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# Distribution of Elements between Coexisting Garnet-Biotite and Muscovite-Biotite Pairs from Polymetamorphic Schists of South-East Beawar, Rajasthan, India

By Ram S. Sharma and V. Narayan (Banaras)\*)

With 12 figures and 2 tables in the text

#### Abstract

Eight garnet-biotite and nine muscovite-biotite pairs from polymetamorphic schists of southeast Beawar in northwest Peninsular India have been studied in regard to their distribution of Mg, Fe, and other elements.

The distribution coefficient for Mg-Fe in garnet-biotite is found to depend on Mg/Fe ratio of the host rock and on the octahedrally coordinated Al in biotite. This is explained by nearly uniform composition of garnets, presumably owing to their refractory nature, in contrast to the coexisting biotites which show variable and correlated composition with the parent rocks during their repeated crystallization-deformational history. The  $K_{D} \frac{G-B}{Mg-Fe}$  ranges from 0.135 to 0.224 and is comparable to the K<sub>D</sub> values found in garnet-biotite pairs from other areas.

In the muscovite-biotite pairs the distribution of alkalies is irregular but Al and Ti show a consistent distribution relation. The  $K_D \stackrel{Ms-Bi}{Mg-Fe}$  varies only slightly in different samples of a single zone and the variation is attributable to the nature of the assemblage. From the distribution of Al and Ti, and the near identical values of  $K_D \stackrel{Ms-Bi}{Mg-Fe}$ , despite distant locations of the samples, it is suggested that chemical equilibrium has attained in these polymetamorphic rocks.

# INTRODUCTION

Since RAMBERG and DE VORE (1951) proposed the thermodynamic equations of the distribution ratios for two ideal mixtures, and KRETZ (1959) discussed actual partitioning of elements between coexisting phases from gneisses, the distribution of elements amongst mineral pairs has been widely employed as a test of chemical equilibrium in the rocks. Later studies of KRETZ (1961, 1964), ALBEE (1965a, 1965b), HOUNSLOW and MOORE (1967), SAXENA (1968), SEN and CHAKRABORTY (1968) and others confirmed the relations found by

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KRETZ. The concept of the elemental distribution rests on the fact that rocks which contain the same equilibrium assemblage and which formed under identical conditions should have identical cation fractionations between the phases, regardless of the proportions of the phases present in the rocks.

Within the range of uncertainty, the distribution of elements, for example Mg and Fe between coexisting garnet and biotite may be related by the equation

$$\mathrm{K_{D\,Mg}.Fe}_{\mathrm{Mg}} = rac{\mathrm{X_{Mg}^{G}\,X_{Fe}^{B}}}{\mathrm{X_{Fe}^{G}\,X_{Mg}^{B}}} \cong 1.$$

Both theoretical considerations and mineralogical studies by various workers have, however, shown that the distribution coefficient for exchangeable cations between mineral pairs, such as garnet-biotite, is not constant. It is rather dependent on several factors which can be summarized as follows:

# **Physical Factors:**

- a) Temperature: RAMBERG and DE VORE (1951), FROST (1962), KRETZ (1959, 1963), ALBEE (1965a), SEN and CHAKRABORTY (1968), HIETANEN (1969), LYONS and MORSE (1970), and others.
- b) Pressure: RAMBERG and DE VORE (1951), ALBEE (1965a), EVANS (1965), and others.

# Chemical and Mineralogical Factors, which include:

I. Effect of exchangeable cations other than Mg and Fe.

- a) Effect of Mn and/or Ca in garnets: KRETZ (1959), STURT (1962), ALBEE (1965b), NANDI (1967), SEN and CHAKRABORTY (1968), LYONS and MORSE (1970), and others.
- b) Effect of Al<sup>VI</sup> and Ti in biotites: ALBEE (1965a), SAXENA (1968), DAHL (1969), and others.

II. Non-ideality of Fe-Mg substitution, particularly effective in polymetamorphic rocks and could be due to:

- a) Presence of a nonreactive or refractory mineral such as garnet: (Hollister, 1969).
- b) Re-equilibration of Fe-Mg to new metamorphic conditions may be slower than the reaction giving rise to garnet, biotite etc.: EVANS and GUIDOTTI (1966).
- c) Variation in oxidation ratio: CHINNER (1960), HOUNSLOW and MOORE (1967), and others.
- d) Growth of retrograde phases such as chlorite and muscovite during postmetamorphic recrystallization.

III. Garnet/Staurolite ratios: CARD (1964), HIETANEN (1969).

### Distribution of Elements in Polymetamorphic Schists

Mechanical Factors, which include:

- a) Impurities of samples.
- b) Analytical errors.

In light of the above factors, eight garnet-biotite and nine muscovitebiotite pairs have been studied in regard to their elemental distribution. And an attempt is made to enquire which of the several factors controlled the distribution of elements in the mineral pairs, and whether or not the phases showing stable association have attained chemical equilibrium in the polymetamorphic rocks.

# GEOLOGICAL OUTLINE

The schists from which the minerals have been studied belong to the Banded Gneissic Complex which is considered as the oldest stratigraphic unit in the northwest Peninsular India (HERON, 1953; CRAWFORD, 1970). They are evidently polymetamorphic (SHARMA and NARAYAN, in press) and, on the basis of their index minerals, are divisible into two metamorphic zones: a broad staurolite-kyanite zone and a narrow medial zone of sillimanite-muscovite. The analyzed minerals and their parent rock contain the following paragenesis in the two zones.

# Staurolite-kyanite zone

1. kyanite-staurolite-garnet-biotite-muscovite	D 41)
2. kyanite-garnet-biotite-muscovite	D 3
3. staurolite-garnet-biotite-muscovite	C 3
4. staurolite-biotite-muscovite	C 2
5. garnet-biotite-muscovite	<b>B</b> 2
Sillimanite muchonite an	20.0

#### Sillimanite-muscovite zone

1.	sillimanite-staurolite-garnet-biotite-muscovite	<b>E</b> 4
2.	sillimanite-garnet-biotite-muscovite	<b>E</b> 3

### MINERAL SEPARATION

The rock samples were crushed to pass through an 80-mesh sieve (ASTM). The pure mineral fractions were obtained first by separating the powder with bromoform and then

<sup>&</sup>lt;sup>1</sup>) The symbols D 4, D 3, C 3 etc. refer to the nature of the assemblage, wherein the alphabets B, C, D, E denote an assemblage with the highest rank index mineral garnet, staurolite, kyanite, sillimanite respectively. Arabic numeral indicates the number of phases representable on Thompson's AFM diagram, and the additional Greek number I, II, as used in different diagrams helps in differentiating between two similar assemblages.

							Stau	rolite-ky	zanite z	one	
		$B_2$		C			$C_{3i}$			$C_{3\ ii}$	
	G	Bi	Ms	Bi	Ms	G	Bi	$\mathbf{Ms}$	G	Bi	$\mathbf{Ms}$
SiO <sub>2</sub>	37.14	36.34	49.15	35.80	47.68	36.58	35.99	48.75	37.00	35.75	47.05
$Al_2O_3$	19.86	14.95	29.68	16.44	31.54	20.15	15.94			16.04	
$\operatorname{TiO}_2$						0.29					
	$\begin{array}{c c} 0.34\\ 0.99\end{array}$	$\begin{array}{c} 1.60 \\ 1.84 \end{array}$	0.58	$\begin{array}{c} 1.46 \\ 2.11 \end{array}$	$\begin{array}{c} 0.42 \\ 1.94 \end{array}$	1.29	$\begin{array}{c} 1.53 \\ 2.44 \end{array}$	$\begin{array}{c} 0.37 \\ 2.17 \end{array}$	0.08	1.39	0.42
${ m Fe_2O_3} { m FeO}$			1.79						1.40	1.84	2.19
	34.96	23.04	1.42	20.72	1.12	34.60	21.36	1.20	34.80		1.34
MnO MO	1.12	0.03	0.01	0.04	0.12	1.15	0.07	0.09	0.94	0.05	0.00
MgO	2.90	8.36	0.83	9.59	0.79	2.14	9.09	0.69	2.62	9.54	0.7
CaO	2.63	0.15	0.30	0.08	0.23	2.46	0.40	0.45	2.45	0.05	0.60
Na <sub>2</sub> O	-	0.26	1.14	0.46	0.59		0.35	0.66	-	0.33	0.78
K <sub>2</sub> O	_	9.50	10.00	9.20	9.70		9.00	9.60	-	9.60	9.70
$H_2O^+$		3.93	4.99	4.05	5.20		3.84	4.94		4.17	4.74
Total	99.94	100.00	99.89	99.95	99.33	98.63	100.01	99.13	99.09	99.97	99.88
								1	Number	of ior	s on
Si	5.99	5.63	6.55	5.48	6.35	5.99	5.55	6.51	5.93	5.50	6.40
Al	0.01	2.37	1.45	2.52	1.65	0.01	2.45	1.49	0.07	2.50	1.60
Al	3.78	0.38	3.20	0.44	3.30	3.86	0.44	3.27	3.74	0.40	3.34
${f Ti}$	0.04	0.19	0.06	0.17	0.04	0.03	0.18	0.04	0.01	0.16	0.04
${f Fe^{3+}}$	0.14	0.21	0.19	0.24	0.19	0.15	0.28	0.22	0.17	0.20	0.23
${ m Fe}^{2+}$	4.74	2.99	0.15	2.64	0.12	4.75	2.75	0.14	4.73	2.72	0.14
Mn	0.16	0.01	0.00	0.01	0.01	0.16	0.01	0.01	0.13	0.01	0.00
Mg	0.70	1.93	0.17	2.18	0.16	0.52	2.08	0.14	0.63	2.19	0.14
Ca	0.45	0.03	0.04	0.02	0.03	0.43	0.07	0.06	0.43	0.01	0.09
Na		0.07	0.29	0.13	0.14		0.11	0.18		0.09	0.19
K	<u> </u>	1.89	1.70	1.80	1.65		1.76	1.64		1.89	1.6!
OH		4.07	4.42	4.14	4.61		3.94	4.40		4.04	4.24
				1		<u> </u>		Distril	oution c	oeffici	ents a
		$B_2$		0	0 <sub>2</sub>		$C_{3i}$			Сз іі	
(Mg/Fe) <sup>G</sup>		0.148			_		0.110			0.132	
$(Mg/Fe)^{Bi}$		0.650		0.8	324		0.758			0.801	
$(Mg/Fe)^{Ms}$		1.100			330		1.000			1.001	
$\mathbf{K}_{\mathbf{D}} \mathbf{M}_{\mathbf{g}-\mathbf{F}e}^{\mathbf{G}-\mathbf{B}}$				1 1.0							
	1	0.224				1	0.145			0.165	
n <sub>D Mg-Fe</sub>		1.700		1.6	610		1.321			1.240	
(Ca/Mn) <sup>G</sup>		3.620		-			2.700			3.250	
$(Al^{IV}/Z)^{Bi}$		0.296			315		0.306			0.312	
$(Al^{IV}/Z)^{Ms}$		0.183			206		0.186			0.200	l .
$(K/Na+Ca+K)^{Bi}$		0.950			923		0.907			0.950	
$(K/Na+Ca+K)^{Ms}$	1	0.836		1 0 0	<b>906</b>	1	0.874		1	0.855	

Table 1. Chemical analyses of coexisting garnet, biotite and muscovite

Analyst: V. NARAYAN and R. S. SHARMA.

						Sillimanite-muscovite zone								
$D_3$		D <sub>4</sub>			E <sub>3i</sub>			E <sub>3 ii</sub>			$\mathbf{E_4}$			
G	Bi	Ms	G	Bi	Ms	G	Bi	Ms	G	Bi	Ms	G	Bi	Мs
$36.69 \\ 19.55$	$35.24 \\ 16.29$	$47.80 \\ 31.25$	$35.56 \\ 19.35$	$34.66 \\ 16.77$	$47.99 \\ 31.59$		$\begin{array}{c} 34.44 \\ 17.38 \end{array}$	and the second second	$\begin{vmatrix} 34.56\\21.08\end{vmatrix}$		$\begin{array}{c} 46.48\\ 31.64 \end{array}$	36.50 19.81	$34.89 \\ 16.94$	
0.08	1.66	$0.55 \\ 1.82$	0.19	1.53 1.86	$0.47 \\ 1.05$	0.20 1.86	$1.50 \\ 2.65$	$0.37 \\ 2.15$	$ \begin{array}{c} 0.11 \\ 1.48 \end{array} $	$1.45 \\ 1.26$	0.47 1.60	0.07	0.96	0.25
$35.50 \\ 1.00$		$\begin{array}{c} 1.48 \\ 0.06 \end{array}$	$\begin{array}{c} 37.61 \\ 0.89 \end{array}$	$\begin{array}{r} 22.03 \\ 0.05 \end{array}$	$\begin{array}{c} 1.16 \\ 0.04 \end{array}$	$\begin{array}{c} 35.36\\0.92\end{array}$	$\begin{array}{c} 20.54 \\ 0.05 \end{array}$	$\begin{array}{c} 1.22 \\ 0.04 \end{array}$	36.82 0.94	$20.52 \\ 0.09$	$\begin{array}{c} 2.00 \\ 0.03 \end{array}$	$35.90 \\ 1.06$	$\begin{array}{c} 21.59 \\ 0.08 \end{array}$	$\begin{array}{c} 1.26 \\ 0.04 \end{array}$
$\begin{array}{c} 2.71 \\ 2.78 \end{array}$	$\begin{array}{c} 7.88 \\ 0.28 \end{array}$	$\begin{array}{c} 0.64 \\ 0.42 \end{array}$	$\begin{array}{c} 2.16 \\ 2.33 \end{array}$	$\begin{array}{c} 9.28 \\ 0.10 \end{array}$	$\begin{array}{c} 0.74 \\ 0.49 \end{array}$	$\begin{array}{c} 2.44 \\ 2.38 \end{array}$	$\begin{array}{c} 9.76 \\ 0.35 \end{array}$	$\begin{array}{c} 0.68 \\ 0.44 \end{array}$	$\begin{array}{c} 2.58 \\ 2.38 \end{array}$	$\begin{array}{c} 8.76 \\ 0.09 \end{array}$	$\begin{array}{c} 0.84 \\ 0.20 \end{array}$	$\begin{array}{c} 2.49 \\ 2.45 \end{array}$	$\begin{array}{c} 9.68 \\ 0.32 \end{array}$	$\begin{array}{c} 0.96 \\ 0.43 \end{array}$
	0.24 9.50			$0.12 \\ 10.00 \\ 2.00$	$\begin{array}{c} 0.94 \\ 9.94 \\ 5.17 \end{array}$		$0.25 \\ 9.54 \\ 2.50$	and the second second		0.70 8.80	1.11 10.00		0.18 9.66	0.81 9.79
99.60	3.86 99.91	<b>4.4</b> 0 <b>99.3</b> 0	99.98	$\frac{3.60}{100.00}$	5.17 99.48	99.92	3.50 99.96		99.95	$\frac{3.88}{100.00}$	$\frac{4.20}{98.57}$	99.92	$\frac{3.71}{99.99}$	4.79 99.94

basis of 24 (oxygens (O, OH))

									the second se					
5 00	- 1-	0.05	F 07		0.40	F 00	F 04	0.00	F 0.4	- 0-		500	~	0.00
5.92	5.47	6.35	5.87	0.40	6.40	5.90	5.34	6.29	5.64	5.35	6.35	5.96	5.41	6.32
0.08	2.53	1.65	0.13	2.60	1.60	0.10	2.66	1.71	0.36	2.65	-1.65	0.04	2.59	1.68
3.63	0.46	3.35	3.64	0.49	3.36	3.90	0.53	3.41	3.77	0.77	3.41	3.77	0.50	3.40
0.01	0.20	0.05	0.02	0.18	0.05	0.03	0.18	0.04	0.01	0.17	0.05	0.01	0.11	0.02
0.16	0.24	0.17	0.22	0.21	0.11	0.22	0.20	0.23	0.17	0.15	0.17	0.20	0.24	0.19
4.82	2.97	0.23	5.18	2.86	0.13	4.83	2.66	0.14	5.10	2.62	0.23	4.91	2.79	0.14
0.17	0.01		0.12	0.01		0.13	0.01	1	0.13	0.01		0.15	0.01	
0.67	1.82	0.17	0.53	2.15	0.14	0.60	2.26	0.13	0.62	2.00	0.17	0.61	2.25	0.18
0.47	0.05	0.03	0.41	0.02	0.06	0.41	0.06	0.06	0.42	0.01	0.03	0.43	0.05	0.06
-	0.06	0.30		0.04	0.24		0.07	0.11		0.20	0.30		0.06	0.21
	1.89	1.60		1.98	1.68		1.88	1.79		1.76	1.60		1.92	1.67
	4.00	4.01		3.74	4.58		3.62	4.12		3.71	3.92		3.83	4.26
								14						

D <sub>3</sub>	D <sub>4</sub>	E <sub>3 i</sub>	${f E_{3ii}}$	$\mathbf{E_4}$
0.139	0.101	0.124	0.125	0.124
$\begin{array}{c} 0.622\\ 0.885\end{array}$	$\begin{array}{c} 0.751\\ 1.120\end{array}$	$\begin{array}{c} 0.845\\ 0.940\end{array}$	$\begin{array}{c} 0.760 \\ 0.744 \end{array}$	$\begin{array}{c} 0.802 \\ 1.260 \end{array}$
0.224 1.411	0.135 1.490	$\begin{array}{c} 0.147 \\ 1.112 \end{array}$	$\begin{array}{c} 0.162 \\ 0.985 \end{array}$	$\begin{array}{c} 0.156 \\ 1.501 \end{array}$
$\begin{array}{c} 2.751 \\ 0.316 \end{array}$	$\begin{array}{r} 3.410 \\ 0.325 \end{array}$	$\begin{array}{c} 3.250 \\ 0.332 \end{array}$	$\begin{array}{c} 3.250 \\ 0.330 \end{array}$	$\begin{array}{c} 3.000 \\ 0.324 \end{array}$
0.206 0.950	0.202 0.970	$\begin{array}{c} 0.214 \\ 0.935 \end{array}$	$\begin{array}{c} 0.206 \\ 0.898 \end{array}$	$\begin{array}{c} 0.213 \\ 0.945 \end{array}$
0.850	0.848	0.914	0.832	0.860

other distribution parameters

by running the accumulated grains on a Frantz's magnetic separator, followed in each case by a careful hand-picking under a binocular microscope. In this way about one gram sample of the mineral was collected. For rock analyses the samples were cut into cubes of nearly 8 cm size and were crushed by steel mortar and electric agate mortar. Fine powder of the samples was finally prepared by grinding with alcohol in a hand-driven agate mortar.

#### CHEMICAL ANALYSES

The minerals and rocks were analyzed by the methods mostly based on SHAPIRO and BRANNOCK (1956, 1962) and HOUNSLOW and MOORE (1966). The analytical data on the minerals and the rocks are presented in Tables 1 and 2.

### DISTRIBUTION OF ELEMENTS BETWEEN GARNET-BIOTITE PAIRS

Because of their common association in most rocks, and also being stable over a large range of metamorphic temperatures and pressures, the garnetbiotite pairs have received much attention in regard to their cation fractionation (see KRETZ, 1959; MUELLER, 1960; ALBEE, 1965; SEN and CHAKRABORTY, 1968; DAHL, 1969; HIETANEN, 1969; LYONS and MORSE, 1970; FLEMING, 1972). Their dominant constituents are iron and magnesium whose ionic radii are similar, therefore allowing easy diadochic substitution between the phases. Other cations of slightly larger radius are Mn and Ca, out of which the former is incorporated primarily in garnet. Al and Ti distribution is less interesting in them, because Al is stoichiometrically fixed and Ti can occupy different structural sites. Hence, only the distribution of Mg, Fe and Mn is considered in these mineral pairs.

#### Distribution of Mg, Fe<sup>2</sup>), and Mn

The distribution relations of these cations between eight garnet-biotite pairs from the area is shown in Figure 1. The molecular ratio  $X_{Mn}$  is strikingly regular while that of  $X_{Mg}$  and  $X_{Fe}$  is not; iron distribution is more irregular than the magnesium distribution. As Mn is more or less exclusively contained in garnet, its effect on the distribution of Mg and Fe is examined. In Figure 2, where the Mg/Mg + Fe ratios are plotted, no consistent relationship is evident. Moreover the plots of sillimanite-muscovite zone lie towards the relatively lower  $K_D$  side, which is not in conformity with the general conclusion that  $K_D$  increases with increasing grade of metamorphism. However, this feature

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<sup>&</sup>lt;sup>2</sup>) The Fe<sup>3+</sup> content of garnet and biotite in the present case is sufficiently low to permit disregard of it (see Table 1). A constituent like ferric iron in dilute concentration when added will only slightly decrease the Gibbs free energy of a major constituent of a solid solution (KRETZ, 1964, p. 3–4).



Fig. 2. Magnesium-iron distribution in garnet-biotite pairs from polymetamorphic schists of Beawar area.

can be understood if it is assumed that there was probably not a significant difference in the P-T conditions of the two zones.

In order to enquire about the chemical factor (s) which caused the variation in  $K_D$  in rocks of the similar metamorphic grade, the  $K_{DMg-Fe}^{G-B}$  is plotted against the compositional variables such as Mn, Ca in garnet and Al<sup>VI</sup> in biotite (Fig. 3). There is apparently no relation between the Mn content in garnet and  $K_D$  (Fig. 3a), possibly because of low Mn quantity in the garnets. KRETZ (1959) and ALBEE (1965a) have shown that Mn of garnet affects the Mg-Fe distribution such that  $K_{D Mg-Fe}^{G-B}$  becomes more in those garnet-biotite pairs where the garnet is Mn rich than in the case of Mn-poor garnet coexisting with biotite of the same composition (see also SEN and CHAKRABORTY, 1968). Again, the effect of  $Ca^{G}$  on  $K_{D Mg-Fe}^{G-B}$  is found to be inconsequential in the analyzed samples (Fig. 3b), which may be understood by more or less identical values of calcium in the garnets. Lyons and Morse (1970, p. 231) have, however, shown that  $K_D$  Mg-Fe for garnet-biotite pairs in calcium-rich metamorphic rocks of the garnet to kyanite zone is significantly lower than that in isogradic pelitic schists. Owing to the above-stated reason, the effect of  $(Ca + Mn)^{G}$  and of  $(Ca/Mn)^{G}$  on  $K_{D Mg-Fe}^{G-B}$  is also irregular (Fig. 3c and d),



Fig. 3a. Molecular ratio of Mn in garnet KD Mg-Fe<sup>2+</sup>.



Ca (mol. prop.) garnet o 8 6 9 •D3 •B2 Ε4 F3i 20 0.10 0.00 0.50 0.30 KD Mg-Fe<sup>2+</sup>

C 3ii

Fig. 3b. Molecular ratio of Ca in garnet KD Mg-Fe<sup>2+</sup>.



Fig. 3c. Molecular ratio of (Ca+Mn) in garnet versus K<sub>D Mg-Fe<sup>2</sup>+.</sub>

Fig. 3d. Molecular ratio of Ca/Mn in garnet versus K<sub>D</sub> Mg-Fe<sup>2+</sup>.

although SEN and CHAKRABORTY (1968), using 87 pairs of analyses culled from literature, concluded that  $K_D$  is a systematic function of Ca/Mn ratios in garnets. It should be stated here that LYONS and MORSE (1970) have also not found that  $K_D$  is a function of Ca/Mn in garnets.

The scatter of the plots and their varying  $K_D$  do not also show any correlation with the presence or absence of staurolite and hence with the garnet/ staurolite ratio (Fig. 4). The garnet-biotite pairs (D 4 and E 4) from the schists containing a good amount of staurolite have low  $K_D$  (cf. HIETANEN, 1969), but the general variation does not seem to be in full accordance with the conclusion of HIETANEN (loc. cit., p. 444), who writes that the crystallization of staurolite in the rocks increases the Mg/Fe ratio in the coexisting garnet and biotite, more so in biotite. In the present case the samples containing more modal percentage, however, show lesser  $K_D$  values.





Fig. 5. Relation between oxidation ratio of rock and  $K_{D Mg \cdot Fe^{2+}}^{G-B}$ . Square represents the plots after Hounslow's and Moore's (1967) data.

Fig. 4. Plot of garnet/staurolite ratio (volume %) versus  $K_{D MgFe^{2+}}^{G-B}$ .

There also do not exist relations between the  $K_D$  for Mg/Fe in garnetbiotite pairs and the rock oxidation ratio. CHINNER (1960) and HOUNSLOW and MOORE (1967) report that rock oxidation ratio results in strong variation in Mg/Fe ratios of garnet and biotite. It is rather interesting to note that the minerals pairs biotite-garnet-staurolite assemblages from Fernleigh area (HOUNSLOW and MOORE, loc. cit.) show a strong relationship between  $K_D$  and the rock oxidation ratio (Fig. 5).

ALBEE (1965b) and, more recently, DAHL (1969, p. 311) have suggested that the distribution of Mg and Fe<sup>2+</sup> and hence  $K_D$  in the coexisting garnet-

biotite pairs is dependent on octahedrally coordinated Al in biotite. A plot of  $K_{D Mg-Fe}^{G-B}$  versus Al<sup>VI</sup> in biotite indicates a highly satisfactory relationship in the studied samples (Fig. 6). Again, the different  $K_D$  values in the analyzed mineral pairs from a single zone are found to show a strikingly consistent relationship with the iron and magnesium contents of the rock. This is illustrated in Figure 7, where the  $K_D Mg-Fe$  is plotted against Mg/Fe ratio of the host rock. The dependency of  $K_D$  on Mg/Fe ratio of the rock is likely to occur in



Fig. 6. Plot of Al<sup>VI</sup> in biotite versus Fig. 7. Relation between Mg/Fe (mol.  $K_D^{G-B}_{Mg-Fe^{2+}}$ . prop.) of rock and  $K_D^{G-B}_{Mg-Fe^{2+}}$ .

the area where garnet composition does not vary significantly; the  $K_D$  for Mg/Fe in garnet-biotite must then change with the change in Mg/Fe ratio of the coexisting biotite. In the authors' area, like in most areas (see, e.g. ATHER-TON, 1965, p. 296; FREY, 1969), the Mg-Fe of biotite is found to show a strong dependence upon the Mg-Fe of the rock. The garnet composition remaining more or less uniform, the plot of Mg/Fe rock vs. 1/(Mg/Fe) biotite therefore shows a definite correlation (Fig. 8). Owing to their small amounts, the variations of Mn and Ca will not effect the K<sub>D</sub> in a significant manner, as discussed earlier (see also ALBEE, 1965b, p. 279). On the other hand, if the biotites have varying Mg-Fe, the distribution coefficient for the given mineral pair of garnetbiotite will be of course different in different assemblages even if they come from the neighbouring outcrops. This is considered to be of a great importance for the garnet-biotite pairs from the polymetamorphic rocks in which garnet, owing to its refractory nature, does not internally re-equilibrate while "biotite and chlorite and presumably muscovite continuously internally reequilibrate with the changing external conditions ...." (HOLLISTER, 1969, p. 2489). In the present case, as in most other areas (see HOLLISTER, 1969; DRAKE, 1969;



Fig. 8. Plot of Mg/Fe of rock versus 1/(Mg/Fe) in biotite.



Fig. 9. Relation between Ca content of garnet and anorthite percentage (molecular) of plagioclase.

ATHERTON, 1968), it appears to be almost definite that the outer rim of the garnet, and so also the overgrown garnet (garnet II) of the second metamorphism, are in equilibrium with the coexisting biotite and muscovite in the rocks. Although this matter can only be resolved with the help of electron microprobe analysis of garnets, the effect on  $K_D$  in the individual sample should not be significant and detectable (cf. ALBEE, 1968). It may be added here that the garnet in the rocks shows equilibrium relationship with the coexisting plagioclase in regard to the Ca distribution (Fig. 9).

From this and the preceeding discussion it is considered that the garnetbiotite pairs from the polymetamorphic schists have approached chemical equilibrium. Of course, it is evident that if garnet in the different assemblages shows a nearly uniform composition, as in the studied case, it is the biotite Mg/Fe and its dependency on the host rock composition that result into different  $K_D_{Mg-Fe}^{G-B}$  values even in rocks of the same zone. In this context ALBEE'S (1965b) remark is worth reproducing here. He writes "that  $K_D$  the parameter which we can measure, will vary not only with temperature, but with changes in composition as well. Biotite and chlorite in a single outcrop formed at a single temperature may exhibit a wide range of Fe/Mg values and of Mn, Ti, Fe<sup>3+</sup>, F, Cl and Al contents. This will result in a range of values for K..." (ALBEE, 1965b, p. 277).

The variation in  $K_D M_{g-Fe}^{G-B}$  for the investigated rocks is between 0.135 to 0.224, and thus coincides with the  $K_D$  values given for kyanite to sillimanite zone rocks by HIETANEN (1969) from Idaho area and by LYONS and MORSE (1970) form New Hampshire. The values of  $K_D$  compiled by Lyons and Morse (op. cit. Table 1) is based on the determination Mg/Fe<sup>2+</sup> + Fe<sup>3+</sup> in the garnet-biotite and thus slightly differs from the  $K_D$  values calculated as Mg/Fe<sup>2+</sup> for the mineral pairs in the investigated area.

Index		Sta	Sillimanite-muscovite zone							
No.	Group B		Group (	)	Gro	up D	Group E			
	B <sub>2</sub>	$C_2$	$C_{3i}$	$C_{3ii}$	D <sub>3</sub>	$D_4$	E <sub>3 i</sub>	$\mathbf{E}_{3ii}$	$\mathbf{E_4}$	
Sp. No.	77/588	77/744	77/530	77/700	77/601	78/39	77/639	77/591	77/707	
SiO <sub>2</sub>	61.11	57.26	45.71	53.07	59.43	37.54	43.67	60.52	57.63	
TiO,	0.87	0.98	1.00	1.12	0.89	1.26	1.00	0.42	0.37	
$Al_2O_3$	10.07	19.58	20.64	22.15	18.84	30.48	29.02	21.20	20.95	
Fe <sub>2</sub> O <sub>3</sub>	2.24	1.75	5.87	3.04	1.82	2.80	5.60	1.23	2.86	
FeO	13.43	8.16	11.74	9.87	8.11	13.18	7.96	6.14	7.48	
MnO	0.40	0.06	0.06	0.03	0.05	0.13	0.08	0.07	0.11	
MgO	3.81	3.72	5.33	3.51	3.15	6.16	3.49	3.02	2.83	
CaO	1.25	0.24	0.09	0.16	0.39	0.46	0.62	0.82	0.89	
$Na_2O$	0.34	0.67	0.82	0.83	0.86	0.81	0.61	1.43	0.62	
$K_2 \bar{O}$	3.74	5.08	5.68	3.75	3.98	4.82	5.48	2.20	3.25	
$P_2O_5$	0.31	0.24	0.26	0.26	0.21	0.33	0.29	0.10	0.13	
$H_2O^+$	2.44	2.26	2.80	2.19	2.28	2.98	2.20	2.35	2.82	
Total	100.01	100.00	100.00	99.98	100.01	100.95	100.02	99.50	99.92	
0.R.	13.0	17.4	31.2	21.7	14.4	16.5	38.7	16.0	26.4	
$Mg/Fe^{2+}$	0.51	0.80	0.80	0.64	0.70	0.84	0.78	0.80	0.69	

 Table 2. Chemical composition of the schists from which coexisting garnet, biotite and muscovite are analysed

Analyst: V. NARAYAN and R. S. SHARMA.

# DISTRIBUTION OF ELEMENTS BETWEEN MUSCOVITE-BIOTITE PAIRS

The distribution of cations between coexisting muscovite-biotite pairs, as compared to the garnet-biotite pairs, has received very little attention of petrologists, although the two micas almost always occur together in most pelitic schists. Being complex chemical mixtures, they show considerably large substitutions and hence the problem of elemental distribution in them remains extremely difficult.

Among the important works pertaining to the distribution of Fe, Mg, Al, Ti, alkalies etc. in the coexisting micas those of BUTLER (1965, 1967), SAXENA (1966), EVANS and GUIDOTTI (1966), and GUIDOTTI (1970) are worth mentioning. From Moine schists of Ardnamurchan area in Scotland, BUTLER (op. cit.) reports a consistent distribution of Mg and  $Fe^{2+}$  between coexisting muscovites and biotites. In the rocks of western Maine, EVANS and GUIDOTTI (1966) also found an excellent linear correlation of Mg/Fe ratios in the coexisting micas. They, however, pointed out that due to relatively small variations of Ti in the micas a linear relationship for the Ti distribution could not be detected. In contrast, the mica pairs from Oquossoc area (GUIDOTTI, 1970) do not show any significant difference in Mg/Fe ratios and the distribution coefficient is therefore not discernible according to the grade. SAXENA (1966), on the basis of 20 chemical analyses of the coexisting mica pairs from schist and gneisses, found that Mg-Fe and also K do not show any regularity in their distribution, while Na and to some extent Ti have a tendency to approach equilibrium.

In the following pages, the distribution relations of Mg, Fe, Ti, Al, and alkalies between nine coexisting muscovites and biotites have been discussed. All the mica pairs, except one (C 2), are from the same assemblages from which the garnet-biotite pairs have been dealt with.

#### Distribution of Mg and Fe

In Figure 10 the distribution of  $Mg/Fe^{2+}$  (atomic ratio) shows almost a cluster of the points, irrespective of the metamorphic zones. This indicates that the distribution of magnesium and iron in the micas does not bear any



Fig. 10. Magnesium-iron distribution between coexisting muscovites and biotites from polymetamorphic schists of Beawar area.

relationship with the grade (cf. BUTLER, 1965, p. 202; 1967, p. 255–256; EVANS and GUIDOTTI, 1966, p. 44), or else there is not much difference in the temperature and pressure in the two zones of the area. In the Oquossoc area, GUIDOTTI (1970, Fig. 11, p. 310) also describes a similar cluster on a plot of Mg/Fe (muscovite)/Mg/Fe (biotite), which he attributes to the similar nature of the assemblages.

The mean value of  $K_{D Mg-Fe}^{Ms-Bi}$  in the present study is 1.35 which is very similar to that found by EVANS and GUIDOTTI (1966) in the western Maine where  $K_D = 1.3$ , but is in contrast to 1.56 in that of GUIDOTTI (1970) and to 2.5-3.0 in that of BUTLER (1967). This difference is possibly due to the distinction made in one case and not made in another case between ferrous and ferric iron, although GUIDOTTI (loc. cit.) ascribes this difference to the difference in the metamorphic grade of the areas of western Maine and Oquossoc.

#### Distribution of Al and Ti

A plot of  $Al^{IV}/Z$  ratios in Figure 11a and of  $Ti^{Ms}$  versus  $Ti^{Bi}$  in Figure 11b shows a parallel relationship, indicating therefore that the distribution of  $Al^{IV}$  and Ti is regular in the coexisting micas (cf. BUTLER, 1967; DAHL, 1969). In





Fig. 11a. Distribution of tetrahedral aluminium  $(Al^{IV}/Z)$  in the muscovite-biotite pairs.

Fig. 11b. Distribution of Ti (wt. %) between coexisting biotites and muscovites.

rocks containing Al-silicate minerals the Al in muscovite and biotite appears to have substituted more Si than in the micas of isogradic schists without aluminosilicate minerals. This suggests that the distribution of tetrahedral aluminium in the micas is independent of grade (cf. BUTLER, 1965, 1967). Similarly the partitioning of Ti in these muscovite-biotite pairs is consistent and unrelated to the metamorphic grade (ENGEL and ENGEL, 1960; KWALK, 1968; GUIDOTTI, 1970).

#### **Distribution of Alkalies**

The alkalies as K/Na + K and as K/Na + Ca + K ratios in the coexisting micas do not exhibit any regular distribution (Figs. 12a and b). Similar feature has also been observed by SAXENA (1966, p. 1), who explained it by the fact that the variation of potassium is limited in muscovites but is large in biotites. A plot of K (cations) in the muscovites and biotites from the area displays



- b) Plot of K/(Na+K) (atomic ratios) between coexisting muscovites and biotites.
- c) Potassium distribution in the muscovite-biotote pairs.



that there is a significant deviation from stoichiometry in both micas (Fig. 12c). There appears no ready explanation for the existing variation in the alkalies, as there is no other K-bearing phase present in the rocks. Following SAXENA (1966, p. 14) it may be considered that "the distribution is influenced by other ions present in the mineral and appears to be also influenced by the presence or absence of other phases in the rock".

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