Metallic element contents of biotite collected along the Nishiki river, Southwest Japan—Heavy metal concentration to clay minerals in aqueous solutions. II.

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Metallic element contents of biotite collected along the Nishiki river, Southwest Japan, were investigated by means of atomic absorption spectrophotometry and the results obtained were examined from mineralogical and statistical view points. Biotite in the district is commonly altered to vermiculite and to lesser extent to vermiculite-chlorite interstratified mineral and kaolinite. The main variations of the chemical composition are mostly caused by decomposition and the vermiculitization of biotite.

The content of the representative interlayer cation, K, depends on that of biotite in the parent granite. Rubidium behaves together with K, so that the Rb fraction is almost constant in the interlayer cations (K, Na, Ca and Rb), despite its low content (below 550ppm) of biotite.

Among the possible octahedral cations, substitution of Fe by Mg is remarkable. Contents of minor elements, such as Cu, Zn and Pb, vary locally but no geological evidences for explaining the local enrichments of these elements can be found. Correlation coefficients of Fe and Zn against K suggest that a part of the two elements are contained in the interlayer position.

INTRODUCTION

Takeno *et al.* (1981) demonstrated experimentally that metal ions concentrated remarkably to clay minerals when the minerals were suspended in aqueous solutions containing metal ions. In nature, metal ions in surface water, such as that of rivers and lakes, tend to concentrate in clay minerals suspended in and/or deposited from the water. However, we have little knowledge of this adsorption mechanism. For example, although clay minerals are commonly suspended or sedimented in rivers, few researches on detailed quantitative examinations of clay minerals in rivers have been done before. These clay minerals contain various metal ions and the concentration depends mainly on the geology of the district. Recent water pollutions caused by the extensive development of modern industries veil the natural distribution of the metal concentrations.

Most systematic researches on metal con-

tents of surface water were carried out by Förstner and Müller (1974). Their remarkable contribution is that they distinguish the metal contents of clay particles from the metal ions contained in water. Their results clearly indicate that metal contents of clay constituents are on ppm level whereas those of water are on ppb level. Detailed mineralogical studies on the clay constituents are required. In our previous paper, heavy metal concentration of mica mineral ($2M_1$ muscovite) under various aqueous conditions was examined experimentally (Takeno *et al.*, 1981), and the results show that most of heavy metals such as Zn, Co and Cu concentrate remarkably to the solid, i.e., mica mineral.

Examinations of metal contents of clay minerals in natural environment are rather difficult because of the minor amounts of a certain clay mineral in rivers and/or lakes. Among clay minerals, mica mineral is one of the most abundant in rivers, especially, if granitic rocks are

developed in the district. As an example of such situations, the Nishiki river in Yamaguchi Prefecture, southwest Japan was selected for the investigation of metal contents of biotite from the mouth (Iwakuni city) to the head of the river, and the results of the analyses were examined statistically in relation to the geology of the district as well as to mineralogy. Biotite in the river sands was derived from the weathered part of granite developed in the district. The metal contents were examined for biotites both from river sands and weathered granite. Chemical variation of the biotite during the weathering process will not be treated in this paper.

OUTLINE OF GEOLOGY AND SAMPLES

Figure 1 shows geological map around the

Nishiki river together with the sampling localities. The geology of the district is studied in detail by Nishimura (1971, 1982), especially in relation to the regional metamorphism. According to Nishimura (1971), the basement of the geology of the district is composed of Paleozoic formation of the Tsuno group (Devonian to Carboniferous) and is called Sangun metamorphic rocks (Sg in Fig. 1). The Sangun metamorphic rocks are distributed in the central part of the district and consist of alternating beds of psammitic schists in the lower part and of basic schists in the upper part. The Nishiki group of Paleozoic formation (Permian) is also distributed in the northern part of the Sangun metamorphic rocks separated mainly by tectonic slides. The Nishiki group (Ns) is composed of slightly metamorphosed psammitic rocks, pelitic

Fig. 1. Geological map and sampling localities of the Nishiki river district. 1: Sangun metamorphic rocks, 2: Mikawa group (Paleozoic), 3: Nishiki group (Paleozoic), 4: Kuga group (Mesozoic), 5: Granitic rocks (Mesozoic), 6: Rhyolitic pyroclastics (Mesozoic).

rocks and acidic tuffs and is unconformably overlain by rhyolitic pyroclastics of Cretaceous age (Sy). Mesozoic formation of Kuga group (Triassic to Jurassic) is distributed widely in the southern part of the district. The rocks are separated by tectonic faults from the surrounding rocks and are composed of pelitic rocks, cherts and sandstones (Ku). The Mikawa group of Permian age (Mk) is distributed as a narrow belt between Sg and Ku. These basement rocks are intruded by granitic rocks of the Hiroshima granite of late Cretaceous age (Gr) distributed widely in the southern and northeastern parts of the district. The granitic rocks are coarse grained biotite-granite composed of quartz, K-feldspar, plagioclase and biotite. Hornblende is also a main constituent in the southern part of the Sugano lake. The average size of these minerals is about 1 to 5 mm.

Along the Hongo river, the Kawayama mine of bedded cupriferous iron sulfides ore deposits in the Sangun metamorphic rocks (Takeno, 1965, 1966) was once worked.

About 2 kg of river sands was collected from each locality shown in Fig. 1. A simple bottom sampler was used for collecting the samples from the Sugano lake. In addition to the samples from the rivers and lakes, some slightly weathered parts of the granite were also collected. Samples of ECG-, SUG- and NDG- are those from the weathered part of the granite from which biotite grains were transported into the river. These samples were washed with distilled water in order to remove impurities adhered to mica grains. Then, pure mica grains were picked up under the binocular microscope. These mica grains are usually smaller than about 2 mm in size with platy shape and dark brown to golden yellow in color. In the river sands, the grain size of biotite becomes considerably finer. Samples from the northwestern part of the district such as SU-11, 12 and 13 contain no mica grains since no granitic rocks are distributed in the upper reaches of the river. Samples along the Hongo river (A2 to C in Fig. 1), such as HK-1 and HK-2, contain only rounded or folded mica grains. These mica grains are

muscovite of metamorphic origin and contain fine inclusions of plagioclase and quartz. Samples along the A₃-B contain a very small amount of biotite suggesting that the biotite in the SUG-granite in the south-western part of the district is transported mainly to the south, towards Tokuyama city (Fig. 1). Along A₁-B-C-D-E, on the other hand, a systematic change in amounts of biotite in the river sands can be traced. The current direction of the river is almost perpendicular to the general trend of the geology of the district (NE-SW). Samples of NR-15 and NR-26 were taken from both sides (upper and lower) of a weir which separates the sea water. Therefore, samples from the reaches lower than

Fig. 2. X-ray powder diffraction patterns of biotite grains (NR-17) treated with some reagents.

NR-25 of the river are sediments in brackish water. These mica grains collected were pulverized in an agate mortar for X-ray powder analyses.

X-ray powder patterns of the biotite grains generally reveal some extra reflections at about 14 and 7 Å in addition to the basal reflections of mica mineral. In rare cases, weak reflections of interstratified mineral appear beyond 20 Å. Therefore, several treatments were done to identify the extra reflections. These treatments were as follows: 1) ethylene glycol, 2) KCl (1M) at 95°C (1h), 3) KCl (1M) + KOH (1M) at 95°C (1h), 4) HCl (6M) (1h) and 5) heating at 300° and 500°C (1h) in air. An example of the results of these treatments for one sample is shown in Fig. 2. Except two biotites from relatively fresh granite, all biotite grains exhibit distinct reflections at 14 Å. The 14 Å spacing does not expand by ethylene glycol treatment indicating absence of smectite (Harward and Brindley, 1965). Therefore, the 14 Å reflection can be ascribed to vermiculite or chlorite. By the KCl treatment, the intensity of the 14 Å reflection becomes weak but remains clearly, suggesting the existence of chlorite, since 14 Å reflection of vermiculite shifts toward 10 Å by the treatment (Sudo, 1974). Existence of kaolinite should be confirmed by some treatments since the second order reflections of vermiculite and chlorite appear also at 7 Å. For this purpose, the HCl treatment was done, because chlorite and vermiculite are decomposed by warm HCl whereas kaolinite is resistive (Brindley, 1961). As is seen in Fig. 2, the 14 Å reflection disappears by the HCl treatment but the 7 Å reflection remains in the case of NR-7 showing the existence of some kaolinite. Further confirmation of kaolinite was done by heating at 500°C for one hour. Movement of some reflections from 14 Å to 13.3 Å by the KCl + KOH treatment suggests the existence of vermiculite-chlorite interstratified mineral (mixed-layer mineral; Sudo, 1974). Therefore, chlorite found by the KCl treatment is that of vermiculite-chlorite interstratified mineral. Figure 3 shows the most representative X-ray

powder patterns of biotite grains from granite and from river sands. As the results of the above treatments, the constituent minerals are found to be mainly mica mineral (10 Å) and vermiculite (14 Å) with small amounts of vermiculite-chlorite interstratified mineral (14 Å) and kaolinite (7 Å). The vermiculite-chlorite interstratified mineral is found mainly in river sands. Mica grains of HK-1 and HK-2 (along A₂-C) derived from the Sangun metamorphic rocks are composed of mixtures of very fine grained mica clay mineral (muscovite), quartz and plagioclase.

About 100mg of these biotite grains was dissolved in mixed hydrofluoric and hydrochloric acids and 50ml solutions were obtained.

Fig. 3. X-ray powder diffraction patterns of biotite grains collected from granite (ECG-3) and from river sands (NR-13).

The concentrations of elements were determined by atomic absorption using Model AA-646 atomic-absorption spectrophotometer by the flame method. Minor elements such as Cr, Co, Ni, Cu and Pb were measured by carbon-tube flameless method.

EXPERIMENTAL RESULTS

Metal contents of biotite are listed in Table 1 in ppm except for K, Na, Mg, Mn and Fe (wt.%). Among the measured 14 elements, it is generally accepted that the first 4 elements (K, Na, Ca and Rb) occupy the interlayer position and the rest belong to the octahedral positions (e.g. Deerr *et al.*, 1962). The two main constituent elements of the mica mineral, Si and Al, could not be measured because of technical difficulties by atomic-absorption method.

For the comparative study, metal contents of biotite in the typical Hiroshima granite collected in the western part of Hiroshima city (Koi-machi) were also examined. Three samples of A-1, A-4 and A-6 in Table 1 are taken from the weathered part of granite, 0-10cm, 40cm and 60cm depths from the surface of the outcrop, respectively. Characteristics of the variation of metal content of biotite from the depths to the surface are now being studied and will be reported elsewhere. The numbers from 1 to 32 in the Table 1 are samples collected along the A₁-B-C-D-E in Fig. 1 (from the lower to the upper reaches) together with those of the parent granite of the district. The mean and standard deviation (S.D.) in Table 1 were calculated from the data of these 32 samples since biotites of these localities probably constitute a series as was described previously. In general, the pH value of the river water is in the range between 7.0 and 8.0 throughout the year (Iwakuni city, 1979). In Table 1, the first 5 samples are those from brackish water. The Na contents of these samples are higher than those of the adjacent samples taken from fresh water (NR-25, NR-11) and adsorption of Na is compensated by Ca release and adsorption of some metals such as Rb, Li and Zn.

As some typical examples of the major interlayer cations and minor octahedral cations, the distributions of K and Zn contents are shown schematically in Figs. 4 and 5, respectively. In these figures, K and Zn contents of mica grains collected from the river sands are represented by the length of thick lines perpendicular to the river current. The average K and Zn contents of biotite obtained from the granites are also shown (NDG-, SUG- and ECG- in Figs. 4 and 5). Potassium is the most representative interlayer cation of mica minerals and the variation of the content may probably reflect the degree of alteration and/or breakdown. It can be said that K content of mica minerals in river sands relates largely to those of biotite in the parent granites, i.e., those from A₁ to B, A₃ to B and D to E are similar to those of NDG-, SUG- and ECG-biotite, respectively. In other words, K content of biotite is held almost constant even after they are transported into river water and brackish water. Unusually large K contents of those from A₂ to C are due to different species of the mica mineral, i.e., muscovite of metamorphic origin as described previously. The variation range of K content is relatively small (between 1.24 and 5.12wt.% except those of muscovite) compared with other cations. Moreover, the average K content is 2.95wt.% (Table 1) and the value is far lower than that of fresh biotite in granite. According to Deer *et al.* (1962), the K content of fresh biotite in granitic rocks is in the range between 5.8 and 7.5wt.% (equivalent to about 7.0-9.0wt.% of K₂O). As is seen in Table 1, a considerable amount of K release from biotite structure is found even in the parent granite (weathered part). That is, the most part of the K release has proceeded before the transportation of the biotite into the river. Therefore, during the weathering of the host granite, the K release has proceeded to a large extent.

Zn content, on the other hand, varies considerably independent of the content of those of biotite in the parent granites as shown in Fig. 5. There are some possibilities that relatively high Zn contents from C to D in Fig. 5 are

Table 1. Metallic element contents (in ppm) of mica minerals collected from the Nishiki river district, except K, Na, Mg and Fe contents which are given in wt.% (marked by star). The calculations of the Mean and S. D. (Standard deviation) were done with the numbered 32 samples collected along A₁-B-C-D-E (Nos. 1-24) and from the parent granite (Nos. 25-32).

Samples	K*	Na*	Ca	Rb	Li	Mg*	Cr	Mn*	Fe*	Co	Ni	Cu	Zn	Pb
1 NR-28	4.11	0.33	292	456	439	2.99	20	0.27	16.66	30	0	41	728	10
2 NR-27	3.81	0.32	194	547	485	2.02	11	0.29	18.45	17	0	38	917	4
3 EC-2	3.87	0.59	193	516	474	2.10	36	0.32	17.40	23	10	50	701	16
4 EC-1	3.83	0.22	202	367	230	2.40	55	0.31	14.90	29	21	40	488	10
5 NR-26	4.10	0.18	365	356	243	3.00	24	0.27	14.27	21	0	57	471	0
6 NR-25	3.43	0.08	586	379	287	2.57	0	0.27	15.58	21	0	43	518	0
7 NR-11A	4.16	0.07	563	400	157	2.71	25	0.26	15.54	21	0	27	359	1
8 NR-11B	3.64	0.08	609	366	293	2.88	25	0.25	14.95	22	0	30	338	1
9 EC-4	5.12	0.35	431	383	229	3.50	52	0.36	16.40	22	7	91	421	5
10 NR-12	3.66	0.09	687	370	210	2.96	23	0.26	15.47	17	0	34	353	4
11 EC-5B	4.46	0.23	609	403	224	3.00	57	0.31	15.20	24	8	38	330	3
12 EC-5G	3.67	0.17	398	319	180	2.60	47	0.26	14.20	23	17	16	354	7
13 NR-13	3.56	0.18	705	361	350	2.32	15	0.29	15.70	18	0	85	729	34
14 NR-14	2.40	0.22	788	212	274	0.46	5	0.36	17.46	2	0	71	911	105
15 NR-15	3.06	0.14	439	365	418	1.35	10	0.34	17.02	13	0	84	439	49
16 NR-16	2.02	0.22	362	199	332	0.81	8	0.51	18.65	9	0	99	758	77
17 EC-6	1.84	0.52	450	195	406	1.30	0	0.54	24.30	10	3	68	1278	43
18 NR-17	1.76	0.16	603	141	319	0.91	4	0.40	20.01	7	0	47	940	64
19 NR-18	2.81	0.17	420	333	440	1.24	6	0.38	18.22	8	0	24	811	45
20 NR-18	1.84	0.23	503	143	365	0.97	7	0.40	20.29	7	0	26	915	63
ND-2	2.59	0.63	1227	159	184	3.90	125	0.35	16.40	39	34	186	541	9
NR-21	2.20	0.17	534	134	177	2.90	73	0.26	14.45	27	0	116	413	13
NR-22	1.86	0.30	1460	126	206	3.60	61	0.35	17.62	32	0	83	429	5
NR-24	3.13	0.11	847	288	251	2.69	43	0.23	13.85	27	0	70	376	3
NR-23	3.87	0.13	649	403	366	2.57	0	0.35	15.12	22	0	45	476	1
SU-14	2.86	0.23	1601	173	113	3.08	52	0.16	13.40	16	0	84	294	8
HK-2	5.67	1.29	110	196	80	0.80	79	0.10	4.70	9	21	47	177	6
HK-1	4.46	0.33	184	171	80	0.90	83	0.10	4.80	9	23	67	167	6
21 ND-1	1.25	0.39	681	131	370	1.10	36	0.52	20.70	12	20	89	977	65
22 ND-11	1.40	0.19	345	193	372	0.28	0	0.40	19.89	2	0	37	926	87
23 ND-13	1.28	0.29	382	178	436	0.32	0	0.41	20.82	1	0	63	1201	88
24 ND-3	1.57	0.39	232	148	327	0.70	9	0.40	19.00	4	0	40	899	56
25 NDG-1	1.24	0.23	133	102	115	0.70	10	0.27	18.00	5	2	35	922	48
26 ECG-1	3.79	0.24	1660	246	198	3.50	55	0.24	14.50	28	7	12	218	2
27 ECG-2	3.95	0.25	107	338	187	0.70	0	0.27	17.10	3	1	7	614	42
28 ECG-3	2.04	0.15	57	367	438	0.60	5	0.28	18.20	5	4	8	725	3
29 ECG-4	2.03	0.19	299	—	—	1.40	29	0.49	20.70	5	4	8	707	2
30 SUG-2	2.31	0.23	429	205	135	2.20	106	0.19	11.80	23	65	12	269	8
31 SUG-5	3.65	0.23	1422	398	153	3.10	152	0.24	14.30	26	21	27	310	5
32 SUG-6	2.88	0.18	67	340	322	0.80	17	0.24	10.70	7	3	78	437	3
A-1	4.52	0.44	2970	188	218	2.64	8	0.28	18.56	0	0	59	461	5
A-4	4.35	0.50	3950	368	312	2.63	10	0.30	19.00	0	0	28	523	3
A-6	4.10	0.47	4702	297	281	2.62	8	0.29	18.74	0	0	21	522	5
MEAN	2.95	0.24	475	296	294	1.76	27	0.33	16.98	15	6	44	655	30
S.D.	1.11	0.12	342	128	120	1.08	33	0.09	2.99	9	13	27	284	32

caused by the existence of the Kawayama mine, in which Zn was one of the most important products (about 1.0wt.% Zn in raw ore). However, the influence of the mine should be considered together with the mobility (easiness of release or adsorption) of the elements which

will be discussed later based on correlation coefficients of Zn against the other elements.

Examinations of Co, Cu and Pb distributions strongly suggest that these elements sensitively reflect the local enrichments of these ions. For example, the cause of high Co content between

Fig. 4. Schematic representation of K content of mica minerals along the Nishiki river. The length of the thick lines represent K contents.

A₃ and B (Co contents of NR-23, -24, -22, -21 and ND-2 are 22, 27, 32, 27 and 39 ppm, respectively) will probably be ascribed to the local enrichment since the Co content of biotite in the parent granite is very low. The high Pb contents between B and D are ascribed also to the same cause. The cause of such local enrichment of certain elements is not sure at the present stage, since no special hydrothermal activities are found in these subdistricts. Human activities, such as small factories can also be one of the causes.

Correlation coefficient between two elements were calculated with 32 data numbered in Table 1 and the results are shown in Table 2. These 32 samples are collected along A₁-B-C-D-E (Fig. 1) together with those of the parent granite, and all of these may probably have serial genetical relations with each other. The

same coefficients were also calculated with 24 samples which are restricted to the river sands along the same line and the results are shown in Table 3. In the case of 32 samples, the significance level of the coefficient is statistically recognizable above 0.325 with 5% risk and above 0.418 with 1% risk (Fisher, 1963). Therefore, it can be safely said that two elements have surely certain correlations when the values exceed 0.50. In Table 2, the most intimate correlations are found between K-Rb (0.82), Mg-Co (0.93), Mn-Fe (0.84) and Fe-Zn (0.86). The first pair, K-Rb, shows that the both elements are released from or introduced to the interlayer position of biotite structure together. This fact has been reasonably accepted since the intimate geochemical relations between Rb and K were pointed out already by Mason (1966). Rb forms no minerals of its own except in few

Fig. 5. Schematic representation of Zn content of mica minerals along the Nishiki river.

Table 2. Correlation coefficients between two elements, calculated on the numbered 32 samples in Table 1 (see text)

	K	Na	Ca	Rb	Li	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zu	Pb
K	1.00													
Na	-0.11	1.00												
Ca	0.18	-0.15	1.00											
Rb	0.82	-0.02	-0.04	1.00										
Li	-0.20	0.38	-0.28	0.23	1.00									
Mg	0.82	-0.11	0.46	0.58	-0.34	1.00								
Cr	0.34	0.05	0.50	0.19	-0.50	0.57	1.00							
Mn	-0.58	0.41	-0.13	-0.56	0.33	-0.51	-0.38	1.00						
Fe	-0.60	0.42	-0.17	-0.48	0.43	-0.56	-0.52	0.84	1.00					
Co	0.75	0.00	0.38	0.61	-0.22	0.93	0.62	-0.52	-0.58	1.00				
Ni	-0.00	0.13	0.11	-0.07	-0.36	0.22	0.73	-0.25	-0.39	0.38	1.00			
Cu	-0.06	0.27	-0.06	-0.02	0.37	-0.13	-0.21	0.42	0.13	-0.09	-0.21	1.00		
Zn	-0.70	0.46	-0.34	-0.46	0.56	-0.72	-0.60	0.71	0.86	-0.68	-0.35	0.26	1.00	
Pb	-0.69	0.18	-0.06	-0.61	0.33	-0.77	-0.45	0.61	0.60	-0.71	-0.24	0.38	0.71	1.00

cases and, in igneous rocks, it is present in mica minerals (mainly biotite) and potash feldspar. After Mason (1966), K is the only major element which can be replaced by Rb at the crys-

tallization stage of minerals. The present results suggest that Rb behaves in association with K during the decomposition or alteration process of biotite. The coefficient increases to 0.87

Table 3. Correlation coefficients between two elements, calculated on the 24 samples (Nos. 1-24 in Table 1) (see text)

	K	Na	Ca	Rb	Li	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
K	1.00													
Na	-0.17	1.00												
Ca	-0.07	-0.45	1.00											
Rb	0.87	-0.03	-0.27	1.00										
Li	-0.39	0.52	-0.39	0.01	1.00									
Mg	0.92	-0.19	0.03	0.75	-0.48	1.00								
Cr	0.64	0.10	-0.08	0.42	-0.50	0.66	1.00							
Mn	-0.76	0.49	-0.01	-0.74	0.37	-0.71	-0.33	1.00						
Fe	-0.80	0.53	-0.08	-0.63	0.60	-0.75	-0.57	0.86	1.00					
Co	0.86	-0.06	-0.16	0.77	-0.33	0.91	0.72	-0.65	-0.71	1.00				
Ni	0.13	0.30	-0.14	0.03	-0.24	0.19	0.75	0.08	-0.15	0.40	1.00			
Cu	-0.15	0.30	0.16	-0.20	0.18	-0.18	-0.05	0.50	0.24	-0.18	0.04	1.00		
Zn	-0.79	0.53	-0.13	-0.58	0.67	-0.78	-0.63	0.73	0.91	-0.71	-0.18	0.22	1.00	
Pb	-0.86	0.14	0.15	-0.79	0.36	-0.94	-0.58	0.71	0.67	-0.89	-0.19	0.35	0.72	1.00

when samples are restricted to the river sands (see, Table 3). The other interlayer cations such as Na and Ca have very low coefficients to the other elements even to K and Rb. This suggests that the two elements are introduced or released from biotite structure independently as far as the correlation coefficients are concerned. The rest three pairs (Mg-Co, Mn-Fe, Fe-Zn) are considered to be the interrelations among the octahedral cations. These elements behave in association with each other, since the values are positive. Special attention should be paid to the high positive value of Fe-Zn combination. These two elements have almost the same coefficients to the other elements, i.e., the both elements have high negative values to the other interlayer cations, especially to K (Fe-K=-0.60, and Zn-K=-0.70), which means that when K is released from the structure, Fe and Zn are introduced to the structure. These high negative values against K indicate that a part of Fe and Zn occupy the interlayer position replacing K. This can happen in the case of the mineral vermiculite whose formula is represented as

where E is exchangeable cations (Sudo, 1974). The composition, charge relations and cation exchange capacity of vermiculite can be interpreted as replacement of K by some bivalent cations (Foster, 1963; Nagasawa, 1972). Therefore, under the condition of high Zn content of river water, Zn content of the mineral (biotite +

vermiculite) may easily increase replacing the interlayer cations as well as the octahedral cations. Fe and Zn exhibit the same tendencies against the possible octahedral cations, i.e., negative values to Mg, Cr and Co and high positive values to Li, Mn and Pb. These correlation values indicate that the two elements are released from the biotite (or vermiculite) structure together with Li, Mn and Pb but are replaced by Mg with Cr and Co whose ionic radii are almost equal to those of Fe²⁺ and Zn²⁺. It may be also concluded that Pb replaces partly the interlayer cations, especially K and Rb, since Pb has negative correlation coefficients against the two elements, and Pb²⁺ has a relatively large ionic radius compared with those of octahedral cations. In natural silicates, Pb (whose ionic radius is 1.2 Å) displays diadochic substitution for K (1.33 Å) (Ringwood, 1955). However, the greater electronegativity of Pb (1.8) compared with K (0.8) decreases the amount of the substitution (Mason, 1966; Ringwood, 1955). These factors seem to be valid even in natural aqueous environments. The highest negative correlation is found between Pb and Mg (-0.76 in Table 2 and -0.91 in Table 3). Moreover, the two elements show reverse correlations to other elements. For example, Pb has high negative values against K, Rb and Co whereas those of Mg are positive. The satisfactory explanation for the intimate correlations between the two elements remains to be solved.

Fig. 6. Multiple correlations among the possible octahedral cations (A and B) and the interlayer cations (C).

To be noted is that the coefficient between the two representative octahedral cations of biotite, Fe and Mg, is negative. Although the explanations of high negative value of Fe-K and high positive value of Mg-K are not clear, the fact may suggest that the vermiculitization process is controlled partly by the Fe/Mg ratio of the initial biotite, i.e., the higher the ratio the larger the K release resulting in further alteration to vermiculite. These correlation coefficients described above increase clearly when samples are restricted to the river sands (Table 3).

Multiple correlations between the analyzed elements should be also examined and for this purpose, the data of the numbered 32 samples in Table 1 were used. For the calculations, weight percent was converted to ppm and all the measured units were unified. Figure 6-A shows Zn and Li ratios among the minor elements of the octahedral cations. As seen in the figure, Zn and Li show reverse correlation with each other, i.e., the loss or gain of Zn is compensated by Li and vice versa. This relation clearly indicates that Li occupies the octahedral position. Correlations between the major octahedral cations, Fe, Mg and Mn, are shown in Fig. 6-B. Among these elements, Fe and Mg correlate well with each other and the Mn ratio is almost constant in the range between 0.01 and 0.03. The results clearly indicate that Fe in biotite is substituted by Mg. Multiple correlations among the possible interlayer cations are shown in Fig. 6-C. As seen in the figure, K and Na are well correlated with each other. The variation tendency of Ca is almost similar to that of Na. These intimate relations were not found by the examinations of correlation coefficients between two elements. The Rb contents are relatively small and the ratio between the interlayer cations is almost constant in the range between 0.004 and 0.016.

CONCLUSIONS

Metal contents of altered biotite collected along the Nishiki river, southwest Japan were measured and the relation between the metal contents and the geology of the district and

correlation coefficients were examined. Biotite in the river sands are derived from the granitic rocks developed in the district, and the metal contents of biotite in the river sands show, in general, intimate relations to those of biotite in the parent granite. However, no special relation between the geology and the metal content of biotite is found during the transportation in the river water. Partial alteration of biotite to vermiculite with small amounts of vermiculite-chlorite interstratified minerals is commonly observed in rivers and even in the parent granite.

Concentrations of the most representative interlayer cation, K, depends on that of biotite in the parent granite and the loss or gain of K is intimately related to the alteration of the mineral. Among the interlayer cations, K correlates well with Na and Ca and Rb fraction is almost constant.

Characteristics of the possible octahedral cations can be summarized as follows: Substitution of Fe by Mg is commonly observed. Among the minor elements, Cu, Zn and Pb contents vary locally and the local enrichments of these ions are caused probably by some human activities. Examinations of the correlation coefficients between any two elements suggest that a part of Fe and Zn is contained in the interlayer position.

In conclusion, biotite in the district is commonly altered to vermiculite and vermiculite-chlorite interstratified minerals to some extent keeping the morphology of biotite even in the parent granite. Moreover, each granite has different rate or different extent of vermiculitization. The main variation of major elements in these altered biotite can be explained as the results of the alteration and decomposition. In the river sands, grain size of biotite becomes gradually smaller from the upper to the lower reaches, but the alteration process exhibits no further progress. However, minor element contents of both interlayer and octahedral cations change complicatedly depending on the local environments.

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