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Distribution and Chemical Behavior of 21 Elements in River Water in the Yakushima Island

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The concentrations of 21 elements dissolved in the river water collected from around the Yakushima Island were determined by a neutron activation analysis (NAA). From the analytical results, the distribution and chemical behavior of each element in the water were discussed. The chemical composition of the river water was nearly uniform all around the island, and the concentration of each element determined in this work was extremely close to the geochemical background value of river water, since our experimental area had scarcely any pollution. Among the 21 elements chlorine, sodium, and magnesium were mainly supplied into the river water from the ocean, while the others were chiefly driven from the rocks and their efflorescences in the drainage basin. The enrichment factors for the granitic earth crust (F_E-value) were very close to 1 for calcium, strontium, and zinc, while those of selenium, arsenic, tungsten, and antimony were much higher than 1. For the elements such as aluminium, iron, manganese, *etc.*, on the other hand, the F_E-values were very low. These differences in the F_E-values among the elements correspond to differences in their solubilities in the water.

The determination of multi-element concentrations in natural waters is of great importance to substantiate numerous theories on the geochemical migration of the chemical species on the earth surface. However, few articles have dealt with trace element concentrations in river water until recent years,[1-3] for the reason that the analytical methods for the determination of trace elements in the concentration less than part per billion (ppb) were generally quite complicated. More recent developments in instrumental neutron activation analysis (INAA) have facilitated the determination of multi-elements including trace elements. Using INAA, those concentrations in river water have been determined by many workers.[4-11] But no one has mentioned those in a natural freshwater which is perfectly free from pollutions by anthropogeneous sources, even though the analysis of such unpolluted water is very useful to evaluate the geochemical background value of natural water. In a previous paper,[12] it has been reported that the trace element concentrations in the river water collected from the Mikura Island were very close to a geochemical background value, since its basin was virtually unpolluted.

The Yakushima Island, one of the Nansei Islands, lies about 60 km south of Sata Point, the southernmost part of Kyushu, as shown in Fig. 1. It is supposed that the basin in the Island has scarcely any pollution as in the case of Mikura Island, for the reason that our experimental area is thinly populated and is far apart from any big town or industrial area. Furthermore, the streams in the Island flow with a rapid current throughout the year because of its steep topography and abundant rainfall.

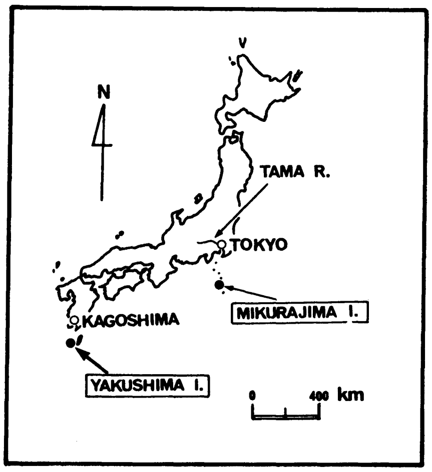

Fig. 1. Locality of the Yakushima Island.

In order to evaluate geochemical background values of river water, the concentrations of 21 elements in the water samples collected from 9 sites in the Island were determined using NAA.

Meanwhile, several workers[13-17] have reported on the chemical species of various elements dissolved in natural water and their solubilities. However, there is also no paper dealing with those of trace elements in unpolluted river water.

In this paper, therefore, the solubilities of trace elements in the river water are discussed; the relation between the enrichment factors for the granitic earth crust of those elements and their ionic potentials is emphasized.

Experimental

Water Sample. The Yakushima Island is composed of three geologic units, the Micocene Yakushima Granite, the Paleogene part of the Shimanto Group and the Quaternary deposits.[18,19] The Miocene Yakushima Granite is distributed most widely in the Island, especially in its basin, as can be seen in Fig. 2.

The river water samples were collected in December 1979 at nine sites in the basin of the Island. All the sampling sites are shown in Fig. 2.

The water samples were filtered within a few hours after the sampling, using a Type HA millipore filter with diameter 142 mm and pore size 0.45 μm. After the filtration, the samples were transferred to a 5-liter polyethylene bottle which was throughly washed with 10% nitric acid, followed by redistilled water, to remove trace element contaminations, and then acidified immediately with 30 ml of nitric acid (Super Special Grade) in order to avoid any adsorption of trace elements on the wall of the bottle.

For the analysis of chlorine, on the other hand, another 1

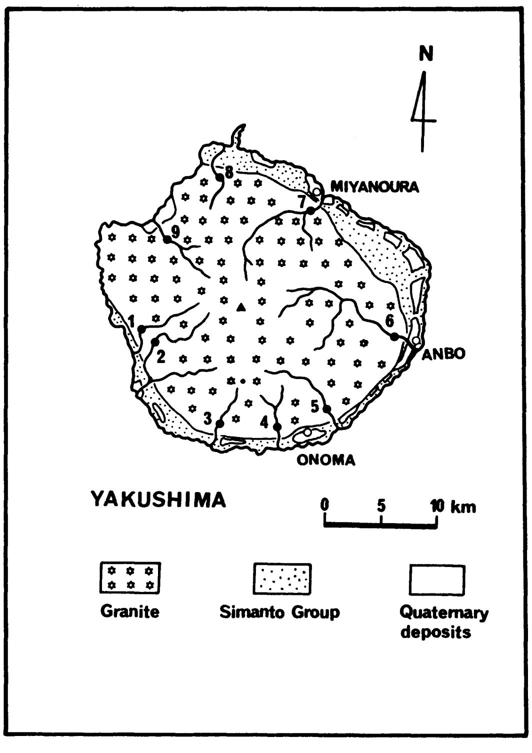

Fig. 2. Geological map of the Yakushima Island showing the sampling sites.

liter of the water sample was taken in another polyethylene bottle without the filtration and acidification.

Preparation of Irradiation Samples. For the NAA in this report, two kinds of irradiation samples, that is an evaporated residue sample and an iron(III) hydroxide coprecipitated one, were prepared from each water sample, according to the process reported in our previous papers.[5,8,20]

Four liters of the water sample were concentrated to 100 ml using a rotary evaporator. The concentrated water sample was then divided into two 50 ml portions.

One was dried on a Pyrex glass dish under an infrared lamp until the weight was constant. The residue was weighed and transferred into a polyethylene bag for neutron irradiation, and then heat-sealed.

The other was diluted with 100 ml of redistilled water, and then boiled for 30 min on a hot-plate after adding 0.5 ml of iron (III) chloride solution (Fe^{3+}: 10 mg/ml) and adjusting to pH 6 with aqueous ammonia. The iron (III) hydroxide precipitate was gathered on a piece of No. 5A filter paper with 5.5 cm in diameter and then rinsed with redistilled water ten times or more. After drying, the precipitate was transferred into another polyethylene bag together with the filter paper, and heat-sealed.

Irradiation and Gamma-counting. The sample and reference standard were encapsulated in a polyethylene capsule for all irradiations. The irradiation was performed by the TRIGA-Mark II Reactor of Rikkyo University, with a thermal neutron flux of 1.5×10^{12} n/cm^2 s. The gamma-spectrometer consists of a Ge(Li) coaxial detector of about 30 cm^3, with 2% efficiency and 2.8 keV resolution, and a 2048 and 4096 channel pulse height analyzer.

The evaporated residue sample was first irradiated for 1 minute to determine the elements induced the short-life nuclides such as Al(^{28}Al), Ca(^{49}Ca), Mg(^{27}Mg), Mn(^{56}Mn), Na(^{24}Na), and V(^{52}V), and these radioactivities were measured for 100 s by the spectrometer. One month later, the same sample was irradiated once more for 12 h to determine the elements induced the long-life nuclides such as Co(^{60}Co), Cr(^{51}Cr), Cs(^{134}Cs), Fe(^{59}Fe), Rb(^{86}Rb), Sb(^{124}Sb), Sc(^{46}Sc), Se(^{75}Se), Sr(^{85}Sr), and Zn(^{65}Zn). The measurement of these long-life activities were carried out for 50000 s after a cooling time of 2—4 weeks to reduce the short or medium-life nuclides.

The iron (III) hydroxide coprecipitate sample, on the other hand, was also irradiated for 12 h to determine the elements induced the medium-life nuclides such as As(^{76}As), La(^{140}La), Sm(^{153}Sm), and W(^{187}W), and after the cooling time of 1 d, these activities were measured for 1000 s.

Analysis of Chlorine. The concentration of chlorine in the river water samples was measured by means of Mohr's method.

Results and Discussion

The concentrations of 20 elements could be determined from the two irradiation samples by NAA. The recovery of several elements, such as arsenic, tungsten, *etc.* in water attendant upon the procedure of iron(III) hydroxide coprecipitation has been reported in the previous papers.[5,20,21]

In Tables 1—3, the concentrations of 21 elements determined in the river water collected from the Yakushima Island are listed, together with the statistical errors based on the gamma-counting.

These tables show that extraordinarily high concen-

TABLE 1. CONCENTRATIONS OF MAJOR ELEMENTS IN THE RIVER WATER COLLECTED FROM YAKUSHIMA ISLAND (units : ppm)

Sample No.	*WT*[a)] °C	pH	Conductivity μΩ^{-1} cm^{-1}	ER[b)]	Cl	Na	Mg	Ca
1	10.0	7.4	28	42.5	7.9	5.0 ± 0.04	0.44 ± 0.11	1.1 ± 0.1
2	9.6	7.3	20	33.6	6.6	3.9 ± 0.04	0.34 ± 0.12	0.74 ± 0.08
3	11.4	7.0	23	38.9	7.2	5.0 ± 0.05	0.45 ± 0.11	0.96 ± 0.09
4	12.5	6.6	22	30.8	6.2	4.0 ± 0.04	0.51 ± 0.14	0.57 ± 0.08
5	9.5	6.6	15	26.2	4.5	2.8 ± 0.03	0.22 ± 0.10	0.42 ± 0.06
6	12.9	6.7	27	39.5	6.7	4.7 ± 0.05	0.41 ± 0.15	1.0 ± 0.1
7	11.3	6.6	23	34.7	7.0	3.8 ± 0.04	0.34 ± 0.11	0.59 ± 0.08
8	14.3	7.0	44	59.1	12.9	7.2 ± 0.05	0.99 ± 0.16	1.1 ± 0.1
9	11.7	7.1	32	46.0	8.3	5.0 ± 0.04	0.70 ± 0.12	1.2 ± 0.1
Average	11.5	6.9	26	39.0	7.5	4.6 ± 0.04	0.49 ± 0.12	0.85 ± 0.09

a) Water temperature. b) Amount of evaporated residue.

Table 2. Concentrations of minor elements in the river water collected from Yakushima Island (units : ppb)

Sample No.	Al	Sr	Fe	Zn	Rb	Mn	As	V
1	68 ± 1	13 ± 0.8	4.5 ± 1.1	1.5 ± 0.2	0.94 ± 0.06	0.36 ± 0.30	0.28 ± 0.02	0.11 ± 0.03
2	58 ± 2	13 ± 0.8	2.6 ± 1.0	1.0 ± 0.2	0.56 ± 0.06	0.77 ± 0.28	0.15 ± 0.02	0.04 ± 0.04
3	80 ± 1	9.0 ± 1.0	7.3 ± 1.2	0.7 ± 0.2	0.90 ± 0.07	0.33 ± 0.30	0.29 ± 0.02	0.10 ± 0.04
4	70 ± 2	6.2 ± 0.7	1.8 ± 1.2	1.7 ± 0.2	0.78 ± 0.06	0.54 ± 0.31	0.08 ± 0.01	0.05 ± 0.05
5	65 ± 1	6.7 ± 0.9	ND	1.1 ± 0.2	0.47 ± 0.06	0.31 ± 0.25	0.05 ± 0.01	0.02 ± 0.03
6	52 ± 2	12 ± 1	5.9 ± 1.1	1.4 ± 0.1	1.3 ± 0.1	1.2 ± 0.4	1.4 ± 0.1[a]	0.07 ± 0.05
7	59 ± 1	9.2 ± 0.7	2.8 ± 0.5	0.9 ± 0.1	0.84 ± 0.07	0.41 ± 0.27	0.42 ± 0.02	0.02 ± 0.03
8	68 ± 2	17 ± 0.8	3.4 ± 1.3	0.7 ± 0.1	1.3 ± 0.1	0.86 ± 0.37	0 20 ± 0.03	0.08 ± 0.05
9	65 ± 1	17 ± 1	110 ± 3[a]	1.3 ± 0.2	1.1 ± 0.2	88 ± 0.8[a]	1.8 ± 0.04[a]	0.09 ± 0.04
Average	65 ± 1	12 ± 0.8	4.0 ± 1.2	1.1 ± 0.2	0.91 ± 0.09	0.60 ± 0.31	0.21 ± 0.02	0.06 ± 0.04

a) These abnormal values are not included in the average values.

Table 3. Concentrations of trace elements in the river water collected from Yakushima Island (unit : ppt)

Sample No.	Cs	Cr	Se	La	W	Sb	Co	Sm	Sc
1	29 ± 2	ND	23 ± 5	28 ± 4	12 ± 3	10 ± 2	10 ± 1	7.4 ± 0.3	5.9 ± 0.2
2	29 ± 1	ND	26 ± 8	29 ± 3	8 ± 4	8 ± 1	23 ± 1	7.5 ± 0.3	5.8 ± 0.2
3	64 ± 2	46 ± 20	23 ± 8	23 ± 4	170 ± 5[a]	17 ± 2	6.4 ± 0.8	8.1 ± 0.4	10 ± 0.2
4	58 ± 2	ND	10 ± 6	21 ± 3	28 ± 4	10 ± 1	8.4 ± 0.9	6.0 ± 0.3	6.9 ± 0.2
5	51 ± 2	ND	23 ± 6	23 ± 3	19 ± 3	9 ± 2	6.0 ± 0.9	7.2 ± 0.3	6.6 ± 0.2
6	100 ± 2	ND	31 ± 5	ND	820 ± 10[a]	17 ± 2	13 ± 1	3.1 ± 0.4	3.1 ± 0.2
7	44 ± 2	ND	27 ± 5	18 ± 3	27 ± 5	11 ± 1	9.0 ± 0.8	5.2 ± 0.3	4.8 ± 0.2
8	48 ± 2	40 ± 20	69 ± 7	ND	25 ± 6	3 ± 1	13 ± 1	2.9 ± 0.4	3.6 ± 0.2
9	74 ± 3	ND	34 ± 8	39 ± 4	ND	29 ± 2	170 ± 2[a]	16 ± 0.5	7.6 ± 0.3
Average	55 ± 2	43 ± 20	30 ± 6	26 ± 3	20 ± 4	13 ± 2	11 ± 1	7.0 ± 0.4	6.0 ± 0.2

a) These abnormal values are not included in the average values.

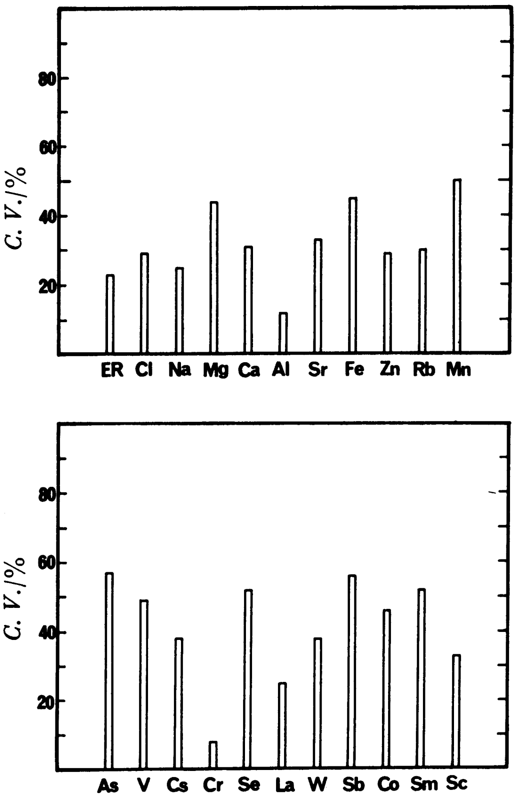

Fig. 3. The coefficients of variation of ER and 21 elements among the 9 sampling sites.

trations were given for heavy metal elements such as iron, manganese, arsenic, and cobalt at sampling site No. 9 (Nagata River), and high concentration of tungsten was found at the No. 3 (Yukawa River) and No. 6 (Anbo River). Utilizing the analytical results, but without these extraordinary values, the coefficients of variation (*C.V.*) were evaluated for 21 elements among all the sampling sites, by the next equation; the results are illustrated in Fig. 3.

$$\sigma = \sqrt{\sum(x_i - \bar{x})^2/n} \qquad (1)$$
$$C.V.(\%) = \sigma/\bar{x}$$

From Fig. 3, it was clarified that the coefficients of variation were less than 50% for almost all elements; those for the elements Cl, Na, Ca, Al, Sr, Zn, Rb, Cr, La, and Sc were less than 30%. These values are generally lower than those in the Tama River[5] and the Mikura Island.[12] Consequently, it can be said that the concentrations of almost all elements in the river water are nearly uniform all over the Island.

The basin in the Island had scarcely any pollution, as mentioned above, so that the values in the concentrations of various elements presented in Tables 1—3 are extremely close to the geochemical background value of the Yakushima's river water.

It is of interest to compare the concentrations of the elements in the Island water with those in river water collected from other districts, such as the drainage basin of the Tama River[5] and the Mikura Island,[12] so

TABLE 4. C_r-VALUES[a)] FOR 21 ELEMENTS IN THE RIVER WATER COLLECTED FROM YAKUSHIMA ISLAND, MIKURAJIMA ISLAND,[12)] AND THE TAMA RIVER[5)]

	Yakushima Island	Mikurajima Island	Tama River
ER	1000	1000	1000
Cl	192	225	14
Na	118	117	40
Ca	22	28	131
Mg	13	17	25
Al	1.7	1.2	1.3
Sr	0.31	0.19	0.75
Fe	0.10	0.12	0.77
Zn	0.028	0.051	0.11
Rb	0.023	0.0071	0.011
Mn	0.015	0.017	0.023
As	0.0054	0.0025	0.035
V	0.0016	0.018	0.021
Cs	0.0014	0.00017	0.00052
Cr	0.0011	0.00056	0.0010
Se	0.00077	—	0.0013
La	0.00067	0.00032	0.0015
W	0.00051	0.00030	0.00041
Sb	0.00033	0.00031	0.0029
Co	0.00028	0.00031	0.00087
Sm	0.00018	0.00010	0.00031
Sc	0.00015	0.00021	—

a) The values are given in milligrams of each element per gram of the amount of evaporated residue (ER).

as to characterize the water quality of the Island. One has to keep in mind, however, that it is unsuitable to compare immediately each element concentration expressed in ppm, ppb and ppt because of their different sampling periods, geological features, *etc.* For this purpose, a relative concentration (C_r-value), using the average values, is evaluated by the next equation; this equation is given in the milligrams quantity of each element per the gram amount of evaporated residue (ER):

$$C_r = \frac{C_i}{C_{ER}} \times 1000, \tag{2}$$

where, C_i and C_{ER} mean the average concentrations of an element i and of the evaporated residue. The C_r-values for various elements in the three different districts are shown in Table 4. From Table 4, the following conclusions are drawn: No large difference in the C_r-values for most elements can be found between the two Islands, although there are some exceptions: the Yakushima Island water is more enriched in rubidium and caesium, and is deficient in vanadium in comparison with those in the Mikura Island water. The disagreement in the C_r-values for these three elements seems to be arise from the differences of their geological features, which is considered in the following way.

The Yakushima Island is mainly composed of the Miocene Yakushima Granite, as previous mentioned, while the Mikura Island is made up by the volcaniclastic rocks of Basalt and Andesite.[22)] The concentration ratios of the former to the latter for rubidium, caesium and vanadium are 4.5, 9.2, and 0.11 respectively, provided the analytical values for two geochemical reference rock samples, JG-1 granodiorite and JB-1 basalt,[23)] are utilized for the two different kind of rocks distributed in the two Islands. These values are close to the same ratios in the river water, 3.2, 8.2, and 0.089 respectively. Consequently, it could be said that the difference of the geological features has a large influence on the concentrations of these elements in the river water.

In the comparison with the amounts in the Tama River water, on the other hand, the Yakushima Island water is more enriched in chlorine, sodium, rubidium and caesium by 2—10 times. The high C_r-values for chlorine and sodium in the Island water can be explained by the assumption that both elements are easily supplied from the ocean; this will be discussed later. The highr C_r-values for rubidium and caesium in the Island water indicate that these elements tend to be derived from the Miocene Yakushima Granite, which is distributed extensively in the Island, as stated above.

Except these four elements, however, the C_r-values for most elements in the Island water are lower than those of the Tama River water by a factor of 2—10. This tendency is evident for the heavy metal elements such as iron, zinc, arsenic, vanadium, selenium, antimony, and cobalt.

It is well known that the difference of origin of the elements in rain water may be indicated by an enrichment factor for the earth's crust or the ocean, F_E or F_O.[24)] The method is applicable not only to rain water, but also to the unpolluted river water.

$$F_E = \frac{C_{Ca}(\text{earth})}{C_{Ca}(\text{sample})} \times \frac{C_i(\text{sample})}{C_i(\text{earth})} \tag{3}$$

$$F_O = \frac{C_{Cl}(\text{ocean})}{C_{Cl}(\text{sample})} \times \frac{C_i(\text{sample})}{C_i(\text{ocean})} \tag{4}$$

Here, C_{Ca}, C_{Cl}, and C_i mean the concentrations of calcium, chlorine and some element i in the earth's crust, the ocean and the water sample, respectively. Calcium is chosen as the reference element for the F_E-values instead of the usually employed sodium, since at the Island sodium is mainly supplied from the ocean. Meanwhile, chlorine is used as the reference element for the F_O-values, because its main source is known to be the ocean.

In Eq. 3, the analytical values of various elements for JG-1[23)] were employed in the place of those for the earth's crust, because the trace element concentrations of the Yakushima Granite have not been determined. For tungsten, however, the analytical value for international geochemical reference rock sample USGS G-1[25)] was utilized, since the value for JG-1 has not been reported.

In Table 5, the enrichment factors (F_E- and F_O-value) are listed for 21 elements. From Table 5, it is recognized that the F_O-values are close to 1 for chlorine, sodium, and magnesium, and those for almost all of the elements except for above three elements are very high. This fact indicates that the origin of chlorine, sodium, and magnesium in the river water could be presumed to be the ocean, but for all of the elements other than chlorine, sodium, and magnesium their main sources should be

Table 5. Average enrichment factors F_E and F_O for various elements

	F_E	F_O
Cl	2400	1.0
Se	210	830
As	31	260
W	5.6	850
Na	3.6	1.2
Sb	2.4	110
Mg	2.0	0.98
Sr	1.2	2.2
Ca	1.0	5.3
Zn	0.60	590
Cs	0.11	470
Rb	0.094	7.0
V	0.054	87
Sm	0.031	31000
Co	0.031	190
Mn	0.027	3900
La	0.024	20000
Al	0.018	170000
Sc	0.015	3900
Cr	0.015	560
Fe	0.0055	3000

assumed to be elsewhere. The river water in the Island is virtually free from the anthropogeneous sources. Furthermore, the influence by naturally occurring organic substances such as humic acids appeared to be negligibly small in our experimental area because of th rocky river bed and abundant flow. Therefore, most of the elements other than the above three elements in the river water are derived from the rocks and their efflorescences in the drainage basin.

The F_E-values are close to 1 for calcium, strontium, and zinc; those for chlorine, selenium, arsenic, tungsten, sodium, antimony, and magnesium are much higher than 1. For aluminium, iron, manganese, *etc.* the F_E-values vanishingly low, as can be seen in Table 5. Chlorine, sodium, and magnesium, showed high F_E-values; these originated from the ocean, as stated above.

It is known that in natural water the elements such as calcium, strontium, zinc, *etc.* are present as divalent cations, and the elements such as aluminium, iron, chromium, *etc.* tend to exist as trivalent species. On the other hand, the great portion (70—100%) of arsenic and antimony are present as pentavalent species such as AsO_4^{3-} and SbO_4^{3-}.[26,27] For selenium and tungsten, it is assumed, according to the example of Garrels and Christ,[13] that those elements exist as hexavalent species, although the chemical species of those elements dissolved in natural water are probably either SeO_3^{2-} and WO_3^{2-} or SeO_4^{2-} and WO_4^{2-}.[28,29]

The relation between the F_E-values for various elements and their chemical valencies is demonstrated by Fig. 4, which is a plot of the logarithm of the F_E-value *versus* an ionic potential that is given in the ratio of chemical valency of the element to its radius.[30] In Fig. 4, it can be considered that the ordinate is one kind of measure of solubility, while the abscissa means the tendency of the cation to bond with anions.

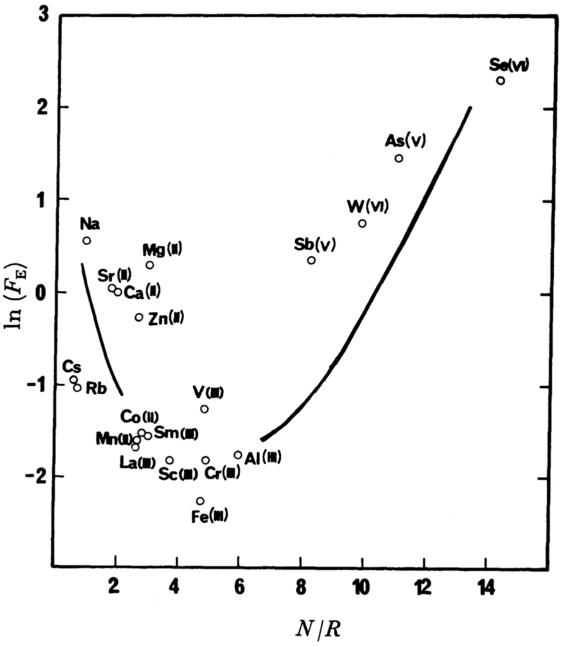

Fig. 4. Plot showing the relation between the logarithm of the enrichment factor (F_E-values) and the ionic potentials of cationic species. A parenthesized Roman numerals show chemical valency (N) of the elements easily formed under the natural conditions. Ionic radii (R) are employed from Shannon and Prewitte.[30]

The diagram shows the following general trends. The scattering pattern of each element in the diagram agrees with those reported by Garrels and Christ,[13] who have studied the behavior of various chemical species in sea water. The relatively high solubilities are found for the elements that form the divalent cations under the range of natural conditions, such as calcium, strontium, and zinc, while the elements that tend to form the trivalent ions such as aluminium, iron, chromium, scandium, *etc.* show very low solubilities. Such trivalent ions not only tend to interact with various anions to form soluble complexes, but also tend to form insoluble hydroxides or oxides in ordinary natural waters. It is well known that the transition elements such as iron, manganese, zinc, vanadium, chromium, cobalt, scandium, *etc.* are being held in the dissolved phase by complexation or chelation with dissolved organic substances in river water.[17,31,32] In our experimental area, however, it is supposed that these organic substances in the river water exist only in very small amounts, as stated above. Thus, the total solubilities for the elements which formed trivalent cations or for the transition elements are still held low in the Yakushima's water.

Zinc shows an exceptionally high solubility among the transition elements; it is extremely hard for zinc to be oxidized to trivalent cation, and easily dissolves in water as a divalent species such as $(Zn(H_2O)_6)^{2+}$.[33] The solubility of vanadium is slightly higher than those of the other transition elements, because a portion of vanadium exists as soluble pentavalent species such as $V_{10}O_{28}^{6-}$,[13] as in the case of arsenic and antimony.

On the other hand, for those elements that form small penta and hexavalent species, such as selenium, arsenic, tungsten, and antimony, the solubilities have very high values, presumably because they react with oxygen to form metal-oxygen anions because of their high ionic potentials, as shown in Fig. 4.

Conclusion

Using NAA method, it was possible to obtain some knowledge about the distribution and chemical behavior of various elements in the riv er water in th Yakushima Island.

The analyzed values for the various element concentrations offered in this paper were close to the geochemical background value of river water, because our experimental area was free from any pollution by anthropogeneous sources. Thus, their values will serve satisfactorily as reference data for the concentrations of the elements dissolved in most river water.

The relation between the F_E-values and ionic potentials showed that the solubilities were relatively high for the elements that form the divalent cations in ordinary natural water, while those for the elements that tend to form trivalent ions were very low. For the elements that easily form the small high valent species, the solubilities were given in very high values. The term solubility indicates not only the tendency of each element to be supplied into the river water from the rocks, but the difficulty of being remove from the river water as deposits.

The geological structure of the Island is rather simple, and the Island forms a kind of closed system, since it is an isolated island. Furthermore, the flow of the water in each river is abundant throughout the year. Therefore, it was supposed that a kind of equilibrium was set up between the rocks and water in the basin as for the behavior of various chemical species, such as the dissolution, precipitation, adsorption, *etc.* These reasons made it easy to study the chemical behavior of the elements in the water.

For a general understanding, however, it would be necessary to evaluate the element concentrations much more than determined in this work, and to substantiate exactly the chemical species for various elements, and also to complete studies conducted on natural freshwaters collected from various different districts.

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