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AN EXPERIMENTAL STUDY OF IRON-MAGNESIUM EXCHANGE BETWEEN BIOTITE AND CLINOPYROXENE

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Abstract

Three electrolyte solutions, 0.5 *M* $MgCl_2$, 0.7 *M* $FeCl_2$ and 1 *M* MgI_2, were tested for their ability to facilitate iron-magnesium exchange in synthetic biotites on the annite-phlogopite join. Synthesis and exchange experiments were carried out, at 1 kilobar of pressure, in standard cold seal pressure vessels with a graphite-methane external buffer. Solid silver-silver iodide was used as an internal buffer for iodide in experiments with magnesium iodide solution.

Chloride solutions proved unsuitable as exchange media because a solvus was produced in the annite-phlogopite series between 500° – 680°C at 1 kilobar.

Using 1 *M* MgI_2 with an Ag-AgI internal buffer to facilitate exchange, the reaction $\frac{1}{3}\ KFe_3^{2+}(AlSi_3O_{10})(OH)_2 + CaMgSi_2O_6 \rightleftarrows \frac{1}{3}KMg_3(AlSi_3O_{10})(OH)_2 + CaFeSi_2O_6$ was calibrated at 500° and 600° at 1 kilobar. The range of distribution coefficients at 600°C and 500°C shows considerable overlap and the reaction is not greatly temperature-dependent.

Iodide solutions can be used to study a wide range of exchange reactions involving hydrous minerals (e.g. garnet-biotite, biotite-cordierite and biotite-amphibole.)

Introduction

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. Because many metamorphic minerals are of variable composition, experimental calibration of exchange reactions is of considerable significance in an understanding of metamorphic conditions. Many minerals important in metamorphic rocks are both ferromagnesian and hydrous and this study outlines the development of a method to study iron-magnesium exchange between hydrous minerals. Previous experimental work on iron-magnesium exchange (Medaris 1969) involved anhydrous phases only.

The hydrous minerals used in the study were synthetic biotites on the annite-phlogopite join and both chloride and iodide solutions were tested as suitable exchange media. The reaction

$$\frac{1}{3}KFe_3^{2+}\ (AlSi_3O_{10})(OH)_2 + CaMgSi_2O_6 \rightleftarrows$$
$$\frac{1}{3}KMg_3\ (AlSi_3O_{10})(OH)_2 + CaFeSi_2O_6$$

between synthetic biotites on the annite-phlogopite join and synthetic clinopyroxenes on the hedenbergite-diopside join was investigated at 500° and 600°C using 1 *M* MgI_2 solution as an exchange medium.

Experimental Methods

Preparation of starting materials

Four biotites on the join annite-phlogopite with Fe/Fe + Mg of 0, 0.166, 0.5 and 1.0, and five clinopyroxenes on the join hedenbergite-diopside with Fe/Fe + Mg of 0, 0.25, 0.50, 0.75 and 1.0, were synthesized from oxide mixes. These oxide mixes were prepared using the 'gel' technique. All biotites and clinopyroxenes used in exchange experiments were synthesized for one week at 1 kilobar pressure, at temperatures between 600° - 730°C in the case of biotites and 600° - 800°C in the case of pyroxenes. The apparatus for synthesis was the same as for exchange experiments and is described below.

Synthesis and exchange apparatus

The experiments were carried out in 12-inch, externally-heated 'cold seal' pressure vessels. Temperature regulation of the furnace was by means of a potentiometer pyrometer. The temperature was measured using a chromel-alumel thermocouple inserted into a well which closely adjoined the sample chamber in the pressure vessel. Once the correct temperature had been reached the variability and uncertainty in temperature readings was always less than ± 5°C and in most cases was ± 2°C.

The pressure medium in all experiments was methane gas and was maintained at 1 kilobar ± 5%. This pressure was transmitted to the charges by the collapse of the silver-palladium (Ag70 Pd30) capsules containing them. The runs were quenched by directing a stream of compressed air on the pressure vessel walls until the temperature was below 200°C.

In order to avoid the formation of 'oxybiotite' (Wones & Eugster 1965) it was necessary to keep the oxygen fugacity at or below the quartz-fayalite-magnetite buffer and this was achieved by the use of the graphite-methane buffer for all experiments. This buffer, first suggested by Eugster & Skippen (1967), produces a fixed hydrogen fugacity which is transmitted through the capsule wall into an aqueous medium and produces an oxygen fugacity at or below that of the quartz-fayalite-magnetite buffer. The pressure of iodide or chloride in the fluid can only reduce oxygen fugacity.

Exchange media

Exchange media were 0.5 *M* $MgCl_2$, 0.70 *M* $FeCl_2$ and 1 *M* MgI_2 solutions. In the case of the first two solutions, about 30 mg of biotite were weighed into a silver-palladium capsule, 30 mg of either ferrous or magnesium chloride solution added, and the capsule welded shut. At the end of the runs (7 - 10 days) the Fe/Fe + Mg of the biotites was determined by *x*-ray diffraction and each run was examined optically. In experiments with 1 *M* MgI_2 solution, about 20 mg of biotite and pyroxene were weighed into separate crimped silver tubes. These were placed in a silver-palladium capsule, and solid AgI and approximately 40 mg 1 *M* MgI_2 solution added. The Ag-AgI was used as an internal buffer for iodide. The capsules were held at 500° or 600° and 1 kilobar for 4 to 5 weeks. The resulting biotites and clinopyroxenes were washed and analyzed by *x*-ray diffraction for Fe/Fe + Mg.

Determination of Fe/Fe + Mg in biotites and clinopyroxenes

Following the work of Wones (1963), Fe/Fe + Mg of the biotites was obtained by accurate determination of $d(060,\bar{3}31)$ using *x*-ray diffraction. There is a systematic increase in $d(060,\bar{3}31)$ with increase in Fe/Fe + Mg (Fig. 1). It is estimated that the maximum uncertainty in the Fe/Fe + Mg of unknown biotites is 0.03.

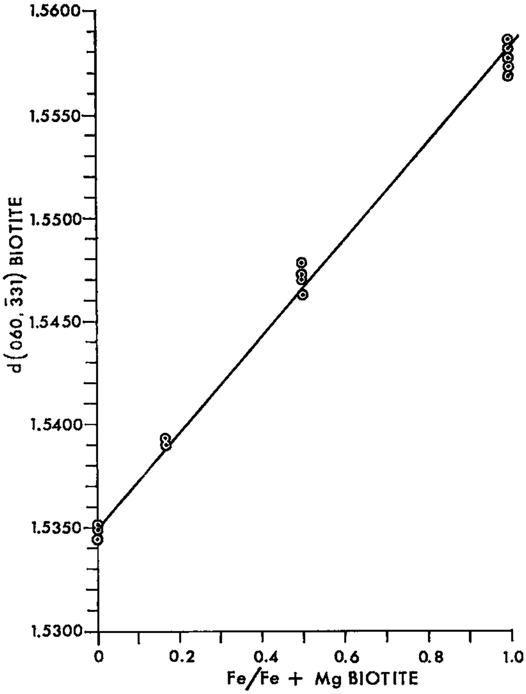

Fig. 1. Curve for the determination of Fe/Fe+Mg in biotites on the annite-phlogopite join.

X-ray films were made of five synthetic clinopyroxenes (Fig. 2) using cobalt radiation with an iron filter. The exposure times were 24 hours and silicon was used as a standard. The 531 line shows the maximum shift between magnesium and iron end members and when $d(531)$ of the pyroxene is plotted against Fe/Fe + Mg a linear relationship is observed (Fig. 2). The maximum uncertainty in Fe/Fe + Mg of the clinopyroxenes is estimated to be 0.02.

RESULTS

The results of runs using 0.5 *M* $MgCl_2$ and 0.07 $FeCl_2$ solutions are shown in Table 1. In all experiments, an iron-rich biotite and a magnesium-rich biotite were produced. The presence of two biotites in the run products was identified 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. No solid phases other than biotite were seen. The Fe/Mg ratios of the chloride solutions in equilibrium with biotite and pyroxene were analyzed by atomic absorption at the conclusion of three experiments (Table 1). These analyses consistently indicate a solution with a high iron content,

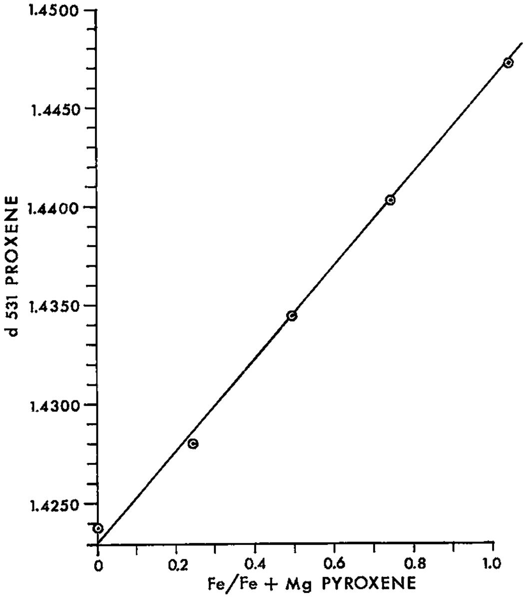

Fig. 2. Curve for the determination of Fe/Fe+Mg in clinopyroxenes on the hedenbergite-diopside join.

i.e. an Fe/Fe + Mg ratio between 0.954 and 0.930.

The Fe/Fe + Mg of the resultant biotites is plotted against temperature in Figure 3. The results suggest the presence of a solvus in the chlor-biotites produced by the use of chloride solutions.

The results of runs using 1 *M* MgI_2 solution as an exchange medium are shown in Table 2. In all runs there was an exchange of ferrous iron and magnesium between biotite and clinopyroxene. Ideal solution was assumed in both biotite and clinopyroxene solid solution series implying that the distribution coefficient,

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

is constant over the entire range of compositions. The results of the runs plotted as log Fe/Mg pyroxene against Fe/Mg biotite are shown in Figures 4 and 5. The possible range of K_D *for* each temperature is indicated. The bracketing lines are not close, indicating that equilibrium is approached slowly in the experiments. K_D at 600°C is between 0.64 and 1.00 and K_D at 500°C is between 0.61 and 0.97. There is considerable overlap between the range of K_D values at 600°C

TABLE 1. RUN RESULTS: BIOTITE + $(Mg,Fe)Cl_2$ SOLUTION

Run Number	Length of run (days)	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
H_3Ex7	10	548±5	1.0	$0.558MgCl_2$	0.91	0.12 0.92	n.d.
H_3Ex8	8	653±5	1.0	$0.558MgCl_2$	0.85	0.9	n.d.
Rb9ExMg2	8	675±3	0.5	$0.558MgCl_2$	0.305	0.38 0.82	n.d.
H_1H_3ExMg2	9	555±2	0.0,1.0	$0.558MgCl_2$	0.275	***	0.954
RH1Ex6	10	548±5	0.0	$0.7FeCl_2$	0.1	0.00 0.95	n.d.
RH9ExFeMg	10	569±2	0.5	$MgCl_2+FeCl_2$		0.45 0.95	n.d.
$RH9ExFe_2$	8	680±3	0.5	$0.7FeCl_2$	0.71	0.47 0.935	n.d.
H_3H_1ExFe1	9	660±2	0.0,1.0	$0.7FeCl_2$	0.82	0.34 0.896	0.937
H_1H_3ExFe2	9	568±2	0.0,1.0	$0.7FeCl_2$	0.78	***	0.930
RH1Ex9	8	650±5	0.0	$0.3FeCl_2$	0.45	0.10 0.81	

*** *x*-ray pattern diffuse

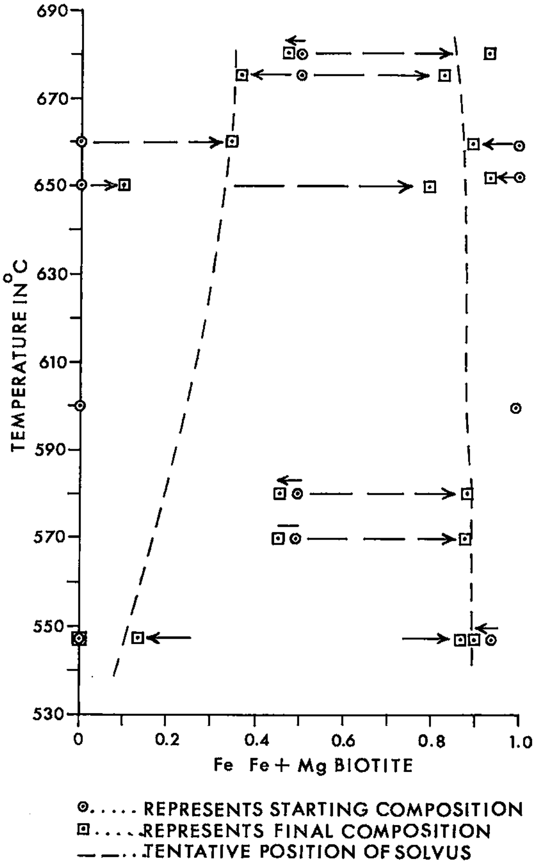

FIG. 3. Solvus produced in the annite-phlogopite series with 0·5 *M* $MgCl_2$ and 0·7 *M* $FeCl_2$.

TABLE 2. RUN RESULTS AT 600°C, 500°C, AND 1 KILOBAR. Ag/AgI INTERNAL BUFFER, 1M MgI_2 SOLUTION. EXTERNAL BUFFER C/CH_4

Run Number	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	$^{d}531$ Final Pyroxene	Fe/Fe+Mg Final Pyroxene	Fe/Mg Final Pyroxene
600°C								
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
500°C								
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

and 500°C and the temperature dependence of the distribution coefficient is quite small.

CONCLUSIONS

The use of chloride solutions as exchange media has proved successful in facilitating exchange of iron and magnesium between synthetic olivines and pyroxenes (Medaris 1969) and in alkali exchange in plagioclase feldspars (Orville 1963, 1972), but appears unsuitable for hydrous minerals because of possible substitution of Cl^- for OH^-.

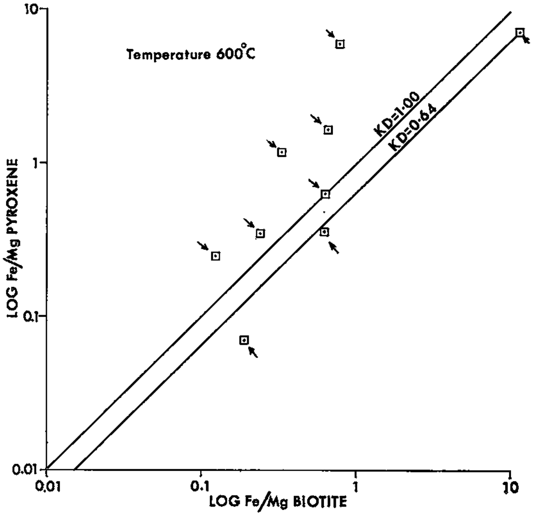

FIG. 4. Log Fe/Mg pyroxene versus log Fe/Mg biotite at 600°C and 1 kilobar.

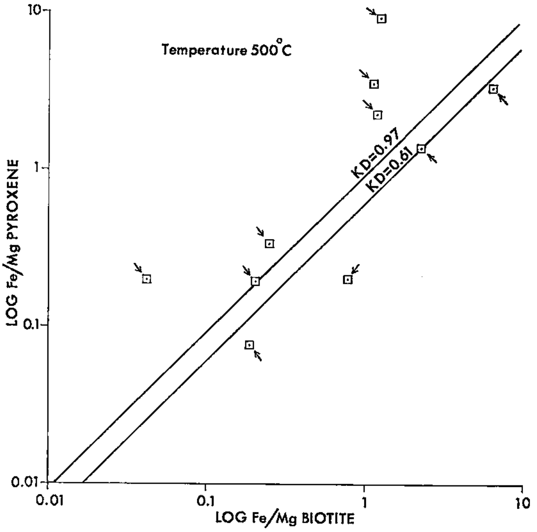

FIG. 5. Log Fe/Mg pyroxene versus log Fe/Mg biotite at 500°C and 1 kilobar.

Gunter. Fe-Mg Exchange in biotites and clinopyroxenes.

This study has demonstrated that magnesium iodide solution can be used to facilitate exchange reactions in hydrous minerals. The presence of the Ag-AgI buffer for the iodide ion will eventually enable the composition of the fluid phase to be calculated although the lack of the dissociation constant for HI at the conditions of the experiments precludes such calculations at present. The temperature dependence of the end member exchange reaction between biotites on the annite-phlogopite join and clinopyroxenes on the hedenbergite-diopside join is apparently small.

Iodide solutions appear to offer a suitable medium for the study of a wide range of important exchange reactions among coexisting minerals, both hydrous and anhydrous. Possible examples are garnet-biotite, biotite-cordierite and biotite-amphibole.

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