DISTRIBUTION OF MINOR ELEMENTS IN COEXISTING HORNBLENDES AND BIOTITES

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ABSTRACT

Twenty pairs of coexisting hornblende and biotite samples were extracted from gneisses and schists whose mineralogy and petrology indicated that they were of epidote-amphibolite facies of metamorphism. Spectrographic analyses were made for seven major and seventeen minor elements, with a view to examining the distribution of minor elements between the two minerals, and the factors that influenced the distributions. Major constituents analysed included SiO_2, Al_2O_3, MgO, FeO, CaO, Na_2O, and K_2O; minor elements included B, Be, Mo, Sn, Ga, V, Zr, Y, Cu, Cr, Co, Ni, Sc, Sr, Ba, Mn, and Ti.

Solution theory predicts that the atomic ratios of an element in biotite plotted against that in hornblende should yield a regular curve, if the elements are in solution and have attained an equilibrium in the two coexisting minerals. Data from the analyses indicate that a number of the minor elements are quite well equilibrated; others show some aberrant points and a few are apparently not equilibrated at all.

Theoretically, the proportions of major elements may influence the fractionation of minor constituents. Evidence for this in the data is scanty, and it is concluded that effects of this type are obscured by contravening effects among the large number of variations possible in the major element concentrations.

An examination of the diagrams shows that some elements are distributed regularly down to very low levels of concentration. Notable among these are Cu, Y, Ni, Co, Sc, Cr, and Ba.

A comparison of data from these rocks with similar from rocks of higher and lower metamorphic facies demonstrates possible variations in distribution coefficients as a function of metamorphic grade.

INTRODUCTION AND BACKGROUND

Element distributions in co-existing minerals have been a problem of interest for some time. In igneous situations, they have been studied by experiment; for example, sub-solidus relations in the alkali feldspars, and by the rules of the reaction series and phase equilibria, as in the use of tie-lines in the study of the compositions of co-existent clino- and ortho-pyroxenes. With metamorphic rocks, much information about facies-composition relationships has come from the study of the equilibria of minerals as expressed by their compositions and the thermodynamic potentials of their constituent elements (Ramberg, 1952 a, b, and 1953; Kretz, 1959, 1961; Mueller, 1960, 1961).

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Comparatively little attention has been directed to minor element distributions in co-existing minerals. Howie (1955) has analysed several igneous rocks with respect to the trace constituents of their component minerals, with the object of finding their relative abundances in the minerals of each rock. His analyses included one pair of biotite and hornblende, five pairs of hornblende and ortho-pyroxene, and six pairs of ortho- and clino-pyroxene. Howie gave no interpretation of his results.

In their study of rocks of the Southern California batholith Sen, Nockolds & Allan (1959) included trace element analyses for a number of combinations of ferromagnesian minerals. There were too few samples of each pair, however, to reveal more than the directions of fractionation of the minor constituents and that these directions were similar to that in the minerals of other batholithic masses.

Nickel (1954) showed data for ten pairs of coexisting hornblende and biotite and for ten pairs of biotite and chlorite. Trace analyses were made for Co, Ni, Cr, Zr, Sc, and V. An interpretation of the data was made in terms of the relative electronegativities of the major and minor elements involved.

DeVore (1955) examined a large number of mineral analyses from the literature and sought to explain major and minor element distributions in terms of ionic properties and bonding mechanisms.

Carstens (1958) listed five pairs of associated ortho- and clino-pyroxenes from basalts for which he gave only Mg, Fe, and Al analyses, and Ni, Cr, Co, and Mn trace analyses, and noted that "trends are apparent" in the distribution of elements between these two mineral species.

Kretz (1959) presented a thorough treatment of co-existing biotites, hornblendes and garnets in gneisses of the amphibolite facies. He examined the distributions of Fe, Mg, Mn, Ti, V, Cr, Zr, Y, and Sc, plotted distribution diagrams of his results, and evaluated the distributions in terms of chemical-phase theory. His work was mainly directed toward the major constituents Ca, Fe, and Mg, and to Ti and Mn, for which the data plot up quite well. His results with respect to Sc, Y, Ba, and Cr are somewhat uncertain, however, and the points on the distribution diagrams are quite scattered. This is somewhat puzzling in view of the orderly distributions found for the elements Fe, Mg, Ca, Mn, and Ti, and in view of the regular behaviour of the minor elements as reported for igneous rock series. Almost certainly, the minor elements are more subject to erratic distribution effects, such as crystal imperfections, but this may have been due at least in part to the fact that for the minor elements (except for Ti and Mn) the spectrographic method employed was operating near the limits of its sensitivity.

Kretz found the use of a distribution diagram to be a useful tool in the study of his data. In this graphical presentation, also called a Roozeboom diagram, the concentration or atomic ratio of an element in one phase is plotted against its concentration, or atomic ratio in the other phase. In such a diagram, if an element is regularly distributed between two minerals, and if each point represents a mineral pair, the points will define some regular curve or straight line. The slope of the line, at low concentrations, will be a graphic representation of the distribution coefficient. Kretz was able to demonstrate that such a regular distribution was, in some cases, influenced by the concentration of another element, *i.e.*, the slope was a function of the concentration of some other element. It was shown, for instance, that Mn concentration in garnet affects the distribution of Mg between garnet and biotite.

In view of these considerations, a similar graphical approach to the distribution of minor elements would be revealing, provided a more sensitive analysis method were employed and a larger number of these elements were determined. In addition, analysis of the major element composition of the minerals and calculation of their atomic ratios would permit examination of possible major element influences on minor element distributions.

In this study, twenty pairs of biotite and hornblende were analyzed spectrographically for seven major and seventeen minor components, using a method suitable to each group. It is possible to demonstrate relationships by the graphical method briefly described above. In addition an attempt is made to interpret the distributions in the light of the structures of the two minerals and of the ionic properties of the minor and major elements involved. The main questions considered in this paper, therefore, may be summarized as follows:

(*a*) which elements are regularly and which are randomly distributed?

(*b*) what are the factors, chemical and structural, that account for regular distributions?

(*c*) what are the factors that may influence the value of the distribution coefficient?

(*d*) to how low a concentration is equilibrium maintained in these minerals, with respect to these various elements?

SPECIMENS AND GEOLOGICAL SETTING

Specimens were gathered by the writer in an area in the Precambrian of northwestern Ontario. The general geology has been described by Donaldson (Geological Survey Map 50-1960) and is typical of much of the northern Ontario shield area.

The oldest rocks apparent in the area are Keewatin-type meta-volcanics and meta-sediments. These lie as NW-SE trending basins and synclines, usually strongly faulted and tightly folded. The belts are of the order of four to ten miles across and up to thirty miles long; five main belts of this type are seen on the North Spirit Lake sheet.

The remaining area, comprising some 80-90 per cent of the total area, is underlain by younger (?) granitoid rocks of various ages whose relationships are difficult to understand because of their compositional variations and structural complexities. Four main types may be recognized:

(*a*) Coarse-grained quartz diorite and granodiorite showing strong foliation. These rocks are 10–40 per cent hornblende and biotite, 40–60 per cent plagioclase, 10–30 per cent potash feldspar, 0–20 per cent quartz, and contain minor sphene, epidote, magnetite, and apatite.

(*b*) Porphyritic and porphyroblastic granodiorite and granite. Foliated, phenocrysts usually aligned.

(*c*) Medium-grained granodiorite and quartz monzonite. Contains 0–20 per cent hornblende and biotite, 30–50 per cent plagioclase, 20–50 per cent potash feldspar, 10–30 per cent quartz. Grey to white, faintly foliated.

(*d*) Granite. Pink, fine-grained, massive, few or no mafic minerals.

The rocks of unit *a* are often strongly banded, and locally migmatitic in character. Those of unit *d*, at the other extreme, show cutting relationships to their surrounding rocks and often contain inclusions of older gneisses. Although the exact relationships are not always clear, the suggested age sequence is *a*, *b*, *c*, *d*. This sequence, *a* through *d*, shows an increase in the potash feldspar to plagioclase ratio, a decrease in mafic mineral content, and a decrease in foliation. Such trends are suggestive of large scale granitization. Aplitic dykes and pegmatites, and the aforementioned inclusions suggest at least some melt of granitic character.

Specimens showing hornblende and biotite were collected from the granitoid rocks, and in some cases from their inclusions. Most specimens are of rocks of type *a* above, with a lesser number representing type *c*, and a few from the inclusions. Some of the inclusions are petrographically very similar to the type *a* gneisses, and the rest of the inclusion specimens are of indeterminate origin.

The geology of the North Spirit Lake map area and characteristics of the specimens themselves demonstrate that the materials analysed were well-suited to this study; specifically—

(1) The terrain sampled is a regionally metamorphosed one of great age, and has probably been influenced by more than one regime of metamorphism. This would seem to afford the most favorable conditions for the attainment of chemical equilibrium between the two minerals of concern.

(2) All specimens are believed to have undergone the same degree of metamorphism, that is, epidote-amphibolite facies, since this facies is apparently persistent over the whole map area. (Donaldson, 1960).

(3) In most of the rocks, hornblende and biotite are the only ferromagnesian minerals present. This presents a simple two-phase situation to most of the transition group elements. Small amounts of magnetite are commonly present, however.

(4) Hand specimens were kept reasonably small. Kretz (personal communication) stresses the importance of small specimens (4–5 cm. in each dimension, or less) to insure that local equilibrium conditions exist throughout.

(5) Fortunately, minor element concentrations are sufficiently varied to permit examination of the distributions over a satisfactory range of values. That is to say, the values do not cluster about points. Most elements show at least a three- or four-fold variation in concentration among the samples analysed.

ANALYTICAL METHODS

Separations

Twenty specimens of schists and gneisses were selected for further work, on the basis of their having sufficient fresh biotite and hornblende for extraction. These specimens were crushed, screened to 100-200 mesh, and the hornblende and biotite isolated using a Frantz isodynamic separator, by "riffling" the grains on coarse paper, and by some hand-sorting where necessary. The separates were examined under a binocular microscope equipped with a counting graticule for impurities present in the form of foreign grains and intergrowths. It is believed that the fractions used in the analysis were at least 98 per cent pure, by volume.

Spectrographic analysis

The major elements in the minerals were determined by a fluxing technique developed by O. Joensuu which employs boric acid and Li_2CO_3. This method has been discussed elsewhere by Goldsmith, Graf, & Joensuu (1955). Working curves were established using chemically analysed ferromagnesian minerals, and calculations were made using the method of Honerjäger-Sohm & Kaiser (1944). Tests performed on N.B.S. standard samples showed that the major element analyses had a relative error usually less than five per cent, which is satisfactory for the methods involved.

Minor elements were determined by a method similar to that of Shaw (1960). Standards consisted of mixtures of Johnson-Matthey Spec-pure compounds and the minor elements were introduced by means of Spex-mix—a mixture of 43 metal oxides, each present at 1.34 per cent concentration (available from Spex Industries Inc.). Standards were prepared covering the range 1 to 1000 p.p.m. at half decade intervals. Analysis of G-1 and W-1 showed that, except for Ba and Sr at low concentrations, the minor element method was satisfactory, giving an error of the order of that experienced by Shaw.

Alkali analysis

Analyses of Na and K in the minerals were made by flame photometry using a Beckman DK-2 spectrophotometer with flame attachment. The Na and K were rendered soluble and extracted by a calcium carbonate-ammonium chloride leach treatment. Standard solutions were made up from C. P. alkali salts. The method, as tested on G-1 and W-1, has a relative error of about 5 per cent for Na_2O and 3 per cent for K_2O.

ANALYTICAL RESULTS

Tables 1 and 2 give the results of the major element analyses of the hornblendes and biotites respectively. Iron was determined as elemental Fe and is recalculated in the table to FeO. All figures are per cent values.

Tables 3 and 4 present the results of the minor element analyses, respectively, for hornblendes and biotites. Lithium was also sought but was found to be below its level of sensitivity in all samples examined.

Notes on the symbols and conventions used follow the tables.

TABLE 1. MAJOR ELEMENT ANALYSES—HORNBLENDES

Sample	6009	6014	6023	6024	6032	6034	6035	6036	6047	6049
SiO_2	48.	46.	48.	48.	50.	45.	47.	45.	44.	42.
Al_2O_3	8.7	9.1	9.3	10.9	5.5	8.1	7.8	9.9	9.2	7.4
TiO_2	0.96	1.04	1.20	1.04	0.46	0.86	0.84	0.86	1.18	1.06
FeO	15.2	16.6	15.2	17.5	11.1	14.5	14.5	16.7	16.3	14.5
Fe^{o}	11.8	12.9	11.8	13.6	8.6	11.3	11.3	13.0	12.7	11.3
MnO	0.23	0.335	0.31	0.335	0.275	0.30	0.3	0.36	0.535	0.425
MgO	7.5	9.4	6.8	9.4	9.8	8.6	8.6	6.9	8.75	8.4
CaO	9.1	8.9	8.4	7.2	12.4	8.6	8.6	7.2	8.05	8.85
Na_2O	2.40	2.15	1.15	2.10	1.60	1.50	1.25	1.70	1.75	2.35
K_2O	1.25	2.1	1.4	2.35	0.65	1.39	1.7	1.4	1.70	1.9

Sample	6050	6051	6055	6056	6057	6058	6060	6061	6064	6065
SiO_2	50.	46.	42.	42.	47.5	47.	46.	42.	47.	48.
Al_2O_3	7.8	8.3	8.6	14.	10.3	9.1	10.5	13.	9.1	7.4
TiO_2	1.25	1.18	0.76	1.16	1.28	0.88	1.31	1.65	1.06	1.13
FeO	13.5	14.2	13.5	14.5	15.2	14.5	17.1	16.6	13.4	11.9
Fe^{o}	10.5	11.0	10.5	11.3	11.8	11.3	13.3	12.9	10.4	9.3
MnO	0.425	0.370	0.225	0.35	0.287	0.385	0.332	0.330	0.350	0.117
MgO	10.3	8.6	11.7	7.7	7.5	9.0	8.2	7.0	10.5	11.5
CaO	12.5	10.0	9.7	9.8	7.2	9.6	7.65	6.35	8.8	12.0
Na_2O	1.15	1.50	2.40	2.65	2.50	1.05	1.15	1.35	1.25	0.95
K_2O	1.9	1.6	1.0	1.7	1.0	1.90	1.80	1.4	1.60	1.0

TABLE 2. MAJOR ELEMENT ANALYSES—BIOTITES

Sample	6009	6014	6023	6024	6032	6034	6035	6036	6047	6049
SiO_2	41.	40.	41.	39.5	39.	39.	39.	37.	39.5	39.
Al_2O_3	12.5	15.	17.	17.2	17.	15.5	15.6	16.	15.3	14.0
TiO_2	2.0	1.60	1.25	1.35	1.02	1.50	1.40	1.60	1.68	1.75
FeO	19.4	19.4	20.6	20.0	14.8	16.8	17.4	21.3	17.4	16.1
Fe^o	15.	15.	16.	15.5	11.5	13.	13.5	16.5	13.5	12.5
MnO	0.150	0.225	0.240	0.252	0.218	0.252	0.198	0.252	0.415	0.230
MgO	7.1	11.5	10.2	13.0	15.5	12.5	10.5	8.6	11.7	12.0
CaO	0.7	0.6	0.9	0.6	0.6	0.6	0.5	0.7	0.5	1.0
Na_2O	0.40	0.42	0.80	1.50	0.35	0.30	0.80	1.10	1.75	1.65
K_2O	6.85	7.45	7.10	8.35	9.10	7.3	6.3	7.2	8.2	6.9

Sample	6050	6051	6055	6056	6057	6058	6060	6061	6064	6065
SiO_2	40.	40.	40.	35.5	36.	37.	36.	36.	40.	36.
Al_2O_3	14.4	12.5	18.	15.8	16.5	16.5	14.	16.8	18.0	13.3
TiO_2	1.98	1.64	1.95	2.00	2.02	2.00	1.85	2.25	1.68	2.15
FeO	16.8	16.1	16.5	15.5	17.8	17.5	17.4	20.0	18.7	14.4
Fe^o	13.	12.5	12.8	12.0	13.8	13.6	13.5	15.5	14.5	11.2
MnO	0.198	0.325	0.150	0.227	0.188	0.220	0.210	0.230	0.230	0.073
MgO	11.7	10.0	12.5	10.3	10.4	10.5	9.2	9.9	14.2	12.5
CaO	1.1	2.1	0.55	0.8	0.4	0.6	1.1	0.5	1.1	0.8
Na_2O	0.50	1.80	0.80	1.00	1.00	0.75	1.25	0.95	0.75	1.2
K_2O	6.6	6.3	8.1	8.1	8.35	7.3	6.75	7.4	6.55	6.75

TABLE 3. MINOR ELEMENT ANALYSES—HORNBLENDES

Sample	6009	6014	6023	6024	6032	6034	6035	6036	6047	6049
B	28	33	59	45	31	34	38	33	41	30
Ga	—	—	—	—	92	—	21	—	—	34
V	250	190	258	265	520	240	218	242	220	210
Be	—	—	—	—	—	—	—	—	3.6	2.5
Mo	22	22	38	10	52	30	15	22	24	$\sim$10
Sn	27	29	—	40	tr	48	40	tr	30	$\sim$28
Cu	24	17	38	31	7	17	13	31	10	12
Y	31	47	42	44	—	38	36	—	63	37
Zr	155	120	185	128	370	110	95	85	125	108
Ni	83	108	74	115	440	110	110	33	41	—
Co	63	57	57	66	150	64	52	49	56	47
Sr	37	35	50	37	16	40	22	45	24	28
Sc	84	66	90	78	140	85	60	57	64	43
Cr	235	300	230	310	$\sim$2850	490	400	235	54	530
Ba	135	88	130	180	10	82	47	340	56	66

Sample	6050	6051	6055	6056	6057	6058	6060	6061	6064	6065
B	26	28	35	47	52	60	52	52	47	33
Ga	46	22	29	46	42	—	—	50	—	46
V	210	190	265	750	300	360	290	290	260	425
Be	—	2.9	—	—	—	—	—	—	—	—
Mo	19	22	17	30	27	32	31	26	31	21
Sn	33	31	—	42	30	60	50	40	40	26
Cu	48	33	33	45	65	105	35	62	42	32
Y	36	56	37	56	60	60	47	70	41	32
Zr	110	115	250	270	195	160	145	160	140	145
Ni	170	130	132	110	95	98	46	41	360	412
Co	56	54	57	54	83	82	70	50	88	114
Sr	29	26	14	47	52	36	77	66	31	27
Sc	46	59	54	138	92	155	70	92	60	58
Cr	820	380	395	700	230	625	72	66	740	390
Ba	50	47	34	204	260	125	405	485	125	112

TABLE 4. MINOR ELEMENT ANALYSES—BIOTITES

Sample	6009	6014	6023	6024	6032	6034	6035	6036	6047	6049
B	48	42	50	52	34	45	53	43	28	29
Ga	88	—	—	—	—	90	—	~90	42	—
V	335	272	345	265	590	315	360	340	235	185
Be	—	—	—	—	—	—	—	—	—	—
Mo	33	31	30	30	25	26	33	31	25	17
Sn	—	—	—	—	—	—	tr	tr	—	24
Cu	27	32	51	79	18	34	31	68	14	12
Y	37	36	38	40	32	37	44	22	38	41
Zr	490	315	225	195	185	138	125	200	215	160
Ni	144	230	144	204	940	220	235	45	74	330
Co	104	105	105	110	245	120	110	71	83	83
Sr	38	55	57	26	31	51	74	50	68	40
Sc	39	25	31	27	32	30	36	30	31	26
Cr	185	370	205	380	7600	610	530	37	70	670
Ba	~2450	580	420	600	600	385	350	1680	250	280

Sample	6050	6051	6055	6056	6057	6058	6060	6061	6064	6065
B	25	30	23	36	42	42	50	45	39	25
Ga	—	—	—	42	78	57	78	90	—	—
V	175	215	265	720	305	330	320	337	275	440
Be	—	~3	—	—	—	—	—	—	—	—
Mo	31	20	21	30	37	37	42	45	28	21
Sn	12	31	—	—	—	—	—	—	—	—
Cu	160	27	60	65	45	295	60	65	130	70
Y	30	83	33	29	52	63	56	60	39	105
Zr	140	170	144	340	195	205	225	280	205	204
Ni	350	180	230	130	172	172	120	87	570	760
Co	76	76	66	71	120	99	123	114	129	195
Sr	23	42	19	36	42	33	92	91	30	31
Sc	27	46	23	37	36	57	35	42	32	21
Cr	700	260	210	660	165	570	48	51	705	360
Ba	520	120	220	1900	900	540	1600	1250	480	1125

Notes on Tables 3 and 4.

Values are given in parts per million.

All analyses were made in triplicate, and the mean taken as the most acceptable value.

A dash (—) denotes that the element was sought and found not present, or at a level too low for the analysis method.

Trace amounts, symbol "tr," denotes that the element was observed but at a level below the significant portion of the working curve.

The symbol (~) denotes approximate values. This usually refers to values determined by extrapolation of the working curve.

DISTRIBUTION OF ELEMENTS

Chemical equilibrium theory

The chemical principles involved in the consideration of solid solution systems have been thoroughly discussed in papers by Ramberg & DeVore (1951), Kretz (1959, 1961), Mueller (1960, 1961) and others and need only be briefly recapitulated here. In essence, these writers have shown that the major components in co-existing minerals of variable composition are distributed among the minerals according to the principles of solution theory and heterogeneous equilibria. By extension, minor elements in minerals form dilute solid solutions, and are therefore amenable to treatment in terms of the physical chemistry of dilute solutions.

Some points which emerge from these theoretical treatments may be outlined as follows:

(*a*) If the elements are in solution, the concentration (or atomic ratio) of an element in one phase (mineral) plotted against the concentration of the same element in a co-existing mineral for a range of concentrations, will define a series of points forming a curve known as a distribution curve.

(*b*) This curve will be a straight line of unit slope, or will be symmetrical about such a line, if the element forms an ideal mixture in both phases; if the element does not form such a mixture in one or both phases, the curve will, in general, be irregular.

(*c*) At dilute concentrations, the curve becomes a straight line passing through the origin. This is the graphic expression of Nernst's distribution law, and is important in this paper because it describes the case for minor elements. This line will be straight, whether or not the element in question forms an inideal solution in one or both phases, and its slope will be the distribution coefficient K_D.

(*d*) The slope of the distribution curve, *i.e.* K_D, is dependent on pressure and temperature. The pressure dependence is negligible, but wide temperature variations cause noticeable differences in distribution (Kretz, 1961).

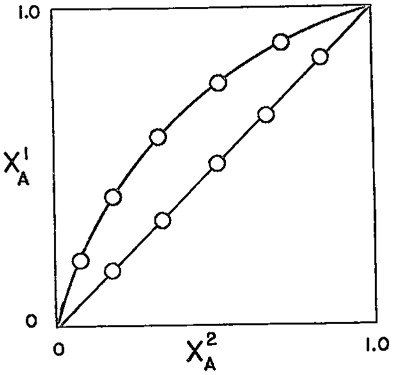

FIG. 1. Diagram showing two hypothetical distribution curves relating the concentration of component A in phase 1 ($X_A{}^1$) to the concentration of A in phase 2 ($X_A{}^2$). (After Kretz, 1961).

(*e*) The distribution of an element is dependent upon the ratios of other elements in the phases, especially major constituents. Inter-element effects among minor constituents will not be great, as minor elements do not have the effect on the general energetic environment in the crystal that major elements have.

(*f*) An examination of Fig. 2 is of interest. It is seen that chemical potential decreases exponentially with decreasing concentration; hence changes in concentration at the dilute level are accompanied by relatively large changes in chemical potential, μ. Since μ is the partial Gibbs Free Energy of a component, we should expect that small concentrations of a component will be quite sensitive to their environment, and we should expect minerals to strive towards an equilibrium

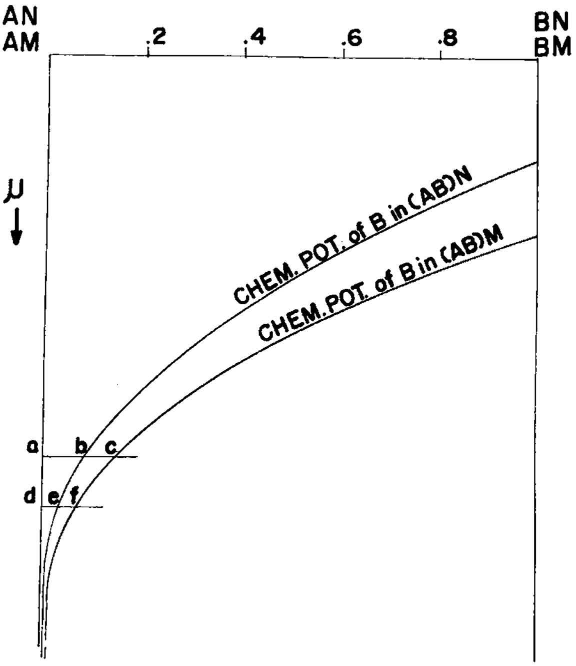

FIG. 2. Diagram showing the chemical potential-atomic ratio relationship in two coexisting hypothetical minerals (AB)M and (AB)N.

distribution of elements, even if present at very low levels. At some very low level, presumably, material transfer of components will become kinetically inhibited, and equilibrium will no longer be achieved.

The curves in Fig. 2 are drawn to represent the chemical potential of element B in two co-existing minerals of type $(AB)M$ and $(AB)N$. The relationship between chemical potential and atomic ratio (or concentration) is given by the equation

$$\mu_B = \mu_B^0 + RT\ln X_B . f_B, \tag{1}$$

where $\mu^0{}_B$ is the chemical potential of B in the pure end-member BM or BN, X_B is the atomic ratio of B, and f_B is the activity coefficient of B in such a mixture; Fig. 2 gives a graphical presentation of two of these equations. If the two minerals are in equilibrium, their chemical potentials with respect to B are equal, and the atomic ratio of B in the two minerals should exist in some ratio determined by equations of type (1). Two examples are shown. The ratio $B/(A+B)$ in mineral $(AB)N$ to the same ratio in mineral $(AB)M$ should be as ab/ac, or as de/df. Conversely, if A and B form ideal mixtures in these two minerals, it should be possible, knowing the *ab/ac* ratio (the slope of the distribution curve), to calculate the difference in Gibbs Free Energy between the two end members *BN* and *BM*, since

$$\mu_B{}^{BN} + RT\ln X_B{}^{(AB)N}.f_B{}^{(AB)N} = \mu_B{}^{(AB)N} = \mu_B{}^{(AB)M} = \mu_B{}^{BM} + RT\ln X_B{}^{(AB)M}.f_B{}^{(AB)M} \tag{2}$$

whence

$$\frac{X_B^{(AB)N}}{X_B^{(AB)M}} = \exp\frac{\mu_B^{BN} - \mu_B^{BM}}{RT} = \frac{ab}{ac}. \tag{3}$$

In general, however, this is not possible since the values of $f_B{}^{(AB)N}$ and $f_B{}^{(AB)M}$ will deviate unpredictably from unity for most elements.

Mineral structures

It is certain that fractionation of minor elements between amphiboles and biotites will be greatly influenced by the nature of the structure of these two minerals. Let us consider the fundamental differences in the structures, and what their effects will be on element selection.

The amphibole is a double chain of silica tetrahedra of infinite length, with some tetrahedra sharing three oxygens, and the remainder sharing only two. The biotite anion group similarly consists of silica tetrahedra, but the network extends infinitely in two directions. The net effect of this difference is that six-elevenths of the oxygens in the amphibole are "active" oxygens, whereas only four-elevenths of the oxygens in the biotite are "active", *i.e.*, form Si-O-cation bonds. In consequence, the active oxygens in biotite will have more double-bond character than in amphiboles, and hence the *M*-O (metal-oxygen) bond in biotites will be of different strength than in amphiboles.

The structure of amphibole was first elucidated by Warren (1930) who established the structural formula as

$(OH,F)_2\, X_{2-3}\, Y_5 Z_8 O_{22}$, where
X – Ca, Na, K
Y – Fe‴, Fe″, Al‴, Mg, Mn and Ti.
Z – Si, Al

The *X* cations are monovalent or divalent ions, whose radius is greater than .90Å.[1] The *Y* cations are ions of intermediate radius, usually divalent, octahedrally coordinated to neighbouring oxygens. The octahedral positions in amphiboles can quite easily accommodate ions up to the size of Mn(0.80 Å); Warren (*ibid.*) quotes an analysis bearing almost 17 per cent MnO, though this must be unusual. The *Z* cations are tetrahedrally coordinated ions, principally Si and Al.

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[1] The ionic radii quoted in this and subsequent sections are those of Ahrens (1952) for six-fold coordination.

Fig. 3A is a section of the amphibole structure in the *a-b* plane, looking down the Z-O chains, and shows the placement of the cations in the structure, the directions of the M-O bonds, and the placement of the hydroxyl groups. It can be seen that the environment of the M sites is not the same for all atoms. The M_1 and M_3 sites (Whittaker's notation) are quite similar, but the M_2 site has somewhat different surroundings, being partly linked to neighbouring Z-O chains. The M_4 site is yet more different, having very long bonds to the O_6 atoms of neighbouring chains, as well as being shared by two pairs of Z-O chains. The large size permits this site to hold ions in eight-fold coordination, using Ca and Na. According to Whittaker (1960), when the M_4 site takes a large ion of this size, there is a tendency for the M_2 site to accept an ion smaller than the mean size of occupants in M_1 and M_3 sites.

The first complete analysis of the mica structure was made by Jackson & West (1930, 1933) for muscovite. The general formula given for the group is

$$(OH,F)_2\, X_1\, Y'''_2\, Z_4\, O_{10}$$

or

$$(OH,F)_2\, X_1\, Y_3''\, Z_4\, O_{10}$$

The X cations are in twelve-fold coordination and are largely K, with lesser Na and Ca. Y cations are in six-fold coordination and are sandwiched between the two layers of tetrahedral SiO_4 groups. The Y ions, linked to oxygen and to hydroxyl groups, are most commonly Fe, Mg, Mn, Ti, and Al. As in amphiboles, the Z cations are in tetrahedral coordination, and consist of Si and Al. The ratio of Si to Al in the Z group is usually about three to one, or slightly greater (Foster, 1960).

Figure 3B is a diagram of the mica structure in the plane *a-c*. The two layers of ZO_4 tetrahedra sandwich the Y sites, and it can be seen that all the Y sites are structurally similar. Thus there is less latitude in the Y sites in biotites for ions larger or smaller than the ions occupying the bulk of these sites, *e.g.*, Mg and Fe''.

A major structural difference between the two mineral groups is in the fact that the micas provide a place for ions up to the size of K, Rb, and Cs (1.69 Å). In micas a layer of such large ions is a regular feature of the structure. No such provision exists in the amphiboles, the largest ion in the regular structure being in the M_4 site whose upper limit appears to be of the order of 1.00 Å. Whittaker (*op. cit.*) and others, however, suggest an A position, so-called, in the cavity of the amphibole structure, which accommodates the excess over two formula units in the X category, and can accommodate up to one formula unit.

Certain general similarities in the structures are also to be noted, *viz.*, —the similarity of the anion network previously mentioned;

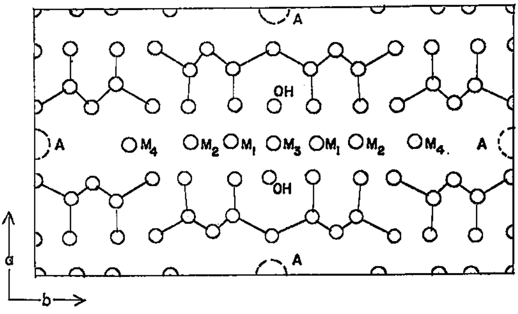

Fig. 3a. Structure of amphiboles, projected on (001).

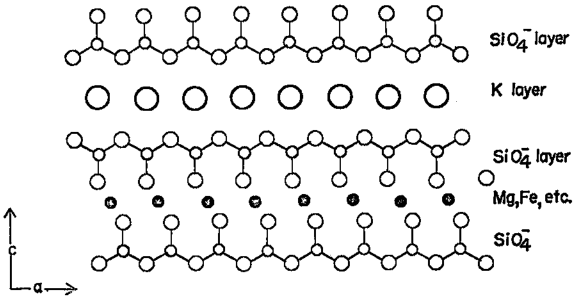

Fig. 3b. Structure of micas, projected on (010).

Fig. 3. Structure of (a) amphiboles and (b) micas.

- —the greatest variety of cations are in octahedrally, coordinated positions, in six-fold coordination;
- —there is provision for eight- and twelve-fold coordination of cations;
- —hydroxyl groups are present in analogous positions in both structures.

Minor element incorporation

In considering the extent of solution of a "solute" element in two co-existing "solvent" minerals, it is insufficient to consider the weight of the element dissolved in each phase. It is more meaningful to calculate the proportion of atomic sites filled by the minor element, out of the number of sites available to that element, in each phase. This is the atomic ratio. To determine the sites in these minerals that are available to the various elements, we have discussed the crystal chemistry and structures of hornblende and biotite, together with the elements usually associated with the various atomic positions.

On the basis of the ionic character of the major element occupants in the lattice sites of these two minerals, we might reasonably expect the following minor element substitutions to occur:

Group	Coordination	Radius	Ions
Z	4	0.35–0.64 Å	B^3, Ti^4, Cr^3, Ga^3, Be^2.
Y	6	0.65–0.90	Ti^4, Cr^3, Ni^2, Co^2 Mo^4, Cu^2, V^3, Zr^4 Mn^2, Sc^3, Y^3, Sn^4.
X	8–12	>0.90	Sr^2, Ba^2, (Y^3, Sn^2).

With this scheme in mind, atomic ratio calculations were carried out for major and minor elements. Atomic ratios of Fe, Mg, Mn, and Ti for the octahedral (*Y*) positions in the minerals were calculated first. Then the atomic ratios for all minor elements in hornblende were calculated, on the basis of their filling octahedral positions in that mineral, and the same data were derived for the biotite specimens. In addition, B, Cr, and Ti have been calculated as if occupying the tetrahedral (*Z*) position in both minerals, and Ba, Sr, and Y have similarly been calculated as if occupying the large sites occupied in the main by Ca, Na, and K in these species.

With these data it will be possible to observe the extent of solution (the atomic ratio) in hornblende versus that in biotite; if the distribution theory is valid, a linear plot of distribution points should result, within the limits imposed by analytical error and disequilibrium effects.

In the same way, it will be possible to assess which structural position is accommodating those elements whose properties suggest that they may occupy more than one position in these minerals. For instance, it has been suggested (as discussed in Rankama & Sahama, 1949, p. 622) that Cr^3 may occupy tetrahedral sites in silicate minerals. If this ion does so, then presumably it will show a better, more linear distribution when the atomic ratios are calculated and plotted on the supposition that the ion is in the tetrahedral *Z* site than it will if considered to be in the *Y* site. This calculation will be applied to B^3, Ga^3, Ti^4, Cr^3, which elements can conceivably occupy the *Y* and *Z* positions in these minerals. In the same way we can apply this test to Ba^2, Sr^2, Y^3, and Sn^2, which ions can conceivably occupy the *Y* sites as well as the large Ca-Na-K sites to a limited degree. Data for Ga and Sn are too sketchy, however, to permit a valid comparison to be made. All other ions are treated only as if occupying octahedrally coordinated *Y* sites, since it seems unlikely, on general crystal chemical considerations, that they will occupy other structural sites to more than a very limited degree.

The slopes of the distribution curves will also permit a comparison of the behaviour of minor elements with major components such as Mg, Fe, Ca and K.

The atomic ratios of minor constituents were calculated as follows: for the tetrahedral position in both minerals the atomic ratio of element E was calculated as

$$\frac{\text{gram atoms of } E}{\Sigma \text{ gram atoms of Si} + \text{Al}}$$

For the octahedral position, the calculation was

$$\frac{\text{gram atoms of } E}{\Sigma \text{ gram atoms of Fe} + \text{Mg} + \text{Mn} + \text{Ti}}$$

For the large 8 and 12 fold coordinated structural positions, the atomic ratio was calculated as

$$\frac{\text{gram atoms of } E}{\Sigma \text{ gram atoms of Ca} + \text{Na} + \text{K}}$$

More strictly, of course, the denominators of the above fractions should include the sum of the atomic ratios of all the possible minor elements associated with that structural position. Besides making the calculation rather unwieldy, this changes the atomic ratio only negligibly —in most cases less than the analytical error involved. The objection may be raised that the atomic ratio calculation for the Ca–Na–K positions in these minerals implies that these positions are chemically equivalent. Although this may be not quite true, as is discussed in the following section, there does not seem to be a better way to discuss the distribution of minor components such as Ba and Sr.

Major element distributions

Magnesium distributions are shown in Fig. 4, in which the atomic ratio of Mg in hornblende (Mg/Mg + Fe + Ti + Mn) is plotted against the atomic ratio of Mg in biotite (Mg/Mg + Fe + Ti + Mn). Ca and Al (six-coordinated) were not included in this calculation because positions occupied by these ions are not, or may not be, equivalent (Kretz, 1959). Within the limits of analytical error, the points lie about a line that passes through the origin and has a slope slightly less than one; hence, the distribution coefficient is, in the notation of Kretz and others, $K_{\text{Mg}}^{\text{Hb-Bio}} \simeq .95$. This curve, and others, are established empirically.

The distribution of *iron* is shown in Fig. 5, in which the atomic ratio (Fe/Mg + Fe + Ti + Mn) in hornblende is plotted against the same value in biotite. Here again the ratios fall close to a straight line passing through the origin, within the limits of error. The slope is unity. This relationship is, of course, to be expected, since Fe and Mg form the larger part of the atoms in the group (Fe + Mg + Ti + Mn). As Kretz points out, a closer estimation of iron distribution would demand know-

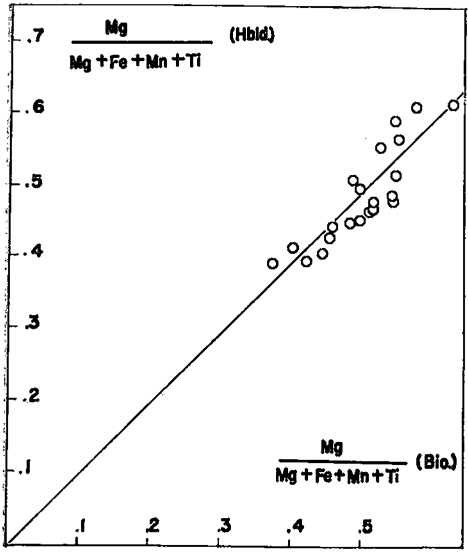

FIG. 4. Distribution of magnesium between hornblende and biotite.

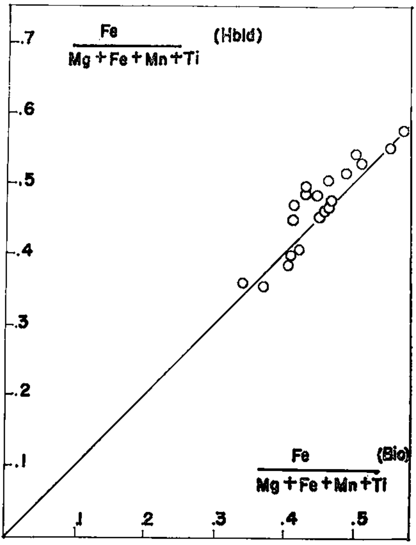

FIG. 5. Distribution of iron between hornblende and biotite.

ledge of the Fe^2/Fe^3 ratio, and a wider range of Fe/Mg ratios. The distributions of Fe and Mg indicate that equilibrium is approached in the rocks under study. The regular distribution also indicates that the conditions of formation of all minerals have been quite similar, since, for any distribution point on the graph, it is unlikely that a disequilibrium effect would be corrected by a countering P-T-X effect.

Aluminum attains higher values in the biotites than in the hornblendes, and occupies a higher proportion of tetrahedral sites. This is the usual situation in these minerals, and is in line with theoretical views of element distribution (e.g. Ramberg 1952b). The Al content in tetrahedral positions in biotites is very consistent, lying between 1.25 and 1.00 formula units. The octahedrally coordinated aluminum fills a somewhat higher proportion of octahedral sites in hornblendes than in biotites; this is probably a consequence of the establishment of electrical neutrality in the two minerals, but an answer to this cannot be attempted without use of a more accurate silica analysis method and the measurement of the Fe^2/Fe^3 ratio.

Calcium distribution in these two minerals is, as expected, strongly disproportionate, the hornblendes having between 7 and 12 per cent CaO and the biotites less than 1 per cent CaO. This is an outcome of the structural demands of the two minerals: the M_4 sites of the amphiboles readily accommodate the doubly valent Ca ion in eight-fold coordination. The biotite, on the other hand, cannot accommodate Ca ions except in the twelve-coordinated K sites, which are much better suited to the large singly charged alkali cations.

Potassium is, conversely, present at very low concentrations in the amphiboles, and at about 7 to 9 per cent in the biotites. The K in the amphiboles is largely accommodated in the *A* sites.

Sodium is somewhat favored in the hornblendes; recalculated formulae suggest that most Na is in the M_4 site in the hornblendes, and the remainder is in the *A* sites. Its valence and size suggest this is probable. In biotites the mineral formulae suggest that it is present in the twelve-coordinated layer, occupying up to 25 per cent of these sites. Apparently this site is less favoured than the M_4 sites in the coexisting hornblendes.

In this section no more has been attempted than to give a general discussion of the major element distribution as it pertains to the aims of this paper. The major element distributions demonstrate that equilibrium has been attained in these minerals, that these distributions are in line with our expectations from knowledge of the mineral structures, and that in view of their general similarity of composition, all were formed under similar environmental conditions.

Minor element distributions

For the purposes of this paper we shall consider minor elements to be those that do not influence physical parameters and properties to an observable degree. Although this probably applies to titanium and manganese in the minerals in question, they are tabulated with the major elements since they were determined by the same analytical method. In discussion we shall consider them as minor elements. The remainder of these elements are discussed in the order in which they appear in Tables 3 and 4. The atomic ratios in the coexisting minerals are plotted in the accompanying figures. Because these atomic ratios are very small, for convenience in discussion they have all been multiplied by 10^6, yielding a number meaning the number of atoms of element E per million sites available to element E—referred to herein as atoms per million.

Manganese distribution is shown in Fig. 6, in which the ratio of $Mn/Mg + Fe + Mn + Ti$ in hornblendes is plotted against the same quantity for biotites. As the figure shows, Mn is favored in the hornblende structure, the distribution coefficient having a value about 1.7. Kretz's samples whose Mn contents lie in the same range of values, show a distribution coefficient of 3.0, indicating that in those rocks Mn is favored in hornblende even more strongly. This will be discussed later.

The distribution of Mn is considered to be, at least partially, a con-

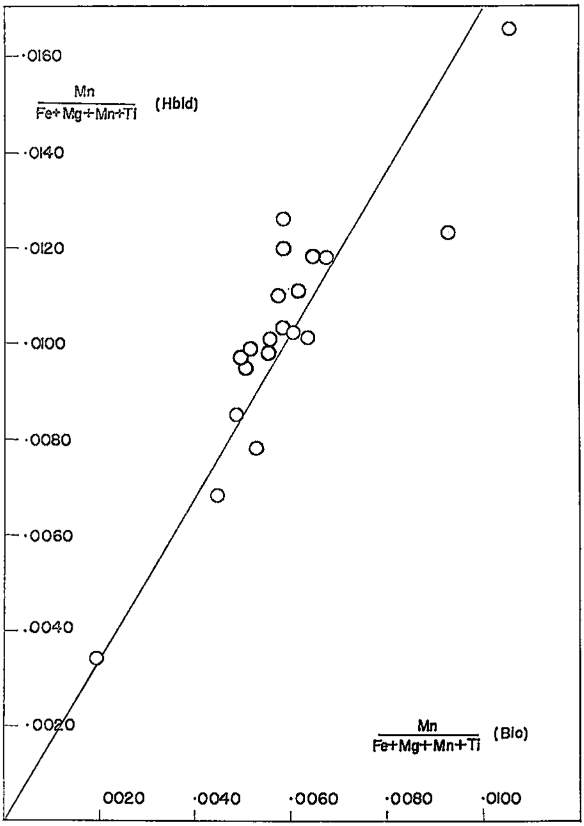

FIG. 6. Distribution of manganese between hornblende and biotite.

sequence of its size (0.80 Å), which lies near the upper limit of the six-fold coordination range. By virtue of its size and charge, it is readily accommodated in the M_4 sites in the amphibole structure. It is evident that while biotite can possibly take Mn into its six-fold sites, this substitution will be more limited because sites equivalent to the M_4 do not exist, and the size of the ion is close to the limit that a six-fold site will tolerate.

Titanium distribution points are plotted in Fig. 7, in which atomic ratios of Ti are plotted for hornblende versus biotite. A tentative distribution curve is placed through the points, indicating a distribution coefficient of about 0.75; although the points are somewhat more scattered than in the Mn diagram, the trend of the points is evident. In Kretz's (1959, Fig. 15) diagram, which covers a somewhat higher range of atomic ratio values, the Ti distributions exhibit a comparable deviation from

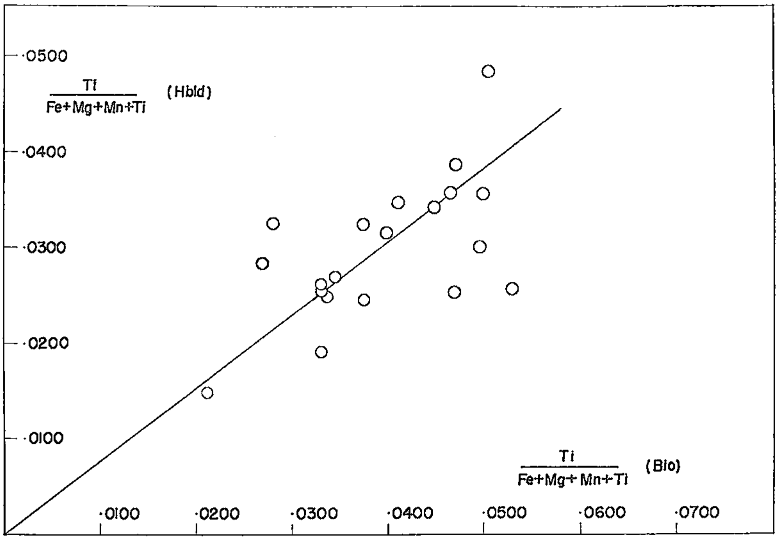

FIG. 7. Distribution of titanium between hornblende and biotite.

linearity; similarly, Nickel's (1954) analyses, covering lower range, show a like scatter of points. The reasons for these deviations are unclear, and they are unrelated to other elements or atomic ratios in any evident way. Calculation of atomic ratios made on the assumption of Ti occupying tetrahedral sites yields a group of distribution points that shows an approximately equal degree of scatter, so that there is no support for this possibility. The existence of some Ti as microlites of ilmenite or rutile within the ferromagnesian minerals seems the most likely reason for these aberrant points.

Boron in both the hornblendes and biotites is present at between 30 and 60 p.p.m. The atomic ratios, calculated on the basis of B in octahedral positions, are shown graphically in Fig. 8. It can be seen that 12 of the distribution points fall into a linear group whose distribution coefficient is about 1.5. The remainder of the points form a separate group. It would be desirable to find some compositional difference to account for this; no chemical, mineralogical, or petrographic pattern can be found, however, to explain this divergence and it is concluded that it is an unreal division.

The ionic properties of B suggest that it may substitute for Si in ZO_4 tetrahedra ($r = 0.23$ Å) and Rankama (1950) concludes that most B in the earth's crust is located in this manner in silicate minerals "although the substitution must be a limited one in view of the small size and

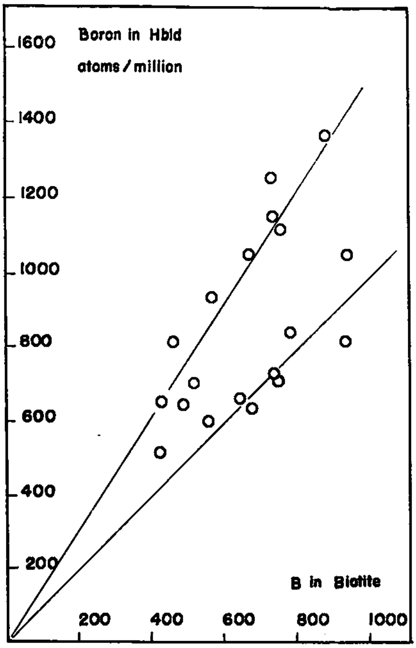

FIG. 8. Distribution of boron between hornblende and biotite, assuming boron in octahedral co-ordination.

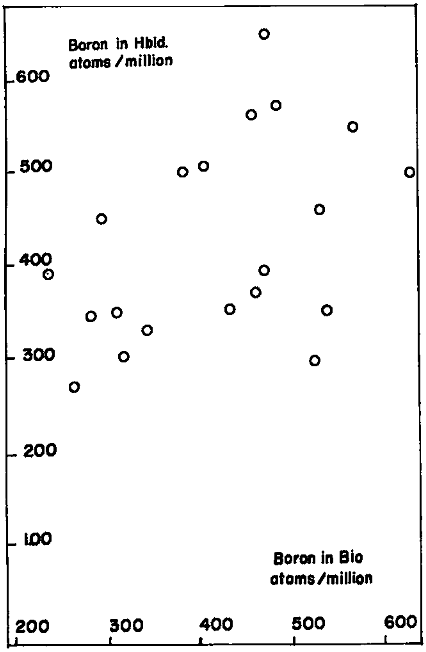

FIG. 9. Distribution of boron between hornblende and biotite, assuming boron in tetrahedral co-ordination.

trivalent nature of the B^3 ion." Calculation of boron to tetrahedral positions in the minerals studied yields a scattered diagram with no linearity of distribution apparent, suggesting that boron is equilibrated as if occupying octahedrally coordinated positions in these minerals (Fig. 9). From Fig. 8 it appears that in these rocks boron is slightly concentrated in the hornblende component.

Gallium data is incomplete, since in most specimens this element is present near its limit of sensitivity. An examination of Tables 3 and 4 would suggest that this element is approximately equally distributed between these two minerals, as would be in keeping with its chemistry which is similar to that of Al. No attempt has been made to present Ga distribution graphically, since only three distribution points are available.

Vanadium values are higher than those of most other elements, extending over a range from 200 to 700 p.p.m. in both minerals. The distribution diagram for vanadium (calculated for octahedral positions) is presented in Fig. 10, showing a distribution coefficient $K_V^{Hb\text{-}Bio} \simeq 1.1$. The spread of the distribution points among the lower concentration values is not related to any other element distribution in the two minerals; the deviation was checked against Fe, Mg, Ca, and Al distributions with no relationship becoming apparent.

The vanadium in ferromagnesian minerals is present as V^3, according to Goldschmidt; as such it has an effective radius of 0.74 Å, and should be admitted to positions of six-fold coordination with about equal ease in either mineral.

Kretz found the vanadium to have about the same distribution coefficient in his rocks as in the author's. In Nickel's minerals, vanadium has a distribution coefficient of about 0.6, biotite containing the greater proportion of the element. It is noteworthy that in Nickel's minerals, total iron has a distribution coefficient of about 0.66, whereas in Kretz's hornblendes and biotites, and in those in this study, total Fe is about equally distributed between the minerals. This would seem to demonstrate quite clearly that the behaviour of V in ferromagnesian minerals is analogous to that of Fe.

Beryllium is present in all mineral samples at a very low level, the highest measured value being 3.6 p.p.m., and with the majority of values lying below the 2.5 p.p.m. limit of sensitivity. Beryllium data is not

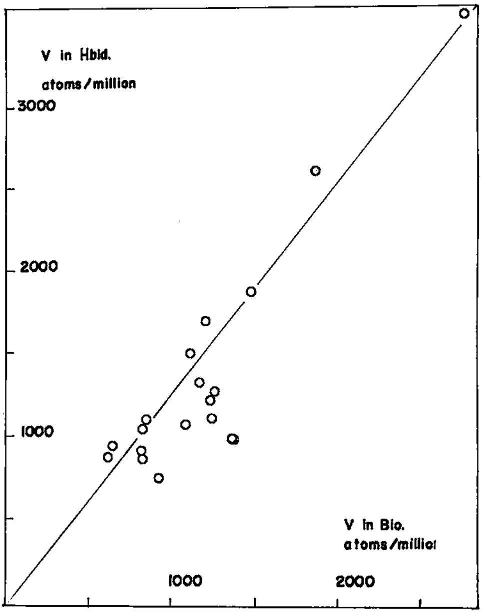

FIG. 10. Distribution of vanadium between hornblende and biotite.

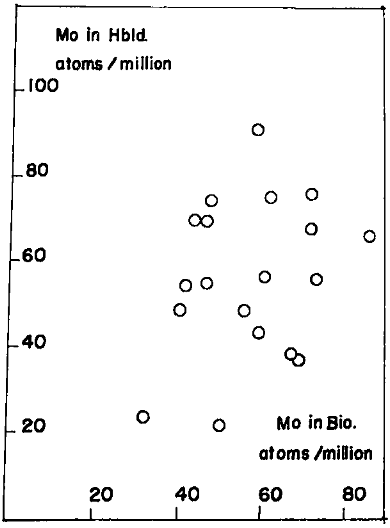

FIG. 11. Distribution of molybdenum between hornblende and biotite.

plotted; for the values see Tables 3 and 4. According to Goldschmidt (1944) and Rankama (1944, p. 444), it is believed to replace Si in ZO_4 tetrahedra.

Molybdenum presents quite a scattered array of distribution points (Fig. 11), the concentrations in both minerals centering on about 30 p.p.m. In view of the high ionization potential and consequent highly sulphophile character of Mo, it is commonly reluctant to enter silicate structures; an equilibrium should be established nonetheless, unless Mo is present as a separate sulphide or oxide phase. The distribution diagram only suggests that Mo is present in both minerals to an approximately equal degree.

Tin distribution data, as shown in Tables 3 and 4, are quite incomplete; values were obtained for most of the hornblendes, but for only three of the biotites. The values for these pairs of minerals are not plotted. These results would indicate that concentrations are generally higher in the hornblendes, those in biotites being in most cases below the limit of sensitivity. Sn does enter silicate structures (Ottemann, 1941), although only in rocks of pneumatolitic origin does it attain high values. Ottemann found 300 p.p.m. Sn in some biotites of pneumatolitic rocks.

Copper distribution, as a function of other octahedrally coordinated cations, is shown in Fig. 12. In view of its crustal abundance copper reaches quite high concentrations in the hornblendes and biotites—295 p.p.m. in one biotite sample. This element appears to be concentrated in biotites, although the relationship is less clear at low concentrations. As shown in Fig. 12, almost all the distribution points fall, within limits

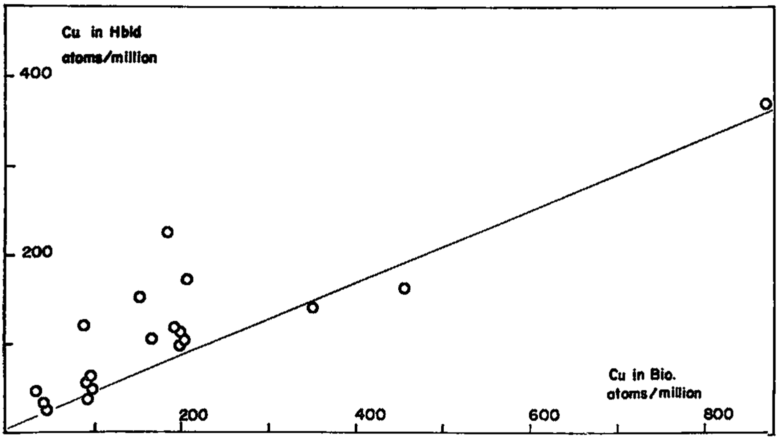

FIG. 12. Distribution of copper between hornblende and biotite.

of error, along a line whose slope is about 0.35. The four points representing rocks 6023, 6051, 6056, and 6061 show no consistent differences in mineralogy, chemistry or petrology from the majority of rocks to explain their erratic position; and one must conclude that Cu is not equilibrated in these samples or that the samples have suffered contamination.

Yttrium distribution is presented in Fig. 13. Unfortunately the concentrations of Y in the minerals studied did not vary greatly, and the distribution points are rather clustered, so that the distribution over a wider range of values cannot be observed. A tendency toward equilibrium is evident, with the hornblende phase being somewhat favoured.

If Y occupies octahedral positions we should expect that it will be favoured in the hornblende structure, since its large size (0.92 Å) would indicate that it would be incorporated with restriction in the biotite structure. Calculation of Y distribution on the basis of its occupying the *X* position in both minerals yields a more scattered distribution of points than that shown in Fig. 13, as does a computation based on the possibility that this element is in *Y* positions in hornblendes and *X* positions in biotites.

It is perhaps pertinent to mention that distribution points 6056 and 6047, apparently out of equilibrium with respect to yttrium, are also rocks in which Fe distribution is out of equilibrium, to a smaller degree, in the same direction (see Tables 1 and 2), which indicates the possibility of Fe exerting a control of yttrium distribution.

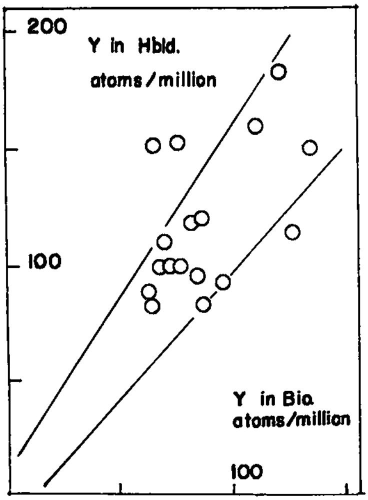

FIG. 13. Distribution of yttrium between hornblende and biotite.

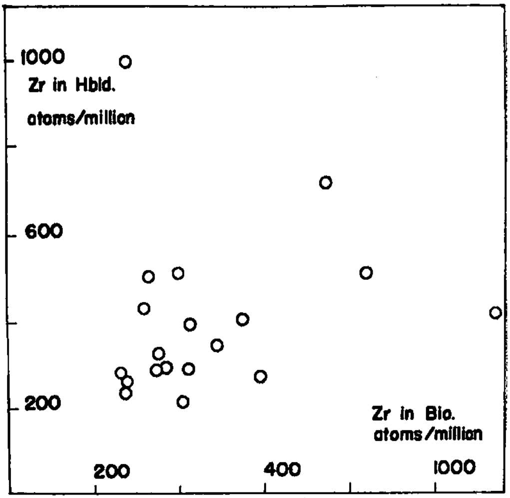

FIG. 14. Distribution of zirconium between hornblende and biotite.

Zirconium, according to the distribution diagram shown in Fig. 14, shows a strong scattering of points. Kretz (1959) found a similar degree of scattering, though Nickel (1954) found a distribution in his rocks that, while irregular, was somewhat more closely grouped than the writer's. DeVore (1955) also observed considerable variation in the ratio of Zr in hornblendes to that in biotites. Degenhardt (1957), who undertook a detailed study of Zr distributions in rocks and minerals, points out that values for Zr in ferromagnesian minerals are often questionable because a large proportion of the amount present is frequently small inclusions of zircon and woehlerite. Zirconium, with its very high lattice energy (E-value) tends strongly to form a separate silicate phase. Studies of element distribution would seem to lend credence to this view. Under these circumstances it will be difficult to learn anything of the extent of true solution of Zr in these minerals, or of its distribution coefficient.

Nickel distribution, as shown in Fig. 15, is quite regular throughout its range of concentration; there can be little doubt that an equilibrium has been established for this element, with the distribution coefficient $K_{\mathrm{Ni}}^{\mathrm{Hb\text{-}Bio}} \simeq 0.70$.

On the basis of charge and radius Ni may participate in the structure of most femic minerals. Despite its well known coherence in basic and ultrabasic rocks with Mg (Rankama & Sahama, 1950, p. 683), its distribution in these two minerals is quite different from that of Mg. Nickel (1954) in his study of these minerals found the distribution coefficient to be somewhat displaced toward biotite, relative to the samples used in this study. As mentioned earlier, the Fe-Mg equilibrium is significantly different in Nickel's rocks.

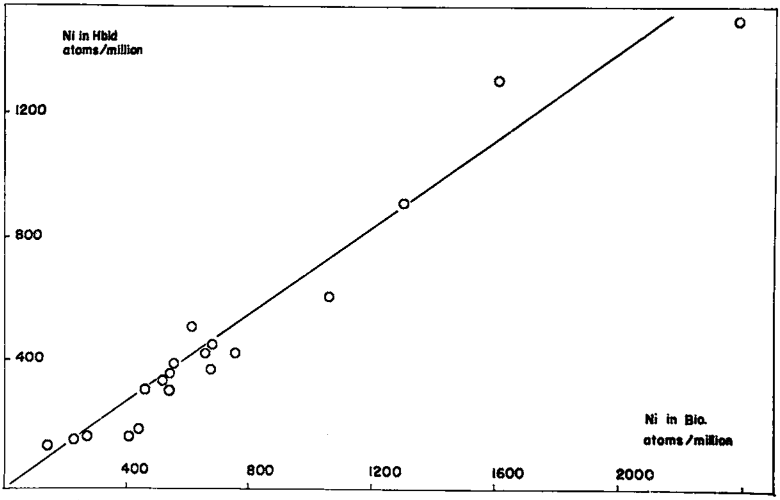

FIG. 15. Distribution of nickel between hornblende and biotite.

Cobalt distribution is illustrated in Fig. 16. This element is present over a shorter range of concentration than nickel, with which it is often closely associated in nature. Its size, like that of Ni^2, is close to those of Mg^2 and Fe^2; its distribution coefficient is of the same order as that of Ni-$K_{Co}{}^{Hb\text{-}Bio} \simeq 0.75$; the equilibration is not as good as that for Ni, but the direction of the equilibrium distribution curve is apparent in Fig. 16. Carr & Turekian (1961) noted that while the total amount of Co in a rock or mineral is often closely correlative with the total of concentrations (or atomic ratios) of Mg and Fe, its behaviour in coexisting minerals seems akin to neither one. This appears to be true here: neither the slope of the distribution curve nor the lateral spread of distribution points can be related to Mg or Fe distributions.

Strontium has a well-known geochemical coherence and similarity of behaviour with Ca (Turekian & Kulp, 1956). Since Ca is strongly limited to one of the minerals in these pairs, it was expected that Sr would reflect this behaviour, or would at least be regular. The distribution of Sr, calculated as a function of Ca + Na + K, in these two minerals appears to be somewhat random (Fig. 17); apparently an equilibrium was not established. A tentative distribution curve was

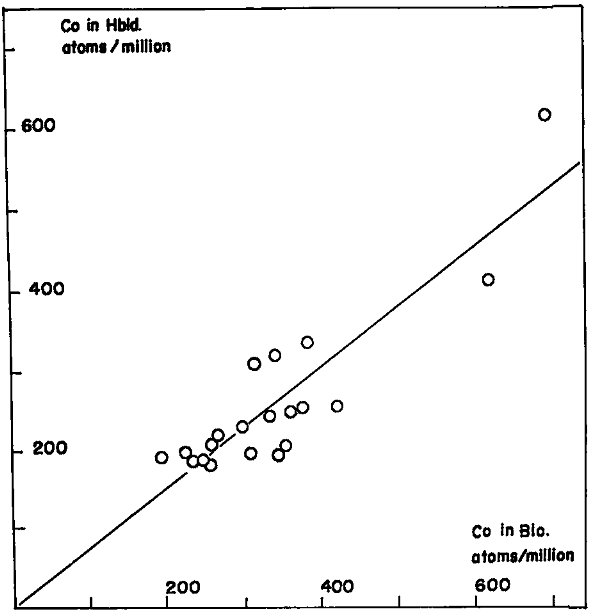

FIG. 16. Distribution of cobalt between hornblende and biotite.

drawn to represent mean atomic ratio in biotite vs. mean atomic ratio in hornblende. The slope is 0.74, suggesting that the Sr is indeed somewhat favoured in biotite. Despite considerable effort to find one, no relationship was observed between the spread of Sr distribution points in Fig. 17 and any other elements or atomic ratio values in the two minerals. Despite the similarity in ionic radius, charge, ionization potential, and electronegativity, these two minerals are apparently partitioning Ca and Sr in quite different proportions. DeVore (1955), found a similar erratic distribution of Sr between nine coexistent pairs of biotite and hornblende.

A calculation of Sr distribution based on the premise that it is perchance occupying octahedrally coordinated positions in the minerals yields a completely erratic distribution of points. (Fig. 18.)

Scandium distribution is shown in Fig. 19. It can be seen from this diagram that Sc is considerably concentrated in hornblende over biotite—the mean atomic ratio of Sc in hornblende is 390 atoms per million, that in biotite is 136 atoms per million. Kretz, who reported Sc values for some of his mineral pairs, found a similar ratio, although his points are much more scattered than these. With the exception of two points in Fig. 19, all points lie within a distance from the line equal to the margin of error; Oftedahl (1943) quoted several mineral analyses of coexistent minerals which demonstrated a similar trend with respect to Sc. Nickel (1954) found a distribution similar to that found in this paper.

Goldschmidt (1931) found that pyroxenes generally contain more Sc

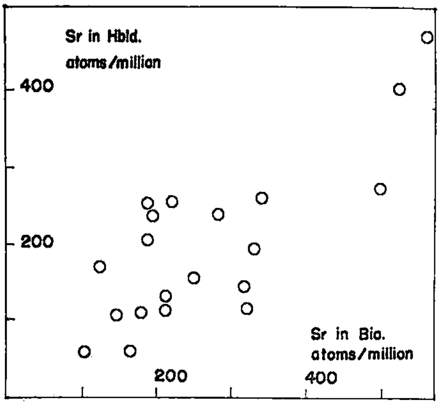

FIG. 17. Distribution of strontium between hornblende and biotite, assuming strontium in [Ca Na K] position.

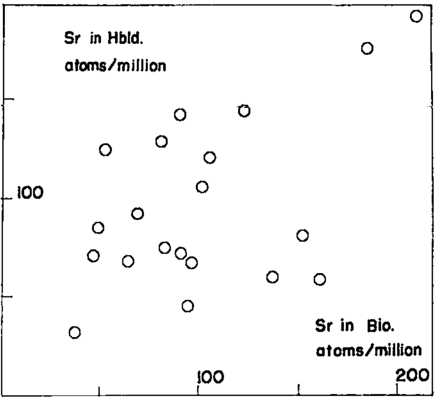

FIG. 18. Distribution of strontium between hornblende and biotite, assuming strontium in octahedrally coordinated positions.

than amphiboles, which in turn contain more than biotite, although biotites of themselves of pegmatitic origin have been found containing up to 1000 p.p.m. Sc (Rankama & Sahama, 1950, p. 512).

Scandium, according to these writers, probably replaces Mg in the structure of these two minerals; its substitution is limited, however, by its trivalency. The Sc ion has a large radius (0.81 Å), which places it near the upper limit of the size range of ions capable of establishing six-fold coordination. This means that it may be easily accommodated in hornblende in M_4 sites, but it will be accepted in biotites with some restriction, much in the manner of manganese (see Fig. 6). Yttrium, on the other hand, a larger trivalent ion in the same periodic group as Sc, is distributed more equally between these two minerals (see Fig. 13), although it would seem able to enter M_4 sites without severe restriction. Hence a geometrical explanation for the distribution pattern of these two elements is less than satisfactory.

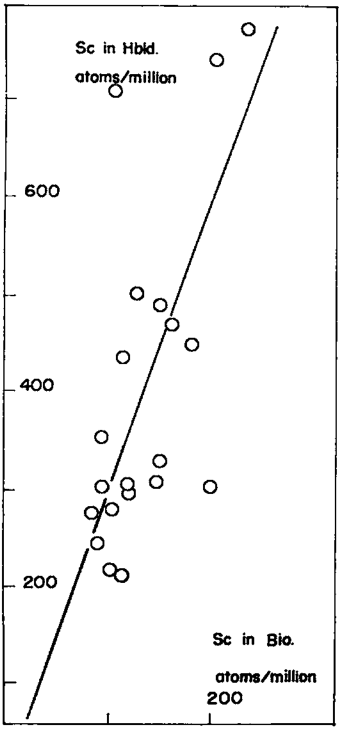

FIG. 19. Distribution of scandium between hornblende and biotite.

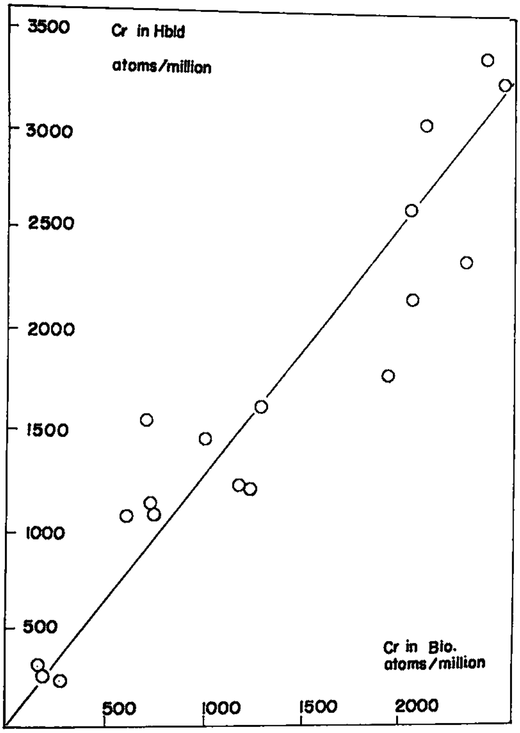

FIG. 20. Distribution of chromium between hornblende and biotite.

Chromium distribution is presented in Fig. 20. Although there is some point spread, the distribution curve that passes through these points has a slope of approximately 1.3.

The lateral spread of points shows some correlation with the ratio [tetrahedral Al in Hb/tetrahedral Al in Bio]. This may indicate (1) that Cr^3 is coherent with Al^3, or (2) that changes in Al distribution changes the relative polarizing power of the two mineral structures, thereby changing the equilibrium distribution of Cr. Plotting the distribution of Cr as a function of the tetrahedral position, which yields a more scattered distribution, suggests that the latter is more likely.

In Nickel's (1954) study, Cr is concentrated in biotite over hornblende by an average factor of four. It is recalled that Fe distribution in those minerals is displaced toward biotite also—$K_{Fe}{}^{Hb\text{-}Bio} \simeq 0.66$—whereas in the present rocks Fe is equally distributed, pointing up the relationship between these elements. A closer examination of Fe would be possible if Fe^2/Fe^3 ratios were available.

Barium (Fig. 21), is calculated as occupying the (Ca + Na + K) sites. It can be seen that Ba is strongly displaced toward biotite, as may be expected from the large size of the Ba ion (1.33 Å).

The mean potassium distribution is shown in the dashed line in Fig. 21. The distribution coefficient of Ba is practically identical with that of K, suggesting that Ba forms a practically ideal solution in K sites in these minerals. The distribution point representing sample 6032, nearest the lower margin of Fig. 21, has the lowest K content (atomic ratio) of the hornblendes, as well as the lowest Ba atomic ratio, emphasizing the relationship between K and Ba.

Summary. In the light of observable geometrical factors, major element relationships, and known patterns of geochemical behaviour, the minor element distributions may be briefly presented as follows:

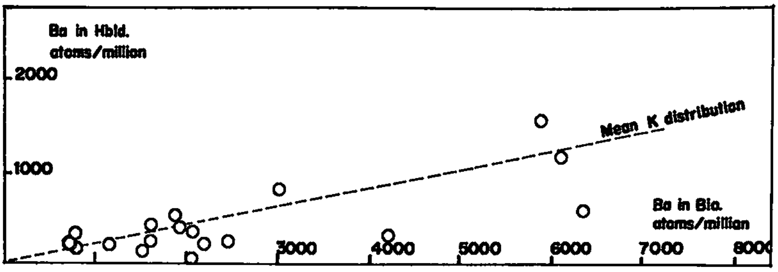

FIG. 21. Distribution of barium between hornblende and biotite, assuming barium in the [Ca Na K] position.

1. B—The minerals approach an equilibrium. The data suggest that B is in octahedrally coordinated positions.
2. Ga, B, Sn—Too little data is available; however the figures give some idea of the concentrations and distributions in these minerals.
3. Mo, Zr—Equilibrium is apparently not established, or else these elements are present as inclusions and microlites of zircon, and perhaps molybdenite.
4. Ti, Cu, Y, Sr—There appears to be a tendency toward equilibrium, although in each case there are a number of exceptions to the general trend of distribution points. Sr gives evidence of existing in the positions occupied by Ca, Na and K, as expected.
5. Mn, V, Ni, Co, Cr, Sc, Ba—These elements show a definite distribution coefficient, and hence give evidence of forming true solid solutions in octahedrally coordinated positions (with the exception of Ba, which apparently fills K sites).
6. Mn, Sc, Ba—For these elements, ionic size effects may account at least in part for the distributions found; a geometrical control on partitioning factors.

Discussion

Lower limits of equilibrium distribution

An examination of the distribution diagrams permits an appraisal of the lower limits to which we can say that the crystals are equilibrated with respect to each element. At some low concentration, presumably, the number of atoms of minor constituent become so few that equilibration becomes kinetically, if not thermodynamically, difficult. We may also expect a certain number of minor constituent ions to be associated with inhomogeneities such as dislocations and grain boundaries; at some low level of concentration these will comprise a significant proportion of the element in question. Which of these two conditions occurs, or which will become dominant first, as concentration is decreased, is difficult to say.

For gallium, tin and beryllium, data are insufficient. Boron is not well equilibrated, but its distribution becomes better above 800 atoms per million. Similarly, vanadium distribution becomes regular above 1200 a.p.m. Copper distribution appears irregular below 100 a.p.m. in hornblende and 200 a.p.m. in biotite. Yttrium, with exceptions, is fairly well equilibrated down to 80 a.p.m. in the minerals, although yttrium distribution in general is not as good as some others. Zirconium data on the writer's minerals as well as on Kretz's and Nickel's materials make it seem doubtful that this element ever achieves good equilibrium distribution in ferromagnesian minerals, apparently preferring to form a subphase of some type (dislocation, zircon, microlite, etc.). Nickel and cobalt are equilibrated down to their lowest concentrations in these minerals—about 200 a.p.m. Chromium, with two exceptions, is moderately well equilibrated to the same level. Scandium achieves regular distribution down to about 100 a.p.m. Strontium, as mentioned earlier, is not regularly fractionated throughout the range encountered in these minerals. Barium is in accord with an equilibrium distribution in those pairs in which it has lowest concentration, i.e., 200 and 750 a.p.m. in hornblendes and biotites respectively; judging from its behaviour, it would presumably reach equilibrium distribution at even lower levels.

The principal fact emerging from this cursory survey of the distribution plots is that some elements, notably Cu, Y, Ni, Co, Sc, Cr, and Ba have achieved quite regular distributions between these two minerals down to remarkably low levels, of the order of 200 a.p.m. This observation attests strongly to the power of chemical potentials,—that two solids, in juxtaposition at an elevated temperature over a long period of time, can fractionate a component present at a level of only one atom in every 5000.

Distributions and major elements

It was among the original purposes of this study to seek relationships between the properties of minor constituent ions and their distribution coefficients, between the properties of the structures and the distribution of elements, and between major elements and minor element distributions. These attempts have been discussed in an earlier section dealing with element distributions, and have on the whole been not very fruitful. Mn, Sc, and Ba appear to be subject to a geometrical control in their distribution, and V and Y appear to show a relationship to Fe distribution, as seen from the distribution points of some aberrant mineral pairs. Major element mineralogy should in principle affect minor element distribution, but it has been difficult to find evidence of this in point spreads in the distribution diagrams. An explanation for this may be that these influences are indeed present, but are obscured by contravening effects of changes in Fe, Mg, Al, Ca, and alkali concentrations in the sample rocks. From this point of view it would be enlightening to study minor element distributions between minerals of more simple chemistry, for example olivine and pyroxene, or orthoclase and plagioclase feldspars, where major element substitutions are not quite as complex.

Table 5 gives a compilation of the ionic properties of those elements

Table 5. Distribution Coefficients and Ionic Properties of Some of the Elements

Distribution coefficient (slope)	Element and valence	Radius (Å)	Ionization potential	Electro-negativity	Lattice energy (Ek)
2.85	Sc^{3}	.81	25.0	1.3	1190
1.70	Mn^{2}	.80	15.6	1.4	2330
1.30	Cr^{3}	.63	32.1	1.6	1220
1.25	B^{3}	.23	37.9	2.0	1535
1.15	Y^{3}	.92	20.5	1.3	1010
1.10	V^{3}	.74	26.5	1.4	1360
1.00	Fe^{2}	.74	16.2	1.7	543
.95	Mg^{2}	.67	15.0	1.2	540
.75	Co^{2}	.72	17.4	1.7	551
.70	Ni^{2}	.69	18.2	1.7	558
.35	Cu^{2}	.72	20.3	2.0	538

presumably in six-fold coordination in hornblendes and biotite, arranged in order of decreasing distribution slope. There appears no strong relationship between any ionic property, and distribution coefficients. The distribution coefficients are graphically compiled in Fig. 22 (1).

Nickel, in his earlier (1954) study of the distribution of iron and magnesium and various minor elements in hornblende, biotite and chlorite, found that iron was somewhat concentrated in biotite, with respect to hornblende, and magnesium was concentrated in hornblende over biotite. Similarly, Co, Ni, Cr, V and Ti, the iron-like elements in terms of electronegativity, were more abundant in biotites, and the minor constituents of lower electronegativity were more abundant in hornblendes. Nickel interpreted the distribution of Fe and Mg in terms of Ramberg's (1952) polymerization models, in which the more electronegative Fe^{2} ion would be accepted preferentially in the more electropositive biotite silicate-framework. These findings are presented graphically in Fig. 22 (2). It now appears, in light of Kretz's work and this paper, that the relationship is not nearly as simple as such a theory would suppose. (Cf. Figs. 22 (1) and 22 (3)).

While it is probably true that the fractionation of the minor constituents is a function of the relative abundance and distribution pattern of the major elements Fe and Mg, it would appear that the distribution patterns of Fe and Mg in Nickel's rocks were fortuitous, from the point of view of electronegativity. In Ramberg's hypothesis, the relative Al/Si ratios in tetrahedral positions in coexisting ferromagnesian minerals can also influence the distribution of such ions as Fe and Mg; formula calculations show that these are not significantly different among the three sets of rocks, so this cannot be appealed to.

Such observations lend support to the view that element selection by

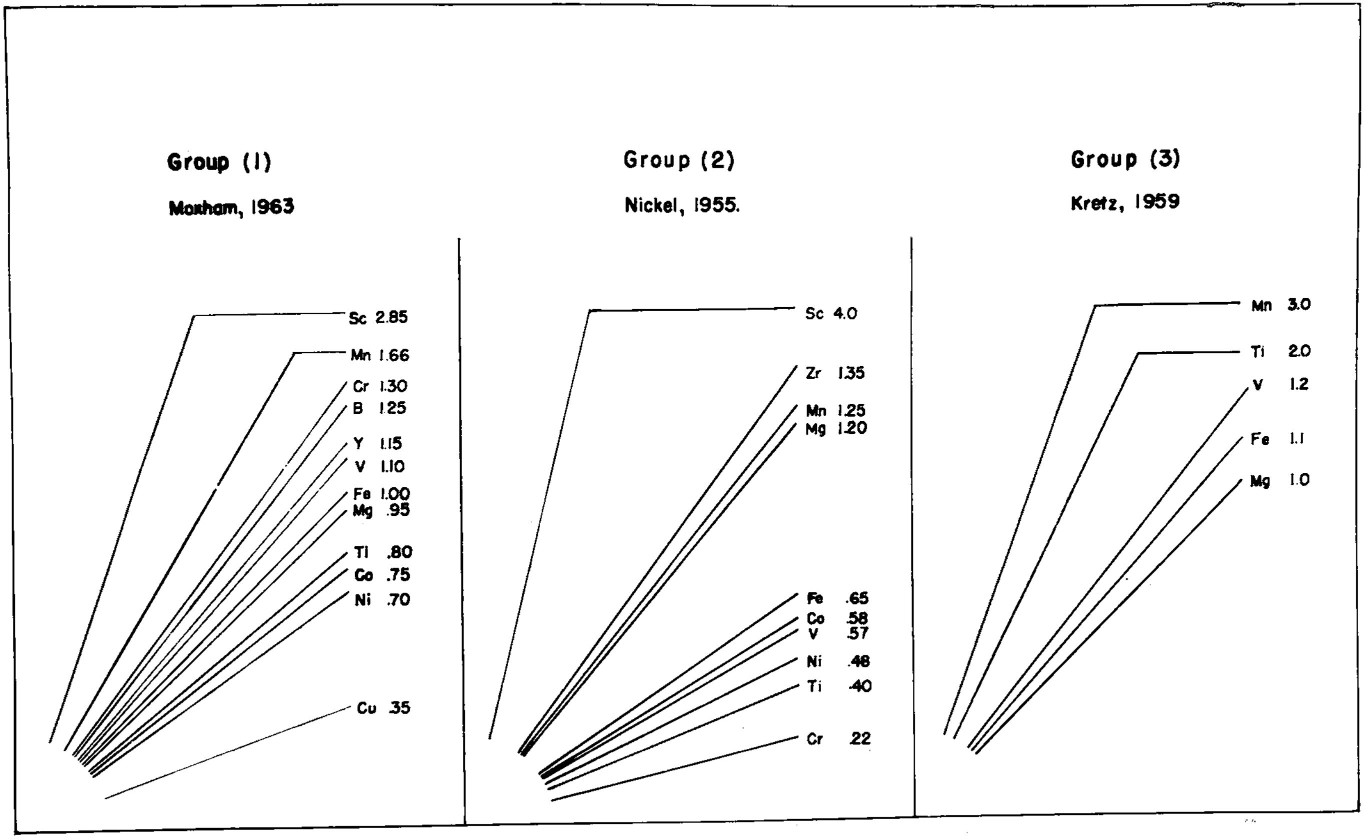

FIG. 22. Graphical presentation of some distributions, as found by Moxham (1), Nickel (2), and Kretz (3).

minerals is not a matter of the mineral seeking ions with certain properties; it is a matter of the relative 'solubilities' of an ion in two or more minerals. These will vary with conditions as expressed in equations shown by Kretz (1960), the basic requirement being that the chemical potential of the ion in each phase be equal. The chemical potentials, as expressed by the μ values, are a function of pressure and temperature. The activity coefficients (f), as discussed earlier, are a function of ionic interactions, and the relative abundances of other components in the phases (minerals) in question.

The activity coefficients are also a function of pressure and temperature. The interplay of these three variables (P, T, and the composition of the system) cause the chemical potentials, and hence the distribution coefficients, to assume values which, at the present time, are unpredictable except in situations of fairly simple mineralogy.

The various properties of the individual ions (ionization potential, valence, radius, etc.) are no doubt all contributive factors to the chemical potential, but the way in which they combine to yield a certain chemical potential and distribution coefficient is not readily evident, except in some cases in which one factor obviously dominates (e.g. Ba distribution in hornblende and biotite being a consequence of its large radius).

Metamorphic facies and distribution patterns

It is not always easy to determine the metamorphic facies of the common gneisses and schists because the assemblage of quartz, potash feldspar, soda plagioclase, mica and hornblende is stable through a wide range of the epidote—amphibolite facies (Ramberg's usage) of metamorphism; gross compositional differences make comparisons of mineralogy uncertain. It is suggested, however, that Nickel's rocks are of lower epidote-amphibolite facies, Moxham's are of upper epidote amphibolite facies, and Kretz's are well into the amphibolite facies of metamorphism. This is suggested on the basis of the following points:

1. In Nickel's rocks, garnet is apparently not stabilized, plagioclase is albitic, epidote is stable. Chlorite is, of course, common.

2. In the writer's rocks plagioclase, generally albitic, is more calcic in a few rocks, up to An 20–25. No chlorite is present and epidote is rare. In a few rocks pyroxene is present. Garnet, though not present in any of the samples, is common. Hornblendes are more aluminous than in Nickel's rocks.

3. In Kretz's rocks, pyroxenes are more common and sillimanite exists in some specimens. Plagioclase is apparently more calcic.

With these seeming differences in metamorphic grade in the three groups of rocks in mind, it may be possible to examine the possibility of an influence of metamorphic grade on distribution coefficients. A complication exists in that, as was discussed earlier, differences in bulk chemistry will also play a part in element distributions; such differences exist both within and among the three groups of rocks under discussion. Assessment of this latter factor is made more difficult by the fact that Nickel did not obtain complete analysis data for his minerals.

Table 6 presents a compilation of distribution slopes in the three groups of rocks, for elements for which data is available from all three groups. For iron, titanium, manganese and vanadium, there is a regular shift in the distribution coefficients through the three groups of rocks listed in order of decreasing grade of metamorphism; these elements exhibit a shift in distribution toward the hornblende member of the mineral pair. With magnesium the situation is less clear, but the opposite effect seems to hold, as would be expected if it behaves reciprocally with respect to iron. Chromium distribution seems to parallel that of the other iron-like elements; but Kretz's data on chromium distributions are not good enough to make this clear.

TABLE 6. TABLE SHOWING VARIATION IN DISTRIBUTION COEFFICIENTS IN THREE GROUPS OF ROCKS OF DIFFERENT METAMORPHIC GRADE

	Facies	Fe	Mg	Ti	Mn	V	Cr
Kretz	Amph.	1.10	1.00	2.00	3.00	1.20	1.2?
Moxham	U. Ep.-amph.	1.00	.96	.80	1.66	1.10	1.30
Nickel	L. Ep.-amph.	.65	1.20	.40	1.25	.57	.22

It should be pointed out that the distribution coefficients of Fe and Mg given in Table 6 and shown in Fig. 22 are not correct since these elements are present at levels well above the lower, straight-line portion of the distribution curve (see Fig. 1) near the origin, as the minor element levels are. The values given are not far removed from the true values and are, in any case, relatively correct.

Since the possibility exists that these shifts in distribution are a function of composition, and not of metamorphic grade, an examination of other element trends is in order. Data on alkalis and calcium, not available for Nickel's materials, is not greatly different in Kretz's mineral pairs and the writer's. Titanium and manganese values are somewhat different in the three groups. Average Ti and Mn concentrations in the two minerals for the groups are given in Table 7. Also, Al distribution differs in the three groups, as shown in the lower part of the table. Two possible explanations for these observations are suggested.

1. The supply of Ti and Mn was different in the three areas, and hence these were taken up to a different degree by the hornblendes and

TABLE 7. TABLE SHOWING ATOMIC RATIOS OF Mn, Ti, AND Al IN THREE GROUPS OF ROCKS OF DIFFERENT METAMORPHIC GRADE (MEAN VALUES)

Element	Mineral	Kretz	Moxham	Nickel
Titanium	Hbld.	.0400	.0300	.0100
	Bio.	.0800	.0450	.0200
Manganese	Hbld.	.0400	.0100	.0050
	Bio.	.0150	.0060	.0035
Aluminum (tetrahedral)	Hbld.	.22	.10	.10
	Bio.	.3	.3	.4
	Hbld./Bio.	.7	.33	.25

biotites of each area. Either or both of these elements, in turn, influenced the fractionation of Fe, Mg, Ti, Mn, V and Cr, and perhaps Al.

2. The distribution of Fe, Mg, Ti, Mn, V, and Cr is a function of temperature. It is, however, generally conceded that the tetrahedral Al content of hornblendes rises with increasing degree of metamorphism so that this is also a function of temperature. Perhaps higher temperatures acted to increase the tolerance of the two mineral structures for Ti and Mn.

The second view seems more likely in view of the fact that within the groups of rocks no relationship exists between Mn abundance, Ti abundance or Al distribution, and the distribution of other elements. It is tentatively suggested that the distribution coefficients in these groups of rocks, on the available evidence, are a function of metamorphic grade; since pressure in general has less effect on distributions than does temperature (Kretz, 1961), it is further suggested that these distribution shifts are largely a result of temperatures of metamorphism.

CONCLUSIONS

The tendency to regular distributions on the part of the majority of the minor constituents supports the view that they occupy structural sites in these minerals. Compositional variables among the mineral pairs examined, as well as analysis error, lead us to expect deviation from perfectly regular distributions.

Attempts to relate the value of the distribution coefficients of minor elements with atomic properties were not fruitful. The distribution coefficient for a particular element is a function of its chemical potential in the two minerals, and this factor is dependent upon a complex summation of the effects of bonding properties, atomic properties, and the character of the crystal structure in question, and the value assumed by the distribution coefficient relative to that of other elements is not predictable at this time. Exceptions exist in the case of atoms whose distribution and location in the two minerals is controlled by unusual size, for example, Ba.

Among the elements that exhibit a tendency toward regular distribution, the regularity persists to a lower limit, for most elements, of around 200 atoms per million. Below this lower level two possibilities exist: the elements have not been able to achieve equilibrium due to a kinetic inhibition, or regular distribution is obscured by disequilibrium concentrations of the element in dislocations and stacking faults.

A comparison of the distribution patterns obtained in three groups of hornblende and biotite bearing rocks of apparently different degrees of metamorphism suggests that the distributions do indeed shift as a function of metamorphic facies, as theory would indicate. This shift is probably more temperature- than pressure-dependent.

A study of minor element distribution between coexisting minerals of simpler chemistry may reveal relationships between major element and minor element distributions. This in turn may lead to clearer ideas on element incorporation in rock-forming minerals.

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