MAGNESIUM-IRON DISTRIBUTION IN COEXISTING BIOTITE AND HORNBLende FROM GRANITIC ROCKS

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Coexisting biotites and hornblendes from the rocks of the Tabito plutonic complex were analysed chemically. The Mg-Fe⁺² distribution coefficients in the two mafic minerals, ranging from 0.74 to 0.93, are directly proportional to the Al^{IV} contents in the hornblendes. The relation is universal in the calc-alkaline granitic rocks of various districts.

INTRODUCTION

Concerning granite petrology, the distribution of elements in coexisting biotite and hornblende has been a current problem, as the two silicates are usually the main mafic constituents in granitic rocks. On the basis of the Mg-Fe⁺² distribution between coexisting biotite and hornblende, Hietanen (1971) presented some petrogenetic discussions for the granitic plutons of the Northern Sierra Nevada. It was pointed out by Ray and Sen (1970) that tetrahedral Al in hornblende exerted a major control on the variation of the Mg-Fe⁺² distribution coefficient between pyroxene and hornblende. Kanisawa (1972) showed that the Mg-Fe⁺² distribution coefficient between biotite and hornblende depended largely upon Al contents in the two minerals. According to Gorbatscev (1972), the total Fe-Mg distribution coefficient between coexisting biotite and Ca-amphibole from metamorphic rocks and igneous rocks, mainly from the former, was controlled by the octahedral substitutions as well as the tetrahedral ones.

Thus, there is a doubt whether the distribution coefficient between biotite and hornblende is sufficiently useful as an indicator of temperature or pressure, because the compositional dependence of the distribution coefficient may not be ignored.

During a petrological study of the Tabito plutonic complex in the Abukuma plateau, northeast Japan, twelve biotite-hornblende pairs were analysed chemically. Based on them and other data from the calc-alkaline granitic rocks of various districts, the partition of Mg-Fe⁺² in biotite and hornblende is discussed in this paper.

GEOLOGICAL OUTLINE OF THE TABITO COMPLEX

The Tabito plutonic complex, according to Shido (1958), occupying an area of about 250 Km², consists of a granitic body and small gabbroic masses. The age of the Tabito complex obtained from Rb-Sr mineral dating is 92 m.y. (Ueno, 1968), 95 m.y. by K-Ar mineral dating (Fukasawa and Onuki, 1972), and 150 m.y. by Rb-Sr whole rock dating (Maruyama, 1972). A

detailed study of the northern part of the complex was made recently by the present author (Tanaka, 1974), and it is briefly summarized below.

The granitic body of the northern part of the Tabito plutonic complex is composed mainly of granodiorite and quartz diorite. The body is divided into three intrusive units, namely, the Myojin-ishi, Komuro and Iritabyuto types, and they are considered to have intruded successively in this order. Gabbroic masses consisting mainly of hornblende gabbro with a small amount of cordierite and gabbro pegmatite are intruded by granitic veins of the Iritabyuto type.

The Myojin-ishi type is characterized by prismatic hornblende and often contains a small amount of cummingtonite and pyroxenes. The Komuro type having no cummingtonite or pyroxene is intruded by networks of leucocratic veins at many places derived from the Iritabyuto type. The Iritabyuto type, the most leucocratic among the three, contains dark inclusions mainly of plagioclase, biotite and hornblende with a small amount of quartz, and correspond to quartz diorite or diorite in mineralogical composition.

MODES OF OCCURRENCE OF BIOTITE AND HORNBLENDE

Biotite and hornblende are the major mafic constituents in the Myojin-ishi type, the Komuro type and the dark inclusions. In the Iritabyuto type, though the amount of biotite is fairly large, the associated hornblende is usually only a little and sometimes not detected.

Biotites are generally subhedral or anhedral, and occur as independent grains or contiguous ones with hornblendes. Minute

biotite replacing hornblendes however are seen sometimes. Accordingly the biotites may have crystallized almost simultaneously with hornblendes, or slightly later than the latter. Most of them are brown in Z-axial color, and the rest are reddish brown.

In the Myojin-ishi type, the hornblendes being usually subhedral prismatic crystals rarely contain in the core clinopyroxene or cummingtonite, and very rarely orthopyroxene. In the other two types and the dark inclusions the hornblendes are subhedral acicular crystals or ragged ones. Hornblendes from the Myojin-ishi and Komuro types are brown, brownish green or green in Z-axial color, and sometimes show the zoning in this order from core to margin. On the other hand, those from the Iritabyuto type and the dark inclusions are generally bluish green, and the bluish tinge is probably due to their high $Fe^{+3}/(Fe^{+2} + Fe^{+3})$ ratio.

CHEMICAL COMPOSITIONS OF BIOTITE AND HORNBLENDE

Eleven pairs of biotite and hornblende were separated by means of the Franz Isodynamic Separator, heavy liquid, and tapping on paper, and they were analysed chemically. In addition, one biotite-hornblende pair from a gabbro in which the mode of occurrence of each mineral is similar to that in the Myojin-ishi type was also analysed. Chemical compositions of the analysed minerals and their structural formulae calculated on the basis of 24 (O, OH) are shown in Tables 1 and 2. Chemical compositions of all host rocks except No. 7372402B were reported by Tanaka (1974).

The SiO_2 content of the analysed biotites covers a narrow range (i.e. 34.4–35.8 wt.%), and is slightly poorer than those from most calc-alkaline granitic rocks.

Table 1. Chemical compositions of biotites.

Rock Type	Myojin-ishi			Komuro			Iritabyuto		Dark inclusions			Gabbro
Anal. No.	3	1	4	19	20	21	23	26	37	42	41	13
D.I.	42.93	44.45	49.65	45.78	50.33	51.31	59.06	64.18	35.84	48.09	62.11	29.06
SiO ₂	35.78	35.20	35.50	35.68	35.40	34.91	34.38	35.27	35.17	35.48	35.05	35.27
TiO ₂	3.43	3.85	3.80	3.86	3.99	3.92	3.61	3.81	2.71	3.51	3.72	3.52
Al ₂ O ₃	15.84	15.73	14.67	15.44	15.22	16.13	16.47	14.99	16.11	15.92	15.65	15.76
Fe ₂ O ₃	1.73	1.05	2.39	1.62	1.95	1.11	3.64	2.30	1.65	2.27	2.59	1.62
FeO	17.94	19.33	18.83	18.03	19.31	20.61	18.53	20.37	19.66	19.41	20.46	19.35
MnO	0.30	0.25	0.32	0.17	0.21	0.27	0.37	0.38	0.18	0.28	0.40	0.13
MgO	11.96	10.95	10.74	12.00	10.49	10.22	9.50	8.71	11.10	10.09	8.54	11.24
CaO	0.56	0.44	0.40	0.54	0.40	0.74	1.14	0.95	0.50	0.34	0.57	0.44
Na ₂ O	0.76	0.77	0.51	0.72	0.72	0.70	0.55	0.80	0.79	0.55	0.63	0.85
K ₂ O	8.53	8.60	9.03	8.60	8.90	7.86	7.64	8.68	8.20	8.83	9.01	8.20
H ₂ O+	3.41	3.72	3.38	3.97	3.63	4.11	4.47	3.42	4.06	3.49	3.40	3.87
H ₂ O-	0.18	0.13	0.06	0.12	0.02	0.19	0.20	0.02	0.26	0.10	0.02	0.11
Total	100.42	100.02	99.63	100.75	100.24	100.77	100.50	99.70	100.39	100.27	100.04	100.36
Si	5.439	5.382	5.486	5.373	5.420	5.292	5.194	5.483	5.344	5.438	5.437	5.358
Al ^{IV}	2.561	2.618	2.514	2.627	2.580	2.708	2.806	2.517	2.656	2.562	2.563	2.642
Al ^{VI}	0.272	0.212	0.153	0.108	0.162	0.168	0.121	0.224	0.224	0.209	0.293	0.175
Ti	0.391	0.442	0.440	0.436	0.458	0.446	0.409	0.444	0.309	0.404	0.433	0.401
Fe ⁺³	0.197	0.120	0.277	0.183	0.224	0.126	0.412	0.268	0.188	0.261	0.301	0.185
Fe ⁺²	2.272	2.463	2.425	2.262	2.464	2.603	2.333	2.639	2.490	2.479	2.645	2.450
Mn	0.039	0.032	0.042	0.022	0.027	0.035	0.047	0.050	0.023	0.036	0.052	0.017
Mg	2.727	2.511	2.490	2.710	2.409	2.324	2.153	2.031	2.530	2.320	1.987	2.561
Ca	0.091	0.072	0.066	0.087	0.066	0.120	0.185	0.158	0.081	0.056	0.095	0.072
Na	0.224	0.228	0.152	0.210	0.213	0.205	0.161	0.241	0.232	0.163	0.189	0.250
K	1.655	1.679	1.781	1.653	1.740	1.521	1.473	1.723	1.591	1.728	1.784	1.590
OH	3.455	3.792	3.482	3.985	3.705	4.153	4.502	3.544	4.113	3.566	3.616	3.920
Mg/Fe ⁺²	1.20	1.02	1.03	1.20	0.98	0.89	0.92	0.77	1.02	0.94	0.75	1.05

Analyst: H. Tanaka.

- 3: Hornblende biotite quartz diorite (No. 7272011).
 1: Hornblende biotite quartz diorite (No. 7281409).
 4: Clinopyroxene bearing biotite hornblende quartz diorite (No. 7272613).
 19: Biotite hornblende quartz diorite (No. 7272216).
 20: Hornblende biotite quartz diorite (No. 7272315).
 21: Hornblende biotite quartz diorite (No. 51505).
 23: Hornblende biotite granodiorite (No. 7272307).
 26: Hornblende biotite granodiorite (No. 51506).
 37: Dark inclusion (No. 7281511A).
 42: Dark inclusion (No. 7372402B).
 41: Dark inclusion (No. 7331402B).
 13: Biotite cummingtonite hornblende quartz gabbro (No. 80204).

So these biotites are rich in Al^{IV} and show a composition near to the siderophyllite-eastonite series.

In the hornblendes from the Myojin-ishi and Komuro types SiO₂ tends to decrease with increasing D.I. of the host rocks, and Al₂O₃, TiO₂, (Na₂O+K₂O) and

MnO show the reverse tendency. So in them, the increase of Al^{IV} is balanced by increasing tri- and quadri-valent cations in the Y-site and by substitution of (Na+K) in the A-site of hornblende structure. On the other hand, the trend opposite to that of the former two types is noticed in the

Table 2. Chemical compositions of hornblendes and the calculated K_D values.

Rock Type	Myojin-ishi			Komuro			Iritabyuto		Dark inclusion			Gabbro
Anal. No.	3	1	4	19	20	21	23	26	37	42	41	13
D.I.	42.93	44.45	49.65	45.78	50.33	51.31	59.06	64.18	35.84	48.09	62.91	29.06
SiO ₂	46.15	45.39	44.44	46.77	45.68	45.07	42.49	44.26	44.61	43.03	43.63	44.95
TiO ₂	1.59	1.72	1.96	2.19	2.34	2.77	2.97	2.00	1.65	2.15	1.65	2.15
Al ₂ O ₃	8.38	8.45	8.49	7.68	8.23	8.56	8.68	7.90	9.75	10.12	9.07	9.16
Fe ₂ O ₃	3.01	2.01	3.86	2.14	2.58	3.46	5.62	4.69	3.23	4.68	4.94	2.88
FeO	13.34	15.20	14.49	13.99	15.48	15.51	14.95	16.17	16.29	15.22	16.03	15.42
MnO	0.43	0.47	0.54	0.45	0.53	0.58	0.64	0.64	0.47	0.55	0.62	0.37
MgO	12.03	11.14	10.25	12.52	10.55	9.51	8.28	8.40	10.04	9.02	7.82	10.47
CaO	11.55	10.90	11.16	10.78	10.72	10.52	11.03	11.23	10.15	11.00	11.30	10.49
Na ₂ O	1.06	1.12	1.38	0.92	1.27	1.22	1.29	1.28	1.30	1.18	1.13	1.16
K ₂ O	0.60	0.62	0.79	0.42	0.42	0.53	1.02	0.80	0.55	0.60	1.06	0.60
H ₂ O ⁺	1.91	2.14	2.08	2.18	2.05	2.31	2.25	2.10	2.15	2.13	2.25	2.15
H ₂ O ⁻	0.18	0.14	0.08	0.18	0.21	0.16	0.12	0.07	0.11	0.11	0.08	0.08
Total	100.23	99.30	99.52	100.22	100.06	100.20	99.34	99.54	100.30	99.79	99.58	99.88
Si	6.815	6.783	6.675	6.862	6.797	6.699	6.466	6.717	6.641	6.475	6.615	6.688
Al ^{IV}	1.185	1.217	1.325	1.138	1.203	1.301	1.534	1.283	1.349	1.525	1.385	1.312
Al ^{VI}	0.271	0.269	0.175	0.188	0.238	0.196	0.020	0.128	0.349	0.267	0.233	0.291
Ti	0.176	0.193	0.221	0.241	0.261	0.309	0.339	0.228	0.184	0.243	0.188	0.240
Fe ⁺³	0.333	0.225	0.435	0.236	0.288	0.386	0.642	0.534	0.361	0.528	0.562	0.321
Fe ⁺²	1.641	1.893	1.814	1.710	1.920	1.921	1.896	2.045	2.021	1.908	2.025	1.912
Mn	0.054	0.059	0.069	0.056	0.067	0.073	0.082	0.082	0.059	0.070	0.079	0.047
Mg	2.665	2.497	2.309	2.755	2.355	2.120	1.890	1.912	2.242	2.036	1.779	2.337
Ca	1.827	1.745	1.796	1.695	1.709	1.675	1.798	1.826	1.619	1.773	1.836	1.672
Na	0.303	0.324	0.401	0.261	0.366	0.351	0.380	0.376	0.375	0.344	0.332	0.334
K	0.113	0.118	0.151	0.079	0.080	0.101	0.198	0.155	0.105	0.115	0.205	0.114
OH	1.880	2.132	2.083	2.132	2.034	2.289	2.283	2.125	2.134	2.137	2.274	2.132
Mg/Fe ⁺²	1.62	1.32	1.27	1.61	1.23	1.10	1.00	0.93	1.10	1.07	0.88	1.22
K_D	0.74	0.77	0.81	0.74	0.80	0.81	0.93	0.82	0.92	0.88	0.86	0.86

Analyst: H. Tanaka.

hornblendes from the Iritabyuto type, though they have a lower content of SiO₂ and higher contents of (Na₂O+K₂O) and MnO than those from the former. The hornblendes from the dark inclusions are slightly richer in Al₂O₃ than those from the three types. The hornblendes mentioned above are all rich in TiO₂ and have more than 1.1 atoms of Al^{IV} in a half unit cell.

One pair of biotite and hornblende from the gabbro have compositions very similar to those from the Myojin-ishi and Komuro types, and their Mg/Fe ratios are not so high as would be expected from the low

D.I. value (i.e. 29.06) of the host rock.

DISTRIBUTION OF Mg AND Fe⁺² IN COEXISTING BIOTITE AND HORNBLLENDE

Here we assume the exchange reaction of Mg and Fe⁺² between biotite and hornblende is expressed as:

The apparent distribution coefficient of Mg-Fe⁺² is:

$K_D = (\text{Mg}/\text{Fe}^{+2})_{\text{biotite}}/(\text{Mg}/\text{Fe}^{+2})_{\text{hornblende}}$. In Table 2 are shown the calculated K_D values for the pairs analysed. The K_D value increases in the Myojin-ishi and Komuro types, and decreases in the Iritabyuto type and the dark inclusions with increasing D.I. of the host rocks. The values of the former group are smaller than those of the latter group.

In general, the apparent distribution coefficient K_D is a function of temperature, pressure and the chemical compositions of the system. In the Tabito plutonic complex, the K_D value covers a fairly wide range from 0.74 to 0.93, and from -0.30 to -0.07 in logarithm. It is evident in Fig. 1 that the K_D value is controlled mainly by the Al^{IV} content in hornblende. Although some analysed hornblendes show zonal structure, all K_D values are plotted on or near a straight line in Fig. 1. The fact indicates that the analysed biotite-hornblende pairs were equilibrated on the Mg-Fe⁺² partition to some extent.

Fig. 1. Relations between the logarithmical value of K_D and the Al^{IV} content in hornblende for the rocks from the Tabito plutonic complex.

- 1: The Myojin-ishi type, 2: The Komuro type,
3: The Iritabyuto type, 4: Dark inclusions,
5: Gabbroic rock.

In Figs. 2 and 3, the logarithmical values of K_D for the total 72 biotite-

Fig. 2. Relations between the logarithmical value of K_D and the Al^{IV} content in biotite for the calc-alkaline granitic rocks of various districts. Twelve data from the Tabito plutonic complex are shown by plus symbols.

Fig. 3. Relations between the logarithmical value of K_D and the Al^{IV} content in hornblende for the calc-alkaline granitic rocks of various districts. Plus symbols the same as used as in Fig. 2.

hornblende pairs from the calc-alkaline granitic rocks of various districts are plotted versus the Al^{IV} contents in biotite and hornblende, respectively. The data used are from the contributions by Haslam (1968), Dodge *et al.* (1968, 1969), Kanisawa (1969, 1972, 1974), Dodge and Ross (1971), Hietanen (1971), Kato (1972), Albuquerque (1973, 1974) and Kato and Tanaka (1973). Some data that show significant deviations from others in each district are omitted in Figs. 2 and 3. These abnormal data could be ascribed to the following reasons:

1. The equilibrium condition was not

attained for the distribution of Mg-Fe⁺² in the coexisting biotite and hornblende.

2. The separation or chemical analysis of the mineral was not complete.
 3. Although in a few cases, the aberrant values of K_D were obtained from the pairs of which the mineral chemistry seemed to be reflected by the extremely oxidized or reduced conditions. This feature may be a sign of the dependance of K_D on the chemistry of the rocks.
- For comparison, the data from the Tabito plutonic complex are plotted together in Figs. 2 and 3.

With respect to biotite, no consistent relation is noticed between the logarithm of K_D and the Al^{IV} content. On the contrary in hornblende, the same trend as in the case of the Tabito plutonic complex can be seen, and all data are plotted near the straight line in Fig. 3. Accordingly it is universally said that the logarithmical values of K_D for Mg and Fe⁺² in coexisting biotite and hornblende are directly proportional to the Al^{IV} contents in hornblendes. The fact is in harmony with the theory of Ramberg (1952) that the substitution of Al for Si influences the lattice oxygen to favor Fe in preference to Mg in octahedral sites.

The similar compositional effect of hornblende upon the distribution coefficient for Mg and Fe⁺² are also seen in clinopyroxene-hornblende and orthopyroxene-hornblende pairs (Ray and Sen, 1970). In conclusion, the Al^{IV} content in hornblende exerts a strong influence on the Mg-Fe⁺² distribution in pairs involving hornblende. Therefore, when the apparent distribution coefficient is used as the indicator of temperature or pressure, much attention must be paid to the compositional effect of hornblende.

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花崗岩類中の共存する黒雲母と角閃石の Mg-Fe 分配

田 中 久 雄

阿武隈高原の田人深成複合岩中体の 12 対の共存する黒雲母と角閃石の化学分析を行った。分析した黒雲母と角閃石の Mg-Fe 分配値は 0.74 から 0.93 と比較的幅広い範囲にわたるが、その自然対数値は角閃石の Al^{IV} 原子数に比例している。同様の関係は他地域のカルクアルカリ岩系の花崗岩類においても一般に認められる。同様の分配率の組成依存性は、単斜輝石-角閃石対及び斜方輝石-角閃石対においても認められることが既に報告されている。従って角閃石を含む対においては、分配率と岩石生成の P-T 条件とを単純に結びつけることは不可能であり、分配率を P-T 条件の解析に利用する場合には、角閃石の組成の影響を十分に吟味しなければならない。

The Myojin-ishi type	明神石型
The Komuro type	小室型
The Iritabyuto type	入旅人型