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TITLE OF THESIS... Fe-Mg Exchange in Synthetic Biotites on the
Join Annite-Phlogopite and Synthetic Clinopyroxene
on the Join Hedenbergite-Diopside
UNIVERSITY... Carleton
DEGREE FOR WHICH THESIS WAS PRESENTED... M.Sc.
YEAR THIS DEGREE GRANTED... 1973

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NL-91 (10-68)

Fe-Mg EXCHANGE IN SYNTHETIC BIOTITES
ON THE JOIN ANNITE-PHLOGOPITE, AND SYNTHETIC
CLINOPYROXENES ON THE JOIN HEDENBERGITE-DIOPSIDE.

by

Avril Ellis Gunter, B.Sc.

A thesis submitted to the Faculty of Graduate
Studies in partial fulfillment of the
requirements for the degree of
Master of Science.

Department of Geology,
Carleton University
Ottawa, Ontario
May, 1973

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1973

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ABSTRACT

Four synthetic biotites on the join annite-phlogopite, and five synthetic clinopyroxenes on the join hedenbergite-diopside, were prepared from reduced oxide mixes. Minerals were synthesized in standard cold seal pressure apparatus at 1 Kbar pressure, at temperatures between 600 - 750° C and under the oxygen fugacity conditions of the graphite-methane buffer.

In an attempt to study the exchange of Fe and Mg between biotite and an aqueous solution, chloride solutions proved unsuitable because a solvus was produced in the annite-phlogopite series between 500 - 680° C at 1 Kbar.

A method using iodide solutions was developed to facilitate the exchange of Fe and Mg between synthetic biotites and clinopyroxenes. The reaction

$$1/3\text{KFe}_3^{2+}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{CaMgSi}_2\text{O}_6 \rightleftharpoons 1/3\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 + \text{CaFeSi}_2\text{O}_6$$

was calibrated at 500 and 600° C and 1 Kbar. The exchange medium was 1M MgI_2 solution with solid Ag / AgI as an internal buffer for f_{I_2} . The biotite and clinopyroxene solid solution series were assumed ideal; and therefore

$$\left(\frac{x_{\text{Pyroxene}}^{\text{Fe}}}{x_{\text{Pyroxene}}^{\text{Mg}}} \cdot \frac{x_{\text{Biotite}}^{\text{Mg}}}{x_{\text{Biotite}}^{\text{Fe}}} \right) = K_D = K_{\text{eq}} = e^{\frac{-\Delta G^\circ}{RT}}$$

At 600° C K_D is 0.80 (range 1.00 - 0.64) and at 500° C K_D is 0.77 (range 0.93 - 0.61). These distribution coefficients are in good agreement with observed values in some naturally occurring biotite-clinopyroxene pairs. The variation of $\ln K_D$ is insufficient to constitute a useful indicator of metamorphic grade. As in most solid-solid reactions ΔS° and ΔV° are small (0.16 cal deg⁻¹ and 0.41 cc).

This method should be applicable to the study of a wide range of exchange reactions involving hydrous minerals (eg. garnet-biotite, amphibole-biotite and chlorite-biotite).

ACKNOWLEDGEMENTS

The writer extends her appreciation to those involved in the preparation of this thesis. I am indebted to Dr. G.B. Skippen of Carleton University, for initiating this study, for the use of his laboratory facilities and for his many helpful suggestions. Dr. E. Froese of the Geological Survey of Canada was most helpful in discussing the evaluation of experimental data and in critical reading of the manuscript.

I should like to thank Dr. G. Chao of Carleton University, for his helpful suggestions on X-ray techniques. Miss J. Baker helped in the preparation of many X-ray films.

Dr. W. Reinhardt of the Geological Survey of Canada, had previously prepared three biotite mixes, on the annite-phlogopite join, and for the use of these I am most grateful. Mr. L. Williams prepared many of the illustrations.

Financial assistance for the thesis was received in the form of:

- (1) an Ontario Graduate Fellowship
- (2) a Carleton Graduate Scholarship.
- (3) a Research Grant from Dr. G.B. Skippen

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INTRODUCTION

Many common minerals of metamorphic rocks are characterized by a wide range of composition, for example minerals of the garnet, cordierite, biotite, muscovite, amphibole, chlorite and ortho- and clinopyroxene groups. In many cases, there is complete solid solution between two or more end members. (In many minerals (e.g. biotites) the total number of possible substitutions is very large). The coexistence of minerals of variable composition implies exchange reactions among the elements common to these minerals. Following the work of Kretz (1959) on the distribution of elements in coexisting garnet, biotite and hornblende in gneisses, many workers have concluded from regularities in element distribution that equilibrium has been approached in metamorphic rocks. Consequently exchange reactions are of considerable significance in an understanding of metamorphic conditions.

Because many metamorphic minerals are ferromagnesian silicates the exchange of iron and magnesium is of particular importance. Many workers, including Ramberg and DeVore (1951), Saxena (1968), Hietanen (1969) and Davidson (1968), have attempted to use the distribution of iron and magnesium between coexisting minerals (olivines and pyroxenes, garnet and clinopyroxene, garnet, staurolite and biotite, ortho- and clinopyroxene), as indicators of metamorphic grade. Experimental calibration

of distribution coefficients would provide an indication of their usefulness as geothermometers and barometers.

Many of the ferromagnesian minerals in metamorphic rocks, particularly at lower grades of metamorphism, are hydrous. Previous work on exchange reactions involves anhydrous minerals (Medaris 1969, Orville 1963, 1972) with the exception of a study of the Rb-K exchange between phlogopite and chloride solution in an iron-free system. The purpose of the present study is twofold. The first and main objective is the development of an experimental method to facilitate iron-magnesium exchange between hydrous minerals. The second objective is to calibrate a particular exchange reaction and to estimate its potential as an indicator of metamorphic grade.

The present study involves the iron-magnesium exchange between biotites on the join phlogopite-annite, and clinopyroxenes on the join diopside-hedenbergite, in a fluid medium. Electrolyte solutions are frequently used in the experimental determination of exchange reactions to improve the kinetics. Thermodynamic relationships will be developed using this example.

It is convenient at this point to define the symbols and constants to be used in this study.

ΔG°	The change in standard free energy of the reaction where the standard state of any component is taken as the pure substance at any specified T & P.
ΔS°	The standard entropy change during the reaction
ΔV°	The standard change in volume during the reaction
K_{eq}	The equilibrium constant for the reaction
K_D	The distribution coefficient
T	Temperature in $^\circ K$
P	Pressure in bars
X	The atomic fraction of either iron or magnesium in the lattice position occupied by these elements
γ	Activity coefficient
f	Fugacity of a gas
R	Gas constant

The coexistence of biotite and clinopyroxene implies the following reaction between the end members:

The equilibrium constant of this reaction is

$$K_{eq} = \left(\frac{x_{Fe}^{Pyroxene}}{x_{Mg}^{Pyroxene}} \cdot \frac{x_{Mg}^{Biotite}}{x_{Fe}^{Biotite}} \right) \left(\frac{\gamma_{Fe}^{Pyroxene} \gamma_{Mg}^{Biotite}}{\gamma_{Mg}^{Pyroxene} \gamma_{Fe}^{Biotite}} \right)$$

$$\text{The distribution coefficient } K_D = \left(\frac{x_{Fe}^{Pyroxene}}{x_{Mg}^{Pyroxene}} \cdot \frac{x_{Mg}^{Biotite}}{x_{Fe}^{Biotite}} \right)$$

If both minerals are ideal solutions the activity coefficients are all unity. In this case the equilibrium constant K_{eq} is equal to the distribution coefficient K_D .

Wones (1972) has presented evidence that Fe-Mg substitution in the annite-phlogopite series is ideal. Grover and Orville (1969) concluded that the M_2 site in clinopyroxene is filled with Ca and that Fe and Mg occupy the M_1 site only. In this case it is probable that the Fe-Mg substitution in the hedenbergite-diopside series is close to ideal. Therefore, in the reaction under consideration $K_{eq} = K_D$. The equilibrium constant is related to the standard free energy change by

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

We can assess the effect of temperature and pressure on the equilibrium constant by considering the variation of ΔG° .

$$\left(\frac{\partial \Delta G^{\circ}}{\partial P} \right)_T = \Delta V^{\circ}$$

$$\left(\frac{\partial \Delta G^{\circ}}{\partial T} \right)_P = - \Delta S^{\circ}$$

The larger ΔS° the more effect temperature will have on a reaction and the larger ΔV° the more effect pressure will have on a reaction.

1. EXPERIMENTAL METHODS

(a) Synthesis of oxide mixes

Four biotites on the join annite-phlogopite $\text{KFe}_3^{2+}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 - \text{KMg}_3(\text{Al}_3\text{SiO}_{10})(\text{OH})_2$ with Fe/Fe + Mg of 0, 0.166, 0.5 and 1, and five clinopyroxenes on the join hedenbergite-diopside $\text{CaFeSi}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6$ with Fe/Fe + Mg of 0, 0.25, 0.5, 0.75, 1.0, were synthesized from oxide mixes. These oxide mixes were prepared using a modification of the gel technique of Boyd and Schairer (1964). The mixes were prepared using Analar Grade reagents and double deionized water. The source of calcium was calcium carbonate, that of iron was iron sponge, magnesium was weighed out as magnesium oxalate, aluminium as aluminium wire, potassium as potassium bicarbonate and silica as tetraethyl orthosilicate (T.E.O.S.). About ten grams of each oxide mix were made up. For the preparation of clinopyroxene mixes the exact quantities of reagents to supply the cations for ten grams of mix were weighed out and dissolved in nitric acid. For the preparation of biotite mixes the aluminium was weighed out first and dissolved in conc nitric acid. The potassium, magnesium and iron components were then calculated to correspond to the amount of aluminium and added to the solution of aluminium in nitric acid. Further procedure was the same for both clinopyroxene and biotite mixes. The nitrate solutions of the cations were diluted and heated on a steam bath until the majority of the nitrates

had been driven off. Ten ml of ethyl alcohol was added to the solution which was then placed in an ice bath. The exact amount of T.E.O.S. was then weighed out as rapidly as possible (to minimize loss of T.E.O.S. by evaporation) and added to the solution of cations. Concentrated ammonia solution was then added with constant stirring until precipitation was complete. The resulting gels were dried on a water bath for several days and then heated, gently at first, until most of the ammonium nitrate and oxides of nitrogen were driven off. The mixtures were ground for an hour in an automatic grinder and fired in an alundum crucible for five hours at 1000° C. The material was then reground for an hour to ensure homogeneity of the mixes. All mixes containing iron were reduced by passing a stream of hydrogen over them for two hours at 600° C. The biotite oxide mixes of Fe/Fe + Mg 0, 0.5, and 1.0 were prepared by Dr. Wade Reinhardt of the Geological Survey of Canada. The biotite mix Fe/Fe + Mg 0.166 was prepared by the author. All the clinopyroxene mixes were prepared by the author.

(b) Synthesis and Exchange Apparatus

The apparatus used in the synthesis of biotite and clinopyroxenes from oxide mixes was the same as that used later in exchange experiments.

The experiments were carried out in an externally heated "cold seal" pressure vessel about 12 inches long. Temperature regulation of the furnace was by means of a

Figure 1. Apparatus used in synthesis and exchange experiments.

potentiometer pyrometer. Each furnace had been calibrated to determine the length and position of its "hot spot." The temperature was measured using a chrome alumel thermocouple inverted into a well in the pressure vessel which closely adjoined the sample chamber. (See Figure 1)

The temperature was monitored continuously during the experiments with a Leeds Northrup strip chart potentiometer recorder (readability $\pm 2^{\circ}$ C) and were checked periodically by an independent cold junction (ice-waterbath) and potentiometer with a readability of $\pm 0.1^{\circ}$ C. Once the correct temperature had been reached the variability and uncertainty in temperature readings were always less than $\pm 5^{\circ}$ C and in most cases were $\pm 2^{\circ}$ C.

Methane gas was used as the pressure medium and pressure was maintained using an air piston pump and read from a Bourdon tube pressure gauge. Each "cold seal" pressure vessel had an independent valve connecting it to the main pressure system. The pressure for all synthesis and exchange experiments was maintained at 1 Kbar $\pm 5\%$. This pressure was transmitted to the charges by the collapse of the walls of the silver palladium (Ag 70 Pd 30) capsules containing them. The runs were quenched by directing a stream of compressed air on the pressure vessels until the temperature was below 200° C.

(c) The Graphite-Methane Buffer

The physical constants of minerals containing iron vary according to the oxygen fugacity conditions

under which they are synthesized (Wones, 1963). In this case the graphite-methane system was used to buffer all synthesis and exchange experiments. The graphite-methane buffer assemblage was first suggested by Eugster and Skippen (1967). The reaction $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$ is a two phase system (solid and gas) with two components (C and H). By the phase rule the fugacities of the gases are fixed if P and T are fixed. (Fugacity coefficients for CH_4 were obtained from the reduced variable chart of Hougen and Watson (1946), for H_2 from Shaw & Wones (1964) and equilibrium constants for the reaction from the JANAF tables.) The f_{H_2} produced by the graphite-methane buffer for a fixed T and P can be transferred across a semi-permeable membrane to fix f_{H_2} inside a charge system. If the gas in the charge system consists of water, the externally imposed f_{H_2} fixes f_{O_2} since for any P and T the dissociation constant of the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$ is known. The graphite was supplied by graphite filler rods in the pressure vessel. The oxygen fugacity conditions of the graphite-methane buffer approximate those of the quartz-fayalite-magnetite buffer system at temperatures over the range 500 - 700° C. Figure 2 shows a comparison between oxygen fugacity variation with temperature of the graphite-methane system and those of various solid buffer assemblages, magnetite

Figure 2. Buffer curves at $P_{\text{total}} = 1000$ bars (Eugster and Wones, 1962).

iron, haematite-magnetite, magnetite-wustite, wustite-iron and nickel-nickel oxide. Compared to the magnetite-haematite and nickel-nickel oxide systems the graphite-methane buffer represents low oxygen fugacity conditions (Eugster and Wones, 1962).

(d) Capsule Material

The capsules containing the experimental charges were made of silver palladium alloy. Two main sizes of tubing were used with wall thicknesses of .012 cm and 0.005 cm. The latter was used in the majority of runs. There were two main reasons for the use of silver palladium as material for the capsules. The first reason was that silver-palladium acts as a semi-permeable membrane for the passage of hydrogen allowing the hydrogen fugacity generated by the graphite-methane buffer to be transmitted into the charge capsule thereby fixing the hydrogen fugacity of the fluid phase surrounding the charge. The other reason for the use of silver palladium as capsule material was to minimize the loss of iron to the capsule walls. Platinum is an excellent semi-permeable membrane for the passage of hydrogen but readily absorbs iron and since in this study it was important that the total amount of iron in the system be kept constant, silver palladium was preferred to platinum.

(e) Synthesis Experiments

In the biotite synthesis runs, between 0.05 to 0.1 grams of oxide mix were weighed accurately into a silver palladium capsule. Double deionized water was added, the amount necessary to hydrate the oxide mix plus an excess of about 20 mg. The capsule was welded shut, checked for leaks and placed in the cold seal pressure vessel. Magnesium-rich biotites were synthesized at temperatures between 650 - 750° C and iron-rich biotites at temperatures between 600 - 650° C. The length of runs varied from three days to three weeks. Optical examination and X-ray diffraction showed that biotites synthesized for three days were identical in size, degree of crystallinity and optical properties with those synthesized for three weeks. Thus in the majority of cases biotites were synthesized for about one week. All synthesized material was checked optically to ensure that only one phase was present. A total of 40 synthesis runs were made with biotite mixes.

The procedure for synthesis of the clinopyroxenes was similar except that 0.1 to 0.15 gm of oxide mix was used and only 20 - 30 mg of water. All the clinopyroxenes were synthesized at temperatures of 700° C for one week. A total of 30 synthesis runs were made with clinopyroxene mixes.

2. DETERMINATIVE METHODS

(a) Biotite

There are two main methods of determining the Fe/Fe + Mg of an unknown biotite; one is by optical methods and the other using X-ray diffraction. In this study X-ray diffraction proved the more useful method as run products were very fine grained (5-10 μ) and often contaminated with solid buffer material so that it was difficult to determine indices of refraction with any precision. The X-ray diffraction method, following the work of Wones(1963), is to measure accurately $d_{(060, \bar{3}31)}$. The biotites are mixed with potassium bromate, which acts as a standard, and mounted on glass slides. (Potassium bromate has two reflections which closely bracket the (060, $\bar{3}31$) doublet of biotite). Determinations were made using a Siemens diffractometer, a copper tube and iron filter at 35 kV and 22 mA. The goniometer speed was $\frac{1}{4}^\circ$ /minute and the chart speed 1 cm/minute. At least three oscillations were made between the standard and unknown peaks. The measurements were averaged and $d_{(060, \bar{3}31)}$ checked against a determinative curve produced by plotting $d_{(060, \bar{3}31)}$ against Fe/Fe + Mg for synthesized biotites of known Fe/Fe + Mg (Figure 3). Following Wones a linear relationship was drawn through these points. There is a systematic increase in $d_{(060, \bar{3}31)}$ with increase in Fe/Fe + Mg.

Figure 3. Biotite determinative curve.

The maximum uncertainty in the measurement of the 2θ $\text{CuK}\alpha$ value of the 060, $\bar{3}31$ peak was $\pm 0.01^\circ$. This corresponds to a maximum uncertainty in the Fe/Fe + Mg ratio of biotites of 0.03.

(b) Clinopyroxenes

The phase relations of clinopyroxenes on the join diopside-hedenbergite were determined by Turnock (1962) who confirmed the existence of a complete series of monoclinic pyroxenes in the subsolidus region. Synthetic pyroxenes on this join have been described by Turnock (1962), Nolan (1969) and most recently by Turnock, Lindsley and Grover (1973). The two latter studies show that the unit cell dimensions show an almost linear change with composition. The a and b dimensions increase with increasing iron content of the clinopyroxene while the c dimension remains almost constant.

X-ray films were made of five synthesized clinopyroxenes using a Debye-Scherrer Powder camera (diameter 114.59mm), Cobalt radiation with an Fe filter at 30 kV and 16 mA. The exposure times were 24 hours and silicon was used as a standard. Three lines, 041, 150 and 531, which appeared to show the most sensitivity to Fe-Mg substitution were tested as possible determinative curves. The 531 line showed the maximum shift between the magnesium and iron end members and was also a prominent line. When the d_{531} values of the clinopyroxenes are plotted against Fe/Fe + Mg (Figure 4)

Figure 4. Clinopyroxene determinative curve.

a linear relationship is observed with d_{531} increasing with increase in iron content of the pyroxene. This line could be measured with an accuracy of $\pm 0.01^\circ$ for the $2\theta_{531} \text{ CoK}\alpha$ which corresponds to an uncertainty in $\text{Fe}/\text{Fe} + \text{Mg}$ of ± 0.02 .

3. Fe-Mg EXCHANGE BETWEEN BIOTITES AND CLINOPYROXENES. IN 1M MgI_2 WITH AN INTERNAL Ag/AgI BUFFER.

(a) Experimental Details

About 20 mg of biotite and pyroxene were weighed by difference into separate crimped silver tubes. These were placed in a $\text{Ag}_{70}\text{Pd}_{30}$ capsule welded shut at one end and solid AgI was added. About 40 mg of a 1M MgI_2 solution were added to the capsule by syringe and the weight measured by difference. The capsule was then welded shut and tested for leaks. The capsules were placed in cold seal pressure vessels under 1 Kbar pressure and held at 500 or 600° C for 4 - 5 weeks under the oxygen fugacity conditions of the graphite methane buffer. (The apparatus used and the methods for controlling temperature and pressure were those described in Section 1b). At the end of each run the capsules were cleaned and reweighed to see if there had been leakage of solution during the run. The resulting biotites and pyroxenes were washed and analyzed for Fe/ Fe + Mg.

(b) The Oxybiotite Problem

Under oxidizing conditions two of the ferrous ions in the biotite annite $\text{KFe}_3^{2+}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ are oxidized to ferric iron and two hydrogen atoms lost from the molecule to give oxyannite $\text{KFe}^{2+}\text{Fe}_2^{3+}\text{AlSi}_3\text{O}_{12}$.

Figure 5. Effect of oxygen fugacity on the oxybiotite content of the annite-phlogopite series (Wones and Eugster, 1965).

Dashed lines represent compositions of "buffered" biotites, the shaded area represents compositions physically impossible to obtain.

Wones and Eugster (1965) investigated the percentage of oxybiotite occurring in biotite solid solutions under the oxygen fugacity conditions of various solid oxygen buffers.

As can be seen in Figure 5 (Wones and Eugster, 1965) the amount of oxybiotite in the biotite solid solution is very small at oxygen fugacities at or below those of the quartz-fayalite-magnetite buffer. In order to avoid the formation of oxybiotites all synthesis and exchange runs were buffered with the graphite-methane buffer. This buffer, at temperatures between 500 - 700° C gives oxygen fugacities very close to those of the quartz-fayalite-magnetite buffer.

(c) Composition of the Fluid Phase

It is desirable but not essential that the composition of the fluid phase be known. As was seen in the previous paragraph oxygen fugacities at or below those produced by the quartz-fayalite-magnetite buffer are necessary during exchange experiments in order to ensure that biotites produced remain along the annite-phlogopite join. The graphite-methane buffer by itself meets this requirement but it is necessary to consider what effect the Ag/AgI MgI₂ system has on the oxygen fugacity.

At temperatures of 500 - 600° C and 1 Kbar pressure we can consider the fluid phase to be in the supercritical

region so that equilibria can be treated as gas reactions. In the following calculations log K data for HI, H₂O and CH₄ were obtained from the JANAF tables and log K data for AgI from Robie and Waldbaum (1968). Fugacity coefficients for H₂ were obtained from Shaw and Wones, (1964) and the fugacity coefficients for H₂O from Holser, (1954). The critical constants for HI were obtained from "The Handbook of Chemistry and Physics" 41st edition 1959. The fugacity coefficients for HI and CH₄ were estimated using the Universal gas activity coefficient chart (Hougen and Watson, 1946).

From the external buffer

Inside capsule

$$P_{\text{total}} = \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} + \frac{f_{\text{H}_2\text{O}}}{\gamma_{\text{H}_2\text{O}}} + \frac{f_{\text{HI}}}{\gamma_{\text{HI}}} \quad (5)$$

Equation 1 is the graphite-methane buffer reaction. This has a fixed hydrogen fugacity for a particular P and T. This hydrogen fugacity is transmitted through the Ag₇₀Pd₃₀ capsule wall to fix f_{H_2} inside the capsule. The presence of Ag and AgI buffers the fugacity of iodine according to reaction (2).

If the hydrogen and iodide fugacities are known the hydrogen iodide fugacity can be calculated from equation (3).

The $f_{\text{H}_2\text{O}}$ can be calculated from equation (5) as P_{total} , f_{H_2} , f_{HI} and the fugacity coefficients for H_2 , HI and H_2O are known. (P_{I_2} and P_{O_2} are so small that they can be ignored).

Once $f_{\text{H}_2\text{O}}$ is known f_{O_2} can be calculated using equation (4). Table 1 below shows the calculated values for the fluid phase inside the capsule at 800°K (527°C) and 1000 bars for both the iodide system and the H_2O system, each system buffered externally by the graphite-methane buffer.

Table 1. Comparison of Fluid Phases in H_2O and Iodide Systems.

	H_2O system	Iodide solution system	Temperature 800°K (527°C) Pressure 1000 bars External buffer C/CH_4
$f_{\text{H}_2\text{O}}$	499.4	492.7	
f_{H_2}	31.28	31.28	
$\log f_{\text{HI}}$	-	-2.528	
$\log f_{\text{I}_2}$	-	-7.37	
$\log f_{\text{O}_2}$	-24.17	-24.18	

It can be seen that the presence of the iodide solution changes the oxygen fugacity only to a very minute extent and that in the direction of decreasing oxygen fugacity.

Table 2. Run results at 600° C and 1Kbar. Ag/AgI internal buffer, 1M MgI₂ solution. External buffer C/CH₄.

Run No.	Fe/Fe+Mg Initial Biotite	d(060 $\bar{3}$ 31) Final Biotite	Fe/Fe+Mg Final Biotite	Fe/Mg Final Biotite	Fe/Fe+Mg Initial Pyroxene	d531 Pyroxene	Fe/Fe+Mg Final Pyroxene	Fe/Mg Final Pyroxene
6Ag1Mg	0.00	1.5375	0.11	0.125	0.25	1.4276	0.19	0.24
6Ag2Mg	0.50	1.5441	0.39	0.64	0.25	1.4290	0.265	0.36
6Ag3Mg	0.50	1.5441	0.39	0.64	0.75	1.4320	0.39	0.64
6Ag4Mg	1.00	1.5562	0.92	11.5	0.50	1.4441	0.88	7.34
6Ag5Mg	1.00	1.5572	0.96	24.0	0.75	1.4436	0.89	8.09
6Ag1MgR	0.167	1.5390	0.16	0.19	0.00	1.4247	0.065	0.07
6Ag2MgR	0.167	1.5396	0.195	0.24	0.25	1.4292	0.26	0.35
6Ag3MgR	0.167	1.5412	0.25	0.33	0.75	1.4416	0.54	1.17
6Ag4MgR	0.50	1.5440	0.40	0.66	0.75	1.4373	0.62	1.63
6Ag5MgR	0.50	1.5443	0.44	0.79	1.00	1.4439	0.86	6.14

Table 3. Run results at 500° C and 1Kbar. Ag/AgI Internal buffer.
1M MgI₂ solution. External buffer C/CH₄.

Run No.	Fe/Fe+Mg Initial Biotite	d(060 331) Final Biotite	Fe/Fe+Mg Final Biotite	Fe/Mg Final Biotite	Fe/Fe+Mg Initial Pyroxene	d531 Final Pyroxene	Fe/Fe+Mg Final Pyroxene	Fe/Mg Final Pyroxene
5Ag1Mg	0.00	1.5360	0.04	0.042	0.25	1.4269	0.165	0.20
5Ag2Mg	0.50	1.5460	0.47	0.89	0.25	1.4268	0.16	0.191
5Ag3Mg	0.50	1.5476	0.54	1.17	0.75	1.4395	0.69	2.22
5Ag4Mg	1.00	1.5511	0.695	2.28	0.50	1.4482	0.58	1.38
5Ag5Mg	1.00	1.5551	0.865	6.41	0.75	1.4412	0.77	3.34
5Ag1MgR	0.167	1.5387	0.155	0.185	0.00	1.4367	0.07	0.075
5Ag2MgR	0.167	1.5388	0.17	0.205	0.25	1.4268	0.165	0.20
5Ag3MgR	0.167	1.5397	0.2	0.25	0.75	1.4287	0.255	0.33
5Ag5MgR	0.50	1.5476	0.55	1.22	1.00	1.4424	0.90	9.0

(d) Experimental Results

Experimental data for partitioning at 600° C are listed in Table 2 and the data for partitioning at 500° C are listed in Table 3. The biotites and clinopyroxenes were identified using the determinative methods given in section 2. Two methods of plotting the data have been used. The first (Figures 6 and 7) shows Fe/Fe + Mg of coexisting biotite and clinopyroxene pairs initially and at the completion of the runs. The second method of treating the data is to plot log Fe/Mg pyroxene against log Fe/Mg biotite (Figures 8 and 9). This latter type of plot is a straight line with a 45° slope for ideal solutions.

(i) Partitioning at 600° C

Figure 6 shows that in all runs exchange of Fe²⁺ and Mg²⁺ has taken place between biotite and clinopyroxene. The position of the distribution curve was approached from both sides. From Figure 8 a range of distribution coefficients for partitioning at 600° C was calculated. Ideal solution was assumed in both biotite and clinopyroxene solid solution series implying that

$$K_D = \left(\frac{x_{\text{Fe}}^{\text{Pyroxene}}}{x_{\text{Mg}}^{\text{Pyroxene}}} \cdot \frac{x_{\text{Mg}}^{\text{Biotite}}}{x_{\text{Fe}}^{\text{Biotite}}} \right) \text{ is constant}$$

over the whole range of compositions. The upper limit of K_D is 1.00 and the lower limit of $K_D = 0.64$.

Figure 6. Fe/Fe+Mg pyroxene and Fe/Fe+Mg biotite at 600° C and 1 Kbar. Circles represent coexisting pairs at beginning of run. Squares represent coexisting pairs at end of run.

Figure 7. Fe/Fe+Mg pyroxene and Fe/Fe+Mg biotite at 500° C and 1 Kbar. Circles represent coexisting pairs at beginning of run. Squares represent coexisting pairs at end of run.

Figure 8. Log Fe/Mg pyroxene and log Fe/Mg biotite at 600° C and 1 Kbar.

Figure 9. Log Fe/Mg pyroxene and log Fe/Mg biotite at 500° C and 1 Kbar.

(ii) Partitioning at 500° C

The data at 500° C are similar to those at 600° C. (One anomalous point resulted; 5Ag₂Mg). A calculation of distribution coefficients from Figure 9 gives an upper limit of 0.97 and a lower limit of 0.61.

There is considerable overlap between the range of K_D values at 600° C and 500° C.

(e) Theoretical Considerations

The distribution coefficients calculated refer to the following reaction:

$$K_D = \left(\frac{x_{\text{Fe}}^{\text{Pyroxene}} \cdot x_{\text{Mg}}^{\text{Biotite}}}{x_{\text{Fe}}^{\text{Biotite}} \cdot x_{\text{Mg}}^{\text{Pyroxene}}} \right)$$

Since we have assumed an ideal solution model

$$K_D = K_{\text{eq}} = \exp \left(- \frac{\Delta G^\circ}{RT} \right)$$

$$\Delta G^\circ = - RT \ln K_D$$

There are no theoretical reasons for assuming that the equilibrium K_D value is intermediate between the upper and lower K_D limits. The equilibrium K_D value is probably that K_D value corresponding to a ΔG° intermediate between the ΔG° values of the upper and lower K_D values.

T°C	T°K	K _D	lnK _D	G° (cals)	Mean G° (cals)	Equilibrium K _D
600°	873°	1.00	0.0000	0.0	386.9	0.80
600°	873°	0.64	-.4463	773.8		
500°	773°	0.97	-.0305	46.8	402.90	0.77
500°	773°	0.61	-.4943	759.02		

The distribution coefficients for the reaction at 600° C and 500° C are 0.80 and 0.77.

(i) Variation of ΔG° with T and calculation of ΔS°

The variation of ΔG° with temperature is given by the relationship $\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\Delta S^\circ$

For solid-solid reactions ΔS° commonly is constant over a small temperature range. If the mean values of ΔG° at the two temperatures are accepted, it is possible to obtain ΔS° by plotting ΔG° against T (Figure 10).

The range in ΔG° gives rise to considerable but unknown uncertainties in ΔS° .— Nevertheless the very small calculated value of 0.16 cal.deg.⁻¹ is very reasonable for a solid-solid reaction (Thompson, 1955). Furthermore, a small positive volume change (see next section) generally requires a small positive entropy for a solid reaction (Fyfe, Turner and Verhoogen, 1958).

Figure 10. Variation of ΔG° with temperature.
Pressure = 1 Kbar

(ii) Variation of ΔG° with P

The following molar volume data is taken from Robie, Bethke and Beardsley (1967) and is for minerals at 298° K and 1 atm.

$$V^\circ \text{ annite} = 154.30 \text{ cc}$$

$$V^\circ \text{ phlogopite} = 149.91 \text{ cc}$$

$$V^\circ \text{ hedenbergite} = 68.30 \text{ cc}$$

$$V^\circ \text{ diopside} = 66.09 \text{ cc}$$

For the reaction $\Delta V^\circ = 0.41 \text{ cc}$ at 298° K and 1 atm.

This reaction has a small ΔV° and should not be greatly affected by change in pressure.

(iii) Variation of $\ln K_D$ with T and P

The reaction was plotted on a pressure temperature grid for values of $\ln K_D$ - .17 to - .27 (Figure 11). Use was made in the calculation of this grid of the equilibrium K_D values determined at 500 and 600° C and the two relationships:

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\Delta S^\circ = -0.16, \quad \left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T = \Delta V^\circ = 0.41$$

Over the range 500 - 700° C at a pressure of 1 Kbar, the $\ln K_D$ changes from -.26 to -.19. This represents a change in K_D from approximately 0.77 to 0.83. This change in K_D is too small for accurate use as a geothermometer. At 600° C the change in $\ln K_D$ from 1 - 5 Kbar is from -.22 to -.25 which represents a change in K_D from 0.80 to 0.78. This reaction is very insensitive to change in pressure.

Figure 11. Variation of $\ln K_D$ with temperature and pressure.

(f) Conclusions

Magnesium iodide solution has proved to be a suitable medium for the exchange of iron and magnesium between biotites and clinopyroxenes. The presence of the silver-silver iodide buffer for the iodide ion enables the composition of the fluid phase to be calculated. Run times of two to three months instead of the four to five weeks used in this study may enable equilibrium to be more closely approached. At both 500° C and 600° C iron slightly favours the biotite molecule. The effect of temperature and pressure on the reaction

is very small over the range 400 - 700° C and 1 - 5 Kbars and probably over a much larger range. This follows from the small ΔS and ΔV typical of solid-solid reactions.

4. THE EFFECT OF MgCl_2 AND FeCl_2 SOLUTIONS ON BIOTITES ON THE JOIN ANNITE-PHLOGOPITE

(a) Introduction

Chloride solutions have proved in the past to be useful exchange media. Medaris (1969) used chloride solutions to facilitate exchange between coexisting synthetic olivine and orthopyroxene, and Orville (1972) used chloride solutions in investigating exchange reactions in plagioclase feldspars. It appeared reasonable, therefore, to use chloride solutions as an exchange medium for biotites and clinopyroxenes. The major disadvantage of using chloride solutions appeared to be the difficulty of calculating the composition of the fluid phase. If we take the simple approach of assuming that at temperatures of 600°C and 1 Kbar all solutions are super-critical and treat all relationships as simple gas equations it is impossible to calculate the fugacity of f_{O_2} and f_{Cl_2} . The equations to be considered are as follows:

From the external buffer

Inside capsule

Inspite of this disadvantage the effect of chloride solutions of biotites on the join annite-phlogopite was investigated.

(b) Experimental Details

The experimental apparatus used was the same as that described in the experimental methods Section 1b.

Biotite was weighed into a silver palladium capsule, chloride solution added and the capsule welded shut.

The chloride solutions were made up using Andar reagents and double deionized water. The MgCl_2 was 0.50 N and the FeCl_2 0.70 N. For three runs $\text{H}_1\text{H}_3\text{ExMg2}$, $\text{H}_1\text{H}_3\text{ExFe1}$ and $\text{H}_1\text{H}_3\text{ExFe3}$ the solutions were washed out of the capsules at the end of the run, diluted to 25 ml with double deionized water and the Fe/Fe + Mg of the solutions calculated by determining Fe and Mg by Absorption Analysis. All runs were examined optically.

(c) Results and Conclusions

All results are shown in Table 4. Except in two runs $\text{H}_1\text{H}_3\text{ExMg1}$ and $\text{H}_1\text{H}_3\text{ExFe3}$ where the capsules had split and the solution lost two biotites, an iron-rich biotite and a magnesium-rich biotite, were produced. The presence of two biotites in the run products was identified both by two distinct 060 peaks in the X-ray diffraction patterns and by the appearance of two biotites of distinctly different refractive indices when run products were examined optically. Within the limits of experimental error the Fe/Fe + Mg of the solutions examined had a

Run Number	Temp in °C	Starting Biotites Fe/Fe+Mg	Solution	Fe/Fe+Mg Starting System	Fe/Fe+Mg Final Biotites	Fe/Fe+Mg Solution at end of run	Length of run	Comments
H ₃ Ex7	548±5	1.0	0.558 MgCl ₂	0.91	0.12	0.92	n.d.	10 days
H ₃ Ex8	653±5	1.0	0.558 MgCl ₂	0.85		0.9	n.d.	8 days
RB9ExMg2	675±3	0.5	0.558 MgCl ₂	0.305	0.38	0.82	n.d.	8 days
H ₁ H ₃ ExMg2	555±2	0.0	1.0 0.558 MgCl ₂	0.275	pattern diffuse		0.954	9 days
H ₁ H ₃ ExMg1	663±2	0.0	1.0 0.558 MgCl ₂	0.28	0.48		n.d.	9 days tube leaked solution lost
RH1Ex6	548±5	0.0	0.7 FeCl ₂	0.1	0.00	0.95	n.d.	10 days
RH9ExFeMg	569±2	0.5	MgCl ₂ +FeCl ₂		0.45	0.95	n.d.	10 days
RH9ExFe ₂	680±3	0.5	0.7 FeCl ₂	0.71	0.47	0.935	n.d.	8 days
H ₃ H ₁ ExFe1	660±2	0.0	1.0 0.7 FeCl ₂	0.82	0.34	0.896	0.937	9 days
H ₁ H ₃ ExFe2	568±2	0.0	1.0 0.7 FeCl ₂	0.78	X-ray pattern diffuse		0.930	9 days
H ₁ H ₃ ExFe3	602±3	0.0	1.0 0.7 FeCl ₂	0.72	0.51		n.d.	7 days tube leaked solution lost
RH1Ex9	650±5	0.0	0.3 FeCl ₂	0.45	0.10	0.81		8 days

Table 4. Run results: Biotite + (MgFe) Cl₂ solution.

constant value in the high iron-rich region. In order to ensure that only biotite phases were present in run products they were carefully examined optically and full X-ray diffraction patterns were made over a 2θ K α Cu range from $65 - 5^\circ$. No evidence was found for the presence of any other solid phase of any kind.

The Fe/Fe + Mg of run product biotites was plotted against temperature in $^\circ$ C (Figure 12). (The two runs where the capsules had split open and the solution lost were not plotted). The results seem to indicate the presence of a solvus in the biotite solution series. However since the majority of biotites found in rocks are in the intermediate Fe/Fe + Mg range and an intermediate biotite was formed in the two cases where capsules had split open and the solution lost; it appears that the solvus must be caused by the use of chloride solutions. One possible anionic substitution in the biotite molecule is Cl^- for $(\text{OH})^-$. It is possible that Cl^- has entered the biotite lattice and that a solvus exists in the chlorine biotite solid solution series. Another possibility is that Cl^- preferentially replaces $(\text{OH})^-$ in either magnesium-rich or iron-rich biotites. Beswick (1973) investigated the exchange of K and Rb between phlogopite and alkali chloride vapour. Beswick showed that a complete solid solution series exists between $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ and $\text{RbMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ at 800° . In measurements of the distribution coefficient of the partitioning of Rb and K between phlogopites and alkali-chloride vapour $K_D^{P/V}$ he found a very rapid increase in

Figure 12. Solvus produced in anorthite-phlogopite series with (Fe-Mg) Cl_2 solution.

$K_D^{P/V}$ for phlogopites vapour of Rb/K of 0.2 - 0.4. At a vapour Rb/K of approximately 0.41 K_D becomes infinite while the coexisting phlogopites have Rb/K of 0.4 - 1.5. Such a relationship implies a solvus (See Figure 13). Beswick did not see two phases produced but pattern of tielines between solid and vapour at 500° C (See Figure 14) indicates the presence of a solvus between phlogopites of approximately 20 and 60 mole per cent of the Rb end members. Beswick does not consider the possibility that chlorine entered his K/Rb phlogopites but it is significant that he finds a solvus at 500° when chloride solutions are used as an exchange medium. His results at 700° C could also be interpreted as indicating a small solvus as the K_D values show a marked increase at Rb/K vapour values of 0.3 - 0.5 (Figure 15).

Various attempts to mount run products and analyse them for chlorine using the electron microprobe proved unsuccessful as did several attempts to synthesize a pure chlorine phlogopite. It is therefore only a suggestion that the presence of a solvus in the annite phlogopite series is produced by the introduction of chlorine into the biotite molecule.

In natural biotite analyses, chlorine is rarely one of the elements determined. It is possible that the occurrence of chlorine in biotites is more widespread than is generally recognized. It is suggested that where the presence of chloride solutions is indicated during metamorphism (and in certain ore forming solutions) any biotites in the rock should be analyzed for chlorine.

Figure 13. Log-log plot for phlogopite-solution Rb/K values at 500° C and 2000 Kg/cm² (Beswick, 1973).

Figure 14. Tieline diagram for phlogopite-solution equilibria at 500° C and 2000 Kg/cm² (Beswick, 1973).

Figure 15. Log-log plot for phlogopite-solution, Rb/K values at 700° C and 2000 Kg/cm² (Beswick, 1973).

5. UNSUCCESSFUL ATTEMPTS AT FACILITATING EXCHANGE

(a) Ag/AgCl Chloride Solution

(i) Method

Chloride solutions have been used successfully as exchange media for plagioclase feldspars (Orville 1972) and (Medaris 1969). It was decided to investigate their use as an exchange medium for biotites on the join annite-phlogopite. In order that the composition of the fluid phase might be calculated, solid silver chloride was added as a buffer for f_{Cl_2} . The experimental details for these exchange experiments were analogous with those described in section 3 except that only one solid phase (biotite or clinopyroxene) was used in each run.

A total of 12 runs was made with biotites at temperatures between 550 and 700° C at 2 kbar with an external C/CH₄ buffer. Two runs were made with clinopyroxenes.

(ii) Experimental Results

The experimental results are reported in Table 5.

The initial biotite went into solution in all these runs. The only solid phase left was α cristobalite which was identified by its X-ray pattern. Run H₃SAEx2 also showed an X-ray pattern which was tentatively identified as andalusite. Run RHIEx2 split open during

Table 5. Ag/AgCl chloride solution run results.

Run No.	Fe/Fe+Mg Initial Biotite	Solution used	Temp.	Run Products	Time
H ₃ SAEx1	1.0	0.5 _M MgCl ₂	655° C	crystalite	8 days
H ₃ SAEx2	1.0	0.5 _M MgCl ₂	510° C	crystalite	8 days
H ₃ Ex3	1.0	0.5 _M MgCl ₂	560° C	crystalite andalusite	7 days
H ₃ Ex4	1.0	0.5 _M MgCl ₂	450° C	crystalite	6 days
RB9ExMg1	0.5	0.5 _M MgCl ₂	550° C	crystalite	7 days
RH1Ex1	0.0	0.7 _M FeCl ₂	700° C	insufficient solid to X-ray	11 days
RH1Ex2	0.0	0.7 _M FeCl ₂	700° C	cordierite	11 days
RH1Ex3	0.0	0.7 _M FeCl ₂	543° C	crystalite	7 days
RH1Ex4	0.0	3.5 _M FeCl ₂	545° C	crystalite	7 days
RH1Ex5	0.0	0.2 _M FeCl ₂	550° C	crystalite	5 days
Run No.	Fe/Fe+Mg Pyroxene	Solution used	Temp.	Run Products	Time
CP5Ex1	1.0	0.5 _M MgCl ₂	525° C	crystalite	10 days
CP5Ex2	1.0	0.5 _M MgCl ₂	545° C	crystalite	6 days

the run and much of the chloride solution was lost. The run product in this case was cordierite. In run RHIEx the solid Ag Cl was omitted from the capsule but the biotite was still enclosed in a crimped silver tube. Here too the resulting solid product was α cristobalite.

(iii) Conclusion

Magnesium and ferrous chloride solutions in the presence of solid Ag/AgCl are unsuitable exchange media for biotites and clinopyroxenes. In the presence of the fluid phase produced by this system both solid phases are completely broken down. Only silica in the form of α cristobalite remains undissolved. There was a possibility that in one run an aluminium silicate; andalusite, was produced. This system was abandoned after the fourteen runs described.

(b) KOH Solution

(i) Method

The experimental method used was that described in section 4 except that 1N KOH solution replaced the Ag/AgI+MgCl₂ solution. The bulk compositions of the solid phases were chosen to be as Fe/Fe + Mg of approximately 0.1, 0.3, 0.5, 0.7 and 0.9. Runs were made at 500° C and 600° C and 1 kbar. The run products were analysed using the determinative methods given in section 2.

The solutions were removed at the end of the run and analyzed by atomic absorption for Fe and Mg.

(ii) Experimental Results

The experimental results are given in Table 6.

All the solutions analyzed contained magnesium but no iron.

(iii) Conclusion

It was hoped that the $(OH)^-$ ions in the potassium hydroxide solution would act as a catalyst for the transfer of iron and magnesium between the solid phases. This hope was not realized. Exchange of iron and magnesium has taken place between the solid phases but magnesium has been extracted from the solid phases to enter the solution. It would appear that the majority of the magnesium has been extracted from the biotites as run product biotites are all iron-rich. When $Fe/Fe + Mg$ of pyroxene is plotted against $Fe/Fe + Mg$ biotite the points are scattered and do not define an equilibrium curve.

The use of 1N KOH as an exchange medium was abandoned after the ten runs described.

Table 6. KOH solution run results.

Run No.	Temp.	Fe/Fe+Mg initial biotite	Fe/Fe+Mg initial pyroxene	Fe/Fe+Mg bulk composition	Fe/Fe+Mg Resulting biotite	Fe/Fe+Mg Resulting pyroxene
6K1	600° C	0.0	0.25	0.13	0.785	0.09
6K2	600° C	0.5	0.25	0.42	0.84	0.20
6K3	600° C	0.5	0.5	0.50	0.67	0.35
6K4	600° C	1.0	0.5	0.76	0.835	0.56
6K5	600° C	1.0	0.75	0.90	1.0	0.86
5K1	500° C	0.0	0.25	0.13		
5K2	500° C	0.5	0.25	0.42	0.675	0.44
5K3	500° C	0.5	0.5	0.5	0.59	0.625
5K4	500° C	1.0	0.50	0.74	0.98	0.605
5K5	500° C	1.0	0.75	0.86	1.0	0.80

GEOLOGIC APPLICATIONS

Biotites on the annite-phlogopite join and clinopyroxenes on the hedenbergite-diopside join, were chosen for this study because of the ideal mixing in their solid solution series. Although not abundant, coexisting biotite and clinopyroxenes occur in metamorphic rocks and the distribution of iron and magnesium in several natural assemblages is now compared with the experimental data given in this study.

Caution should always be used in the application of experimental data to natural assemblages. The coexisting biotites and clinopyroxenes used in this study represent the least aluminous system possible. Generally natural biotites have an Al/Si greater than those of the annite-phlogopite series. Aluminium is present in nearly all natural clinopyroxenes. An increase in the aluminium content of the system changes the distribution coefficients (Kretz, 1960; Albee, 1965). Titanium, manganese and other cations commonly occur with iron and magnesium in octahedral sites. It is often assumed that these other cationic elements act only as dilutants which do not affect the distribution of iron and magnesium between the phases. This assumption may be justified in the case of manganese and titanium in clinopyroxene but is almost certainly not justified in

the case of titanium in biotite. Two studies of coexisting biotite-clinopyroxene are considered; one from skarn deposits (Kretz, 1960) and the other from a gabbro-metagabbro complex (Hermes, 1970).

Skarn deposits are formed by the pneumatolytic or hydrothermal transfer of elements across a granite-carbonate boundary. If the original carbonate rocks were dolomitic in character, the assemblage formed is often diopside-tremolite-phlogopite. Kretz (1960) investigated the distribution of certain elements, including iron and magnesium, in calcic pyroxenes, calcic amphiboles and biotites, in skarn deposits occurring in Grenville gneisses and limestones of southwestern Quebec. All the biotites and clinopyroxenes analyzed were very magnesium-rich. There was considerable variation in the Al content of both biotites and clinopyroxenes, and in the Ti content of biotite. The Mn content of all minerals analyzed was low. K_D values for eight biotite-pyroxene pairs from these skarns are given in Table 7 together with the weight percent of FeO, MgO, Al_2O_3 , TiO_2 and MnO in each mineral. The only sample which can legitimately be compared with the experimental data determined in the present study, is no. 9, which is the least aluminous and also low in Ti and Mn. Kretz considers that the skarn deposits, like the enclosing gneisses and limestones, crystallized within the upper region of

Table 7. K_D values from skarns of S.W. Quebec.
(Data from Kretz, 1960)

Sample No.	Clinopyroxene					Biotite					K_D
	FeO Wt %	MgO Wt %	Al ₂ O ₃ Wt %	TiO ₂ Wt %	MnO Wt %	FeO Wt %	MgO Wt %	Al ₂ O ₃ Wt %	TiO ₂ Wt %	Mn Wt %	
1	0.64	17.6	1.70	0.10	0.04	0.68	23.5	13.0	0.90	0.015	1.25
2	1.13	7.6	0.95	0.055	0.065	2.3	26.0	14.5	0.70	0.03	0.73
4	1.17	17.6	2.3	0.03	0.07	1.7	25.5	13.0	0.21	0.03	1.00
6	2.8	16.5	2.1	0.04	0.135	2.7	25.0	12.3	0.17	0.05	1.57
7	3.2	17.2	1.7	0.125	0.085	6.3	22.5	16.0	1.75	0.04	0.66
9	0.48	17.3	0.33	0.01	0.035	0.96	25.0	9.8	0.06	0.01	0.72
11	1.49	16.0	1.7	0.09	0.09	1.28	24.0	13.0	0.19	0.035	1.75
12	5.65	13.8	1.1	0.06	0.15	12.3	16.4	13.0	2.5	0.05	0.55

Analytical Errors:

FeO $\pm 2\%$
MgO $\pm 10\%$
Al₂O₃ $\pm 5\%$

MnO $\pm 5\%$
TiO₂ $\pm 10\%$

the amphibolite facies. This would indicate temperatures of 550 - 650° C and pressures of 3 - 5 Kbars (Turner 1968). The K_D value of 0.72 determined for sample 9 is well within the range determined by the experimental data. Samples 1, 4, 6 and 11 all contain high alumina pyroxenes and have K_D values greater than 1. Samples 7 and 12 contain biotites with high Ti content and the K_D values for these two samples are lower than the experimental data would suggest. The distribution of iron and magnesium between biotite and clinopyroxene appears dependent on other elements (i.e. Al and Ti) present in the phases.

Hermes (1970) has studied the coexisting mafic silicates of the Mecklenburg gabbro-metagabbro of North Carolina. The gabbro formed from a melt under relatively rapid cooling disallowing large scale fractionation. The metagabbro grades from varieties showing relict igneous textures to varieties showing completely recrystallized granoblastic textures. None of the mafic minerals showed zoning under microprobe analysis. There is very little variation in the Al or Ti content of biotite or pyroxene across the complex. Hermes considers that the crystallization of the gabbro took place about 400° C higher than the metagabbro. The biotites are intermediate in Fe/Fe+Mg with high Ti content. The clinopyroxenes are low in Al and Hermes describes them as salites. K_D values were calculated from the average compositions of clinopyroxenes and biotites, from gabbro,

intermediate metagabbro, and completely recrystallized metagabbro. These values were 0.78, 0.65 and 0.54. Since there is little change in Al and Ti content of minerals across the complex, these values probably reflect the decrease in temperature of crystallization from gabbro to metagabbro. These values are slightly lower than those determined in the present study possibly because of the high titanium content in the biotites.

CONCLUSIONS

This study has demonstrated that iodide solutions can be used to facilitate exchange reactions in hydrous minerals. (Chloride solutions proved unsuitable as exchange media probably due to the smaller size of the chloride ion (1.81 Å), compared to the iodide ion (2.16 Å), which enabled it to be incorporated into the lattice of hydrous minerals in place of the hydroxyl ion.) Solid Ag/AgI acted as an internal buffer for f_{I_2} while only minimally affecting the f_{O_2} conditions produced by the external hydrogen buffer (C/CH₄).

This method was used to calibrate the reaction

at 500° and 600° C and 1Kbar. The distribution coefficient of this reaction at 600° C was found to be 0.80 (range 0.64 - 1.00) and the distribution coefficient at 500° C was found to be 0.77 (range 0.61 - 0.93). The reaction has a small ΔS (0.16 cal deg⁻¹) and a small ΔV (0.41 cc). This gives a $\frac{\Delta S}{\Delta V} = 0.4$ which is a typical value for a solid-solid reaction. (Fyfe, Turner and Verhoogen, 1958, p. 30). A plot of $\ln K_D$ values on a pressure temperature grid (Figure 11) indicate that this reaction is very insensitive to changes in pressure. The change in $\ln K_D$ with temperature is too small for use as a geothermometer.

Where coexisting biotites and pyroxenes of similar composition to those used in the present study occur in rocks, they are found to have similar distribution coefficients. Any variation in composition particularly in Al or Ti content has an appreciable effect on the distribution coefficient. The variation in K_D with composition is much greater than the variation with temperature or pressure.

It is hoped that the iodide solution method for facilitating exchange reactions can be used in studying reactions in various coexisting minerals (eg. garnet-biotite, biotite-amphibole, chlorite-biotite).

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APPENDIX

RESULTS OF SYNTHESIS EXPERIMENTS

Tables 6 and 7 give the temperatures and length of run for all the synthesized materials used in exchange experiments. There was a tendency for synthesis runs made towards the end of the study to be at lower temperatures and for shorter periods of time. It was found that runs of two to three days were sufficient to ensure complete conversion of mix into crystalline mineral. Lower temperatures improved the crystallinity and grain size of synthesized material slightly, probably by a reduction in the nucleation rate. The physical properties; refractive index and X-ray patterns were identical regardless of the length of the run or the temperature of synthesis.

Possible reasons for considering synthesized material to be unsuitable for exchange experiments are summarized below.

- (1) Unreacted mix was present in synthesized material.
- (2) The capsule had leaked during the run.
- (3) Phases other than the biotite or clinopyroxene synthesized were present.

The oxide mixes used were well on composition and no runs were rejected for reason (3). At times it was difficult to determine if the capsule leaked as they

were sometimes damaged externally on removal from the bomb. (Graphite deposition from the methane buffer tended to weld the capsules to the side wall of the bomb.) This lead to an apparent weight loss when the capsule was weighed. However if when the capsule was opened a gas hiss was heard it was presumed that the capsule had not leaked during the run.

Table 8. Synthesis Runs on Biotites

Run No.	Fe/Fe+Mg	Temp.	Duration of run in days	Run No.	Fe/Fe+Mg	Temp.	Duration of run in days
RH1-S-1	0.00	730° C	6	RB9-S-8	0.50	640° C	2
RH1-S-2	0.00	730° C	6	RB9-S-9	0.50	650° C	2
RH1-S-3	0.00	740° C	8	RB9-S-10	0.50	700° C	5
RH1-S-4	0.00	710° C	9	RB9-S-11	0.50	655° C	5
RH1-S-5	0.00	650° C	7	A-S-1	0.167	715° C	3
RH1-S-6	0.00	715° C	4	A-S-2	0.167	635° C	3
RH1-S-7	0.00	718° C	4	H3-S-1	1.00	635° C	18
RH1-S-8	0.00	712° C	4	H3-S-2	1.00	650° C	18
RH1-S-9	0.00	718° C	4	H3-S-3	1.00	655° C	8
RH1-S-10	0.00	750° C	6	H3-S-4	1.00	650° C	9
RH1-S-11	0.00	710° C	15	H3-S-5	1.00	630° C	7
RH1-S-12	0.00	650° C	5	H3-S-6	1.00	650° C	4
RH1-S-13	0.00	690° C	3	H3-S-7	1.00	650° C	6
RH1-S-14	0.00	640° C	3	H3-S-11	1.00	660° C	15
RB9-S-1	0.50	658° C	18	H3-S-12	1.00	645° C	6
RB9-S-2	0.50	650° C	18	H3-S-13	1.00	650° C	2
RB9-S-3	0.50	650° C	2	H3-S-14	1.00	645° C	5
RB9-S-4	0.50	710° C	10				
RB9-S-5	0.50	670° C	4				
RB9-S-6	0.50	665° C	5				

Temperature readings are all $\pm 5^{\circ}$ C.

Table 9. Synthesis Runs on Clinopyroxenes

Run No.	Fe/Fe+Mg Pyroxene	Temp.	Duration of run in days	Run No.	Fe/Fe+Mg Pyroxene	Temp.	Duration of run in days
CP1-S-1	0.00	800° C	9	CP3A-S-4	0.50	655° C	2
CP1-S-2	0.00	815° C	9	CP4A-S-1	0.75	660° C	11
CP1-S-3	0.00	750° C	9	CP4A-S-2	0.75	665° C	8
CP1-S-4	0.00	730° C	3	CP4A-S-3	0.75	675° C	6
CP1-S-5	0.00	700° C	5	CP4A-S-3	0.75	695° C	5
CP1-S-6	0.00	700° C	3	CP5-S-1	1.00	700° C	5
CP1-S-NNO	0.00	750° C	14	CP5-S-2	1.00	700° C	5
CP2A-S-1	0.25	700° C	11	CP5-S-3	1.00	700° C	7
CP2A-S-2	0.25	690° C	5	CP5-S-4	1.00	600° C	3
CP2A-S-3	0.25	690° C	4	CP5-S-5	1.00	600° C	5
CP2A-S-4	0.25	680° C	5	CP5-S-6	1.00	660° C	5
CP2A-S-5	0.25	685° C	3				
CP3A-S-1	0.50	700° C	9				
CP3A-S-2	0.50	720° C	3				
CP3A-S-3	0.50	700° C	2				

Temperature readings are all $\pm 5^\circ$ C.