D/H FRACTIONATION OF COEXISTING BIOTITE AND HORNBLLENDE IN SOME GRANITIC ROCK MASSES

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The deuterium content (δD_{SMOW}) of the water extracted from coexisting biotite and hornblende in granitic rocks was measured. The relationship between δD of biotite and hornblende suggested an isotopic equilibrium in the rocks of four granitic bodies in the Kitakami mountains (Northeast Japan), and the maximum temperature of isotopic equilibration of biotite and hornblende was estimated to be 700–1,000°C, provided that the minimum temperature was 450–550°C. The δD value obtained for the water with which these minerals equilibrated was $-29 \sim -37\text{‰}$ and is definitely enriched in deuterium relative to the present local surface water.

On the other hand, the relationship between δD of biotite and hornblende in the Ryoke metamorphic belt contiguous to the Median Dislocation Line (Southwest Japan) indicated an isotopic disequilibrium. In this case a complicated history of formation of these granitic rocks in terms of the interaction of water and hydrous silicates was inferred.

1. INTRODUCTION

Friedman and Smith (1958) first measured the deuterium content (δD) of the water in coexisting obsidian and perlite and found that there seemed to be no close correlation between their δD values. They also found that δD of perlite was some 40‰ lower than that of the local surface water. Later, Godfrey (1962) and Taylor and Epstein (1966) measured δD of water in pairs of natural hydrous silicates, and estimated the fractionation factor (α) to be 1.009–1.053 in the muscovite-hornblende pair. According to their results, deuterium is most enriched in muscovite among these minerals. Shieh and Taylor (1969) and Forester and Taylor (personal communication) extended the scope. Sheppard *et al.* (1969), Savin and Epstein (1970) and Lawrence (1970) also estimated the fractiona-

tion factors of deuterium between water and hydrous silicates including clay minerals.

Suzuoki and Epstein (1970), (1972) first conducted an experimental determination of α between water and various hydrous minerals under hydrothermal conditions, and found that δD of the hydrogen in the lattice of the mineral is controlled by the composition of the cations in the octahedral position of minerals, as well as the temperature of equilibration and δD of the coexisting water. On this basis, Suzuoki and Epstein (personal communication) have already made some applications to the pairs of natural hydrous silicates.

Origin of the hydrogen included in the lattice of hydrous minerals and of the water of the fluid inclusion of various minerals is one of the most important problems in petrology. This problem is related to the

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question of the presence or non-presence of the juvenile water in the mantle, and to the isotopic composition of crustal water as a function of region and depth. Sheppard and Epstein (1970) measured δD of phlogopites from various kimberlites and estimated δD of "juvenile water" to be $-48 \pm 20\text{‰}$. In this paper we deal with biotite-hornblende pairs in granites in order to confirm the chemistry and temperature dependence of hydrogen isotope ratios in natural systems and further to estimate δD of the water present in granite magmas.

2. SAMPLE DESCRIPTION

The biotite-hornblende pairs were taken from four granitic bodies, viz., the Hitokabe mass, the Kesengawa mass, the Tono mass, and the Hirota mass in the

Kitakami mountains, the Northeast Japan, and from two bodies, i.e., the Hiji mass and the Minakata mass, in the Ryōke metamorphic belt, the Southwest Japan. The localities of these granitic bodies are shown in Fig. 1.

The four bodies in the Kitakami mountains were intruded during the Cretaceous period and have given contact metamorphism to the enclosing Paleozoic and Mesozoic formations. According to Kawano and Ueda (1965), K-Ar ages of biotites from these bodies are 110–120 m.y. The Hitokabe mass (Kanisawa, 1969), SiO_2 content of which ranges from 61 to 68%, consists of hornblende-biotite granodiorite and hornblende-biotite quartz diorite. In this mass, dark inclusions of quartz diorite with SiO_2 content of about 56% are plentiful. The Tono mass, the SiO_2 content of which varies from 56 to 70%, the largest granitic mass in the Northeast Japan, is composed of biotite-granodiorite, biotite-hornblende granodiorite and hornblende-biotite quartz diorite, sometimes containing clinopyroxene. The Kesengawa mass, the SiO_2 content of which ranges from 57 to 65%, consists of biotite-hornblende granodiorite and biotite-hornblende quartz diorite, sometimes containing clinopyroxene. The Hirota mass, the SiO_2 content of which is rather uniform in the range from 61 to 63%, is small in scale and composed of clinopyroxene-biotite-hornblende granodiorite. This mass seems to be formed under shallower condition than the other three.

The chemistry of biotite and hornblende in these masses is typical of these minerals in granite as already described by Kanisawa (1972). The $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios of biotite and hornblende are 0.35–0.52 and 0.34–0.46 respectively. $K_D (\text{Mg}/\text{Fe})_{\text{biot/hornb}}$ is 0.64–0.81, and the numbers of Al^{IV} of

Fig. 1. Locality of the granitic masses investigated.

M.D.L.: Median Dislocation Line,
I.S.L.: Itoigawa-Shizuoka Line.

biotites and hornblendes in the formula calculated on the basis of 24 (O, OH) are 2.13–2.49 and 0.72–1.30 respectively.

The Hiji and Minakata masses belong to the Older Ryôke granitic rocks. The Hiji mass the absolute age of which has been determined to be 95 and 110 m.y. by Pb-a studies of zircon (Karakida *et al.*, 1965), and 83 m.y. by Rb-Sr of biotite (Hayase, 1967), is slightly younger than the Minakata. Both seem to be protoclastic intrusions the origin of which had some relation to the activity of the Median Dislocation Line. The SiO₂ content is lower in the Hiji mass, 60–64%, than the Minakata mass, 67–70%. The chemistry of biotite and hornblende is rather peculiar in that both minerals have high iron-magnesium ratios, Fe/(Fe+Mg), of 0.51–0.76 in biotite and 0.48–0.76 in horn-

blende. The reason for the high Fe/(Fe+Mg) ratios of the minerals in these masses compared to that of the masses in Kitakami is not clear. It is interesting, however, to note that biotite-hornblende pairs from these rocks exhibit an apparent disequilibrium with respect to the behavior of hydrogen isotopes as described later.

3. EXPERIMENTAL

Mineral separations were carried out using magnetic and heavy liquid methods, after pulverizing the samples to 100 mesh-size. The purity of separates was higher than 98%, except for the biotites of HJ-2 and MN-1, where the separation of chlorite was impossible (see Table I).

The extraction of water from hydrous silicates such as biotite and hornblende was

Table 1. Analytical results and pertinent chemical information.

No.	SiO ₂ host rock (wt. %)	biotite				hornblende			
		δD (‰) (SMOW)	H ₂ O (wt. %)	Fe/(Fe+Mg) (atomic frac.)	Al ^{VI} (No. on basis of (O,OH) ₂₄)	δD (‰) (SMOW)	H ₂ O (wt. %)	Fe/(Fe+Mg) (atomic frac.)	Al ^{VI} (No. on basis of (O,OH) ₂₄)
HK-1*	55.44*	-78.3	3.66	0.51	0.292	-69.2	2.06	0.45	0.246
HK-2*	55.58*	-72.2	3.54	0.50	0.348	-68.4	2.04	0.43	0.186
HK-3	60.66	-69.5	3.98	0.47	0.227	-65.6	2.11	0.42	0.139
HK-6	63.63	-73.1	3.53	0.52	0.213	-69.8	2.19	0.45	0.177
HK-9	66.77	-72.2	3.78	0.51	0.104	-70.4	2.19	0.46	0.169
HR-2	61.56	-72.4	3.02	0.46	0.151	-62.6	1.89	0.36	0.007
HR-3	62.77	-73.9	3.22	0.46	0.000	-63.2	2.11	0.36	0.056
HR-4	62.53	-76.2	3.34	0.45	0.000	-69.7	1.94	0.37	0.000
TN-1	56.52	-65.6	3.34	0.51	0.265	-58.8	1.92	0.42	0.193
TN-2	62.34	-80.0	3.96	0.43	0.000	-69.2	2.07	0.34	0.084
TN-3	67.01	-74.3	3.78	0.43	0.268				
TN-4	70.35	-73.9	3.90	0.35	0.055				
KS-1	57.11	-58.7	3.78	0.48	0.184	-52.4	2.00	0.38	0.183
KS-2	64.97	-63.7	4.06	0.44	0.000	-58.7	2.03	0.36	0.109
HJ-1	62.86	-67.1	4.13	0.51	0.297	-67.7	2.15	0.52	0.365
HJ-2	64.13	-64.0	5.33**	0.55	0.035	-70.4	2.37	0.53	0.107
HJ-3	62.42	-78.2	4.35	0.51	0.169	-94.0	2.07	0.48	0.269
HJ-4	59.95	-85.7	4.85	0.55	0.088	-102.0	1.92	0.54	0.289
MN-1	69.73	-65.2	5.48**	0.76	0.000	-74.9	1.73	0.76	0.296
MN-2	69.96	-60.0	4.01	0.76	0.061	-64.7	1.94	0.74	0.201
MN-3	66.98	-86.1	3.86	0.62	0.280	-80.6	2.07	0.58	0.344
MN-4	68.00	-76.8	4.33	0.69	0.074	-78.2	1.97	0.69	0.373

*: dark inclusions, **: probably containing some amounts of chlorite.

HK: Hitokabe, HR: Hirota, TN: Tono, KS: Kesengawa, HJ: Hiji and MN: Minakata.

performed by the dehydration technique using high frequency induction heating similar to that described by Friedman and Smith (1958) and Godfrey (1962). The dehydration vessel modified by Epstein and Taylor (1970) was used in this study. The pre-heated platinum crucible and the powdered sample were handled in a moisture-free chamber to protect completely the sample from possible contamination by extraneous water.

Usually, water vapor and hydrogen gas were evolved simultaneously in the dehydration process of mineral treated. Hydrogen gas was converted to water by heating it with CuO (500~600°C) which was trapped to enhance the quick pumping of evolved gases from the dehydration vessel. This procedure minimizes the glow-discharge during the induction heating. A heavy glow-discharge gives erratic results on δD measurement. The water extracted was passed over hot uranium metal (700°C), and converted to molecular hydrogen (Bigeleisen *et al.*, 1952). After measuring the volume of the evolved hydrogen the isotopic composition of the gas was determined using a specially constructed mass spectrometer.

The D/H ratio is presented by the following expression,

$$\delta D (\text{‰}) = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{SMOW}}}{(D/H)_{\text{SMOW}}} \times 1,000$$

where SMOW refers to Standard Mean Oceanic Water.

A repeated run of a laboratory-reference muscovite gave the standard deviation of $\pm 1.5\%$ and $\pm 0.06\%$ for δD and water content respectively.

4. RESULTS

In Table 1 are listed δD values and

Fig. 2. Relationship between δD and $Fe/(Fe+Mg)$ of biotite and hornblende of the granitic masses in the Kitakami mountains. Notation in the figure is the same to that in Table 1.

the yield of water extracted from biotite and hornblende together with pertinent chemical information. As shown in Fig. 2, the biotite-hornblende pairs from four granitic masses in Kitakami mountains seem to approach equilibrium with respect to deuterium partition, because the tie-lines between the coexisting biotite and hornblende on the δD versus $Fe/(Fe+Mg)$ diagram are nearly parallel to the "equilibrium line" (the broken line in Fig. 2) that was experimentally determined by Suzuoki and Epstein (1970), (1972). The actual equilibrium line moves up and down on the diagram depending on the temperature of equilibration (or crystallization) and the value of δD of coexisting water. According to Suzuoki and Epstein (1970), (1972), the equilibrium partition of deuterium between biotite and hornblende is almost even, provided that the Fe/Mg ratios of minerals are the same. The equilibrium fractionation between biotite and hornblende can be regarded as being a function of the difference between their Fe/Mg ratios.

On the pairs of the low temperature side such as TN-2, however, δD value of

biotite is slightly lower than the equilibrium line, provided that δD value of hornblende is just on the equilibrium line. In Fig. 2, the δD and Fe/Mg data for coexisting biotite-hornblende pairs from the Hitokabe and Hirota masses show little scatter. Data for the Kesengawa and Tono masses plot in different positions. The tie-lines of the Tono mass are widely separated. The tie-lines of coexisting biotite and hornblende from host rocks with less SiO_2 content appear in the higher δD side of Fig. 2. The exceptions are HK-1 (SiO_2 : 55.44%) and HK-2 (SiO_2 : 55.58%) from the Hito-

kabe mass. However, these samples may not be the product of magmatic differentiation but are the inclusions, which were influenced physically and chemically by the host granite.

As seen in Figs. 3 and 4, there is an inverse relationship between δD and water content of biotite and hornblende in the individual mass, Kesengawa, Tono and Hirota, i.e., the higher the content of water, the lower the value of δD is. On the other hand, such relationship is not seen in the Hitokabe mass. This may have some connection to the fact that the range of water content of both biotite and hornblende of Hitokabe mass is narrower than those of the other three.

As seen in Fig. 5, the tie-lines of biotite and hornblende of the Hiji and the Minakata masses from the Ryôke metamorphic belt exhibit a quite different inclination from those of four masses in the Kita-

Fig. 3. Relationship between δD and H_2O content of biotite of the granitic masses in the Kitakami mountains.

δD values are normalized to $\text{Fe}/(\text{Fe}+\text{Mg})=0.40$.

Fig. 4. Relationship between δD and H_2O content of hornblende of the granitic rocks in the Kitakami mountains.

δD values are normalized to $\text{Fe}/(\text{Fe}+\text{Mg})=0.40$.

Fig. 5. Relationship between δD and $\text{Fe}/(\text{Fe}+\text{Mg})$ of biotite and hornblende of the granitic masses in the Ryôke metamorphic belt. Notation in the figure is the same to that in Table 1.

Fig. 6. Relationship between δD and H_2O content of biotite and hornblende of the granitic rocks in Ryōke.

δD values are normalized to $Fe/(Fe+Mg)=0.50$. HJ-2 and MN-1 are excluded because of the contamination of chlorite.

kami mountains shown in Fig. 2. The tie-lines are almost perpendicular to the "equilibrium line," i.e., δD of biotite is mostly higher than that of hornblende. However, there are some exceptions. The tie-lines of MN-3 and HJ-1 show nearly equilibrated conditions as those of the pairs already found in the Kitakami mountains. The biotite-hornblende pairs with perpendicular tie-line apparently represent disequilibrium situation with respect to the deuterium exchange. Moreover, the relationship between δD and SiO_2 content of the host rock is rather reversed when compared with that of the Kitakami mountains.

As seen in Fig. 6, there seems to be no conspicuous relationship between δD and water content of biotite and hornblende, in contrast to the relationship found in the masses of Kitakami.

5. DISCUSSION

According to Suzuki and Epstein (1970), (1972), the fractionation factor, $\alpha=$

$(D/H)_{\text{mineral}}/(D/H)_{\text{water}} = (1000 + \delta D_M)/(1000 + \delta D_W)$, of both biotite and hornblende can be represented by a linear combination of the temperature and chemistry dependent terms as,

$$10^3 \ln \alpha_{M-W} = -22.4 \times 10^6 T^{-2} + 28.2 + (2X_{Al} - 4X_{Mg} - 68X_{Fe}) \quad (1)$$

where T denotes the absolute temperature and X the mole fraction of the six-coordinated cations. The left-hand side of eq. (1) can be approximated to $\delta D_M - \delta D_W$ where the suffices M and W represent mineral and water respectively. When the amount of the mineral is negligible to the amount of water in an equilibrium mixture, δD_W is virtually invariant and δD_M only is subjected to a change with the change in chemical composition of the mineral even under the same temperature. Biotite and hornblende can be regarded as the "same" hydrous mineral with different chemical composition.

The inclination of the broken line shown in Fig. 2 gives the chemistry dependence of δD_M when the presence of six-coordinated aluminium is negligible. Since X_{Al} of most of the samples in this study is small (refer to Table 1), the contribution of X_{Al} term can be safely neglected. When a biotite-hornblende pair can be regarded as being in equilibrium, e.g. Kitakami masses in this study, δD value at $X_{Fe}=0$ can be obtained by the extrapolation using the same inclination as that of the broken line in Fig. 2. Then Eq. (1) is simplified to

$$\delta D_M^* - \delta D_W = -22.4 \times 10^6 T^{-2} + 24.2 \quad (2)$$

where δD_M^* denotes the normalized δD value of the mineral.

On the basis of the results obtained for biotite-hornblende pairs from masses in the Kitakami mountains, a following consideration is made using Eq. (2). If the δD value

of the coexisting water in Kitakami mountains was the same throughout, the biotite-hornblende pair of TN-2 was regarded to be equilibrated under the lowest temperature as indicated in Fig. 2. Although the δD value of biotite of TN-2 seems to be slightly lower than the equilibrium value, the biotite-hornblende pair is assumed to be crystallized or isotopically equilibrated with the water in magma in the temperature range from 450 to 550°C. Judging from the texture under the microscope the rock of TN-2 is neither recrystallized nor of non-magmatic origin. Then the temperature of 450–550°C may be taken to be the minimum temperature during the magmatic stage.

Provided that the temperature of TN-2 pair is set and δD of the water in magma is the same throughout the crystallization of magma, the equilibrium temperature of biotite-hornblende pair of KS-1 (apparently the highest temperature pair) is estimated to be about 700–1,000°C. Such a temperature value is also acceptable for the highest crystallization temperature of a granitic magma. The equilibrium temperature of the other pairs in Kitakami should lie in the range from 450–550°C to 700–1,000°C. The change in SiO_2 content is also conformable to the estimation.

The already mentioned inverse correlation between δD and water content can be interpreted in terms of the temperature effect; viz., the water content of hydrous silicate increases when the temperature of equilibration is lowered.

If the above consideration is valid, δD of the water in the granitic magma would be about $-29 \sim -37\%$ which is definitely higher than $-60 \sim -70\%$ of the present local surface water in the Kitakami mountains. The high δD value of the water in this

granitic magma may be attributed either to the crustal water of which δD varies with region and depth, or to the contribution of "juvenile water" from the mantle.

On the other hand, most of the biotite-hornblende pairs from the Hiji and Minakata masses in the Ryôke metamorphic belt, showed apparent disequilibrium situation with respect to the deuterium partition. At the present time, it is difficult to give any decisive interpretation consistent with both chemical and geological information for the apparent disequilibrium. A simple and premature interpretation is that the biotite in granitic masses of Ryôke might have been subjected to the exchange of deuterium with the water of high δD value after their formation, while the exchange of deuterium between hornblende and water might have taken place to a lesser extent after their formation.

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若干の花崗岩体中の共存する黒雲母と角閃石の水素同位体

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北上山地の遠野、広田、気仙川、人首の4花崗岩体中の黒雲母と角閃石の δD を測定した。黒雲母、角閃石、マグマの水は水素同位体的に平衡であったと考えられる。その時の温度の最低が450-550°Cであったと仮定すると、最高の温度は700-1000°Cとなり、マグマの水の δD は-29~-37‰となる。高温と推定される花崗岩はより塩基性で、低温と推定されるものはより酸性である。

領家帯の非持、南向両岩体のものについても同じ測定をしたが、これは北上山地の例とくらべて、まったく異なった結果を示し、黒雲母、角閃石、マグマの水は水素同位体的に非平衡であった。そのことの理由はよく分らないが、これらの花崗岩体の形成史が単純でなかったことを示すものであろう。