3+}), the symmetry of the iron site (tetrahedral or octahedral) and to determine site occupancy factors. The Mössbauer centre shift is very sensitive to the high spin oxidation state of iron and Fe^{2+} and Fe^{3+} are readily distinguished. There is a range of centre shift for Fe^{2+} and Fe^{3+} depending on the coordination number and the site symmetry. Iron bearing cordierites show pronounced pleochroism and Mössbauer spectra have been studied for clues to the mechanism of this effect.

Mössbauer spectra of natural cordierites have been studied by Duncan and Johnson (1964) and Rossman (1976) but no spectra have yet been published of synthetic cordierites.

In the structure of cordierite there are eight crystallographically equivalent octahedral sites in which Me atoms are accommodated. However, there are two alternative sites for Fe^{2+} . These are the ring cavity sites A and B. Site A is situated in the plane of the Al-Si six-membered rings with a radius of $1.4\text{\AA}$ and site B between two adjacent six-membered rings, larger in size, with a radius of $2.2\text{\AA}$. Cohen et al (1977) place water molecules occurring in cordierite in site B and any alkali metals in site A. Fe^{3+} replaces Al^{3+} in the large T_1 tetrahedra.

As was noted in section 1 of this chapter there is disagreement over the presence or absence of structural Fe^{2+} in the ring channels (Duncan and Greenwood, 1974, Rossman, 1976).

(b) Experimental Details

Mossbauer spectra of synthetic hydrous cordierites of $(\text{Fe}/\text{Fe} + \text{Mg})$ 0.25, 0.50 and 1.00, dehydrated cordierites of $(\text{Fe}/\text{Fe} + \text{Mg})$ 0.50 and 1.00 and natural iron rich cordierites $\text{Fe}/\text{Fe} + \text{Mg} = 0.9$ from Dolní Bory, Czechoslovakia were prepared in the Chemistry Department at Carleton University by C. Bordeleau. The Mossbauer spectra were obtained from weighed samples pressed between two cellulose tapes and mounted on a perforated cardboard disc. The amount of sample used varied between 10 and 25 mg.

The spectrometer consisted of a vibration generator driven at constant acceleration with a triangular wave from the Hewlett-Packard 3300A function generator. A Northern Scientific Multichannel Scalar (NS636), operated in the multiscaling mode, was used to record the data in 1024 channels and the transmitted radiation was detected with a Reuter Stokes proportional counter (RSG-61-M₂) filled with Xe and CO₂. The pulses from the detector were then fed to the analyser which was gated to accept pulses from the 14.4 Kev gamma ray of ^{57}Co . The distance between the source and the analyser was kept constant at 10cm in all experiments. Experiments were conducted at room temperature.

Sample	Peak Assignment	Area Under Peak	Peak Position mm/sec	Centre Shift mm/sec	Quadrupole Splitting mm/sec	% Fe ²⁺ in Second site
Synthetic Hydrous (Fe/Fe + Mg) = 0.25	Fe ²⁺ oct	523114 (9110)	2.310	1.182	2.257	0%
	Fe ²⁺ oct	513472 (9521)	0.053			
Natural Hydrous (Fe/Fe + Mg) 0.90	Fe ²⁺ oct	1439398 (10482)	2.309	1.213	2.193	0%
	Fe ²⁺ oct	1441988 (10854)	0.116			
Synthetic Hydrous (Fe/Fe + Mg) 0.50	Fe ²⁺ oct	872103 (10832)	2.307	1.215	2.184	32.4%
	Fe ²⁺ oct	862743 (12494)	0.123			
	Fe ²⁺ site 2	416238 (112018)	1.701	0.941	2.520	
	Fe ²⁺ site 2	416238	0.181			
Synthetic Hydrous (0.46 mqls H ₂ O) (Fe/Fe + Mg) 1.00	Fe ²⁺ oct	1543326 (9475)	2.310	1.240	2.140	21.1%
	Fe ²⁺ oct	1549770 (10296)	0.171			
	Fe ²⁺ site 2	412425 (97421)	1.675	0.936	1.478	
	Fe ²⁺ site 2	412425	0.197			

Table 9 Mössbauer spectra parameters of synthetic hydrous

cordierite of (Fe/Fe + Mg), 0.25, 0.50 and 1.00 and of a natural iron-rich cordierite.

Figure 11. Mössbauer spectrum of a natural synthetic cordierite.
(Fe/Fe + Mg) = 0.25.

SAMPLE: NATURAL CORDIERITE $Fe/Fe+Mg = 0.90$ CORD3SA

Figure 12 Mössbauer spectrum of a hydrous natural cordierite
of $(Fe/Fe + Mg)$, 0.90.

The velocity scale was calibrated with .001" iron foil using a ^{57}Co (Pd) source and the absolute zero velocity was determined by running spectra of the same foil at different attenuation.

Spectra were analysed by fitting Lorentzian curves to the experimental points by use of a non-linear least squares regression programme. The isomer shifts are quoted relative to the centroid of iron.

(c) Experimental Results

The spectra of the hydrous cordierites are of two distinct types. The low iron ($\text{Fe}/\text{Fe} + \text{Mg}$) 0.25 synthetic cordierite and the natural iron-rich cordierite ($\text{Fe}/\text{Fe} + \text{Mg}$) >0.8 (an analysis of this cordierite is given in Appendix 2) showed a simple quadrupole spectrum with an isomer shift characteristic of Fe^{2+} high spin. (See Table 9 and Figures 11 and 12). These spectra show all the iron to be in the octahedral site. It is possible that spectra on a single crystal of the natural cordierite (similar to the oriented spectra prepared by Duncan and Johnson) would show evidence of Fe^{2+} in a second site.

In contrast to the spectra just described the spectra of the synthetic cordierites ($\text{Fe}/\text{Fe} + \text{Mg}$) 0.50 and 1.00 showed a pronounced hump on the high velocity peak. A best fit to the experimental data was obtained by fitting two quadrupole doublets. Both components of the doublet in the second site were constrained to have equal areas but the peak position was unconstrained. The computer

SAMPLE: SYNTHETIC CORDIERITE $Fe/Fe+Mg = 0.50$ CORD2SA

Figure 13 Mössbauer spectrum of a hydrous synthetic cordierite
of $(Fe/Fe + Mg) = 0.50$.

SAMPLE: SYNTHETIC CORDIERITE $\langle \text{Fe}/\text{Fe}+\text{Mg} \rangle = 1.00$ CORD45B

Figure 14 Mössbauer spectrum of a synthetic cordierite of $\langle \text{Fe}/\text{Fe} + \text{Mg} \rangle = 1.00$.

fitting to these spectra is shown in Figures 13 and 14 and the peak positions and areas in Table 9. Comparisons of the areas under the peaks indicates that 32.4% of the total iron in the intermediate cordierite and 21.1% of the total iron in the Fe-cordierite are present as Fe^{2+} in the second site. The centre shift of this second site indicates a lower coordination for this site than for the octahedral site. The water content of the intermediate cordierite was unknown but the hydrous Fe-cordierite contained 0.46 mols water per formula unit as measured by TGA.

When synthetic material with a $(\text{Fe}/\text{Fe} + \text{Mg}) > 0.50$ is heated in vacuum there is a colour change from grey to reddish brown indicating that oxidation has taken place. Spectra of dehydrated material of composition $(\text{Fe}/\text{Fe} + \text{Mg})$ 0.50 and 1.00 had lost the hump on the high velocity peak and this had been replaced by one on the low velocity peak. (See Figures 15 and 16). Two quadropole doublets were fitted to the experimental points (see Table 10). One has a centre shift characteristic of Fe^{2+} in the octahedral site and the other is an Fe^{3+} doublet. 23% of the total iron in the intermediate cordierite and 23.4% of the total iron is present as Fe^{3+} in the dehydrated samples.

(d) Discussion

There are two possible explanations for the presence of a second Fe^{2+} site in the hydrous samples. The first is that the extra peaks result from impurities in the original material and the second that

Sample	Peak Assignment	Area Under Peak	Peak Position mm/sec	Centre Shift mm/sec	Quadrupole Splitting mm/sec	% Total Fe as Fe ³⁺
Synthetic anhydrous (Fe/Fe + Mg) 0.50	Fe ²⁺ oct	650830 (9749)	2.303	1.198	2.209	23.1%
	Fe ²⁺ oct	576847 (12071)	0.094			
	Fe ³⁺	434651 (3487)	0.778			
	Fe ³⁺	184651 (131295)	-0.003	0.339	0.877	
Synthetic anhydrous (dehydrated 0.46 mols sample) (Fe/Fe + Mg) 1.00	Fe ²⁺ oct	761939 (9125)	2.303	1.220	2.165	23.2%
	Fe ²⁺ oct	735340 (10256)	0.138			
	Fe ³⁺	226194 (10256)	0.708			
	Fe ³⁺	226194 (100389)	-0.191	0.259	0.899	

Table 10 Mössbauer spectra parameters of anhydrous synthetic cordierite of (Fe/Fe + Mg) 0.50 and 1.00.

SAMPLE: HEATED CORDIERITE $\text{Fe}/\text{Fe}+\text{Mg} = 0.50$ CORD7SA

Figure 15 Mössbauer spectrum of an anhydrous synthetic cordierite ($\text{Fe}/\text{Fe} + \text{Mg}$), 0.50.

SAMPLE: HEATED CORDIERITE <Fe/Fe+Mg> = 1.00 CORD6SB

Figure 16 Mössbauer spectrum of an anhydrous synthetic cordierite of (Fe/Fe + Mg), 1.00.

part of the iron in cordierite is present in a second non-octahedral site as suggested by Duncan and Johnson (1974). The gels from which the cordierites were prepared were made up stoichiometrically and any iron in cordierite occupying a non-octahedral site must be structural. If 21% of the iron in cordierite is occupying a second site (presumably in the channels as suggested by Duncan and Johnson) this implies corresponding vacancies in the octahedral sites. This large a proportion of vacancies is crystallographically difficult to envisage. The centre shift of the second Fe^{2+} site indicates a coordination number for the site of four and is identical to those seen in spinels (Bancroft 1973). Spinels occur as impurities in the iron-rich cordierite material and it has been noted that these spinels change colour from green to reddish brown on heating while the cordierite remains unchanged. It is suggested that the magnitude of the Fe^{2+} in the second site in the hydrated material and the Fe^{3+} peaks seen in dehydrated material are an indication of the amount of impurity in the original material and are not associated with the cordierite. If iron-rich cordierites have a large proportion of their total iron in a non-octahedral site it would have been expected that the iron-rich natural cordierite would show the same phenomenon. The natural cordierite shows only a simple Fe^{2+} quadrupole spectrum indicative of all the iron in the octahedral site. Fe_2O_3 and Al_2O_3 can form solid solutions with an inverse spinel structure (Deer, Howie and Zussman, 1963).

The reddish brown high-refractive index phase seen in the dehydrated material is assumed to be an inverse spinel and is taken to be responsible for the Fe^{3+} peak in the Mössbauer spectra. Although sufficient impurities were observed in the iron-rich cordierites to account for the Mössbauer spectra there may be a small contribution from iron in a channel site. The distorted trigonal bipyramidal site in the ring channels that Duncan and Johnson (1974) postulated could be occupied by Fe^{2+} , would have a similar centre shift to Fe^{2+} in spinels and the peaks would not be resolvable. Rossman (1976) found no evidence for structural iron in the channels of natural cordierites and it is quite possible that this is the case with synthetic cordierites also.

6. CONCLUSIONS

Synthetic cordierites were prepared across the entire Mg-Fe join but iron-rich cordierites showed up to 20% of impurities which were FeMg spinels and quartz. Determinations of the distortion index and the infrared spectra indicated that all the synthetic material was orthorhombic low-cordierite. Cell parameters a , b and V increase with increase in $(Fe/Fe + Mg)$ whereas c decreases with increase in $(Fe/Fe + Mg)$. There is a small increase in cell volume for a particular composition when the cordierite is dehydrated but there is no increase in the amount of deviation of the cell from hexagonal geometry. Stout's (1975) hypothesis that dehydration will markedly increase the distortion index is not confirmed by the synthetic cordierites.

The infrared studies confirmed earlier work that all water in cordierite is present as molecular H_2O and can be removed from the cordierite structure by heating to $750^\circ C$. There are no differences in the infrared spectra of Mg-cordierites and Fe-cordierites. No conclusive evidence was found for the presence of iron in non-octahedral sites for iron-rich cordierites. The extra peaks in the Mossbauer spectra could be accounted for by spinel impurities.

CHAPTER II WATER CONTENT AND REFRACTIVE INDICES OF SYNTHETIC CORDIERITE

1. INTRODUCTION

The work of Schreyer and Yoder (1964) on the system Mg-cordierite-water showed that the H_2O content of cordierite varied with the conditions of synthesis, decreasing with increase in temperature and increasing with increase in pressure. They also showed that the refractive index is a function of H_2O content. There has been speculation (e.g. Wood, 1973) that $(Fe/Fe + Mg)$ in cordierite influences the amount of water taken up by the mineral. Experimental studies on the distribution of Fe and Mg between garnet and cordierite by Hensen and Green (1972) and Currie (1971) are in disagreement and Wood suggests that this disagreement can be reconciled if iron-cordierites contain more water than magnesium-cordierites under the same temperature and pressure conditions. The experiments of Hensen and Green were performed under dry conditions while those of Currie were at conditions where $P_{H_2O} = P_{TOTAL}$.

Cordierites are very easily hydrated and dehydrated and this has lead to analogies with the zeolite group of minerals which behave in the same way. The zeolite analogy was considered by Newton (1972) in a study of the high pressure stability limits of Mg-cordierite under wet and dry conditions. Newton found that the upper pressure stability limit of hydrous cordierite was 11.2 kilobars while under anhydrous conditions the stability limit was

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only 8.2 kilobars. He compared these findings with the work of Greenwood (1961), on the zeolite, analcime, the stability field of which is considerably reduced when $P_{H_2O} < P_{TOTAL}$.

The aim of the present study is to find a method whereby the H_2O content of cordierites synthesised under various conditions of temperature, total pressures and the activity of water can be measured. Also, to study the relationship between refractive index and H_2O content and further to determine if the amount of water is compositionally dependent.

2. WATER CONTENT DETERMINATIONS

(a) Synthesis of Cordierites

The cordierites used in this study were synthesised on the graphite-methane buffer, $(\text{GH}, \text{CH}(\text{X}, \text{OH}))$ and the nickel-bunsenite buffer, $(\text{NNO}, \text{OH}(\text{GH}, \text{COH}))$. (The buffer notation is that of Eugster and Skippen, 1967). The temperature of synthesis was from 500 to 800°C and pressures of 1 to 3 kilobars. All the cordierites used in water determinations were first subjected to X-ray diffraction and optical-microscopy.

The samples of magnesium-rich cordierites, $((\text{Fe}/\text{Fe} + \text{Mg}) 0.0 \text{ and } 0.25)$, contained few impurities and the samples used in water determinations were all better than 95% pure. The occurrence of impurities in the cordierites of $(\text{Fe}/\text{Fe} + \text{Mg}) 0.50, 0.65 \text{ and } 1.00$ has been discussed in Chapter I section 3,c, and the presence of quartz and Fe-Mg spinels noted. These impurities must be accounted for in the measurement of H_2O content.

In attempts to synthesise cordierites of all compositions at low temperatures, (550 and 600°C), the metastable phases chlorite and pyrophyllite were encountered. (The work of Schreyer and Yoder, 1964, and Richardson, 1968, had indicated the stability of cordierite at these temperatures). The metastable phases could be eliminated if the temperature at the beginning of a synthesis run was initially raised to 700°C and then after a few hours reduced to the required temperature for several days. This procedure produced cordierites without chlorite or pyrophyllite.

When a previously synthesised cordierite was hydrothermally treated, under the same or different conditions, water determinations appeared to show a large increase in H_2O content. This was a particular problem in reversal runs when previously synthesised cordierites of high H_2O content were hydrothermally treated under conditions expected to give lower H_2O values. Optical examination of these runs showed that the refractive index of the cordierites had been lowered indicating that there had indeed been a decrease in H_2O content. Examination of the material with a high power lens showed that it contained fluid inclusions. The grain size in these runs was larger than the original material and the fluid inclusions possibly resulted from the amalgamation of two or more grains trapping water between them. (Fluid inclusions were not observed in freshly synthesised material). The H_2O content of reversal runs was therefore estimated by refractive index measurements only.

(b) Water Determination

(i) Thermogravimetric analysis equipment

Analyses of natural cordierites usually give an H_2O content of 1-3 weight percent. The method used in determining the H_2O content of the synthetic material was required to accurately determine this percentage of water in the small samples, (5-15 mg), available for analysis. Thermogravimetric analysis (T.G.A.) proved a suitable method. The sample was heated in a small platinum cup at a controlled rate of heating and the weight loss against

Figure 17 Thermogravimetric analysis equipment.

increase in temperature was monitored on a two pen recording chart. The equipment consisted of a Cahn model RG electrobalance, a Cahn time-derivative computer with a Fisher accessory stand, a model 260F furnace, a model 360 linear temperature programmer and thermocouple reference. All but a few of the magnesian end-member water determinations were carried out in vacuum using a General Electric vacuum pump giving a vacuum of 0.5mm mercury. A schematic diagram of this equipment is seen in figure 17.

Since the expected weight loss was so small (0.1-0.2mg) great care was taken to ensure that all the equipment was completely anhydrous. The platinum cup was heated to 1000°C in a muffle furnace and transferred via a dessicator to the T.G.A. equipment. All tweezers, spatulas, sample containers etc., were kept in a dessicator at all times. The balance was calibrated frequently using a Cahn 10mg reference weight. Preparation of the samples themselves is described in the section on quench techniques.

(11) Accuracy and reproducibility of T.G.A. equipment.

It is a characteristic of the T.G.A. apparatus that a blank determination shows an apparent weight loss and in vacuum this weight loss is several times the actual weight loss. It is therefore necessary to cool the equipment to room temperature and allow it to re-equilibrate before taking the final weight readings (usually several hours or overnight).

<u>Run Number</u>	<u>Size of Sample(mg)</u>	<u>Calculated Wt Loss %</u>	<u>Observed Wt Loss %</u>
1	10.73	2.198	2.143
2	10.97	2.198	2.279
3	11.62	2.198	2.169
4	12.03	2.198	2.244
5	9.74	2.198	2.402
6	12.05	2.198	2.075
			<u>2.219+</u> .257.

Table 11(a) TGA determinations on a mixture of Al_2O_3 and $CaCO_3$.

<u>Run Number</u>	<u>Size of Sample(mg)</u>	<u>Wt % Water</u>	<u>Mols Water</u>
1Co-S-14Q1	8.1	1.77	0.58
1Co-S-14Q1	8.46	1.90	0.63
1Co-S-14Q1	10.73	1.72	0.57
1Co-S-14Q1	10.50	1.90	0.63
Co-S-47	7.64	1.75	0.63
Co-S-47	7.86	1.79	0.64
3Co-S-2	16.25	1.00	0.35
3Co-S-2	6.38	1.08	0.40
1Co-R-2	10.00	2.05	0.68
1Co-R-2	6.74	1.97	0.67

Table 11(b) Duplicate TGA runs to demonstrate reproducibility of the equipment

To test the accuracy of the T.G.A. equipment in the desired weight loss range, a 5 gram mixture of nineteen parts 'Analar' grade Al_2O_3 and one part 'Analar' grade $CaCO_3$ was made up as a standard. These reagents were mixed by grinding under acetone for a total of five hours. The theoretical weight loss for this mixture is 2.198 weight percent. Analyses were performed on approximately ten milligram samples. The results of the six analyses on the standard are given in Table 11(a). These results give a mean value of 2.2187 weight loss percent with a standard deviation of $\pm .257$. As the standard sample was weighed on a different balance to that used in the T.G.A. analyses and the size of the standard (5 gms) was large compared with the samples used for T.G.A. these results provided a reasonable indication of the accuracy of the T.G.A. equipment. As an additional check on the reproducibility of the T.G.A. equipment, duplicate determinations were made on several cordierite samples and these results are given in Table 11(b). These data indicate that the accuracy and reproducibility of the T.G.A. equipment are better than 0.15% weight loss percent which represents $\pm .04$ mols H_2O in cordierite.

(iii) Quench techniques and preparation of material.

Thermogravimetric analysis is capable of measuring the H_2O content of synthetic cordierites to the required degree of accuracy and reproducibility but it is also most important to know if the H_2O contents measured

Run Number	Type of Quench	Drying Conditions	Maximum Temperature of Dehydration	Weight Percent Loss	No. Mols Water
3Co-S-12Q2	Isobaric Fast	110° over 3 days	1000°C	1.80	0.63
3Co-S-12Q2	Isobaric Fast	110° over 3 days	1000°C	1.59	0.59
3Co-S-12Q1	Isobaric Slow	110° over 1 day	1000°C	1.64	0.60
3Co-S-12Q1	Isobaric Slow	110° over 1 day	Vacuum 3 days 25°C Same sample then heated to 900°C	0.3	0.62
3Co-S-12Q1	Isobaric Slow	110° over 1 day		1.48 } 1.78	
3Co-S-12Q1	Isobaric Slow	150° over 1 day	900°C	1.53	0.54
3Co-S-12Q1	Isobaric Slow	150° over 6 days	950°C	1.49	0.51
3Co-S-12Q3	Isothermal Fast	110° over 2 days	1000°C	1.32	0.46
3Co-S-12Q3	Isothermal Fast	150° over 3 days	1000°C	1.23	0.43

Table 12 Quench and drying technique TGA results.

represent the equilibrium amount at the conditions of synthesis. Various quench techniques were used to investigate this problem. Cordierites are easily dehydrated by heating to only a few hundred degrees and Schreyer and Yoder (1964) found that at 750°C and 1 atmosphere pressure, dehydration is almost instantaneous. Hydration is almost as rapid and Schreyer and Yoder obtained complete hydration in one hour at 900°C and 1000 bars pressure. There are two main quench techniques, i.e. (1) isobaric in which the run is cooled rapidly at constant pressure, and (2) isothermal, in which the pressure is reduced rapidly at constant temperature. The isobaric quench results in absorption of water on cooling and results in a higher H_2O content than the equilibrium. In an isothermal quench, the sudden release of pressure tends to extract water out of the structure, resulting in a low value. The equilibrium H_2O content must lie somewhere between the values for the isobaric and isothermal quench. In isobaric quench, experiments for material synthesised at 650°C and 2000 bars on the graphite-methane buffer, some runs were cooled as quickly as possible in a stream of compressed air and reached a temperature of under 150°C in a minute and one half. The pressure was released at this point. Other runs were simply removed from the furnace and allowed to cool slowly in air and reached a temperature of 150°C in about thirty minutes. (These two methods are referred to as fast and slow quench in Table 12.) It was found that for

Figure 18 Weight loss in synthetic Mg and Fe-cordierites with increase in temperature. (heating rate 10°/minute).

runs made at 650°C and 2000 bars on the graphite-methane buffer there was no difference in measured H₂O content using the slow and fast isobaric quenching techniques. At temperatures (800°C or higher) water is almost certainly absorbed on cooling and results in this region are unreliable. Only one isothermal quench was made on a run at 650°C and 2000 bars on the graphite-methane buffer for the same composition as the isobaric quench experiments. The isothermal quench gave an H₂O content of 1.32 weight percent against 1.59-1.81 weight percent for isobaric quench. The quench problem has been extensively studied by Duncan and Greenwood (1977) and they suggest that at temperatures below 750°C, the isobaric quench results are close to equilibrium H₂O contents.

Treatment of the material after removal from the capsule is also important. The cordierite is ground under acetone twice and then dried for various periods of time. It was found that drying in an 110°C oven for up to two weeks did not change the H₂O content but if the oven temperature was 150°C or higher, there was a reduction in H₂O content with increase in drying time. If the weight loss as a percentage of total weight loss is plotted against increase in temperature, (heating rate 10°/min) it can be seen (Figure 18) that weight loss commences between 150°C-250°C. It is complete for Fe-cordierite, dehydrated under vacuum, at 650°C and for Mg-cordierite, dehydrated in air, by 750°C. The fact that all water in the synthetic

Number	(Fe/Fe+Mg)	Type of Experiment	Initial Temperature Mean RI	°C	Pressure in bars	Buffer	Final Mean RI
1Co-R-3	0.00	Reversal	1.5445	750	1000	GH(X, OH)	1.538
1Co-S-4	0.00	Ordinary Synthesis	N/A	750	1000	"	1.536
2Co-R-1	0.25	Reversal	1.550	750	1000	"	1.540
2Co-S-3	0.25	Ordinary Synthesis	N/A	750	1000	"	1.540
3Co-R-2	0.50	Reversal	1.560	750	1000	"	1.554
3Co-S-2	0.50	Ordinary Synthesis	N/A	750	1000	"	1.553
4Co-R-1	0.65	Reversal	1.562	750	1000	"	1.557
4Co-S-2	0.65	Ordinary Synthesis	N/A	750	1000	"	1.556
Co-R-1	1.00	Reversal	1.585	750	1000	"	1.569
Co-S-27	1.00	Ordinary Synthesis	N/A	750	1000	"	1.568
1Co-H-1	0.0	Rehydration	1.524	650	2000	"	1.544
1Co-S-14Q1	0.0	Ordinary Synthesis	N/A	650	2000	"	1.5445
Co-H-1	1.00	Rehydration	1.556	650	2000	"	1.5845
Co-S-28	1.00	Ordinary Synthesis	N/A	650	2000	"	1.584

Table 13 Reversibility and rehydration experimental results

cordierites is completely removed by heating to 750°C is confirmed by infrared spectra (Chapter I, section 4(c)), which show all water removed from material heated to 750°C .

To determine whether water could be extracted from a cordierite by reduced pressure, an intermediate cordierite was held at room temperature, under vacuum, for three days before the sample was heated. Approximately ten percent of the total weight was removed in this way.

The general treatment of material prior to T.G.A. was an isobaric fast quench with the pressure released when the temperature fell below 150°C , followed by grinding under acetone twice and drying overnight in an 110°C oven. Using these techniques it is felt that H_2O content determinations on different runs, synthesised under the same conditions, are reproducible to ± 0.06 mols water.

(iv) Reversibility and hydration experiments

Several experiments were performed to see if the reaction between cordierite and water is a reversible process. Previously synthesised cordierites with a high H_2O content (0.60 mols) were treated hydrothermally at 750°C and 1000 bars on the methane buffer. An H_2O content of 0.32 mols had been found for cordierites synthesised under these conditions. Due to the fluid inclusion problem mentioned in section 2(a) reversals were checked by change in the refractive index of the material. The results of these reversal runs are given in Table 13. Also included are the refractive indices for material which was rehydrated at high temperatures and pressures following

Run Number	(Fe/Fe + Mg)	Temperature °C	Pressure In Bars	Buffer	Weight Percent Loss	No. Mols Water
1Co-S-14	0.00	650	2000	GH(X, OH)	1.72	0.57
1Co-S-14	0.00	650	2000	" "	1.90	0.63
3Co-S-12Q1	0.50	650	2000	" "	1.80	0.63
3Co-S-12Q2	0.50	650	2000	" "	1.64	0.57
Co-S-47	1.00	650	2000	" "	1.75	0.65
Co-S-24	1.00	650	2000	" "	1.82	0.66
1Co-S	0.00	675	2000	" "	1.39	0.49
Co-S-57	1.00	675	2000	" "	1.32	0.49
1Co-S-12	0.00	700	2000	" "	1.28	0.43
Co-S-36	1.00	700	2000	" "	1.24	0.46
1Co-S-1	0.00	750	1000	" "	1.03	0.34
2Co-S-1	0.25	750	1000	" "	1.08	0.36
2Co-S-2	0.25	750	1000	" "	1.05	0.34
3Co-S-1	0.50	750	1000	" "	0.99	0.35
4Co-S-1	0.65	750	1000	" "	1.01	0.35
Co-S-26	1.00	750	1000	" "	0.92	0.35

Table 14 TGA results for cordierites of different compositions

synthesised under the same conditions.

treatment of the sample by T.G.A. These results show full reversibility for all compositions. Of particular interest is the capacity of T.G.A. treated anhydrous material to react with H_2O to the same extent as indicated in the synthesis experiments.

(v) Composition dependence of water content.

To test the composition dependence of the H_2O content, cordierites of different compositions were synthesised under identical conditions. At $750^\circ C$, 1000 bars, with the graphite-methane buffer, cordierites of (Fe/Fe + Mg), 0.0, 0.25, 0.50, 0.65 and 1.00 were synthesised. At $650^\circ C$, 2000 bars, with the graphite-methane buffer cordierites of (Fe/Fe + Mg), 0.00, 0.50 and 1.00 were synthesised. The two end-member cordierites at $700^\circ C$ and 2000 bars, again using the graphite-methane buffer, were also compared. Within the limits of experimental error there is no compositional dependence on the H_2O content of a cordierite, as judged from the weight loss on T.G.A. (Table 14). However, the presence of oxidisable impurities in the iron-rich cordierites, (and the possible presence of easily oxidisable Fe^{2+} within cordierite itself) complicate the determination of the H_2O content of Fe-bearing cordierites by the T.G.A. method. It will be shown in section 3, following, that the refractive index is a more reliable indicator of H_2O content than T.G.A. measurements.

3. REFRACTIVE INDICES OF SYNTHETIC CORDIERITES

(a) Introduction

Schreyer and Yoder (1964) showed that the refractive index of synthetic Mg-cordierite increases with increase in H₂O content and give an equation for the relationship: $N_m = 1.525 + .0075 \text{ H}_2\text{O}$. H₂O is in weight percent and $N_m = \frac{N_\gamma + N_\alpha}{2} \dots 2 - 1$

The relationship between refractive indices of natural cordierites and H₂O content has been studied by Lepezin et al (1976). They used wet chemical techniques to obtain analyses for 74 natural cordierites and an additional 27 natural cordierites were analysed by electron microprobe. The H₂O contents of 58 of these natural cordierites were determined by Penfield's method. (Hildebrand et al, 1953, pp 827-828). Refractive indices of the remaining 44 cordierites were measured on both the original samples and on material that had been dehydrated in vacuum. The H₂O content was calculated by using the difference in the refractive indices of the natural and dehydrated material in the equation determined by Schreyer and Yoder (1964) and given in the previous paragraph. A regression analysis was carried out by Lepezin et al on their data to produce equations relating (Fe/Fe + Mg), H₂O content and refractive indices for cordierites. The following equation is given for cordierites rich in magnesium.

$$H_2O(N_m, F) = 132.933N_m - .044F - 206.66. \quad .2 - 2$$

For application to cordierites rich in iron the following equations are given:

$$H_2O(N_x, F) = 97.858N_x - .034F - 149.159 \quad .2 - 3$$

$$H_2O(N_y, F) = 112.624N_y - .0329F - 171.043. \quad .2 - 4$$

H_2O is weight percent and F is $(Fe/Fe + Mg)$.

As well as H_2O , natural cordierites may contain $(O_2, He$ and A in the large cavities between two adjacent six-membered rings. (Lepezin and Melenevsky, 1977). Often present also are alkali and other cations (Na^+, K^+, Ca^{2+}, Cs^+) within the ring channels in the plane of the six-membered ring (Cohen et al, 1977). Cordierites from granulite facies terrains may contain 0.6-0.8 weight percent CO_2 (Suknev et al, 1971). The refractive indices measured by Lepezin et al (1976) reflect the influence of these other elements and molecules which makes comparison with the refractive indices of the synthetic cordierites difficult. However, when natural cordierites are heated in vacuum, A, He and CO_2 will be removed together with H_2O and the refractive indices of the anhydrous synthetic cordierites have been compared with refractive indices of anhydrous natural cordierites calculated from the equations of Lepezin et al.

(b) Measurement of refractive indices

It proved impossible to measure three refractive indices of the synthetic cordierites as the material is very fine-grained. The stated values in Tables 15 and 16

Run Number	Pressure of synthesis in bars	Temperature of synthesis in °C	Buffer used	Mols water in cordierite	Minimum RI(A)	Maximum RI	Mean RI (A+B)/2
1Co-S-5 TGA			dehydrated material	0.0	1.520	1.528	1.524
1Co-R2 TGA			dehydrated material	0.0	1.521	1.530	1.5255
1Co-S-2	1000	750	GH, (X, OH)	0.34	1.533	1.539	1.536
1Co-S-4	1000	750	GH, (X, OH)	0.34	1.533	1.539	1.536
1Co-S-5	2000	750	GH, (X, OH)	0.39	1.536	1.542	1.539
1Co-S-12	2000	700	GH, (X, OH)	0.45	1.539	1.545	1.542
Co-S-14Q1	2000	650	GH, (X, OH)	0.61	1.541	1.548	1.5445
1Co-S-13	1000	650	GH, (X, OH)	0.46	1.539	1.543	1.541

Error in water content estimated as ± 0.06 mols

Table 15 Mean refractive indices of Mg-cordierites of known water content.

Figure 19 Variation of mean refractive indices of Mg-cordierite with H_2O content.

are for the mean refractive index which was determined as follows: The oil or mixture of oils which most closely matched the minimum refractive index (A) of all the cordierite grains in a slide was determined using white light, this was refined using NaD light and the refractive index of this oil measured using a Bausch and Lomb refractometer. The maximum value of refractive index (B) was determined in the same way. The range of values given for each sample represents at least two determinations measured on separate occasions and where these determinations differ, both sets of values are given. The mean refractive index is defined as $(A + B)/2$ and is analogous to the parameter, N_m , reported by Schreyer and Yoder (1964).

(c) Refractive indices of magnesium cordierite.

The water contents of the magnesium cordierites in Table 15 were determined by thermogravimetric analysis and the refractive indices by the method just described. The water content is reported as the number of mols of water per formula unit. The refractive index of Mg-cordierite agrees well with a value of 1.524 obtained from the equation of Lepezin et al for Mg-cordierites (2 - 2).

Polynomials of degree 1 and 2 were fitted to the refractive indices and water contents for the Mg-cordierites using a Carleton University Geology Department programme (FILIPU) developed by W. Yzerdraat. A one degree equation fitted the data for the Mg-cordierites and R^2 and the standard error were not significantly improved by a second

degree fit. If W_{Mg} is the number of mols water in cordierite and RI_{Mg} is the mean refractive index of the Mg-cordierite

$$RI_{Mg} = 1.52489 + .03431W_{Mg} \quad .2 - 5$$

$$R^2 = .982$$

$$St\ error = .001$$

$$W_{Mg} = -43.6435 + 28.6381RI_{Mg} \quad .2 - 6$$

$$R^2 = .982$$

$$St\ error = .031$$

The plot of refractive index versus water content for the Mg-cordierites is shown in Figure 19.

(d) Refractive indices of Fe-cordierites

When Fe-cordierite of $(Fe/Fe + Mg)$ greater or equal to 0.50 is dehydrated in vacuum a colour change is observed from pale grey to reddish-brown. It was noted in Chapter I section 3 that this colour change is related not to the cordierite but to the spinel inclusions which change colour from pale green to reddish-brown and increase their refractive indices considerably. Mossbauer spectra indicated that the Fe^{2+} spinel peak is replaced by a peak corresponding to Fe^{3+} . The proportion of the total Fe^{2+} in the spinel peak is a direct indication of the amount of impurity in the original material. It is suggested that the Fe^{2+} in the spinel impurity (hercynite, $FeAl_2O_4$, in the case of Fe-cordierite) has been oxidised to give a haematite-corundum solid solution. (Extensive solid solution between haematite (Fe_2O_3) and corundum Al_2O_3 is possible,

e.g. Deer, Howie and Zussman, 1962 v5 p 14.)

Due to the presence of impurities it is not possible to obtain a direct correlation between the refractive indices of Fe-cordierites and water contents determined from T.G.A. results. As well as uncertainty over the percentage of Fe-cordierite in the material analysed by T.G.A. there is a weight increase caused by the oxidation of hercynite. The problem has therefore been approached indirectly.

The mean refractive indices of these dehydrated synthetic Fe-cordierites were measured and had values of 1.5535, 1.5540 and 1.5545. This agrees well with a value of 1.5535 obtained from the equations of Lepezin et al (1977). From equation 2 - 3, n_α can be calculated and from equation 2 - 4, n_γ can be calculated. The mean refractive index is $(n_\alpha + n_\gamma)/2$. A value of 1.554 was adopted for the mean refractive index of anhydrous Fe-cordierite.

The position of H_2O in cordierites, in the large cavities, radius 2.2Å, between two adjacent six-membered rings is undisputed. (Gibbs, 1966; Cohen et al 1977; Farrell and Newman, 1967; Lepezin and Melenevsky, 1977 and others). None of these workers have suggested any variation in the position of H_2O in cordierite with change in (Fe/Fe + Mg). It would therefore be expected that the effect of water on the refractive index of the mineral should be very similar in both cases. Therefore the assumption was made that the slope of the refractive index versus water content curve for Mg-cordierite was applicable

Run Number	Pressure Temperature of synthesis		Buffer Used	Mols water in cordierite	Minimum		Maximum RI(B)	Mean RI (A+B)/2
	in bars	in °C			RI(A)			
Co-S-47TGA		dehydrated material		0.0	1.549		1.558	1.5535
Co-S-36TGA		"	"	0.0	1.550		1.558	1.554
Co-S-42TGA		"	"	0.0	1.550		1.568	1.564
Co-S-35TGA		"	"	0.0	1.549		1.560	1.5545
Co-S-27	1000	750	GH(X, OH)	0.34	1.565		1.571	1.568
Co-S-26	1000	750	GH(X, OH)	0.35	1.565		1.573	1.568
Co-S-25	1000	750	GH(X, OH)	0.34	1.565		1.573	1.569
Co-S-35	1000	650	NNO, OH(GX, COH)	0.38	1.565		1.573	1.569
Co-S-36	2000	700	GH(X, OH)	0.46	1.572		1.586	1.576
Co-S-33	2000	700	GH(X, OH)	0.51	1.573		1.581	1.577
Co-S-47	2000	650	GH(X, OH)	0.65	1.580		1.588	1.584
Co-S-42A	2000	650	GH(X, OH)	0.61	1.579		1.587	1.5835
Co-S-21	1000	640	NNO, OH(GX, COH)	0.45	1.574		1.582	1.578
Co-S-57	2000	675	GH(X, OH)	0.49	1.573		1.581	1.577
Co-S-32	2000	600	GH(X, OH)	0.77	1.5781		1.5889	1.585

Table 16 Mean refractive indices of Fe-cordierite with water contents
measured by TGA experiments.

Figure 20 Variation of mean refractive indices of Fe-cordierite with H_2O content.

to Fe-cordierite. If the slope obtained from the Mg-cordierite curve is run through the point 1.554 (zero water content) the line shown as the theoretical curve in Figure 20 is obtained. Also shown in Figure 20 are the refractive indices of some iron cordierites from samples containing both Fe-cordierite and Fe-spinel. These refractive indices are plotted against the observed water contents of the samples from T.G.A. measurements (Table 16). The equation of the theoretical curve is given as follows, where RI_{Fe} is the mean refractive index of the iron-end member and W_{Fe} is the number of mols water in Fe-cordierite.

$$RI_{Fe} = 1.554 + .03431 W_{Fe} \dots \dots \dots .2 - 7$$

$$W_{Fe} = -45.293 + 29.146 RI_{Fe} \dots \dots \dots .2 - 8$$

The validity of this line can be checked against the sample of Fe-cordierite plus impurities that was studied by Mössbauer spectroscopy (see Chapter I section 5). The Mössbauer spectra for this sample indicate that between 21 and 23 percent of the total FeO is present in the spinel phase. The starting 'gel' for Fe-cordierite contained 22.1735 weight percent FeO, and it follows that between 4.6 and 5.1 weight percent FeO was present in the spinel. During thermogravimetric analysis the iron in the spinel was oxidised, i.e.

The stoichiometry of this process requires a weight increase of 11 percent from FeO present in spinel to Fe_2O_3 present in haematite-cordierite solid solution. This implies a

Figure 21 Comparison of H_2O content in an Fe-cordierite calculated from Mössbauer spectrum results with theoretical refractive index. H_2O content curve.

weight gain of between 0.51 and 0.56 weight percent. Thus, at the end of the T.G.A. experiment; the apparent weight loss of the sample is the net result of the weight loss due to the extraction of H_2O from cordierite and a weight gain due to oxidation of FeO in spinel. For the sample in question the apparent weight loss was 1.08 - 1.40 weight percent (allowing for uncertainty in T.G.A.) and this added to the weight of oxidation gives between 1.59 and 1.96 weight percent for the total water loss. Allowing for the fact that only 77 - 79 percent of the sample is Fe -cordierite it follows that the water content of the Fe -cordierite was between 2.27 and 2.54 weight percent which corresponds to between 0.82 and 0.92 mols H_2O . The mean refractive index of the material is 1.578. These results are shown in Figure 21 together with the theoretical curve calculated from equation 2 - 7. There is reasonable agreement between the theoretical refractive index line and the Mossbauer result and this provides evidence that the theoretical line is valid.

(e) Prediction of $(Fe/Fe + Mg)$ from mean refractive index.

The $(Fe/Fe + Mg)$ of synthetic cordierites can be determined from the measurement of mean refractive index of anhydrous samples. The close agreement between the mean refractive index of Mg and Fe -cordierites with the values calculated from the equations of Lepezin et al (1976) indicates that $(Fe/Fe + Mg)$ of natural cordierites could also be predicted from the mean refractive index of

Figure 22 Variation of mean refractive indices of anhydrous synthetic cordierites with (Fe/Fe + Mg).

dehydrated samples. The mean refractive indices of dehydrated samples of all compositions lie on a straight line. The equation for the line shown in Figure 22 is

$$F = -52.586 + 34.483RI \dots \dots \dots .2 - 9$$

where $F = (Fe/Fe + Mg)$ and RI_F is the mean refractive index of the sample.

4. WATER CONTENT MODELS

(a) Introduction

Even under laboratory conditions, difficulty is encountered in ensuring that the H_2O content of cordierite represents the equilibrium H_2O content for the conditions of synthesis. (See Section 2, c, iii of this chapter). It is therefore unlikely that the H_2O contents of natural cordierites represent the equilibrium H_2O content at the time of mineral formation. Instead, the contents of the ring channels of natural cordierites reflect the cooling history of the mineral. It is necessary to know the water content of natural cordierites at the time reactions observed in the rocks actually took place in order to calculate meaningful phase relationships. Models are needed that will allow calculation of the H_2O content of natural cordierites at any specified temperature and water fugacity. Water distribution data from synthetic cordierites prepared under controlled conditions makes calculation of these models possible.

(b) Water content model for Mg-cordierite (Model A)

Data on the distribution of water in synthetic Mg-cordierite are available from this study, from Duncan and Greenwood (1977) and from the work of Schreyer and Yoder (1964).

There is room in the cages between two adjacent six-membered rings of cordierite for one molecule of water only. (Lepezin and Melenevsky, 1977). This would

	Temperature Centigrade	Pressure In Bars	Buffer Used			$\ln K =$ $-\ln f_{H_2O} + \ln X$ $-\ln(1-X)$	
				$\ln f_{H_2O}$	X		$-RT \ln K$
*	750	1000	GH(X,OH)	6.581	0.25	-7.6796	15612
*	750	1000	" "	6.581	0.32	-7.3348	14917
*	700	1000	" "	6.546	0.46	-7.0355	13604
*	650	1000	" "	6.493	0.38	-6.6533	12203
Δ	750	1000	None	6.696	0.406	-7.0799	14393
Δ	650	1000	"	6.554	0.52	-6.4739	11874
*	750	2000	GH(X,OH)	7.216	0.38	-7.7055	15802
*	700	2000	" "	7.143	0.45	-7.3437	14199
*	675	2000	" "	7.098	0.49	-7.1380	13447
*	650	2000	" "	7.051	0.59	-6.6870	12266
*	650	2000	" "	7.051	0.61	-6.6037	12112
*	600	2000	" "	6.928	0.76	-5.7753	10019
Δ	750	2000	None	7.291	0.38	-7.7805	15956
Δ	650	2000	"	7.090	0.622	-6.5919	12091
Δ	560	2000	"	6.788	0.815	-5.3052	8676
O	700	2000	None	7.202	0.62	-7.1220	13771
O	600	2000	"	6.953	0.62	-6.4635	11213
*	650	3000	NNO,OH(X,OH)	7.538	0.74	-6.4918	11907

* Results this study.

Δ Results Duncan & Greenwood (1977)

O Results Schreyer & Yoder (1964)

Table 17 Experimental results of water distribution in Mg-cordierite at temperatures between 550°C and 750°C and pressure up to 3 kilobars.

allow a maximum H₂O content for Mg-cordierite of 3 weight percent. No synthetic cordierites have been prepared with more than 3 weight percent water and hydrated inclusions or retrograde minerals in natural cordierites are sufficient to account for the small number of published cordierite analyses containing more than 3 weight percent water. This model proposes that fully hydrated cordierite contains one molecule of water per formula unit and it is suggested that the appropriate stoichiometry of the reaction is:

The molar volumes of the hydrated and dehydrated cordierites are practically identical (see Tables 4, 5 and 6) and the energy arising from the volume change of solids over the pressures involved in this study is negligible. Only temperatures of 750°C or less were considered to minimise quench problems. Results at 1, 2 and 3 kilobars were available from this study. Other distribution data from Duncan and Greenwood (1977) and Schreyer and Yoder (1964) in the temperature range 550 - 750°C and pressures, 1 - 3 kilobars, were also included. In order to calculate an equilibrium constant for reaction, 2 - 10, it is necessary to determine the activity *a*, or fugacity *f*, of each of the participating species. The equilibrium constant for 2 - 10 is written as:

$$K_{\text{Mg}} = \frac{a_{\text{Mg}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18} \text{H}_2\text{O}}}{a_{\text{MgAl}_2 \text{Si}_2 \text{O}_6} \cdot f_{\text{H}_2\text{O}}} \quad \dots \quad 2 - 11$$

Figure 23 Standard free energy change, ΔG° , for the reaction $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} + \text{H}_2\text{O} + \text{MgAl}_4\text{Si}_5\text{O}_{18}\text{H}_2\text{O}$ plotted against temperature.

The fugacity of H_2O is experimentally controlled but a solution model is required to estimate the activities of the remaining components. An ideal solution between $Mg_2 Al_4 Si_5 O_{18}$ and $Mg_2 Al_4 Si_5 O_{18} H_2O$ has been assumed for cordierite with the activity of the hydrous component given by the experimentally determined water content X_{H_2O} , and the activity of the remaining component given by $1 - X_{H_2O}$ since the solution is binary. If the number of mols of water produced for a particular set of conditions is $X(0-1)$ then the equilibrium constant for the reaction at this point is:

$$\ln K = -\ln f_{H_2O} + \ln X - \ln(1-X) \dots\dots\dots 2 - 12$$

(The standard free energy change for reaction 2 - 10,

ΔG° is $-RT \ln K$.) The experimental results and the $\ln K$'s and ΔG° 's calculated from them are shown in Table 17.

Figure 23 shows ΔG° plotted against $T^\circ C$ and $T^\circ K$.

A least squares fit was calculated to give the following equations:

$$\Delta G^\circ = -21647 + 36.0T \dots\dots\dots 2 - 13$$

$$\ln K = \frac{10893}{T} - 18.47 \dots\dots\dots 2 - 14$$

If the temperatures and fugacity of water are known for the synthesis of a particular cordierite, combination of equations 2 - 14 and 2 - 12 allows calculation of the H_2O content from a plot of $\ln X - \ln(1-X)$. This function (see Figure 24) tails off to plus and minus infinity at the two ends and must be considered most sensitive for H_2O content from $X = 0.1 - 0.9$ mols H_2O . It now becomes

Figure 24 Correlation of the function $\ln X - \ln(1-X)$ with number of mols H_2O , (X), in cordierite.

Figure 25 Variation of the H₂O content of Mg-cordierite (in mols) with temperature and pressure where $P_{\text{TOTAL}} = P_{\text{H}_2\text{O}}$.

possible to calculate equilibrium H_2O contents for Mg-cordierite under a range of conditions. In Figure 25 a pressure-temperature diagram contoured with values of H_2O for Mg-cordierite is given, for the condition where $P_{H_2O} = P_{TOTAL}$. The values of the water fugacity used in calculating this diagram were from Burnham, Holloway and Davis (1969).

(c) Water content model for Fe-cordierites (Model B)

The only water distribution data available for Fe-cordierite are from the present study. The H_2O content, X , for each of the experimental points was determined by measuring the mean refractive index of the material and using equation 2 - 8 to calculate the H_2O content.

The activity of $Fe_2 Al_4 Si_5 O_{18} H_2O$ is given by X_{H_2O} and the activity of $Fe_2 Al_4 Si_5 O_{18}$ by $1 - X$. The stoichiometry of the reaction is:

As with Mg-cordierite, equilibrium constants ($\ln K$) and standard free energy changes ΔG° were calculated for each experimental point (Table 18). A plot of ΔG° versus temperature defined a straight line indicating that the model of ideal mixing has some validity. The equations for this straight line are:

$$\Delta G^\circ = -35377 + 49T \quad \dots \quad 2 - 16$$

$$\ln k = \frac{17802}{T} - 24.66 \quad \dots \quad 2 - 17$$

(Figure 26)

At temperatures less than $800^\circ C$ Fe-cordierite contains more water than Mg-cordierite synthesised under the same

Pressure, in Bars	T°C	T°K	Buffer	Mean RI	Calculated		lnk	ΔG°
					Observed Water Content	Water Content X		
1000	750	1023	GH, CH(X, OH)		.34	.44	-6.822	13869
1000	650	923	"	1.5765	.46	.65	-5.8740	10774
2000	750	1023	"	1.571	.38	.505	-7.2710	14782
2000	675	948	"	1.577	.49	.67	-6.3900	12034
2000	650	923	"	1.5835	.61	.86	-5.2357	9604
2000	650	923	"	1.584	.65	.87	-5.1500	9446
2000	700	973	"	1.577	.47	.67	-6.4348	12442
2000	700	973	"	1.576	.45	.64	-6.5676	12699
2000	600	873	"	1.585	.77	.90	-4.7308	8207
1000	650	923	NNO, OH(GX, COH)	1.568	.36	.41	-4.8760	8459
2000	610	883	"	1.574	.45	.58	-5.220	9160

Table 18 Water distribution data in Fe-cordierite at temperatures between 600°C and 750°C at 1 and 2 kilobars pressure.

Figure 26 Standard free energy change, ΔG° , for the reaction $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}\text{H}_2\text{O}$ plotted against temperature.

conditions. This is obvious in a pressure-temperature diagram contoured for values of X_{H_2O} in Fe-cordierite for the situation where $P_{H_2O} = P_{TOTAL}$ (Figure 27). Once again, the values of water fugacity were taken from Burnham, Holloway and Davis (1969).

Figure 27 Variation of the H₂O content of Fe-cordierite (in mols) with temperature and pressure where $P_{H_2O} = P_{TOTAL}$.

5. CONCLUSIONS

Thermogravimetric analysis provided a method for determining the water content of Mg-cordierite to a reproducibility of ± 0.06 mols H_2O . Measurement of the refractive indices of the analysed material gave a correlation of water content of Mg-cordierite with refractive index.

Due to impurities, thermogravimetric analysis did not give an accurate water content for Fe-cordierite. However the water content could be obtained from refractive index measurements using a line with the same slope as the Mg-cordierite, refractive index line, through the refractive index of pure anhydrous Fe-cordierite. Mossbauer spectra of Fe-cordierites showed impurities in the samples as Fe^{2+} in spinel site for the hydrous cordierite and as Fe^{3+} for the dehydrated material. The refractive index, observed water content and percentage of impurity were known for one Fe-cordierite and this provided a means to test the validity of the theoretical refractive index, water content line for Fe-cordierites.

The $(Fe/Fe + Mg)$ of a cordierite can be determined by a measurement of the refractive index of the dehydrated material.

It was assumed that an exchange reaction takes place involving the mixing of water molecules and vacancies within the channel sites of the cordierite. The two end-members of this exchange reaction are anhydrous cordierite and a cordierite containing one mole

of water per formula unit. An assumption of ideal mixing in the channel sites was made and proved adequate for the distribution data of both Mg and Fe-cordierites. Two models were presented for calculating water contents of Mg-cordierite and Fe-cordierite, if the temperature and water fugacity of synthesis are known. There is a definite compositional difference in water content between Mg and Fe-cordierites synthesised under the same conditions.

Those conclusions described above which are dependent on the use of an ideal solution model to calculate the activities of anhydrous and hydrous cordierite species should be regarded as tentative. The use of the solution model in this case does not imply the substitution of one ion for another but the ideal mixing of water molecules and vacancies within the cordierite structure. Although the magnitude of the energy change, caused by the mixing of water molecules and vacancies, has been indicated by the work of Newton (1972) and Greenwood (1961), it would be desirable to experimentally verify that within the pressure-temperature limits used in calculating activities of cordierite species in this study, that the energy change can indeed be represented by an ideal solution model.

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PART TWO
CORDIERITE REACTIONS
AND PHASE RELATIONS

CHAPTER I Fe-CORDIERITE REACTIONS IN THE SYSTEM

1. INTRODUCTION

In Part I, Chapter II, the variation of the water content of synthetic cordierites was studied with respect to temperature, pressure and the fugacity of water. A definite difference in the H_2O content of Mg and Fe-cordierites was found. Fe-cordierites contained significantly more water at low temperatures than Mg-cordierites synthesised under the same conditions. Models were presented for calculating the H_2O content of either end-member if the temperature and water fugacity under which the cordierite was synthesised, are known. Model A is applicable to Mg-cordierite and Model B to Fe-cordierite.

The stability of silicates containing iron is dependent not only on pressure and temperature but on oxygen fugacity. To illustrate the changes in stability of iron minerals with variation in the composition of the fluid, $\log f_{\text{O}_2}$ -T diagrams at constant pressures have commonly been employed. Even for the most oxidising natural systems however, oxygen is an insignificant proportion of the fluid, which may be thought of as a mixture of water and hydrogen. Information given in $\log f_{\text{O}_2}$ -T diagrams may also be presented in terms of T-X sections where X is the mole fraction of hydrogen or water in the mixture.

Experimental work in the system $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ has used buffers to control the hydrogen fugacity and an assessment of the reliability of the buffers used is important. Any assemblage of solids or solids and gases which has a fixed fugacity of either oxygen or hydrogen for a given temperature and pressure can be used in combination with water to fix the proportions of water, hydrogen and oxygen in the reacting fluid. The common buffers in the system OH are given in Table 1. The reliability of these buffers varies greatly. The most reliable buffer is the graphite methane buffer, $\text{GH}, \text{CH}(\text{X}, \text{OH})$, as methane gas is both buffer and pressure medium and the buffer reaction precipitates graphite. This enables very long runs to be made without loss of buffering capacity. There is a danger with any solid-solid buffer, that during a long run, one or other of the phases will be exhausted and the buffering capacity of the system lost. This is a particular problem with buffers fixing a high ratio of hydrogen to water, QFI or MW for example. The buffering capacity of the QFI system is exhausted after runs of a few hours, or at the most a day, and the buffer must be constantly renewed during the time necessary for the direction of a reaction to become apparent. Apart from problems of buffer stability, there have been difficulties encountered in calculating fluid compositions. Poor thermochemical data for magnetite had resulted in inaccurate equations for any buffer containing this phase, but work on the thermochemistry of the iron oxides, by

BUFFER ASSEMBLAGES

4 Fe ₃ O ₄ + O ₂ magnetite	=	6 Fe ₂ O ₃ haematite	(HM)
2 Ni + O ₂ nickel	=	2NiO nickel oxide	(NNO)
3 Fe ₂ SiO ₂ + O ₂ fayalite	=	2 Fe ₃ O ₄ + 3SiO ₂ magnetite quartz	(QFM)
6 FeO + O ₂ wustite	=	2 Fe ₃ O ₄ magnetite	(MW)
$\frac{3}{2}$ Fe + O ₂ iron	=	$\frac{1}{2}$ Fe ₃ O ₄ magnetite	(MI)
2Fe + O ₂ iron	=	2 FeO wustite	(WI)
2 Fe + SiO ₂ + O ₂ iron quartz	=	Fe ₂ SiO ₄ fayalite	(QFI)
C + 2H ₂ graphite	=	CH ₄ methane	graphite-methane

Table 1 Common buffer assemblages in the system OH
used in experimental work involving iron
silicates.

Haas and Robie (1973), has removed this problem. The equation for the MW buffer has been recalculated by Skippen (personal communication) and found to predict accurately the temperature of intersection of the graphite-methane and MW buffer, which has been experimentally determined by the author. The most accurate equation for the QFM buffer is from an experimental determination of the reaction $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 \rightleftharpoons 3\text{Fe}_2\text{SiO}_4 + \text{O}_2$ by Hewitt (personal communication to G.B. Skippen). The equation determined by Hewitt, accurately predicts the hydrogen fugacity determined by Eugster, (personal communication). This author used a hydrogen sensor (consisting of Ag + AgCl and 3M HCl inside a platinum capsule) and equilibrated it with the QFM assemblage. The equations used in the calculation of $\log f_{\text{O}_2}$ for the solid-solid buffers are given in Table 2.

This chapter will attempt to show the significance of variable water content in cordierite on some reactions in the system, $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} - \text{H}_2$, and to show how slight changes in the calculation of buffer curves may also have an important effect on calculated phase relations. A review of the experimental work in this system has been given in the general introduction and will not be repeated here. Of particular interest in this system is the relationship between cordierite and garnet which is important petrologically. The reaction

$$3 \text{ cordierite} \rightleftharpoons 2 \text{ almandine} + 4 \text{ sillimanite} + 5 \text{ quartz}$$

(vapour)

Buffer Assemblage		$\log f_{O_2} = -\frac{A}{T} + B + C \frac{(P-1)}{T}$			Source
		A	B	C	
NiO-Ni	NNO	24930	9.36	.046	Huebner and Sato (1970)
SiO ₂ - Fe ₂ SiO ₄ - Fe ₃ O ₄	QFM	25738	9.00	.092	Wones and Gilbert (1969)
SiO ₂ - Fe ₂ SiO ₄ - Fe ₃ O ₄	QFM	24770	8.47	.092	Hewitt
Fe ₃ O ₄ - 'FeO'	MW	34667	14.45	.083	Skippen
Fe ₃ O ₄ - 'FeO'	MW	32730	13.12	.083	Eugster and Wones (1962)
SiO ₂ - Fe ₂ SiO ₄ - Fe	QFI	29382	7.51	.050	Eugster and Wones (1962)

Table 2 Equations used for calculating $\log f_{O_2}$ for various buffer assemblages.

has been studied by Richardson (1968) and Weisbrod (1973). Both determinations of this reaction (the former author using the QFM buffer and the latter the QFI buffer) show a slight negative slope with garnet produced on the high temperature side of the reaction. If cordierite is treated as an anhydrous phase, this is a solid-solid reaction, which typically has a positive slope in P-T space. Cordierite with its low density should be stable on the low pressure, high temperature, side of the reaction.

Froese, (1973), studied phase relationships in the system, $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{O}_2$, at 2 kilobars, particularly the oxidation of cordierite and almandine. Five isobaric invariant points have been experimentally determined in this system at 2 kb. They are: quartz-almandine-hercynite-cordierite-fayalite, (Hsu 1968); quartz-almandine-hercynite-magnetite, (Hsu 1968); quartz-almandine-hercynite-cordierite-magnetite, (Rutherford and Eugster 1967), quartz-sillimanite-hercynite-cordierite, (Richardson 1968) and quartz-sillimanite-hercynite-cordierite, (Rutherford 1970). (An invariant assemblage is one which has no degrees of freedom, and pressure, temperature, $\log f_{\text{O}_2}$ and the compositions of the phases are all fixed). These phase relations are complicated at high temperatures by the presence of magnetite (Fe^{2+} ($\text{Fe}^{2+}, \text{Fe}^{3+}$) O_4) and hercynite ($\text{Fe}^{2+}(\text{Al}^{3+}) \text{O}_4$) solid solutions. (At low temperatures, the only stable oxide phase is nearly pure magnetite). A solvus exists between

magnetite and hercynite and this has been studied by Turnock and Eugster (1962). Froese fitted a two-constant Margules solution model to the data of Turnock and Eugster and derived activity coefficients for magnetite and hercynite. In Froese's analysis of the phase relations, cordierite was treated as an anhydrous phase and he found that for the reaction,

$$2 \text{ garnet} + 4 \text{ sillimanite} + 5 \text{ quartz} \rightleftharpoons 3 \text{ cordierite},$$

cordierite is stable on the high temperature side of the reaction. The calculations have been repeated taking into account the activity of anhydrous cordierite in cordierite

2. THE REACTION 3 CORDIERITE + 2 ALMANDINE +
4 SILLIMANITE + 5 QUARTZ + VAPOUR

Any reaction involving cordierite implies the simultaneous reaction between cordierite and water. The models developed in Chapter II of Part I of this study assume that cordierite containing one mole of molecular water per B channel site is saturated. (Cordierite monohydrate will henceforth be referred to as hydrous cordierite). The models also imply that ideal mixing of water and vacancies occurs in the channels. Richardson (1968) does not give the refractive index of the Fe cordierites found in his reaction runs but the H₂O content of each experimental point can be estimated using Model B (See Part I Chapter 2). Five experimental points define the reaction. We can consider two end-member equilibria, one involving anhydrous cordierite and the other hydrous cordierite.

The anhydrous equilibrium:

The hydrous equilibrium:

Subtraction of equation 3 - 1 from 3 - 2 and division by three gives the following:

This reaction, 3 - 3, is the Fe-cordierite hydration reaction. If X is the mole fraction of hydrous cordierite

Temp °C	Press in Kbars	Dir'n Reaction	Buffer Used	ln fH ₂ O	$\frac{\Delta VS(P-1)}{RT}$	X	$\frac{\ln K + \Delta VS(P-1)/RT}{\text{anhydrous} \quad \text{hydrous}}$
700	3.5	+	QFM	7.764	-7.336	.80	-2.508 16.625
700	3.0	+	QFM	7.588	-6.288	.77	-1.879 -17.260
750	2.5	+	QFM	7.494	-4.983	.56	-2.520 19.238
775	2.5	+	QFM	7.537	-4.864	.46	-3.015 20.077
775	3.0	+	QFM	7.732	-5.838	.51	-3.698 19.378
<p>Anhydrous $3 \text{ Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18} \rightleftharpoons 2 \text{ Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 4 \text{ Al}_2\text{SiO}_5 + 5 \text{ SiO}_2$</p> <p>lnk = -3ln (1-X)</p>							
<p>Hydrous $3 \text{ Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}\text{H}_2\text{O} \rightleftharpoons 2 \text{ Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 4 \text{ Al}_2\text{SiO}_5 + 5 \text{ SiO}_2 + 3 \text{ H}_2\text{O}$</p> <p>lnk = 3 ln fH₂O - 3 ln X</p>							
<p>Molar Volume Minerals</p>							
				Cordierite	237 cm ³		
				Sillimanite	49.90	$\Delta V_F = -167.40 \text{ cm}^3$	
				Almandine	115.28	$= -4.05 \text{ cal/car}$	
				Qtz	22.688		

Table 3 Calculation of lnK₁ bar anhydrous and lnK₂ bar hydrous for the reaction,
 Fe-cordierite $\rightleftharpoons$ almandine + sillimanite + quartz from the data of
 Richardson (1968).

and (1-X) the mol fraction of anhydrous cordierite, the equilibrium constants of equilibria 3 - 1 and 3 - 2 are as follows:

$$\ln K_{P_{3-1}} = -3\ln(1-X)$$

$$\ln K_{P_{3-2}} = 3\ln f_{H_2O} - 3\ln X$$

The molar volumes of all phases in the reaction, except Fe-cordierites, are taken from Helgeson et al (in press). The Fe-cordierite molar volume of 237 cm³ was calculated from the cell volumes given in Chapter I, Part I. (This value agrees with that of Hsu (1968)).

For each of Richardson's (1968), experimental points the water content of the cordierite, (X), water fugacity, f_{H_2O} , and $\Delta V_s(P-1)/RT$, were calculated. (ΔV_s is the volume change in the reaction given in cal/bar). (Table 3). Values of $\ln K_P + \Delta V_s(P-1)/RT = \ln K_{1 \text{ bar}}$ for both equilibria 3 - 1 and 3 - 2 were plotted against reciprocal temperature. The position of the lines drawn through the two sets of data is constrained by the requirement that

$$\ln K_{3-1} - \ln K_{3-2} = \ln K_{3-3}.$$

The equations for the two lines at 1 bar are as follows:

$$\ln K_{1 \text{ bar } 3-1} = \frac{16500}{T} - 19.125 \text{ (anhydrous)} \quad \dots \quad 3-4$$

$$\ln K_{1 \text{ bar } 3-2} = \frac{-40125}{T} + 58.03 \text{ (hydrous)} \quad \dots \quad 3-5$$

Figure 1. $\ln K - 1/T$ plot for the equilibrium: $3\text{Fe}_3\text{Al}_4\text{Si}_5\text{O}_{18} + 2\text{Fe}_3\text{Al}_3\text{Si}_3\text{O}_{12} = 4\text{Al}_2\text{SiO}_5 + 5\text{SiO}_2$ (Data are from Richardson 1968).

Figure 2. $\ln K - 1/T$ plot for the equilibrium:

For each end-member equilibrium (i.e. 3-1 and 3 - 2) equations were calculated, (using 3 - 4 and 3 - 5), for various activities of either hydrous, or anhydrous cordierite, at a series of pressures. (For example, when the activity of the hydrous cordierite is 0.7, the line generated from equation 3 - 5 ($\ln K_1$ bar for the hydrous end-member reaction) represents the hydrous reaction for a cordierite of water content 0.7 mols. The activity of anhydrous cordierite along the same line is given by $(1 - 0.7)$ or 0.3). Figure 3 shows a P-T diagram, for the situation where $P_{H_2O} = P_{TOTAL}$, which closely approximates the water fugacity of the QFM buffer), contoured with various activities of the anhydrous and hydrous end-member equilibria. The path of the observed reaction passes through the points where the activity of either the hydrous or anhydrous species is the same for both end-member equilibria. The observed reaction has a variable entropy of reaction and the resulting reaction path is curved. It has a negative slope at low temperatures, where cordierite compositions are close to the hydrous end-member, and has a positive slope at higher temperatures, when the cordierite becomes dehydrated. The minimum pressure at which almandine garnet becomes stable is 2.75 kilobars.

This reaction has also been studied by Weisbrod (1973), using the QFI buffer. At the temperatures and pressures of Weisbrod's experiments, the mol fraction of H_2O in the $H_2O - H_2$ gas phase is close to 0.2 and the water

Figure 3 Calculated path for the reaction, Fe-cordierite
+ almandine + sillimanite + quartz when
 $P_{H_2O} = P_{TOTAL}$ from the data of Richardson (1968).

The dashed lines represent equilibrium 3 - 1 contoured for the activity of anhydrous Fe-cordierite (1-X) shown in brackets and for the activity of hydrous Fe-cordierite X. The narrow solid line represents the equilibrium 3 - 2 contoured for the activity of hydrous Fe-cordierite (X) and for the activity of anhydrous Fe-cordierite (1-X) shown in brackets. Also shown are the data points of Richardson (1968).

Figure 3

fugacity is very small. The position of the anhydrous reaction is not dependent on the fugacity of water and remains unchanged. However, the position of the hydrous reaction is greatly affected by change in water fugacity. Figure 4 shows reaction Fe-cordierite = almandine + sillimanite + quartz plotted for the conditions of the QFI buffer. Weisbrod's data produce a line with a slight negative slope passing through the points 750°C, 3.3 kilobars and 900°C, 2.8 kilobars. This line is also shown in Figure 4. The calculated curve for the Fe-cordierite breakdown reaction predicts that the stability field of Fe-cordierite is considerably reduced under the conditions of the QFI buffer, with the minimum pressure for the appearance of almandine reduced to 1.5 kilobars. This does not agree with the experimental work of Weisbrod (1973), who found higher pressure stability for Fe-cordierite using the QFI buffer than Richardson using QFM. However, Newton (1972), working in the magnesium end-member system found that for $P_{H_2O} = P_{TOTAL}$, the highest pressure at which cordierite was stable (for the reaction cordierite $\rightarrow$ enstatite + sillimanite + quartz) was 11.2 kilobars, whereas, in the anhydrous system (for the same reaction) the stability limit was lowered to 8.2 kilobars. Reference was made in the introduction to this chapter of the difficulty in maintaining the buffering capacity of QFI and this may account for the discrepancy between the experimental and theoretical results.

Figure 4 Calculated path for the reaction, Fe-cordierite
 $\rightleftharpoons$ almandine + sillimanite + quartz, when
 $P_{H_2O} = P_{H_2O}$ of the QFI buffer, from the data of
 Richardson (1968).

The narrow dashed lines represent equilibrium 3 - 1
contoured for the activity of anhydrous Fe-cordierite (1-X)
shown in brackets and for the activity of hydrous Fe-
cordierite X. The narrow solid lines represent the
equilibrium 3 - 2 contoured for the activity of hydrous
Fe-cordierite (X) and for the activity of anhydrous
Fe-cordierite (1-X) shown in brackets. Also shown is the
experimental determination of Weisbrod, (1973).

Figure 4

3. THEORETICAL CALCULATIONS IN THE SYSTEMS,

- (a) Reactions in the system $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{O}_2$, ignoring the activity of water in cordierite.

As was noted in the introduction to this chapter five invariant points in the system $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{O}_2$ have been experimentally determined at 2 kilobars. Three points were determined on the QFM buffer, one on the NNO buffer and one on the MW buffer. These points are given in Table 4. The value of $\log f_{\text{O}_2}$ for the various points depends on the buffer equations used. Froese (1973), used the equation of Wones and Gilbert (1969), for the QFM buffer and the equation of Eugster and Wones (1962), for the MW buffer. The calculations of Froese (1973), have been repeated using the equation of Hewitt, (personal communication to G.B. Skippen) and the equation of Skippen, (personal communication to the author), for the MW buffer. The change in the water fugacity for each point by a change in the buffer equations is negligible. H_2O contents of the cordierites were calculated using water content model B (Part I, Chapter 2). Table 5 gives the appropriate oxygen fugacities and the water content of cordierite for each point. In the following calculations, the standard state of the solids has been defined as the pure substance at 2 kilobars, while the standard state of oxygen remains at a fugacity of 1 bar.

<u>Coexisting Phases</u>	<u>T°(C)</u>	<u>Oxygen Buffer</u>	<u>References</u>
Quartz-almandine-hercynite -cordierite-fayalite	875	MW	HSU (1968)
Quartz-almandine-hercynite magnetite	727	QFM	HSU (1968)
Quartz-almandine-hercynite -cordierite-magnetite	700	QFM	RUTHERFORD & EUGSTER (1967)
Quartz-sillimanite-hercynite -cordierite	875	QFM	RICHARDSON (1968)
Quartz-sillimanite-hercynite -cordierite	750	NNO	RUTHERFORD (1970)

Table 4 Experimentally determined invariant points

(at 2 kilobars) in the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-O}_2$.

T(°C)	Buffer	log f_{O_2} Calculated by Froese	log f_{O_2} Calculated for this study	f_{H_2O}	Water Content Cordierite in mols Model B
875	MW	-15.20	-15.60	1387.5	.14
875	QFM	-13.26	-12.96	1692.3	.18
727	QFM	-16.56	-16.12	1397.0	.59
700	QFM	—	-16.80	1327.3	.69
750	NNO	-14.92	-14.92	1464.3	.51

Table 5 Values of log f_{O_2} for the variant points
given in Table 4.

In order to facilitate comparison with the work of Froese, (1973), the same numbering system for the reactions considered has been used. They are numbered 1 to 12 without any prefix. The twelve reactions considered by Froese, and their relationship with each other, are given in Table 6. Also included is an additional reaction, 13, which is the hydration of anhydrous Fe-cordierite to give hydrous Fe-cordierite.

In order to assess the magnitude of changes in phase relations due solely to changes in buffer equations, cordierite was treated as an anhydrous phase, and the calculations of Froese (1973), repeated using the solid-phase buffer data from Table 2.

From equation 1, (the QFM buffer equation at 2 kilobars) at 875°C, the equilibrium constant provides the activity of magnetite at this temperature. From the Wones and Gilbert (1969), equation, Froese (1973), calculated the activity of magnetite (a_{mt}) = .328. The Hewitt buffer equation indicates a_{mt} = .217. (The work of Froese contains expressions from which activity coefficients of magnetite and hercynite can be calculated for any temperature). The coexistence of magnetite and hercynite at this temperature enables the activity of hercynite (a_{hc}) to be determined. The coexistence of magnetite and hercynite at 727°C enables their activities to be determined at this temperature also. With a knowledge of a_{mt} and a_{hc} at 875°C and 727°C, ΔG° for

Reaction Number	Reactions	
1	$4/3 \text{FeO} \cdot 5 \text{FeO}_2 + \text{SiO}_4 \leftrightarrow \text{Fe}_2\text{SiO}_4 + 1/3 \text{O}_2$	
2	$\text{Fe}_2\text{Al}_2\text{Si}_3\text{O}_{12} + 1/3 \text{O}_2 \leftrightarrow 2 \text{FeO} \cdot 5 \text{AlO}_2 + 4/3 \text{FeO} \cdot 5 \text{FeO}_2 + 3 \text{SiO}_2$	
3	$2 \text{FeO} \cdot 5 \text{AlO}_2 + 5/2 \text{SiO}_2 \leftrightarrow \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9$	
4	$6 \text{FeO} \cdot 5 \text{AlO}_2 + 1/2 \text{O}_2 + 3 \text{SiO}_2 \leftrightarrow 2 \text{FeO} \cdot 5 \text{FeO}_2 + 3 \text{Al}_2\text{SiO}_5$	
5	$6 \text{FeO} \cdot 5 \text{AlO}_2 + 5 \text{SiO}_2 \leftrightarrow \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2 \text{Al}_2\text{SiO}_5$	-2/3 ④ ②
6	$\text{Fe}_2\text{SiO}_4 + \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2/3 \text{O}_2 \leftrightarrow 2 \text{FeO} \cdot 5 \text{AlO}_4 + 8/3 \text{FeO} \cdot 5 \text{FeO}_2 + \text{SiO}_2$	① ②
7	$\text{Fe}_2\text{SiO}_4 + \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9 + 1/3 \text{O}_2 \leftrightarrow 4/3 \text{FeO} \cdot 5 \text{FeO}_2 + 2 \text{FeO} \cdot 5 \text{AlO}_2 + 7/2 \text{SiO}_2$	① ③
8	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 1/2 \text{SiO}_2 \leftrightarrow \text{Fe}_2\text{SiO}_4 + \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9$	① ② ③
9	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 1/3 \text{O}_2 \leftrightarrow \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9 + 4/3 \text{FeO} \cdot 5 \text{FeO}_2 + 1/2 \text{SiO}_2$	② ③
10	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 2 \text{Al}_2\text{SiO}_5 + 5/2 \text{SiO}_2 \leftrightarrow 3 \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9$	② -2/3 ④ + 3 ③
11	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 1/2 \text{O}_2 \leftrightarrow \text{FeO} \cdot 5 \text{FeO}_2 + \text{Al}_2\text{SiO}_5 + 2 \text{SiO}_2$	② + 1/3 ④
12	$\text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9 + 1/6 \text{O}_2 \leftrightarrow 2/3 \text{FeO} \cdot 5 \text{FeO}_2 + \text{Al}_2\text{SiO}_5 + 3/2 \text{SiO}_2$	③ + 1/3 ④
13	$\text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9 + 1/2 \text{H}_2\text{O} \leftrightarrow \text{FeAl}_2\text{Si}_2 \cdot 5 \text{O}_9 + 1/2 \text{H}_2\text{O}$	

Table 6 Reactions in the system FeO-Al₂O₃-SiO₂-O₂ considered by

Froese (1973)

Cordierite Asanhydrous phase. Equations of Froese (1973)			Cordierite asanhydrous phase. Uses QFM of Hewitt. MW of Skippen		
$\Delta G^\circ =$	T°C	a _{mt}	T°C	a _{mt}	a _{hc}
1 38950-13.7T.	875	.328	875	875	
2 -33460+9.1T	875	.328	875	.217	.957
3 -1240+0.9T	727	.832	727	.827	.891
4 -66180+31.2T	875		875		.957
5 -10660+31.2T	700		700		.891
6 -72410+22.8T	875	.328	875	.217	.957
7 -37710+12.8T	750	.670	750	.660	.750
8 4250-3.7T					
9 -34700+10.0T					
10 6940-9.0T					
11 -55520+19.5T					
12 -20820+9.5T					

Table 7 Standard free energy changes (at 2 kilobars) for

equations 1 - 12 of Froese (1973) assuming that

Fe-cordierite is an anhydrous phase.

reaction 2 may be calculated (Reaction 2 is the oxidation of almandine to give magnetite and hercynite). At 700°C magnetite and hercynite again coexist enabling a_{mt} and a_{hc} to be determined at this temperature. A knowledge of the a_{hc} at 875°C and 700°C enables reaction 3 to be calculated (Reaction 3 is the breakdown of cordierite to hercynite and quartz). From the ΔG° of reaction 3 at 750°C the activity of hercynite at this temperature may be determined and reaction 4 calculated. The equilibrium constant for reaction 4 is:

$$\ln K = 2 \ln a_{mt} - 6 \ln a_{hc} - 1/2 \ln f_{O_2}$$

This reaction is sensitive to small changes in the activity of magnetite and hercynite and small changes in the oxygen fugacities for buffers, which change the calculated activities for the two minerals causing a large change in this reaction. Combinations of equations 1 to 4 (as shown in Table 6) allow calculation of reactions 5 - 12. The standard free energy change (ΔG°) for reactions 1 - 12 as calculated by Froese (1973) and those obtained using the buffer equation of Hewitt for QFM and that of Skippen for MW, are shown in Table 7, together with the activities of magnetite and hercynite used in the calculations. A comparison can be made between the two sets of data from Figures 5 to 8. Figure 5 shows a temperature-composition diagram, at relatively low oxygen fugacities, calculated by Froese. The contours of $\log f_{O_2}$ represent those for the Wones and Gilbert (1969) QFM buffer equation.

Figure 5 A temperature, X_{hc} plot at 2 kilobars for relatively low oxygen fugacities. (Data are from Froese (1973)).

This figure shows the original calculated positions of reactions 1 - 10 of Froese. The Wones and Gilbert (1969) equation was used for the QFM buffer and the Eugster and Wones (1962) equation for the MW buffer. has been assumed an anhydrous phase.

Figure 5

Figure 6 A temperature $-X_{hc}$ plot at 2 kilobars for relatively low oxygen fugacities. (Data are from this study).

This figure shows the position of reactions 1 - 10 when the equation of Hewitt is used for the QFM buffer and the equation of Skippen for M.W. Cordierite has been assumed an anhydrous phase.

Figure 6

Figure 7 $\log f_{O_2}$ - $1/T$ plot at 2 kilobars showing the phase relations calculated by Froese (1973).

Figure 8 $\log f_{O_2}$ - $1/T$ plot at 2 kilobars showing the phase relations calculated in this study.

Reaction 10, (2 garnet + 4 sillimanite + 5 quartz = 3 cordierite), is independent of $\log f_{O_2}$ and composition of the oxide phases and occurs at 498°C. Figure 6 shows a similar diagram for the same equilibria, calculated using the buffer equation of Hewitt for QFM and the buffer equation of Skippen for MW. The contours of $\log f_{O_2}$ represent those of the Hewitt QFM buffer and it should be noted that these are at slightly higher values than those indicated by the buffer equation of Wones and Gilbert (1969), for the same temperature and composition of the oxide phases. The really significant change in Figure 6 is the position of reaction 10. This has been shifted two hundred degrees to 698°C. The changes this causes in the phase relations are more clearly seen on $\log f_{O_2}$ -temperature diagrams. Figure 7 shows these relationships as calculated by Froese and Figure 8 as calculated using the buffer equation of Hewitt for QFM and that of Skippen for MW. Reactions 9 and 10 have been drastically shifted below the position of the magnetite-hercynite solvus. This represents a very large reduction in the stability field of anhydrous cordierite.

- (b) Reactions in the system $FeO - Al_2O_3 - SiO_2 - H_2 - H_2O$ considering the activity of water in cordierite.

The twelve equations of Froese (1973) may also be calculated taking into account the water in cordierite, (these water contents are given in Table 5 and were calculated using Model B described in Part I, Chapter 2).

Cordierite Hydrous Phase Froese		Cordierite hydrous phase. Hewitt Skippen		Anhydrous Cord		Cordierite hydrous phase. Hewitt Skippen		Anhydrous Cord		Cordierite hydrous phase. Hewitt Skippen		Anhydrous Cord	
1	$\Delta G^\circ = 38950 - 13.7T$	T°C	a_{mt}	a_{hc}	a_{Cord}	T°C	a_{mt}	a_{hc}	a_{Cord}	T°C	a_{mt}	a_{hc}	a_{Cord}
1		875	.328			875	.217			875	.217		
2	-33406+9.1T	875	.328	.956		875	.217	.957		875	.217	.957	
3	5024-4.37T	727	.832	.902		727	.827	.891		727	.827	.891	
4	8824+7.37T	875		.956	$\sqrt{.83}$	875		.957	$\sqrt{.83}$	875		.957	$\sqrt{.83}$
5	7577-4.19T	700		.910	$\sqrt{.31}$	700		.910	$\sqrt{.31}$	700		.910	$\sqrt{.31}$
6	-72410+22.8T	875	.328	.956	$\sqrt{.82}$	875	.217	.937	$\sqrt{.82}$	875	.217	.937	$\sqrt{.82}$
7	-43974+18.07T	750	.358	.924	$\sqrt{.49}$	750	.358	.958	$\sqrt{.49}$	750	.358	.958	$\sqrt{.49}$
8	10514-8.97T												
9	-28436+4.73T												
10	7495-8.92T												
11	-46401+11.56T												
12	-17965+6.83T												
13	-17688+24.5T												

Table 8 Standard free energy changes (at 2 kilobars) for

equations 1 - 12 of Froese (1973) taking into account the activity of water in cordierite.

The method used for calculating reactions 1 - 4 is as described in the preceding section, except that a term for the activity of anhydrous cordierite a_{anco} is included in the equilibrium constants as well as terms for the activities of magnetite and hercynite. Again the calculations were made using two sets of equations for the solid-phase buffers. The standard free energies for the reactions are given in Table 8. For reactions involving cordierite, the equations in Table 8 give the standard free energy change for the pure anhydrous end-member cordierite. The standard free energy changes for the analogous hydrous cordierite reactions can be calculated using equation 13 which is the reaction anhydrous Fe-cordierite + water $\rightleftharpoons$ hydrous Fe-cordierite. Since the H_2O content of cordierite is a function of both temperature and the fugacity of water, (Part I, Chapter 2), it is desirable to represent reactions of this mineral on a diagram that shows the effect of changes in water fugacity more clearly than a $\log f_{O_2} - T$ diagram. One such diagram is a $T - X_{H_2O}$ diagram where X_{H_2O} is the mol fraction of H_2O in an $H_2O - H_2$ mixture.

When we consider the H_2O content of cordierite we are considering a new component, H_2O , without introducing a new phase. Thus invariant points (like the intersections of reactions, 10, 11, 12 and 9, seen in Figures 7 and 8) in the system $FeO - Al_2O_3 - SiO_2 - O_2$

are no longer constrained by the phase rule to be invariant. The position of reactions not involving cordierite remain unchanged by variation in water fugacity.

Reaction 10 of Froese (1973) is the reaction
 $2 \text{ almandine} + 4 \text{ sillimanite} + 5 \text{ quartz} = 3\text{Fe-cordierite}$
 which was determined experimentally by Richardson (1968), and Weisbrod (1973). A theoretical calculation of the Fe-cordierite breakdown reaction from the data of Richardson (1968) indicated that for conditions where $P_{\text{H}_2\text{O}} = P_{\text{TOTAL}}$ the assemblage almandine-sillimanite-quartz is not stable at 2 kilobars, (see Figure 3). Calculations where the water fugacities are those of the QFI buffer indicated that the assemblage almandine-sillimanite-quartz is stable at 2 kilobars between temperatures of 600°C and 740°C . The disagreement between the theoretical calculation of the stability of almandine-sillimanite-quartz on the QFI buffer and the experimental work of Weisbrod (1973), has already been noted. An assessment of the stability of the almandine-sillimanite-quartz assemblage independent of the data of Richardson (1968) is provided from the data given in table 8.

The equation for the standard free energy change of reaction 10, calculated using the buffer equations of Hewitt for QFM and Skippen for MW, is given in Table 8. This is the equation for the anhydrous end-member reaction. The analogous equation for the hydrous end-member reaction is calculated by the addition of 3X reaction 13. These equations are now compared with

similar equations calculated from the data of Richardson (1968). The two equilibria to be considered are the anhydrous equilibrium:

and the hydrous equilibrium:

From the data of Richardson (1968) the following equations were calculated for the equilibrium constants of equilibria 3-1 and 3-2.

$$\ln K_1 \text{ bar } 3-1 = \frac{16500}{T} - 19.125 \quad 3-4$$

$$\ln K_1 \text{ bar } 3-2 = \frac{-40125}{T} + 58.03 \quad 3-5$$

Equations equivalent to 3-4 and 3-5 have been derived from the standard free energy changes of the anhydrous and hydrous reaction 10.

At 2 kilobars the G° for the equilibrium:

is given by:

$$\Delta G^\circ = 22844 - 23.46T \quad 3-7$$

At 2 kilobars the ΔG° for the equilibrium:

is given:

$$\Delta G^\circ = -30220 + 50.04T \quad 3-9$$

Multiplying both equations 3 - 8 and 3 - 9 by -2 to correspond with the sense and stoichiometry of the equilibria 3 - 1 and 3 - 2 we obtain the following expressions for the standard-free energy changes of equilibria 3 - 1 and 3 - 2 at 2 kilobars.

$$\Delta G^{\circ}_{3-1} = -45688 + 46.927 \dots \dots \dots 3 - 10$$

$$\Delta G^{\circ}_{3-2} = 60440 - 100.08T \dots \dots \dots 3 - 11$$

$\ln K_1$ bar for the equilibria 3 - 1 and 3 - 2 can be calculated from the following two relationships

$$\ln K_{2 \text{ kilobars}} = \frac{-\Delta G^{\circ}_{2 \text{ kilobars}}}{RT} \dots \dots \dots 3 - 12$$

$$\ln K_{1 \text{ bar}} = \ln K_{2 \text{ kilobars}} + \Delta V_s \left(\frac{2000 - T}{RT} \right) \dots \dots \dots 3 - 13$$

(The necessary volume data are given in Table 3).

The following expressions were derived:

$$\ln K_{1 \text{ bar } 3 - 1} = \frac{18917}{T} - 23.60 \dots \dots \dots 3 - 14$$

$$\ln K_{1 \text{ bar } 3 - 2} = \frac{-34473}{T} + 50.04 \dots \dots \dots 3 - 15$$

For the anhydrous equilibrium values of ΔH°_R are 32.8 kcals and 37.6 Kcals using equations 3 - 4 and 3 - 14 respectively. For the hydrous equilibrium values of ΔH°_R of -78.7 Kcals and -68.5 Kcals were derived from equations 3 - 4 and 3 - 15 respectively. This indicates approximate agreement only between values calculated from the experimental data of Richardson, (1968) and

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those calculated from the five isobaric invariant points used by Froese (1973).

We have already noted that the experimental work of Weisbrod (1973), indicates that the reaction:

$$3\text{Fe-cordierite} = 2 \text{ almandine} + 4 \text{ sillimanite} + 5 \text{ quartz}$$

is not stable at 2 kilobars for the low water fugacity conditions of the QFI buffer while theoretical treatment of the data of Richardson (1968) indicates that the assemblage almandine-sillimanite-quartz is stable between 600°C and 740°C . (Figure 4). The standard free energies of equations 3 - 10 and 3 - 11, which were calculated using the theoretical treatment of Froese (1973), can be used to provide an independent estimate of the stability of the Fe-cordierite breakdown reaction at 2 kilobars. The anhydrous equilibrium 3 - 1 is independent of water fugacity and this equilibrium plotted on a $T\text{-}X_{\text{H}_2\text{O}}$ diagram (Figure 9) for various activities of anhydrous Fe-cordierite is a series of horizontal lines, ($a_{\text{anhy Fe-co}} = 1-X$, where X is the water content of cordierite in mols H_2O). We can also contour this diagram for the values of $(1-X)$ for T and $X_{\text{H}_2\text{O}}$. (Equilibrium values of $\ln f_{\text{O}_2}$ are calculated for each value of $(1-X)$ at a range of temperatures. These $f_{\text{H}_2\text{O}}$ values were converted first to $P_{\text{H}_2\text{O}}$ using the fugacity coefficients of Burnham, Holloway and Davis (1969), for 2 kilobars and the appropriate temperature and hence to $X_{\text{H}_2\text{O}}$). The anhydrous reaction 3 - 1 can only be stable at points where the $(1-X)$ for reaction 3 - 1 crosses the equivalent $(1-X)$ contour. It can be

Figure 9 $T-X_{H_2O}$ plot at 2 kilobars for reaction 10.

The dashed lines represent the anhydrous equilibrium,
 $Fe_3Al_2Si_3O_{12} + 2Al_2SiO_5 + 5/2SiO_2 \rightleftharpoons 3FeAl_2Si_2.5O_9$,
contoured for the activity of anhydrous Fe-cordierite.

The figures on these contours represent the quantity $(1-X)$
where X is in mols H_2O . The narrow solid lines represent
activity contours of anhydrous Fe-cordierite $(1-X)$ for
the reaction

The wide solid line represents the calculated position
of the reaction, almandine + sillimanite + quartz $\rightleftharpoons$
Fe-cordierite.

Figure 9

seen from Figure 9 that the assemblage almandine-sillimanite-quartz only becomes stable at 2 kilobars, at very low X_{H_2O} . Qualitatively this result agrees with the theoretical treatment of the Richardson (1968) data for low values of X_{H_2O} as represented by the QFL buffer.

4. CONCLUSIONS

For an understanding of Fe-cordierite reactions it is necessary to consider the change in the entropy of Fe-cordierite as its water content varies with changes in temperature and water fugacity. Fe-cordierite reactions should be considered as combinations of anhydrous and hydrous end-member equilibria; the observed path of a Fe-cordierite reaction resulting from the simultaneous solving of the two end-member equilibria for identical activities of hydrous Fe-cordierite.

Theoretical treatment of reactions in the system $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{O}_2$, (Froese, 1973), can give very different results if the solid-phase buffer equations used for the calculations of $\log f_{\text{O}_2}$ are changed slightly.

Contrary to the experimental determination of Weisbrod (1973) two independent theoretical examinations indicate that the assemblage almandine-sillimanite-quartz will be stable at 2 kilobars for very low values of $f_{\text{H}_2\text{O}}$.

CHAPTER II Fe-CORDIERITE REACTIONS IN THE SYSTEM 1. INTRODUCTION

The minerals found in metamorphosed rocks of pelitic composition have often been represented for theoretical consideration by the system, $\text{K}_2\text{O} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ (Albee, 1965; Hess 1969; Grant, 1973; A.B. Thompson, 1976 and others). Even this simplified system, which ignores the important contribution of Na_2O in feldspars and biotites and CaO in plagioclase feldspars and garnet, (to name only two possible extra components) is complex for experimental work. Reactions have been studied in either the magnesium or iron end-member systems. Both of these systems have certain advantages and disadvantages. The magnesium end-member system does not involve two oxidation states, as for Fe, but has the disadvantage that reactions are sluggish and take place at high temperatures and pressures. (Reactions involving pyrope garnet are extremely difficult even in high pressure apparatus). The direction of an iron end-member reaction is usually apparent after runs of two to three weeks and reactions are often possible in conventional hydrothermal apparatus at temperatures 75 to 100° less than the corresponding magnesium end-member reactions. However, careful control of the hydrogen fugacity is necessary to prevent oxidation of the iron silicates.

Many of the minerals of pelitic rocks such as garnet, staurolite, cordierite, chloritoid, chlorite and

biotite contain iron as an important component and iron oxides and spinels are present in these rocks also. This means that an understanding of pelitic rocks cannot be achieved without a knowledge of the iron end-member system and its variation with change in temperature, pressure and the fugacity of both water and hydrogen.

Some of the experimental work in the system $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} - \text{H}_2$ was considered in Part II, Chapter 1 and the difficulties inherent in establishing accurate phase relationships became apparent. Many of the problems are caused by a lack of knowledge of the phases used in the experimental work, the amount of water in the cordierite, composition of magnetite and hercynite, structural state of the feldspars and the composition of staurolite, for example.

Any meaningful model for pelitic rocks must consider the potassium-bearing phases, biotite, muscovite and potash feldspar. Pioneering work on the least aluminous of the iron biotites (annite $\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$) was carried out by Eugster and Wones (1962). Rutherford (1969) investigated the stability of the aluminous iron biotites and their relationship with alkali feldspars.

Metamorphosed pelites containing cordierite have bulk compositions low in Ca and Na (Reinhardt (1968) so that the system $\text{K}_2\text{O} - \text{FeO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O} - \text{H}_2$ is a good approximation for these rocks. This chapter considers two cordierite reactions in the iron end-member system. These are:

biotite + sillimanite + quartz $\rightleftharpoons$ cordierite + sanidine

biotite + sillimanite + quartz $\rightleftharpoons$ cordierite + muscovite

The first of these reactions will subsequently be referred to as the cordierite-sanidine reaction and the second will be referred to as the cordierite-muscovite reaction.

An attempt has been made to characterise all the phases used as fully as possible and the difficulties encountered in extracting good thermochemical data for Fe-cordierite from these reactions are examined.

2. EXPERIMENTAL DETAILS

(a) Preparation and characterisation of phases

(i) Fe-cordierite

The preparation, cell dimensions and refractive indices of Fe-cordierite have been described fully in Part I and are mentioned only briefly here. Fe-cordierite was prepared either from a fayalite-kaolinite mix (with a slight excess of SiO_2) or from a gel of the stoichiometric composition, $2\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. The material used in reaction runs was synthesised hydrothermally at $650\text{--}700^\circ\text{C}$ at 1 to 2 kilobar pressure with the graphite-methane buffer used to control hydrogen fugacity. Fe-cordierite is difficult to synthesise; the runs require seeding with previously synthesised Fe-cordierite and even then (as was seen in Part I) there exist hercynite and quartz impurities which occur as minute inclusions within the fine grained (2μ) Fe-cordierite. Where possible the refractive index of run-product Fe-cordierites has been measured in order to determine the water content.

Theoretical model B (Part I Chapter II) was also used to determine water contents of run-products.

(ii) Biotite

Two biotites were prepared, annite (used in all but one of the reaction runs) and siderophyllite. They were synthesised hydrothermally, at 650°C and 1 kilobar, from 'gels' of compositions $\text{K}_2\text{O} \cdot 6\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (annite) and $\text{K}_2\text{O} \cdot 5\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (siderophyllite). The cell

dimensions of the annite are $a = 5.3971(30)$, $b = 9.3609(6)$, $c = 10.3447(26)$, $\beta = 99.98(5)$, $V = 514.73(\text{\AA}^3)_{196}$. The cell was indexed as the 1M polymorph (Smith and Yoder (1955).

(The powder patterns of the biotite and other phases involved in the Fe-cordierite reactions are given in Appendix 3.) The position of the 060 peak of this biotite is $d = 1.5583 \pm .0003$ as measured by slow ($1/4^\circ/\text{min}$) oscillation over the peak using potassium bromate as a standard. For siderophyllite, only the 060 peak was determined: $d = 1.5527 \pm .0003$. The substitution of Al-Al for Fe-Si that occurs between annite and siderophyllite causes a decrease in the b parameter and this change, as indicated by the change in the 060 peak, is a linear one. (Rutherford 1969).

(iii) Muscovite ($\text{K}_2\text{Al}_4\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$)

The muscovite used in the study was synthesised at 700°C and 1 kilobar pressure using the graphite-methane buffer from a 'gel' of composition $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and water. The mica produced was not the same as the synthetic 2M_1 muscovite prepared by Chatterjee and Johannes (1974). It could be indexed as a 1M polymorph and was similar to a muscovite prepared by Yoder and Eugster (1955). Cell constants for this muscovite are $a = 5.2266(50)$, $b = 8.9954(7)$, $c = 10.2957(10)$, $\beta = 101.932(6)$, $V = 473.591(\text{\AA}^3)$.

It appears probable that the muscovite prepared for the present study is more disordered than the 2M_1 muscovite of Chatterjee and Johannes. The thermochemical properties

of this 1M muscovite will differ slightly from those determined by Chatterjee and Johannes for the 2M₁ polymorph.

(iv) Sanidine

The structural state of a mineral can have very significant effects on its behaviour in reactions. (One explanation for differences in experimental determinations of the reaction, muscovite + quartz $\rightarrow$ potassic feldspar + sillimanite + water, is that some workers have used disordered sanidines and other workers have used well ordered orthoclase.) Hovis (1974) showed that the enthalpy, volume and entropy of sanidine are functions of actual tetrahedral site populations of Al and Si in monoclinic feldspar. The potassium feldspar used in this study was synthesised from a 'gel' of composition $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ at 1 kilobar pressure and 700°C using the graphite-methane buffer. Cell refinements of 38 lines gave the following cell dimensions: $a = 8.6039(20)$, $b = 13.0303(20)$, $c = 7.1818(10)$, $\beta = 115.96(3)$, $V = 723.89(168) \text{ \AA}^3$. These cell constants are very similar to the cell constants for sanidines used by Chatterjee and Johannes (1974) in their determination of the muscovite breakdown curve.

Hovis (1974) defined a long-range ordering parameter, z , for monoclinic potash feldspars. This parameter is an indication of the Al-Si tetrahedral site populations and can be measured directly from cell parameters. Hovis gives the following relationship for z ;

$$z = 7.634a - 4.3584b + 6.8615c.$$

The feldspar synthesised for this study had $z = 0.117$.

Chatterjee and Johannes (1974) found that sanidines with $z = 0.11$ to 0.12 before an experiment become slightly more ordered ($z = 0.17$) at the end of the run if they had been in equilibrium with quartz. An attempt was made to refine cell constants of sanidine from run products of the Fe-cordierite reaction but interference from the lines of the five other phases present in the mixture made this impossible. Quartz is one of the phases present and it is probable that the sanidines of the run products have become slightly more ordered than the starting material. A value of $z = 0.17$ has been adopted to be consistent with the findings of Chatterjee and Johannes (1974).

(v) Sillimanite

Sillimanite was synthesised from a 'gel' of composition $Al_2O_3 \cdot SiO_2$, at $700^\circ C$ and 2 kilobars pressure and had the following cell dimensions: $a = 7.510(\pm 5)$, $b = 7.683(\pm 3)$, $c = 5.759(\pm 4)$, $V = 332.2(\pm 3) \text{ \AA}^3$. Recent calorimetric work on synthetic and natural sillimanites, by Anderson et al (1977), has confirmed the existence of sillimanite disordering enthalpy, the magnitude of which was predicted by Holdaway (1971) and calorimetrically determined by Newton and Kleppa (1973). Although the disordering enthalpy phenomenon in sillimanite had shown itself mainly in the breakdown of andalusite to sillimanite, it was thought advisable to check the position of the

1 kilobar reversal (graphite-methane buffer) of the cordierite-sanidine reaction using natural sillimanite, (from Hungerford Township, Ontario). The position of the 1 kilobar reversal on the graphite-methane buffer was the same for both synthetic and natural sillimanite.

(vi) Quartz

The quartz used in this study was finely ground optical quality quartz provided by Dr. G. Chapoy of Carleton University.

(b) Starting material for reaction runs.

The reactants for runs consisted of annite + sillimanite + quartz mixed in the stoichiometric proportions $K_2Fe_6Al_2Si_6O_{20}(OH)_4 + 6Al_2SiO_5 + 9SiO_2$, (except for a slight excess of quartz), for the cordierite-sanidine reaction and $K_2Fe_6Al_2Si_6O_{20}(OH)_4 + 8Al_2SiO_5 + 7SiO_2$ (with a slight quartz excess) for the cordierite-muscovite reaction. The product mixture for the cordierite-sanidine reaction consisted of $3Fe_2Al_4Si_5O_{18} + 2KAlSi_3O_8$, and for the cordierite-muscovite reaction of $3Fe_2Al_4Si_5O_{18} + K_2Al_4Al_2Si_6O_{20}(OH)_4$. All phases were present for all the reaction runs and the proportion of reactants to product used for each run is noted in Tables 12, 13 and 14. Approximately 10-15mg of materials were used for each reaction run.

(c) Experimental apparatus

The runs were made in standard "Tuttle" type pressure vessels on either the graphite-methane buffer $GH, CH(X, OH)$ or the $NNO, OH(GX, COH)$ buffer. Details of the

methods of control of temperature and pressure and their reliability have been given in Part I, Chapter I. Run times were from 13-46 days. All runs were rapidly cooled in a stream of compressed air and the pressure released when the temperature fell below 150°C .

3. EXPERIMENTAL RESULTS

(a) Determination of reaction direction

The phases stable for a particular reaction run were determined both by observing the change in the relative intensities of the X-ray peaks of the phases, before and after the run, and by optical microscopy. The reactants and products were mixed in various proportions and X-ray diffraction patterns run from $65^{\circ} 2\theta$ Cu $k\alpha$ to $7^{\circ} 2\theta$ Cu $k\alpha$. The intensities of quartz X-ray peaks was very variable from run to run and were unreliable for estimating reaction direction. For all runs where annite was the starting biotite there was an observed decrease in the relative intensity of the sillimanite peaks at the end of a run, even where the assemblage biotite + sillimanite + quartz was stable. (This indicates a probable reaction between annite and sillimanite to produce a more aluminous biotite). Therefore sillimanite X-ray peaks intensities were also unreliable for determining the direction of reaction. The most useful reflections were the cordierite (110,200) doublet, the biotite (001) and (060) peaks, the several sanidine peaks, between 31° - $45^{\circ} 2\theta$ Cu $k\alpha$ and the muscovite (112) peak at $33.9^{\circ} 2\theta$ Cu $k\alpha$.

For the reaction, biotite + sillimanite + quartz + cordierite + sanidine, optical examination of runs where the assemblage, cordierite + sanidine, was stable commonly showed the growth of fresh cordierite and well crystallised sanidine that was occasionally twinned. For runs where

Run Number	Starting Material	Pressure in bars	Temperature °C	Buffer used	Time in days	Direction of Reaction	Comments
15(S)RP2	60% Prod 40% React	1000	626 ± 5	GH, CH(X, OH)	18	+	Growth of new biotite
15(S)RP3	80% Prod. 20% React	1000	644 ± 5	"	36	+	
15(S)RP5	25% Prod 75% React	1000	645 ± 5	"	36	+	
15(S)RP6	25% Prod 75% React	1000	665 ± 5	"	28	+	50% shift
15(S)RP11	40% Prod 60% React	1000	631 ± 5	"	46	+	
15(S)RP15	60% Prod 40% React	1000	617 ± 5	"	13	+	
15(S)RPC2	45% Prod 55% React	1000	595 ± 5	NNO, OH (GX, COH)	21	+	
15(S)RPC3	45% Prod 55% React	1000	603 ± 5	"	18	+	Growth of fresh cordierite
15(S)RPC6	25% Prod 75% React	1000	613 ± 5	"	45	+	
15(S)RPC8	40% Prod 60% React	1000	620 ± 5	"	39	+	
15(S)RPS1	40% Prod 60% React	1000	625 ± 5	GH, CH(X, OH)	18	+	Natural sillimanite, Little change
15(S)RPS2	40% Prod. 60% React	1000	631 ± 5	"	18	+	Natural sillimanite
15(S)RPS3	40% Prod 60% React	1000	620 ± 5	"	28	+	Natural sillimanite
15(S)RPS31	50% Prod 50% React	1000	612 ± 5	"	30	+	Siderophyllite + natural sillimanite

On GH, CH(X, OH) buffer 1000 bars bracket 626 - 631 + 3°C.

On NNO, OH(GX, COH) buffer 1000 bars bracket 603 - 613 + 3°C.

Reaction 15(S)

$K_2Fe_6Al_2Si_5O_{20}(OH)_4 + 6Al_2SiO_5 + 9SiO_2 + 3Fe_2Al_4Si_5O_{18} + 2KAlSi_3O_8 + \text{vapour.}$

Table 9 Reaction runs at 1000 bars on the Fe-cordierite-sapidine reaction.

OF/DE

Run Number	Starting Material	Pressure Temperature		Time in days	Direction of Reaction	Comments
		in bars	$^{\circ}\text{C}$ Used			
15(S)RP7	60% Prod 40% React	1500	634 + 5 GH(X,OH)	26	+	
15(S)RP8	25% Prod 75% React	1500	690 + 5 GH(X,OH)	26	++	50% shift
15(S)RP10	45% Prod 55% React	1500	653 + 5 GH(X,OH)	40	+	
15(S)RP14	40% Prod 60% React	1500	639 + 5 GH(X,OH)	45	++	
15(S)EPC7	40% Prod 60% React	1500	641 + 5 NNO,OH (GX,COH)	31	+	
15(S)EPL2	40% Prod 60% React	2000	672 + 5 GH(X,OH)	44	++	
15(S)EPL3	40% Prod 60% React	2000	655 + 5 GH(X,OH)	40	+	
15(S)EPL6	30% Prod 70% React	2000	645 + 5 GH(X,OH)	40	+	
15(S)EPL7	30% Prod 70% React	2000	639 + 5 GH(X,OH)	26	+	

On GH, (X,OH) buffer 1500 bars bracket 634 - 644 +4 $^{\circ}\text{C}$.

On GH(X,OH) buffer 2000 bars bracket 639 - 645 +3 $^{\circ}\text{C}$

Reaction 15(S)

$\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_4\text{O}_{20}(\text{OH})_4 + 6\text{Al}_2\text{SiO}_5 + 9\text{SiO}_2 + 3\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18} + 2\text{KAlSi}_3\text{O}_8 + \text{vapour}$

Table 10

Table 10 Reaction runs at 1500 and 2000 bars on the Fe-cordierite-sanidine reaction.

Run Number	Starting Material	Pressure in bars	Temperature °C	Buffer Used	Time in days	Direction of Reaction	Comments
8(S)RP1	20% Prod 80% React	1000	546 ± 6	GH, CH (X, OH)	28	+	Biotite eliminated
8(S)RP3	20% Prod 80% React	1000	353 ± 3	"	28		Chlorite, sillimanite quartz only
8(S)RP5	60% Prod 40% React	1000	580 ± 5	"	35	+	
8(S)RP6	60% Prod 40% React	1000	570 ± 5	"	35	+	
8(S)RP7	60% Prod 40% React	1000	583 ± 5	"	23	+	
8(S)RP8	60% Prod 40% React	1000	590 ± 3	"	23	+	No sanidine observed
8(S)RP9	60% Prod 40% React	2000	573 ± 3	"	30	+	
8(S)RP10	60% Prod 40% React	2000	584 ± 2	"	30	+	

Reacción 8(S)

Table 11 Reaction runs at 1000 and 2000 bars on the Fe-cordierite-muscovite reaction.

biotite + sillimanite + quartz were stable, the growth of fresh biotite could be recognized within some of the cordierite grains. It could be distinguished from the hercynite inclusions, (which appeared to have remained unchanged), by its lower refractive index. Optical examination of products from runs using the (NNO, OH(GX, COH) buffer was very difficult due to the presence of finely ground graphite, which is part of the buffer system, and had become mixed with the charge.

All reaction run results are shown in Tables 9, 10 and 11. Reaction runs with the prefix (15(s) refer to the cordierite-sanidine reaction and those with the prefix 8(s) refer to the cordierite-muscovite reaction.

(b) Biotite composition determination

(i) Introduction

The Fe-biotites used in iron end-member reactions may vary in composition considerably. The least aluminous of the biotites, annite ($K_2Fe_6^{2+}Al_2Si_6O_{20}(OH)_4$), was first synthesised by Ostrovskii (1956), and was studied by Eugster and Wones (1962) and has generally been used as the starting biotite in much experimental work.

Deviations from the ideal formula occur in several ways: one is the substitution of $Al^{3+} - Al^{3+}$ for $Fe^{2+} - Si^{4+}$ to give aluminous biotites. Substitution of $Fe^{3+} - Al^{3+}$ for $Fe^{2+} - Si^{4+}$ and the substitution of Fe^{3+} for Fe^{2+} while the charge balance is maintained by the replacement of OH^{1-} by O^{2-} (Eugster and Wones 1962).

Iron biotites in equilibrium with the aluminous phases sillimanite (Al_2SiO_5) and Fe-cordierite ($\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) are more aluminous than annite (Rutherford 1968) and it would be expected that for reaction runs where annite is the starting biotite, a change towards a more aluminum-rich biotite will have occurred by the end of the run. It was noted in the previous section that this change to a more aluminous biotite occurred at the expense of sillimanite. The reaction is of the form, annite + sillimanite $\rightarrow$ 'aluminous' biotite + quartz. It is possible to determine the aluminum content of the run biotites but not their ferric iron content.

(ii) Measurement of aluminum content

According to Rutherford (1968) the substitution of Al-Al for Fe-Si in iron biotites causes a linear change in the position of the 060 peak. The positions of the 060 peaks for synthetic annite and siderophyllite ($\text{KFe}_3\text{Al}_3\text{Si}_5\text{O}_{20}(\text{OH})_4$), which had been synthesised at 650°C and 1 kilobars pressure, were determined by oscillation over the peak at a scanning speed of $1/4^\circ/\text{min}$ and a chart speed of $2\text{cm}/\text{min}$. The radiation used was $\text{Cu K}\alpha$ and potassium bromate (KBrO_3) was used as an internal standard. A plot of the d values obtained for the two biotites against iron content is given in Figure 10. The intensities of the 060 peak of biotite, in the products of a reaction run, are small and the width to height ratio of the peak is large. These factors caused problems in the measurement of 060 of the run product

Figure 10 Determination of the aluminum content of run product biotites from the d spacing of the 060 peak.

The solid line represents the determination curve calculated from the d spacings of the 060 peaks of annite and siderophyllite. The dashed lines are the estimated error limits in the determination of the d spacing.

Figure 10

biotites. In runs starting with annite, two 060 peaks could be observed, one close to $d = 1.585$ which corresponds to the starting biotite and another in the range $d = 1.550$ to $d = 1.5513$. There was little decrease in sillimanite shown for the run where siderophyllite was the starting biotite, and only one 060 peak was observed, at d values between 1.5505 and 1.5513. These peaks are also plotted in Figure 10. The biotites in all reaction runs are in equilibrium with sillimanite and biotite and their composition probably does not vary much with difference in temperature and pressure. The following composition of biotite has been estimated from the d spacing of (060) in run products:

(iii) Activity of biotite.

The run product biotites are much closer in composition to siderophyllite than to annite ($\text{K}_2 \text{Fe}_6 \text{Al}_2 \text{Si}_6 \text{O}_{20} (\text{OH})_4$) but unfortunately, the only reliable thermochemical data for iron biotites are available for Annite. (Helgeson et al 1977). Extraction of useful thermochemical data for Fe-cordierite from the reactions studied requires reliable thermochemical data for all other phases. However, if the activity of the annite component in the equilibrium biotites can be determined, the reactions can still be used to determine thermochemical data for Fe-cordierite. The only model presently available for calculating these activities is

the Temkin model: This method, first discussed by Temkin, (1945) calculates the activity of a component in a solid solution by considering ideal mixing of atoms on the various sites of the crystal. The Temkin method has been applied to many minerals and the following calculations on biotite follow the treatment of Froese (1976). The model must consider mixing of Fe^{2+} and Al^{3+} in octahedral sites, and mixing of Si^{4+} and Al^{3+} in the tetrahedral sites. No allowance is made for the presence of Fe^{3+} in the biotites. The activity of annite in the equilibrium biotites is given by the following expression:

$$a_{\text{annite}} = \left[\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Al}^{\text{oct}}} \right]^6 \left[\frac{\text{Si}}{\text{Si} + \text{Al}^{\text{tet}}} / 0.75 \right]^6 \left[\frac{\text{Al}^{\text{tet}}}{\text{Si} + \text{Al}^{\text{tet}}} / 0.25 \right]^2$$

This gives activities of annite in the equilibrium biotites between 0.12 for $\text{Fe}_{4.7}$ and 0.15 for $\text{Fe}_{4.6}$. The activity of siderophyllite in the equilibrium biotite would be given by:

$$a_{\text{siderophyllite}} = \left[\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Al}^{\text{oct}}} / 0.833 \right]^5 \left[\frac{\text{Al}^{\text{oct}}}{\text{Fe}^{2+} + \text{Al}^{\text{oct}}} / 0.167 \right] \left[\frac{\text{Si}}{\text{Si} + \text{Al}^{\text{tet}}} / 0.625 \right]^5 \left[\frac{\text{Al}^{\text{tet}}}{\text{Si} + \text{Al}^{\text{tet}}} / 0.375 \right]^3$$

This gives activities of siderophyllite in the equilibrium biotites of 0.66 for $\text{Fe}_{4.6}$, and 0.72 for $\text{Fe}_{4.7}$.

4. THE REACTION BIOTITE + SILLIMANITE + QUARTZ
 $\rightleftharpoons$ Fe-CORDIERITE + SANIDINE + VAPOUR

(a) Introduction

This reaction has been previously studied by Hoffer (1976) and Holdaway and Lee (1976). Hoffer used natural materials in the system, $\text{MgO} - \text{FeO} - \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$. Full details of the phases are not given and it is therefore very difficult to compare his results with this study. The K-feldspar was an adularia ($\text{Or}_{90}\text{Ab}_{10}$), the biotite had $(\text{Fe}/\text{Fe} + \text{Mg}) = 0.50$ and the cordierite (which was from the same rock) had $(\text{Fe}/\text{Fe} + \text{Mg}) = 0.34$. Hoffer quotes the following equilibrium conditions: $650^\circ\text{C} \pm 10^\circ$ at 2500 bars $P_{\text{H}_2\text{O}}$, $680^\circ\text{C} \pm 10^\circ$ at 3,000 bars $P_{\text{H}_2\text{O}}$ and $710^\circ\text{C} \pm 10^\circ$ at 3,500 bars $P_{\text{H}_2\text{O}}$. The reaction studied by Holdaway and Lee was in the iron end-member system but the buffer used is not given in the abstract. They quote the breakdown of Fe-cordierite + K feldspar at pressures above a line through 640°C at 2 kb and 710°C at 2.7 kb.

(b) Calculation of equilibrium curve

Four reversals were obtained on the reaction biotite + sillimanite + quartz = Fe-cordierite + sanidine + vapour. Using the graphite-methane buffer, the reversal at 1 kilobar is $626-631 \pm 5^\circ\text{C}$, at 1.5 kilobars, $634 - 644 \pm 5^\circ\text{C}$ and at 2 kilobars $639 - 645 \pm 5^\circ\text{C}$. On the $\text{NNO}, \text{OH(GX), COH}$ buffer, a reversal was obtained at 1 kilobar and $603 - 613 \pm 5^\circ\text{C}$. The uncertainty limits for

temperature control are estimated at $\pm 5^{\circ}\text{C}$ (see Chapter I, Part I) and all calculations have been made using the extremes of these uncertainties. The reversal at 1 kilobar on the graphite-methane buffer has been calculated for 621°C and 636°C , for example. Water contents for Fe-cordierite at each reversal point were calculated using model B, the thermodynamic model from Chapter II, Part I, and were also estimated from mean refractive index measurements. There was good agreement between the two methods of calculating water content. Where differences occur both values were used to calculate an equilibrium constant.

Following the treatment of Fe-cordierite reactions developed in Chapter 2, Part I, the observed reaction was considered in terms of two equilibria, involving two end-members, anhydrous Fe-cordierite and hydrous Fe-cordierite containing one mole of water per formula unit.

The following equilibrium involves the anhydrous cordierite species:

Assuming that sillimanite, α quartz, and sanidine are present in pure phases the equilibrium constant for

4 - 1 is:

$$K = \frac{f_{H_2O}^2 \cdot a_{Fe\ cord}^3}{a_{annite}} \dots \dots \dots 4 - 2$$

The fugacity of H_2O is controlled experimentally and the activity of anhydrous Fe-cordierite is determined by mean refractive index measurements and calculated using the thermodynamic model B (Both methods were discussed in Part I Chapter II). Determination of the activity of the annite species could be accomplished by the use of a solution model to account for the substitution of Al for Si and Fe as discussed previously in Section 3 - (ii) of this chapter. The use of an ideal solution model to account for this substitution is subject to considerable uncertainty and experimental results are therefore reported as a product of the equilibrium constant and the activity of annite, i.e.

$$K \cdot a_{annite} = f_{H_2O}^2 \cdot a_{Fe\ cord}^3 \dots \dots \dots 4 - 3$$

As discussed in section 3 - (iii) of this chapter, the composition of biotites in experiments is nearly constant. Biotites of this composition could be assigned unit activity and the annite term dropped from the above equation. To avoid such an awkward choice of standard state for the biotite species, however, the annite term has been retained.

Experimental results have been adjusted to the pressure of the standard state, 1 bar, using the following equation:

$$\ln K_{1\ bar} = \ln K_p + \Delta V_s (P-1)/RT \dots \dots \dots 4 - 4$$

React Pressure Dir'n in bars	Temp °C	Buffer Used	lnf H ₂ O	$\Delta V_s (P-1)/RT$	Water Content in mols		lnK ₁ bar ^a annite	
					Model B	RI	Hydrous	Anhydrous
+	1000	GH, CH(X, OH)	6.444	1.5677	.82	.82	-5.472	9.311
+	1000	"	6.478	1.5487	.82	.82	-5.525	9.360
+	1500	"	6.746	2.3315	.83		-5.010	10.5076(.83)
							-4.973	10.6782(.83)
+	1500	"	6.794	2.2809	.82	.83	-5.108	10.5518(.83)
							-5.072	10.7223(.82)
+	2000	"	7.020	3.0920	.86		-4.345	11.233 (.86)
							-4.380	11.010 (.87)
+	2000	"	7.052	3.0384	.86	.87	-4.466	11.244 (.86)
							-4.431	11.021 (.87)
+	1000	NNO, OH(GH, COH)	4.670	1.6091	.58		-4.695	8.347
+	1000	"	4.608	1.5730	.52	.52	-4.997	8.587
Hydrous Reaction $K_2Fe_6Al_2Si_6O_{20}(OH)_4 + 6Al_2SiO_5 + 9SiO_2 + H_2O \rightleftharpoons 3Fe_2Al_4Si_5O_{18}H_2O + 2KAlSi_3O_8$								
$\ln K (\text{Hydrous}) = -\ln f_{H_2O} + 3\ln X$								
Anhydrous Reaction $K_2Fe_6Al_2Si_6O_{20}(OH)_4 + 6Al_2SiO_5 + 9SiO_2 \rightleftharpoons 3Fe_2Al_4Si_5O_{18} + 2KAlSi_3O_8 + 2H_2O$								
$\ln K (\text{Anhydrous}) = 2\ln f_{H_2O} + 3\ln(1-X)$								
ΔV_s for both reactions = 2.788 cal/bar								

Table 12. Calculated values of $\ln(K_1 \text{ bar}^a \text{ annite})$, for both the hydrous and anhydrous equilibria involved in the Fe-cordierite-sanidine reaction, for the reversed temperature brackets at 1000, 1500 and 2000 bars pressure.

Figure 11 $\ln(K_1 \text{ bar} \cdot a_{\text{annite}}) - 1/T$ plot for the anhydrous equilibrium, $\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4 + 6\text{Al}_2\text{SiO}_5 + 9\text{SiO}_2 \rightleftharpoons 3\text{Fe}_2\text{Al}_4\text{Si}_{15}\text{O}_{18} + 2\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{O}$

Figure 12 $\ln(K_1 \text{ bar} \cdot a_{\text{annite}}) - 1/T$ plot for the hydrous equilibrium. $K_2Fe_6Al_2Si_6O_{20}(OH)_4 + 6Al_2SiO_5 + 9SiO_2 + H_2O \rightleftharpoons 3Fe_3Al_2Si_5O_{18} \cdot H_2O + 2KAlSi_3O_8$.

Experimental data are shown in Figure 11 and the data used for plotting this figure are given in Table 12. Experimental results from the graphite-methane buffer for the anhydrous species have been represented, as shown in Figure 12, by the expression:

$$\ln(K_1 \text{ bar} \cdot a_{\text{annite}}) = \frac{-126667}{T} + 149.6 \quad .4 - 5$$

The equilibrium involving hydrous Fe-cordierite is written as follows:

Equilibrium 4 - 6 can be derived from equilibrium 4 - 1 by adding the equilibrium (4 - 7) for the formation of the hydrous species as follows:

where the constant for equilibrium 4 - 6 is given by:

$$\ln K_{4.6} = \ln K_{4.1} + 3 \ln K_{4.7} \quad .4 - 8$$

Adding the activity of annite:

$$\ln(K_{4.6} \cdot a_{\text{annite}}) - \ln K_{4.1} \cdot a_{\text{annite}} + 3 \ln K_{4.7}$$

$K_{4.7}$ has been measured as described in Part I, Chapter II and an expression for the equilibrium involving the hydrous end-member can therefore be calculated, i.e.

$$\ln(K_{4.6} \cdot a_{\text{annite}})_{1 \text{ bar}} = \frac{-73261}{T} + 75.62 \quad .4 - 9$$

Experimental results represented in terms of the hydrous end-member are shown in Figure 12 and the data plotted are given in Table 12. Uncertainties in 4 - 9 and 4 - 5 are caused not only by the uncertainties in temperature and pressure (reported in Part I Chapter I) but to a systematic error of unknown magnitude caused by the use of a theoretical line (2 - 8) to calculate H₂O contents for the Fe-cordierite. The uncertainty limits indicated in Figures 11 and 12 for the equilibria 4 - 1 and 4 - 2 have been calculated in the following way. They assume that the expression derived in Part I Chapter II

$$\ln K = \frac{17802}{T} - 24.66 \dots \dots \dots 4 - 10$$

represents the equilibrium

Systematic or other errors accumulated in the derivation of 4 - 10 are not included in the estimates of uncertainty in Figures 11 and 12.

For the conditions at which reversals on the graphite-methane buffer of the cordierite-sanidine reaction were achieved, the H₂O content of the Fe-cordierites varies between 0.82 and 0.87. Thus, the reaction run cordierites are closer in composition to the hydrous end-member. Uncertainty limits for the hydrous end-member equilibrium were assumed as shown in Figure 12. Using the relationship 4 - 8 uncertainty limits can be calculated for the anhydrous equilibrium 4 - 1.

This gives the relatively narrow limits of uncertainty shown in Figure 11.

The expression 4 - 5 which has been quoted representing the hydrous species, cordierite-sanidine equilibrium, represents the mid-points of the uncertainty limits. Equation 4 - 8 was then used to calculate the position of the anhydrous species, cordierite-sanidine reaction and this is the expression 4 - 9 shown in Figure 12.

The reversal obtained on the $\text{NNO,OH}(\text{GH,COH})$ buffer was anomalous when compared to results on the graphite-methane buffer. There are two possible reasons for this anomaly. The first explanation is that there was a problem in obtaining equilibrium with the $(\text{NNO,OH},(\text{GH,COH}))$ buffer. However, only runs where there was confidence that the buffer had been maintained during the whole run have been quoted and errors in estimating the fluid composition of the buffer would have to be extremely large to account for the anomalous result. The second possible explanation appears more likely. Farrell and Newman (1967) detected the presence of CO_2 molecules in infrared studies of natural cordierite. At 1000 bars and 627°C the fluid composition of the $\text{NNO,OH}(\text{GX,COH})$ buffer is 84 percent CO_2 and only 14.5 percent H_2O , with small amounts of H_2 , CO and CH_4 . It appears likely that CO_2 will enter the cordierite molecule under these conditions, either instead of or in addition to water. (A study of the amount of CO_2 in cordierites by Suknew et al (1971) showed up to 0.8 wt percent CO_2 in cordierites from granulite terrains). A study of the effect of CO_2 in cordierites needs to be

Figure 13 Calculated reaction path for the reaction,
aluminous biotite + sillimanite + quartz $\rightarrow$
Fe-cordierite + sanidine + vapour.

This figure shows the anhydrous equilibrium (dashed lined)
contoured with various values of $(1-X)$ mols H_2O . The
narrow solid line represents the hydrous equilibrium
contoured with various values of X . The thick line
represents the calculated reaction path.

Figure 13

carried out before runs on the NNO, OH(GX, COH) buffer can be used to determine cordierite reactions.

The equilibria involving hydrous and anhydrous cordierite can be represented on a P-T diagram for specified H_2O fugacity and cordierite species activity if the activity of the annite species is assumed to be constant. Both equilibria are shown in P-T space in Figure 13 with contours representing varying activity of the appropriate cordierite species at $P_{\text{H}_2\text{O}} = P_{\text{TOTAL}}$. Since these equilibria must apply simultaneously for the observed reaction, this reaction is located at the intersection of contours whose values sum to unity since the mole fractions (i.e. activities in solid solution) of the species must sum to unit value.

5. THE REACTION BIOTITE + SILLIMANITE + QUARTZ $\pm$
Fe-CORDIERITE + MUSCOVITE (VAPOUR)

(a) Introduction

This reaction has not previously been studied experimentally. Thompson (1976) predicts a negative slope for this reaction in P-T space, on the basis of schematic phase relations deduced from field relations.

(b) Experimental Results

At $353 \pm 5^{\circ}\text{C}$. and 1 kilobar, the run products were chlorite, (of undetermined composition)- muscovite and quartz. No attempt was made to determine the position of the chlorite breakdown curve. A run at 590°C and 1 kilobar showed no evidence of sanidine formation. Only one reliable reversal for this reaction was obtained at 2 kilobars between $575^{\circ}\text{C} - 580^{\circ}\text{C} \pm 5^{\circ}\text{C}$. As only one reversal for the Fe-cordierite-muscovite reaction was observed, no calculations of an equation for this reaction were possible.

6. PHASE RELATIONS AMONG THE MINERALS, BIOTITE, MUSCOVITE, SANIDINE, Fe-CORDIERITE, ALMANDINE, SILLIMANITE AND QUARTZ

A.B. Thompson (1976b) considered phase relations between Fe-cordierite, almandine, muscovite, Kspar, aluminosilicate biotite and quartz. He gave a schematic pressure-temperature grid (Figure 14) for reactions involving these minerals. The reactions were considered in terms of the components, Al_2O_3 , FeO and $KA1O_2$ with SiO_2 and H_2O present in excess. (The phase relations were developed using the method of Zen 1966). There are six minerals which can be considered in terms of the components FeO, Al_2O_3 - $KA1O_2$. These are Fe-cordierite, almandine, biotite, potassic-feldspar, muscovite and aluminosilicate. Thompson postulates the presence of four stable invariant points (where five of the six phases occur at fixed temperature and pressure and two metastable invariant points. The stable invariant points are muscovite absent [Mus], garnet absent [Gar], Kspar absent [Ksp], and cordierite absent [Crd]. The metastable invariant points are biotite absent [Bio] and aluminosilicate absent [Als].

Partial quantitative grids for these minerals are presented for the conditions where $P_{H_2O} = P_{TOTAL}$ and for $P_{H_2O} = P_{H_2O}$ of the QFI buffer. The biotite in these two grids is aluminous of a fixed composition identical to the run product biotites produced in the determination of the reaction biotite + sillimanite +

Figure 14 A schematic P-T representation of phase relations in the system $K_2O-FeO-Al_2O_3-SiO_2-H_2O$, determined from natural assemblages (Thompson 1976).

Figure 15 A partial quantitative P-T, grid in the system
 $K_2O-FeO-Al_2O_3-SiO_2-H_2O$ when $P_{H_2O} = P_{TOTAL}$.

The position of the reaction Fe-cordierite + almandine + sillimanite + quartz was calculated from the data of Richardson (1968) as shown in Figure 3 Part II. The position of the reaction aluminous-biotite + sillimanite + quartz + Fe-cordierite + sanidine is as shown in Figure 13. The position of the muscovite + quartz breakdown curve is from the equation of Chatterjee and Johannes (1974). The dotted line represents the approximate position of the reaction: Fe-cordierite + Muscovite + aluminous-biotite + sillimanite + quartz.

Figure 15

quartz $\pm$ Fe-cordierite + sanidine $\pm$ vapour. The aluminosilicate polymorph considered is sillimanite. The potassic-feldspar is high sanidine, identical to those used in the determination of the reaction, muscovite $[2M_1]$ + quartz $\pm$ sanidine + sillimanite, by Chatterjee and Johannes, (1974). For any point along an Fe-cordierite reaction curve, the H_2O content of the Fe-cordierite is the equilibrium H_2O content under the stated conditions.

The positions of the muscovite + quartz $\pm$ sanidine + sillimanite curves were calculated from equation of Chatterjee and Johannes (1974). The position of the reaction Fe-cordierite $\pm$ almandine + sillimanite + quartz was calculated from the data of Richardson (1968), as shown in Part II, Chapter I.

For phase relations where $P_{H_2O} = P_{TOTAL}$, the phase relations are shown in Figure 15. The invariant point [Mus] where sanidine, aluminous-biotite, Fe-cordierite, sillimanite and quartz coexist is at $685^\circ C$, 3.35 kilobars. The invariant point [Gar] where muscovite, sanidine, Fe-cordierite, aluminous-biotite, sillimanite and quartz coexist must occur at low pressures but its exact position cannot be determined due to uncertainty over the position of the muscovite-Fe-cordierite reaction.

The phase relations in Figure 16 are for the condition where $P_{H_2O} = P_{H_2O}$ of the QFI buffer. These conditions do not occur in nature but are of interest because experimental work on almandine and Fe-cordierite has been determined using this buffer. (Hsu, 1968:

Figure 16 A partial quantitative P-T grid in the system $K_2O-FeO-Al_2O_3-H_2O$ when $P_{H_2O} = P_{H_2O}$ of the QFI buffer.

The position of the reaction Fe-cordierite + almandine + sillimanite + quartz was calculated from the data of Richardson (1968) as shown in Figure 4, Part II.

The position of the reaction, aluminous-biotite + sillimanite + quartz + Fe-cordierite + sanidine was calculated from equations 4 - 5 and 4 - 9. The position of the muscovite + quartz breakdown curve is from the equation of Chatterjee and Johannes (1974).

Figure 16

Weisbrod, 1973). Figure 16 also illustrates the phase relations of Fe-cordierite where P_{H_2O} is much less than P_{TOTAL} .

The position of the muscovite + quartz breakdown curve, (again calculated using the equation of Chatterjee and Johannes (1974), has been displaced to temperatures $130^{\circ}C$ lower than for the condition where $P_{H_2O} = P_{TOTAL}$. The position of the observed reaction, biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + sanidine + vapour has remained practically unchanged. However, the stability field of Fe-cordierite under these conditions is greatly reduced with respect to pressure. The invariant point, [Mus] occurs at $640^{\circ}C$ and 1.6 kilobars. It is not known if the reaction, muscovite + Fe-cordierite $\rightleftharpoons$ biotite + sillimanite + quartz + vapour, is stable under conditions of the QFI buffer.

CHAPTER III APPLICATIONS OF EXPERIMENTAL RESULTS TO NATURAL SYSTEMS.

This chapter is devoted to showing the application of experimental results from Parts I and II of this study to natural systems. Most emphasis will be placed on the effect of the H_2O content of natural cordierite on mineral stability and phase relations. While it has been recognized for many years, that the entropy contribution of water in cordierite will affect reactions involving the minerals, (Thompson, 1976; Hutcheon et al, 1973; Hess, 1969; Hensen, 1971; Currie, 1971, 1973) a quantitative assessment of this effect has not been possible.

Before the effect of H_2O content in natural cordierites can be studied, it is necessary to know quantitatively the H_2O content of the mineral at the time reactions were actually taking place. Cordierites very readily adsorb and release water and as was seen in Part I. Chapter 2, rapid quenching is necessary to obtain equilibrium H_2O contents. It is therefore unlikely that the H_2O contents of natural cordierites represent the H_2O contents at the time of mineral formation. Instead, the contents of the ring channels in natural cordierites reflect the cooling history of the minerals. (Lepezin and Melenevsky 1977). As well as water, other gases may be present in the large cavities between two adjacent six-membered rings especially argon. (Smith and Schreyer, 1960) and carbon-dioxide, (Suknev et al, 1971). Alkali

atoms and beryllium are also commonly found in natural cordierites, occurring in a channel site in the plane of the six-membered rings (Cohen et al, 1977). All these variables will affect the optical properties of natural cordierites. Therefore, it is not surprising that Leake (1960), and Hay (1963) were not able to correlate the optical properties of cordierites (especially refractive index) with either metamorphic grade or composition. It was in order to calculate the water contents of natural cordierites under known conditions of temperature and water fugacity that the mathematical models (Part I, Chapter 2, section 4) were developed.

As the H_2O content of cordierite changes with changes in temperature and water fugacity, the entropy contribution of water to the mineral will change also. It can no longer be assumed, (as is generally assumed with experimental reactions), that ΔS_R will remain constant over temperatures of a few hundred degrees and pressures of a few kilobars. (While it has been recognized that the entropy contribution of water in cordierite will affect its role in metamorphism, e.g. Hess, 1969; Currie, 1971, 1973; Hensen, 1971; Hutcheon et al, 1973; Thompson, 1976; Welsbrod, 1973; Newton, 1972; it has not been appreciated that ΔS_R is continually changing along the path of a cordierite reaction). This variable entropy of reaction will be particularly significant in reactions that have hitherto been treated as anhydrous, since the entropy changes in anhydrous reactions are usually small.

Newton (1972) found the breakdown of magnesium-cordierite to enstatite-sillimanite-quartz under anhydrous conditions occurred at 3 - 4 kilobars less than for conditions where $P_{H_2O} = P_{TOTAL}$. It has been suggested by Newton and Newton et al. (1974) that chemical equivalents of Mg-cordierite, enstatite-sillimanite-quartz and sapphirine-quartz, found in many granulite terrains, may have resulted not from a change in pressure and temperature but from a lowering of the activity of water.

In Part II of this study Fe-cordierite reactions were considered as combinations of two end-member equilibria; one involving anhydrous Fe-cordierite and the other involving hydrous Fe-cordierite, containing one mol H_2O per formula unit. Theoretical calculations based on experimental work in the system $FeO - Al_2O_3 - SiO_2 - H_2O - H_2$, indicated a decreased stability of cordierite with respect to pressure when $P_{H_2O} < P_{TOTAL}$. Since the breakdown of cordierite to give garnet is commonly used in natural systems as a geobarometer this decreased stability of cordierite when $P_{H_2O} < P_{TOTAL}$ is of some significance. The assemblage garnet-cordierite-sillimanite is common in regionally metamorphosed rocks; (Wynne-Edwards and Hay, 1963; Reinhard, 1968; Currie 1971; Dallmeyer and Dodd, 1971; Hutcheon et al, 1973; Dougan, 1974 and A.B. Thompson, 1976). The same assemblage, garnet-cordierite-sillimanite may arise due to contact metamorphism. (Best and Weill, 1964 and Okrusch, 1971).

Since the assemblage is common, many attempts have been made to use the distribution of cations (Fe^{2+} and Mg) as indicators of metamorphic temperatures and pressures. Two experimental studies by Currie (1971) and by Hensen and Green (1971) have attempted to determine a correlation between the distribution of Fe^{2+} and Mg^{2+} in garnet and cordierite, temperature and pressure. Unfortunately the experimental results of Hensen and Green (determined under anhydrous conditions) and of Currie (determined under conditions where $P_{\text{H}_2\text{O}} = P_{\text{TOTAL}}$) do not agree.

An example of the difficulties of reconciling the experimental studies of Currie and Hensen and Green with observed natural assemblages is seen in the work of Dougan (1974) on cordierite gneisses from the Guri area, Venezuela. Dougan, using temperatures estimated from coexisting Fe-Ti oxides, and considering the lack of muscovite, presence of sillimanite and lack of migmatization associated with the garnet-cordierite assemblages, estimated metamorphic temperatures of 700 - 800°C, pressures between 4 - 7 kilobars with $P_{\text{H}_2\text{O}} < P_{\text{TOTAL}}$. The distribution coefficients for two garnet cordierite pairs, where $K_D = \left(\frac{\text{Mg}}{\text{Fe}}\right)_{\text{cordierite}} \cdot \left(\frac{\text{Fe}}{\text{Mg}}\right)_{\text{garnet}}$, are 4.70 and 5.08. The experimental study of Currie for these distribution coefficients would give metamorphic conditions of 645°C, 5.8 kilobars and 695°C, 6.0 kilobars. The work of Hensen and Green would indicate metamorphic conditions of 820°C, 5.3 kilobars and 845°C, 6.15 kilobars.

The temperature estimates of Hensen and Green appear too high and those of Currie, too low.

Both Thompson (1976b) and Hutcheon et al (1973) approached the problem of determining metamorphic conditions from Fe-Mg distribution in coexisting garnet and cordierite, from a theoretical consideration of two anhydrous end-member equilibria relating the minerals, garnet, sillimanite, quartz and cordierite.

Hutcheon et al (1973) assumed that at equilibrium the following relationships exist between reactions 5 - 1 and 5 - 2 making the assumption that ΔS and ΔV are constant:

$$\Delta G_{5-1} = \Delta G^\circ_{5-1} - \Delta S^\circ_{5-1}(T-298) + \Delta V^\circ_{5-1}(P-1) + RT\ln K_{5-1} = 0$$

$$\Delta G_{5-2} = \Delta G^\circ_{5-2} - \Delta S^\circ_{5-2}(T-298) + \Delta V^\circ_{5-2}(P-1) + RT\ln K_{5-2} = 0$$

where ΔG° is the standard free energy change of a reaction at 298°K and 1 bar.

$$K = \frac{\left(\frac{a_{\text{cor}}}{a_{\text{Fecor}}}\right)^3}{\left(\frac{a_{\text{gar}}}{a_{\text{alm}}}\right)^2} = \frac{\left[\frac{\text{Fe}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6}{\left[\frac{\text{Fe}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6} \quad \text{cor}$$

$$K = \frac{\left(\frac{a_{\text{cor}}}{a_{\text{Mg-cor}}}\right)^3}{\left(\frac{a_{\text{gar}}}{a_{\text{py}}}\right)^2} = \frac{\left[\frac{\text{Fe}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6}{\left[\frac{\text{Mg}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6} \quad \text{cor}$$

$$K = \frac{\left(\frac{a_{\text{cor}}}{a_{\text{Mg-cor}}}\right)^3}{\left(\frac{a_{\text{gar}}}{a_{\text{py}}}\right)^2} = \frac{\left[\frac{\text{Mg}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6}{\left[\frac{\text{Mg}}{\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca}}\right]^6} \quad \text{gar}$$

These workers used a theoretical equation, derived from experimental work in the system, $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{O}_2$, (Froese, 1973), for equation 5 - 1. As has already been noted, reaction 5 - 2 cannot be experimentally determined and there are no available free energies of formation for pyrope, which would allow equation 5 - 2 to be calculated. Hutcheon et al calculated reaction 5 - 2 from combinations of experimentally determined reactions, by Newton, 1972 and Hensen, 1972, involving the phases, Mg-cordierite, pyrope, sillimanite, quartz and enstatite. If expressions are known for reactions 5 - 1 and 5 - 2 and K_{5-1} and K_{5-2} are known from analyses of coexisting cordierites and garnets, temperature and pressure can be determined. However, the arguments of Hutcheon et al (1973) are based on the premise that ΔS_R is constant. The experimental results of this study show that ΔS_R is not constant, but changes with temperature and pressure, as the water content of the cordierite varies. The Mg or Fe components in cordierite must themselves be considered as consisting of a combination of anhydrous and hydrous end-members and the true values of the expressions K_{5-1} and K_{5-2} require a term for the activity of anhydrous Fe and Mg-cordierites respectively. However, determination of the H_2O content of a cordierite, (and hence the activity of anhydrous Mg or Fe cordierites), requires a knowledge of the temperature and water fugacity of formation!

Thompson (1976) making the assumption that cordierite is an anhydrous phase, considered the following exchange reaction:

anhydrous cordierite species in equilibrium 5 - 3.

If analyses of a pair of coexisting garnet and cordierite are available the following quantities are known:

$$M_{Fe}^{gar} = \left[\frac{Fe}{Fe + Mg + Mn + Ca} \right]^{gar} \quad 5$$

$$M_{Mg}^{gar} = \left[\frac{Mg}{Fe + Mg + Mn + Ca} \right]^{gar}$$

$$M_{Fe}^{co} = \left[\frac{Fe}{Fe + Mg + Mn + Ca} \right]^{cordierite}$$

$$M_{Mg}^{co} = \left[\frac{Mg}{Fe + Mg + Mn + Ca} \right]^{cordierite}$$

$$K_D = \frac{M_{Mg}^{co} \cdot M_{Fe}^{gar}}{M_{Fe}^{co} \cdot M_{Mg}^{gar}}$$

For a coexisting garnet and cordierite, the following equilibria apply:

(These equilibria have been written for the exchange of one atom of Fe and Mg to facilitate comparison with the measured quantity K_D).

Subtracting 5 - 5 from 5 - 4 we obtain the expression:

The following equilibria also apply:

Subtracting 5 - 8 from 5 - 7 we obtain the expression:

Thus, we can relate the exchange reactions 5 - 5 and

5 - 4 with the hydration reactions 5 - 7 and 5 - 8.

The equilibrium 5 - 7 is:

$\ln K$ is known for equation 2 - 15 (Part I, Chapter 2).

Therefore, we calculate:

$$\ln K_{5.7} = \frac{8901}{T} - 12.33$$

Similarly equilibrium 5 - 8 is

$\ln K$ is known for equation 2 - 10 (Part I, Chapter 2).

Therefore, we calculate

$$\ln K_{5.8} = \frac{5446}{T} - 9.24$$

Therefore, we can calculate 5 - 6

$$\ln K_{5.6} = \frac{3455}{T} - 3.1$$

If $a_{\text{hyFe}}^{\text{co}}$ is the activity of the hydrous Fe species,

$\text{FeAl}_2\text{Si}_{12.5}\text{O}_9 \cdot \frac{1}{2}\text{H}_2\text{O}$ in cordierite

$a_{\text{Fe}}^{\text{co}}$ is the activity of the anhydrous Fe species,

$\text{FeAl}_2\text{Si}_{12.5}\text{O}_9$ in cordierite

$a_{\text{hyMg}}^{\text{co}}$ is the activity of hydrous Mg species,

$\text{MgAl}_2\text{Si}_{12.5}\text{O}_9 \cdot \frac{1}{2}\text{H}_2\text{O}$ in cordierite

$a_{\text{Mg}}^{\text{co}}$ is the activity of the anhydrous species,
 $\text{MgAl}_2\text{Si}_{2.5}\text{O}_9$ in cordierite.

$M_{\text{Fe}}^{\text{co}}$ is the total Fe in cordierite

$M_{\text{Mg}}^{\text{co}}$ is the total Mg in cordierite

The following relationships apply:

$$M_{\text{Fe}}^{\text{co}} = a_{\text{hyFe}}^{\text{co}} + a_{\text{Fe}}^{\text{co}} \quad .5 - 9$$

$$M_{\text{Mg}}^{\text{co}} = a_{\text{hyMg}}^{\text{co}} + a_{\text{Mg}}^{\text{co}} \quad .5 - 10$$

$$K_{5.7} = \frac{a_{\text{hyFe}}^{\text{co}}}{a_{\text{Fe}}^{\text{co}} \cdot (f_{\text{H}_2\text{O}})^{1/2}} \quad .5 - 11$$

$$K_{5.8} = \frac{a_{\text{hyMg}}^{\text{co}}}{a_{\text{Mg}}^{\text{co}} \cdot (f_{\text{H}_2\text{O}})^{1/2}} \quad .5 - 12$$

From the preceeding relationships the various activities
 can be calculated for known T , $f_{\text{H}_2\text{O}}$, $M_{\text{Fe}}^{\text{co}}$ and $M_{\text{Mg}}^{\text{co}}$.

$$a_{\text{Fe}}^{\text{co}} = \frac{a_{\text{hyFe}}^{\text{co}}}{K_{5.7} \cdot (f_{\text{H}_2\text{O}})^{1/2}} \quad .5 - 13$$

$$a_{\text{hyFe}}^{\text{co}} + \frac{a_{\text{hyFe}}^{\text{co}}}{K_{5.7} \cdot (f_{\text{H}_2\text{O}})^{1/2}} = M_{\text{Fe}}^{\text{co}} \quad .5 - 14$$

$$a_{\text{hyFe}}^{\text{co}} = \frac{M_{\text{Fe}}^{\text{co}}}{1 + \frac{1}{K_{5.7} \cdot (f_{\text{H}_2\text{O}})^{1/2}}} \quad .5 - 15$$

$$a_{\text{Fe}}^{\text{co}} = M_{\text{Fe}}^{\text{co}} - \left[\frac{M_{\text{Fe}}^{\text{co}}}{1 + \frac{1}{K_{5.7} \cdot (f_{\text{H}_2\text{O}})^{1/2}}} \right] \quad .5 - 16$$

$$a_{\text{Mg}}^{\text{co}} = \frac{a_{\text{hyMg}}^{\text{co}}}{K_{5.8} \cdot (f_{\text{H}_2\text{O}})^{1/2}} \dots \dots \dots 5 - 17$$

$$a_{\text{hyMg}}^{\text{co}} + \frac{a_{\text{hyMg}}^{\text{co}}}{K_{5.8} \cdot (f_{\text{H}_2\text{O}})^{1/2}} = M_{\text{Mg}}^{\text{co}} \dots \dots \dots 5 - 18$$

$$a_{\text{hyMg}}^{\text{co}} = \frac{M_{\text{Mg}}^{\text{co}}}{1 + \frac{1}{K_{5.8} \cdot (f_{\text{H}_2\text{O}})^{1/2}}} \dots \dots \dots 5 - 19$$

$$a_{\text{Mg}}^{\text{co}} = M_{\text{Mg}}^{\text{co}} - \left[\frac{M_{\text{Mg}}^{\text{co}}}{1 + \frac{1}{K_{5.8} \cdot (f_{\text{H}_2\text{O}})^{1/2}}} \right] \dots \dots \dots 5 - 20$$

An experimental study of 5 - 3 has been carried out by Hensen and Green (1971, 1972). Their study involved the exchange of Fe and Mg between garnet and cordierite under anhydrous conditions so that the activities of the hydrous species, $a_{\text{hyFe}}^{\text{co}}$ and $a_{\text{hyg}}^{\text{co}}$ were zero. However, the experiments of Hensen and Green involved the addition of K_2O and CaO to the system which causes some dilution of the Fe and Mg end-members in both minerals. Insufficient data are given to make adjustments in the mole fractions in 5 - 4 and distribution coefficients given in Table 13 for the work of Hensen and Green ignore the presence of these additional components.

Currie, (1971), has also measured the exchange of Fe and Mg between garnet and cordierite in the presence of an H_2O fluid with $P_{\text{H}_2\text{O}} = P_{\text{TOTAL}}$. We have just derived equations (5 - 15, 5 - 16, 5 - 19, and 5 - 20) for the calculation of the activities of cordierite species with conditions of known temperature and H_2O fugacity. This

T	fH ₂ O	M _{Mg} ^{co}	a _{Mg} ^{co}	a _{anMg} ^{co}	M _{Fe} ^{co}	a _{hyFe} ^{co}	a _{anFe} ^{co}	M _{Fe} ^{gar}	M _{Mg} ^{gar}	K _{Dhy}	K _{Danhy}
* 873	4006	.64	.4863	.1537	.36	.3176	.0424	.68	.32	3.25	7.70
* 973	3810	.41	.2538	.1562	.59	.4244	.1656	.89	.11	4.84	7.63
* 973	5086	.66	.4306	.2294	.34	.2541	.0859	.74	.26	4.82	7.60
* 973	6692	.83	.5668	.2632	.17	.1313	.0387	.54	.46	5.07	7.98
* 1073	6021	.67	.3671	.3029	.32	.1851	.1349	.81	.19	8.45	9.57
* 1073	4545	.52	.2667	.2533	.48	.2611	.2189	.89	.11	8.26	9.36
* 1073	7847	.80	.4644	.3356	.20	.1221	.0779	.68	.32	8.08	9.15
* 1073	10096	.86	.5253	.3347	.14	.0896	.0504	.59	.41	8.44	9.56
* 1173	5118	.56	.2354	.3246	.44	.1691	.2709	.91	.09	14.07	12.11
* 1173	6741	.69	.3134	.3766	.31	.1294	.1806	.84	.16	12.72	10.95
* 1173	8722	.80	.3890	.4110	.20	.0898	.1102	.76	.24	13.72	11.81
* 1173	11131	.85	.4392	.4108	.15	.0719	.0781	.69	.31	13.60	11.71
o 1173	0	.81	-	-	.19	-	-	.51	.49	-	4.44
o 1273	0	.80	-	-	.20	-	-	.51	.49	-	4.16
o 1273	0	.89	-	-	.11	-	-	.39	.61	-	5.17
o 1273	0	.80	-	-	.20	-	-	.43	.67	-	3.0
o 1373	0	.67	-	-	.33	-	-	.59	.61	-	2.9
o 1373	0	.82	-	-	.18	-	-	.37	.63	-	2.7

* Data from Currie 1971.

o Data from Hensen and Green (1971, 1972)

Table 13 Calculated activities of anhydrous and hydrous Fe and Mg species in cordierite, and calculated K_D s for Mg-Fe exchange between garnet and either anhydrous or hydrous cordierite.

enables calculation of the mole fractions, of hydrous and anhydrous species, in the experiments of Currie. These mole fractions are used to calculate K_D values for 5 - 4 and 5 - 5. These calculations are summarized in Table 13.

Experimental results from the work of Hensen and Green (1971, 1972), and Currie (1971), for equilibria are shown graphically in Figure 17. Results from the work of Currie give a clear indication of a negative slope for the hydrous species, 5 - 5. The equilibrium constant for this reaction is given by the expression.

$$\ln K_{D_{hy}} = \frac{-4700}{T} + 6.51 \dots \dots \dots 5 - 21$$

As we have seen previously the anhydrous equilibrium 5 - 4 is related to the hydrous equilibrium 5 - 5 by the expression 5 - 6.

The following expression for the equilibrium constant of 5 - 4 is obtained:

$$\ln K_{D_{an}} = \frac{-1246}{T} + 3.41 \dots \dots \dots 5 - 22$$

As seen in Figure 17, 5 - 22 gives a slight negative slope for the anhydrous species and passes closely through the calculated points from the data of Currie. It does not pass through the data of Hensen and Green. This indicates that there are definite inconsistencies between the experimental work of Hensen and Green and Currie. These inconsistencies may be due to the presence of Ca and K_2O in the experiments of Hensen and Green. As previously noted Thompson (1976), using distribution coefficients

Figure 17 $\ln K_D$ -/T plots for

$$K_D = \left[\frac{a_{\text{co}}}{a_{\text{hyFe}}} \cdot \frac{M_{\text{Fe}}^{\text{gar}}}{M_{\text{Mg}}^{\text{gar}}} \right] \quad \text{and} \quad \left[\frac{a_{\text{Mg}}}{a_{\text{Fe}}} \cdot \frac{M_{\text{Fe}}^{\text{gar}}}{M_{\text{Mg}}^{\text{gar}}} \right]$$

Data are from Currie (1971) and Hensen and Green (1971, 1972).

Figure 17

from field studies, gives a plot of $\ln k_D$ against reciprocal temperature indicating a decrease in the distribution

coefficient $\left(\frac{M_{Mg}^{cor}}{M_{Fe}^{cor}} \cdot \frac{M_{Fe}^{gar}}{M_{Mg}^{gar}} \right)$

with increase in temperature. However, the distribution coefficients will be dependent not only on temperature but on the water fugacity. Although the equations for the equilibria 5 - 4 and 5 - 5 in Figure 7 do not necessarily represent the real values for these equilibria they may be used to illustrate the magnitude of the problems inherent in using distribution coefficients between garnet and cordierite as geothermometers. For example, at a temperature of 700°C the distribution coefficient observed for the pure anhydrous species would be 8.4. The observed distribution coefficient for the pure hydrous species would be 5.4. Conversely, an observed distribution coefficient of 7.0 would represent a temperature of 578°C, for the pure anhydrous species, and a temperature of 757°C for the pure hydrous species. In other words, distribution coefficients between coexisting garnet and cordierite are unreliable as geothermometers. It is precisely in the temperature region that is of major interest in cordierite bearing rocks (600° - 750°C) that the H₂O content of the mineral changes most rapidly with temperature and the fugacity of water.

SUMMARY AND CONCLUSIONS

Cordierites of composition, (Fe/Fe + Mg), 0.0, 0.25, 0.50, 0.65 and 1.00 have been hydrothermally synthesised at pressures of 1 to 3 kilobars, at temperatures between 550° - 750°C on the buffer, GH,CN(X,OH) and buffer NNO,OH(GX,COH). These cordierites had orthorhombic symmetry with a distortion index of 0.15. Cell constants have been given for eighteen cordierites and these include representatives of all compositions of both hydrous and anhydrous species. A representative Mg-cordierite had cell constants: $a = 17.010(.007)$, $b = 9.737(.002)$, $c = 9.343(.003)$ and $V = 1547.3(\text{\AA}^3)$. A representative Fe-cordierite had cell constants: $a = 17.125(.010)$, $b = 9.839(.004)$, $c = 9.293(.003)$, and $V = 1574.0(.7)(\text{\AA}^3)$. It is recommended that a molar volume of 237 cm³ be adopted for Fe-cordierite. For hydrous cordierites, a and b and V increase with increase in (Fe/Fe + Mg) while c decreases. The same relationship of cell constants with composition apply to anhydrous cordierites. For a particular composition there is a slight increase in V , a slight decrease in c and for all compositions except (Fe/Fe + Mg) an increase in b for the anhydrous material. Stout (1975) had suggested that the effect of dehydrating a cordierite would be to increase a relative to b . In the synthetic cordierites the reverse relationship was seen, i.e. b was increased relative to a .

Infrared studies indicated that all water in cordierite is present as molecular H₂O which may be

removed by heating to 750°C.

Mössbauer spectra of a synthetic hydrous cordierite with $(\text{Fe}/\text{Fe} + \text{Mg}) = 0.25$ and a sekaninaite of $(\text{Fe}/\text{Fe} + \text{Mg})$ of 0.90 showed a simple quadrupole doublet with a centre shift and splitting characteristic of Fe^{2+} in an octahedral site. The spectra of synthetic hydrous cordierites with an $(\text{Fe}/\text{Fe} + \text{Mg})$, 0.50 and 1.00 showed an additional Fe^{2+} doublet. After dehydration the anhydrous cordierite indicated that the Fe^{2+} in the second site was now present as Fe^{3+} . The additional peak in the hydrous material has been attributed to Fe-Mg spinel impurities which were oxidised during the dehydration of the cordierite to haematite-corundum solid solutions. The ratio of the areas under the spinel doublet to the total area under the peaks was an indication of the amount of impurities in the original material.

The H_2O content of the synthetic cordierites was measured using thermogravimetric analysis. The equipment could measure H_2O content (on 10-15mg samples) with a reproducibility on duplicate samples of ± 0.15 weight percent which represents $\pm .04$ mols H_2O . Rapid isobaric quenching of cordierite synthesis runs was believed to produce cordierites with close to equilibrium H_2O contents for the conditions of synthesis. The reproducibility of H_2O content determinations on cordierites of the same compositions, produced in separate synthesis runs was $\pm .02$ weight percent or $\pm .06$ mols H_2O .

The following relationships between the H₂O content and mean refractive indices of Mg-cordierite were established:

$$RI_{Mg} = 1.52489 + 0.3431 W_{Mg} \dots \dots \dots .2 - 5$$

$$W_{Mg} = 43.6435 + 28.6381 RI_{Mg} \dots \dots \dots .2 - 6$$

Due to the presence of hercynite and quartz impurities measured H₂O contents of Fe-cordierite were in error. A relationship between mean refractive index of Fe-cordierites and their H₂O was developed and was given by:

$$RI_{Mg} = 1.554 + 0.3431 W_{Fe} \dots \dots \dots .2 - 7$$

$$W_{Fe} = -45.293 + 29.146 RI_{Fe} \dots \dots \dots .2 - 8$$

The (Fe/Fe + Mg) of a synthetic cordierite can be determined from the mean refractive index of the anhydrous material.

$$F = -52.586 + 34.483 RI \dots \dots \dots .2 - 9$$

The work of Lepezin et al (1976) indicated that this relationship may also be applied to natural cordierites.

Using water distribution data determined by T.G.A. an equilibrium constant for the reaction:

was determined and is given by:

$$\ln K = 10893/T - 18.47 \dots \dots \dots .2 - 14$$

Due to the negligible change in molar volume for the reaction 2 - 10, the expression 2 - 14 holds for any pressure. A knowledge of the temperature and water fugacity at the time of synthesis enables the water content to be calculated.

Using H₂O contents of Fe-cordierite calculated from equation 2 - 8 an equilibrium constant for the reaction

$$\text{Fe}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18} \text{H}_2\text{O} \quad 2 - 15$$

was determined and is given by:

$$\ln K = \frac{17802}{T} - 24.66 \quad 2 - 17$$

At temperatures less than 800°C Fe-cordierite have a greater H₂O content than Mg-cordierites synthesised under the same conditions.

The data of Richardson (1968) for the reaction:

3 Fe-cordierite + 2 almandine + 4 sillimanite + 5 quartz were considered in terms of two simultaneous equilibria for the anhydrous and monohydrate (hydrous) species in cordierite.

For the anhydrous equilibrium:

the following equilibrium constant was derived

$$\ln K_1 \text{ bar} = \frac{16500}{T} - 19.125 \quad 3 - 4$$

For the hydrous equilibrium:

the following equilibrium was derived:

$$\ln K_1 \text{ bar} = \frac{-40125}{T} + 58.03 \quad 3 - 5$$

The calculated reaction path of the cordierite breakdown reaction 3 - 1 is curved reflecting the effect of the changing entropy of Fe-cordierite with varying water content. The reaction has a negative slope at low temperatures and a positive slope at high temperatures. The

minimum pressure at which almandine became stable for $P_{H_2O} = P_{TOTAL}$ was 2.75 kilobars while when $P_{H_2O} = P_{H_2O}$ of QFI buffer this minimum pressure at which almandine became stable was reduced to 1.6 kilobars. This indicated that hydrous Fe-cordierite was stable to higher pressures than anhydrous Fe-cordierite.

Phase relations in the system $FeO - Al_2O_3 - SiO_2 - O_2$ at 2 kilobars calculated from experimental determinations of five invariant points (Froese, 1973) were greatly changed by small changes in the equations for the QFM and MW buffers. This was due to the sensitivity of magnetite and hercynite activities to small changes in $\log f_{O_2}$ which affected calculation of the oxidation reactions in this system. Consideration of the H_2O content of cordierite introduced an additional component to the system and calculation of the position of cordierite breakdown reaction to garnet-sillimanite and quartz indicated that this reaction was stable at 2 kilobars only at very low mole fractions of H_2O in the fluid.

The reaction, biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + sanidine + vapour was studied experimentally using well characterised phases. The composition of biotites in equilibrium with cordierite and sillimanite at the end of the reaction runs was:

On the methane buffer the following reversal were obtained on the cordierite-sanidine reaction, on the

graphite-methane buffer; at 1 kilobar between 626° - $631^{\circ} \pm 5^{\circ}\text{C}$; at 1.5 kilobars between 634 - $644^{\circ} \pm 5^{\circ}\text{C}$ and at 2 kilobars between 639° - $645^{\circ} \pm 5^{\circ}\text{C}$. On the NNO, OH(GX, COH) buffer a reversal was obtained at 1 kilobar between 603° - $613^{\circ} \pm 5^{\circ}\text{C}$. Due to uncertainty over the CO_2 in cordierites and its effect on the cordierite-sanidine reaction, only reversals using the graphite-methane buffer were considered. For the equilibrium involving the anhydrous species:

$$\ln(K_1 \text{ bar} - \text{annite}) = \frac{-126667}{T} + 149.6 \dots \dots \dots .4 - 5$$

For the equilibrium involving the hydrous species:

$$\ln(K_1 \text{ bar} - \text{annite}) = \frac{-73261}{T} + 75.62 \dots \dots \dots .4 - 9$$

using these equilibria, the cordierite-sanidine reaction path was calculated.

One reversal was obtained on the reaction, Fe-cordierite + Muscovite + biotite + sillimanite + quartz, at 2 kilobars between 575° and $580^{\circ} \pm 5^{\circ}\text{C}$ on the graphite-methane buffer.

Partial quantitative grids for the system K_2O -

FeO - Al₂O₃ - SiO₂ - H₂O, were shown both for the conditions where $P_{H_2O} = P_{TOTAL}$ and where $P_{H_2O} = P_{H_2O}$ of the QFI buffer. The invariant point [Mus] where Fe-cordierite, almandine, sillimanite, aluminous biotite and quartz coexist is at 685°C and 3.35 kilobars where $P_{H_2O} = P_{TOTAL}$ and at 640°C and 1.6 kilobars where $P_{H_2O} = P_{H_2O}$ of the QFI buffer.

This study has indicated that the H₂O content present in natural cordierites does not represent the H₂O content at the time of metamorphism. As the H₂O content of water changes with changes in temperature and water fugacity, the entropy contribution of water to the mineral changes also. The importance of changes in ΔS_R have not previously been recognised. The experimental evidence of Newton (1972) on Mg-cordierite and the theoretical calculations on Fe-cordierite given in Part II of this study have indicated that the stability of cordierites with respect to pressure is greatly reduced when P_{H_2O} is much less than P_{TOTAL} .

The assemblage, garnet-sillimanite-quartz, is common in metamorphic rocks and attempts have been made to use this assemblage as a geothermometer and a geobarometer, (Currie 1971, Hutcheon et al 1973, Thompson 1976). The methods of these authors are theoretically in error as they do not consider the variable entropy of water in cordierite.

The experimental determinations by Currie (1971) and Hensen and Green (1971, 1972) for the exchange of Fe

and Mg between garnet and cordierite (5 - 3) were examined. The work of Hensen and Green involved anhydrous species only. Having derived expressions for the activities of Fe and Mg hydrous and anhydrous species in cordierite, equilibrium constants for the anhydrous equilibrium (5 - 4) and the hydrous equilibrium (5 - 5), from the data of Currie were calculated:

$$\ln k_{5.5} = \frac{-4700}{T} + 6.51 \dots \dots \dots 5 - 21$$

$$\ln k_{5.4} = \frac{-1246}{T} + 3.41 \dots \dots \dots 5 - 22$$

The expression calculated from the data of Currie for the anhydrous species is inconsistent with the work of Hensen and Green. Similar observed K_D 's from natural cordierite assemblages may represent considerable differences in temperature if there were large differences in water fugacity.

Those conclusions described above which are dependent on the use of an ideal solution model to calculate the activities of anhydrous and hydrous cordierite species should be regarded as tentative, pending experimental verification within the pressure-temperature limits used in this study.

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APPENDIX I

PREPARATION OF SYNTHETIC CORDIERITES

A. STANDARDISATION OF STARTING MATERIALS

1. Fe Sponge. Sample No. S1994

Supplier Johnson, Matthey & Co. Ltd.

Method

Two 50ml vitreosil crucibles with lids were heated for an hour in a muffle furnace at 1000°C and cooled in a dessicator for one hour. Approximately one gram of iron sponge was weighed out into each crucible. The crucibles were then heated in the muffle furnace overnight. After removal from the furnace the lid was lifted to remote oxidation. The heating and cooling process was repeated until constant weights were obtained.

Results

	I	II
Wt of crucible + lid + Fe sponge	29.97244	32.32368
Wt of crucible	28.92386	31.00617
Wt of Fe sponge	1.04858	1.31751
Theoretical wt Fe_2O_3	1.49920	1.88370
Wt of crucible + Fe_2O_3	30.41907	32.88375
Wt of Fe_2O_3	1.49521	1.87756
Factor	1.00267	1.00327

Average Fe Factor = 1.00297

2. Tetraethyl orthosilicate (TE OS) Lot No. A38

Supplier Eastman

Method

Three platinum crucibles (30ml with lids) were brought to constant weight by repeated firings at red

heat for 15 minutes followed by one hour of cooling in the dessicator. Five ml of TEOS were added by pipette to each crucible which was then reweighed; immediately 3ml of ethyl alcohol was added and .990 ammonium hydroxide drop-wise while stirring until a white curdy precipitate was formed. The stirrer was wiped with a small piece of ashless filter paper and this was then added to the crucible. The crucibles were placed on top of an oven (115°C inside) until the precipitate was dry. The crucibles were then heated, gently at first and then at gradually increasing temperature until they were at red heat. After one hour of heating the crucibles were cooled in a dessicator for one hour. The crucibles were brought to constant weight by as many firings and coolings as necessary.

<u>Results</u>	I	II	III
Weight of crucible	30.21286 30.21289	30.23605 30.23607	30.04215 30.04212
Mean wt of crucible	30.21287	30.23606	30.04213
Wt of crucible + TEOS	34.64409	34.56723	34.37319
Wt of TEOS	4.43121	4.33117	4.33105
Theoretical wt of SiO ₂	1.278104	1.24914	1.24911
Wt of crucible + SiO ₂	31.48118 31.48123	31.47736 31.47738	31.28517 31.28489 31.28492
Mean wt of SiO ₂	1.26833	1.24731	1.24277
Percentage recovery	99.242	99.373	99.492
Factor	1.00764	1.00631	1.00510

Mean Factor = 1.00635

3 Magnesium Oxalate Lot No. 0488690

Supplier British Drug Houses

Method

Two platinum crucibles (30ml with lids) were brought to constant weight by repeated firings to red heat for 15 minutes and cooling for one hour in a dessicator. Approximately 1gm portions of magnesium oxalate were weighed into each crucible. The crucibles were heated gently at first and then strongly until all carbon dioxide and water had been removed. The crucibles were then placed in a muffle furnace at 1000°C overnight.

Results

Wt of crucible	41.80420	24.27152
	41.80425	24.27156
Mean crucible wt	41.80423	24.27154
Crucible + Mg oxalate	42.78973	25.41003
Weight Mg oxalate	0.98550	1.13841
Theoretical MgO	0.26777	0.30936
Wt of crucible + MgO	42.06862	24.57685
Wt of crucible	41.80423	24.27154
Wt of MgO	0.26439	0.30531
Percentage Recovery	98.74	98.69
Factor	1.01278	1.01326

Mean Factor = 1.01302

4. Al-Wire Lot No. 32437

Supplier J.T. Baker Chemical Co.

Analysis of Al Wire as determined by J.T. Baker

Insoluble in Hcl	0.040%
Silicon (Si)	0.10
Nitrogen Compounds (as N)	0.001
Copper (Cu)	0.010
Iron (Fe)	0.050
Manganese (Mn)	0.001
Titanium (Ti)	0.010

B. CALCULATED QUANTITIES FOR PREPARING CORDIERITE GELS

The calculated quantities of starting materials used in preparing the cordierite gels are given in Tables A1 - A5.

Fe Cordierite $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (Fe/Fe + Mg) 1.00

Molecular wt = 648.044

31.47 wt% Al_2O_3

22.17 wt% Fe O

0.0 wt % Ms O

46.36 wt% Si O₂

Bottle + Al wire 9.92422 gm

Wt of weighing bottle 9.17769 gm

0.74653 gm

Wt Al corresponds to 1.41060 gms Al_2O_3

Wt of FeO required .99374 gm

Wt of Fe sponge .77244 gm

Iron Factor 1.00297

Wt Fe sponge weighed .77473 gm

Wt SiO_2 required 2.07802 gm

Wt TEOS 7.20515 gm

TEOS Factor 1.00635

TEOS weighed 7.25091 gm

Table A-1 Calculated quantities of starting materials
for cordierite $\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}$

Cordierite $\text{Fe}_{1.3} \text{Mg}_{0.7} \text{Al}_4 \text{Si}_5 \text{O}_{18}$.

Molecular wt = 625.97 (Fe/Fe + Mg) 0.65

32.58 wt% Al_2O_3

14.92 wt% Fe O

4.51 wt% Mg O

47.99 wt% SiO_2

Bottle + Al wire	10.14450 gm
Weighing bottle	<u>9.17820 gm</u>
	.96630 gm

Wt Al corresponds to 1.82587 gm Al_2O_3

Wt FeO required 0.83617 gm

Wt Fe sponge 0.64995 gm

Fe sponge factor 1.00297

Fe sponge weighed 0.65188 gm

Wt MgO required 0.25275 gm

Wt MgOx required 0.93019 gm

x Mg factor 1.01297

Mg oxalate weighed 0.94226 gm

Wt SiO_2 required 2.68949 gm

Wt TEOS required 9.32501 gm

TEOS factor 1.00635

TEOS weighed 9.38422 gm

Table A-2 Calculated quantities of starting materials
for cordierite $\text{Fe}_{1.3} \text{Mg}_{0.7} \text{Al}_4 \text{Si}_5 \text{O}_{18}$.

Cordierite $\text{FeMg Al}_4\text{Si}_5\text{O}_{18}$.

Molecular wt = 616.505 (Fe/Fe + Mg) 0.50

33.08 wt% Al_2O_3

11.65 st% Fe O

6.54 wt% MgO

48.73 wt% Si O₂

Bottle + Al wire 10.08533 gm

Weighing bottle 9.17786 gm

.90747 gm

Wt Al corresponds to 1.71471 gm Al_2O_3

Wt FeO required 0.60386 gm

Wt Fe sponge required 0.46940 gm

Fe factor 1.00297

Fe sponge weighed 0.47079 gm

Wt MgO required 0.33900 gm

Wt MgOx required 1.24764 gm

Mg factor 1.01297

MgOx weighed 1.26382 gm

Wt Si O₂ required 2.52593 gm

Wt TEOS required 8.75831 gm

TEOS factor 1.00635

TEOS weighed 8.81392 gm

Table A-3 Calculated quantities of starting materials
for cordierite $\text{FeMgAl}_4\text{Si}_5\text{O}_{18}$.

Cordierite $Mg_{1.5} Fe_{0.5} Al_4 Si_5 O_{18}$.

Molecular wt = 600.74 (Fe/Fe + Mg) 0.25

33.94 wt% Al_2O_3

5.98 wt% Fe O

10.07 wt% Mg O

51.36 wt% Si O_2

Bottle + Al wire 10.14438 gm

Weighing bottle 9.17765 gm

~~0.96673 gm~~

Wt Al corresponds to 1.82668 gms Al_2O_3

Wt FeO required 0.32185 gm

Wt Fe sponge required 0.25017 gm

Fe factor 1.00297

Fe sponge weighed 0.25091 gm

Wt MgO required 0.33900 gm

Wt MgOx 1.24764 gm

Mg factor 1.01297

MgOx weighed 1.26382 gm

Wt SiO_2 required 2.52593 gm

TEOS required 8.75831 gm

TEOS factor 1.00635

TEOS weighed 8.81392 gm

Table A-4 Calculated quantities of starting materials
for cordierite $Fe_{0.5} Mg_{1.5} Al_4 Si_5 O_{18}$.

Mg Cordierite $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$.

Molecular wt = 584.974 (Fe/Fe + Mg) 0.00

34.86 wt% Al_2O_3

0.00 wt% Fe O

13.78 wt% Mg O

51.36 wt% Si O_2

Al wire + bottle

9.99456 gm

Weighing bottle

9.17772 gm

0.81684 gm

Wt Al corresponds to 1.54346 gm Al_2O_3

Wt MgO required

0.61012 gm

Wt MgOx

2.24543 gm

Mg factor

1.01297

Mg oxalate weighed

2.27456 gm

Wt SiO_2 required

2.27401 gm

TEOS required

7.88483 gm

TEOS factor

1.00635

TEOS weighed

7.93490 gm

Table A-5 Calculated quantities of starting material
for cordierite $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$.

C. PREPARATION OF Fe CORDIERITE FROM FAYALITE KAOLINITE MIX

Fe-Cordierite was also prepared from a synthetic fayalite (Fe_2SiO_4) + Kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$). This method was described by Rutherford (1968). The reaction is assumed to be:

The analysis of the kaolinite used is seen in Table A-6. Pure kaolinite contains 39.5 wt% Al_2O_3 and 46.55 wt% SiO_2 as opposed to the analysed kaolinite which contained 37.20 wt% Al_2O_3 and 44.82 wt% SiO_2 . The prepared mix contained a slight excess of both Al and Si and the molecular proportions were:

Sample of Kaolinite, Macon, Georgia, 4

SiO ₂	44.82%
Al ₂ O ₃	37.20
Fe ₂ O ₃	0.41
FeO	0.07
MgO	0.25
CaO	0.58
Na ₂ O	0.40
K ₂ O	0.43
H ₂ O+	12.92
H ₂ O-	1.76
TiO ₂	1.26
MnO	_____
SO ₃	_____
C	_____
	100.10

92.48% Kaolinite: 7.52% impurities
(1.76% is absorbed water).

Table A-6 Analysis of kaolinite used in
the preparation of Fe-cordierite.

APPENDIX II

Microprobe Analyses of Iron Rich Cordierite (Sekaininite)

Element	Sekaininite I			Sekaininite II		
	Wt%	Mols	Oxide Wt	Wt %	Mols	Oxide Wt
Fe	12.92	1.492	16.62	12.84	1.486	16.52
Al	17.35	4.146	32.78	17.32	4.149	32.72
Ce	.04	.006	.05	.03	.004	.04
Na	.64	.178	.86	.57	.159	.76
K	.00	.000	.00	.00	.000	.00
Si	21.42	4.916	45.81	21.40	4.926	45.79
Ti	.00	.000	.00	.00	.000	.00
Mg	1.36	.362	2.26	1.33	.355	2.21
Total	53.72	18.000	98.38	53.49	18.000	98.04

Element	Sekaininite III			Sekaininite IV		
	Wt %	Mols	Oxide Wt	Wt %	Mols	Oxide Wt
Fe	12.84	1.471	16.52	12.75	1.478	16.40
Al	17.38	4.120	32.84	17.28	4.148	32.66
Ca	.03	.006	.05	.03	.005	.04
Na	.56	.157	.76	.64	.180	.86
K	.00	.000	.00	.00	.000	.00
Si	21.74	4.950	46.51	21.33	4.915	45.62
Ti	.00	.000	.00	.00	.000	.00
Mg	1.38	.364	2.29	1.41	.376	2.34
Total	53.94	18.000	98.97	53.44	18.000	97.92

The analyses were performed by Dr. P. Mainwaring of the Carleton University Geology Department.

APPENDIX III

(a) Cell constants of synthetic 1M muscovite

$[K_2Al_4Al_2Si_6O_{20}(OH)_4]$ used in determination of
the reaction: muscovite + Fe-cordierite
biotite + sillimanite + quartz.

$$a = 5.227(5) \quad b = 8.995(1) \quad c = 10.297(1) \quad \beta = 101.93(6)$$

$$V = 473.6(5) \text{ \AA}^3$$

<u>h</u>	<u>k</u>	<u>l</u>	<u>d observed</u>	<u>d calculated</u>
0	0	1	10.069	10.073
0	0	2	5.040	5.037
0	2	0	4.497	4.498
1	1	1	4.366	4.367
0	2	1	4.111	4.107
1	1	2	3.674	3.677
0	0	3	3.358	3.358
0	2	2	3.358	3.355
1	1	2	3.069	3.070
0	2	3	2.690	2.691
1	3	1	2.571	2.571
1	3	1	2.447	2.444
1	3	2	2.403	2.405
0	4	0	2.251	2.249
1	3	3	2.161	2.161
0	0	5	2.014	2.015
1	1	6	1.673	1.673
0	6	0	1.499	1.499

(b) Cell Constants of synthetic 1M annite

$[K_2Fe_6Al_2Si_6O_{20}(OH)]$ used as the starting biotite for the reactions biotite + sillimanite + quartz $\rightarrow$ Fe-Cordierite + sanidine and biotite + sillimanite + quartz $\rightarrow$ Fe-cordierite + muscovite.

$$a = 5.397_{(2)} \quad b = 9.361_{(6)} \quad c = 10.345_{(3)} \quad \beta = 99.980_{(5)}$$

$$V = 514.73_{(2)} \text{ \AA}^3$$

<u>h</u>	<u>k</u>	<u>l</u>	<u>d observed</u>	<u>d calculated</u>
0	0	1	10.192	10.188
1	1	0	4.645	4.622
1	1	$\bar{2}$	3.717	3.713
0	2	2	3.453	3.447
0	0	3	3.392	3.396
1	3	$\bar{1}$	2.659	2.660
2	0	0	2.659	2.658
0	0	4	2.544	2.547
1	3	1	2.544	2.547
2	0	$\bar{2}$	2.544	2.544
1	1	3	2.544	2.559
2	0	1	2.470	2.469
1	3	$\bar{2}$	2.470	2.471
2	0	2	2.204	2.049
1	3	$\bar{3}$	2.204	2.205
0	0	5	2.031	2.037
2	0	4	1.698	1.698
1	3	5	1.698	1.698
0	6	0	1.560	1.560
3	3	0	1.540	1.540

(c) Cell constants of synthetic sanidine [KAlSi_3O_8]
 starting material for the reactions biotite + sillimanite
 + quartz $\rightleftharpoons$ Fe-cordierite + sanidine

$$a = 8.60392(.002), \quad b = 13.03025(.002), \quad c = 7.18176(.001)$$

$$\beta = 115.964(.0003), \quad V = 723.89(.001) \text{ \AA}^3$$

<u>h</u>	<u>k</u>	<u>l</u>	<u>d observed</u>	<u>d calculated</u>
1	1	0	6.6557	6.6517
0	2	0	6.5158	6.5151
I	1	1	5.8740	5.8665
2	0	1	3.9494	3.9492
2	0	0	3.8660	3.8677
1	3	0	3.7779	3.7873
I	3	1	3.6270	3.6232
2	2	1	3.5553	3.5504
I	1	2	3.4571	3.4610
2	2	0	3.3268	3.3259
2	0	2	3.2838	3.2850
0	4	0	3.2556	3.2576
0	0	2	3.2279	3.2284
1	3	1	2.9945	2.9983
2	2	2	2.9334	2.9332
I	3	2	2.7643	2.7671
3	1	2	2.6074	2.6077
2	2	1	2.5889	2.5867
1	1	2	2.5502	2.5515
3	1	0	2.5248	2.3295
2	4	0	2.4903	2.4916
1	5	I	2.4220	2.4224
2	4	2	2.3133	2.3131

(c) Cont'd

<u>h</u>	<u>k</u>	<u>l</u>	<u>d observed</u>	<u>d calculated</u>
0	6	0	2.1710	2.1717
4	2	2	2.0114	2.0136
2	6	1	1.9314	1.9324
2	6	0	1.8941	1.8936
{ 4	2	0	1.8535	1.8539
{ 1	1	3	1.8535	1.8536
3	5	0	1.8344	1.8329
2	6	2	1.8127	1.8116
2	0	4	1.7949	1.7950
4	4	1	1.7809	1.7804
2	4	2	1.7474	1.7484
2	6	1	1.7200	1.7202
{ 2	7	0	1.6767	1.6773
{ 3	5	3	1.6767	1.6766

(d) Cell constants of synthetic sillimanite,
 $[Al_2Si O_5]$ used in the determination of reactions: biotite +
 sillimanite + quartz $\rightleftharpoons$ Fe-cordierite + sanidine and
 biotite + sillimanite + quartz $\rightleftharpoons$ Fe-cordierite +
 muscovite.

$$a = 7.510(^4), \quad b = 7.683(^3), \quad c = 5.759(^4), \quad V = 322.2(^3) \text{ \AA}^3$$

<u>h</u>	<u>k</u>	<u>l</u>	<u>d observed</u>	<u>d calculated</u>
1	1	0	5.3723	5.3703
1	2	0	3.4205	3.4199
2	1	0	3.3759	3.3736
1	2	1	2.8892	2.9404
2	2	0	2.6905	2.6851
1	1	2	2.5390	2.5376
1	3	0	2.4232	2.4238
2	0	2	2.2849	2.2849
1	2	2	2.2051	2.2026
2	3	0	2.1175	2.1157
0	4	2	1.5976	1.5978
3	3	2	1.5200	1.5203

END

END

FIN