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CHEMICAL COMPOPITION OF THE DRAINAGE FROM ASO WELDED TUFF —ON THE ŌNO RIVER—

By

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Abstract

One of the characteristics of river waters in Kyūshū island is high content of SiO_2. The author has investigated the variation of the chemical composition of the river waters with the difference of geological feature.

The results are as follows.

In the Ōno river system, the SiO_2 content of the drainage from Aso welded tuff area is 53.6 ppm (43.4% to the salinity), in tributaries which start from other igneous rocks and flow through Aso tuff it is 42.0 ppm (39.8% to the salinity), and in tributaries which start from argillaceous sedimentary rocks and flow through Aso welded tuff it is 24.8 ppm (26.6% to the salinity). In the Banjō river system, the whole of which basin is covered with argillaceous sedimentary rocks, the SiO_2 content is 12.9 ppm (25.7% to the sallinity). This fact indicates that the SiO_2 content in the water of the rivers varies with the geological feature of their reaches.

The SiO_2 content in the drainage of Aso welded tuff is in direct proportion to HCO_3 content. Therefore the dissolution of rocks is cuased by the water charged with carbon dioxide.

In Aso welded tuff area the Na content in river waters is out of proportion to Cl content. On the other hand, the quantity of $(Na+K)-Cl$ is in direct proportion to SiO_2 content. Accordingly, almost all the quantity of alkali metals in river waters comes from resolution of rocks at Aso welded tuff area. It is concluded that the alkali quantity which comes from rocks is 82% to the total quantity of alkali metals in river waters of Aso welded tuff, and argillaceous sedimentary rock area that percentage is 40.

1. Introduction

In comparing the chemical composition of the rivers in Japan with that of the average of the rivers in other countries, it can be said that the former contains more SiO_2, Na and Cl, and less salinity, Ca and CO_3 than the latter as are shown in Table 1. K. Seno (1961) attributes this to the difference of precipitation and evaporation. The average precipitation per year in Japan and that in the world are 1700 mm and 1000 mm respectively. Accordingly the salt content of the rain in Japan that makes the river waters is less. On the other hand, the moisty climate of Japan restains evaporation, which also makes the salt content in river water less.

Percentage of Na and Cl to the salinity in river water in Japan, 9.41 and 8.21, are larger than 5.79 and 5.68 of the world average respectively. We can attributes this to the geographical characteristic of Japan surrounded by the ocean which makes the supply of these contents by rain and dryfallouts easier than in other countries. Moreover, abundance of hot springs in this country is another reason for the increase of Na and Cl in the river water.

As far as Ca and CO_3, the contents in the river water in Japan are smaller than in other coutries. This can be attributed to the geological distribution peculiar to Japan. In Japan the sedimentary rock area is smaller than in other coutries, and more rivers are situated in the igneous rock area.

The average percentage of Ca and CO_3, the content to the salinity of 12 rivers in Japan which drainage from sedimentary rock area 22.6 (Ca) and 35.9 (CO_3) and that from igneous rock area is 8.8 (Ca) and 19.0 (CO_3) respectively. There is a sharp distinction in the content of these elements according to the properties of rocks and soil in the catchment area.

SiO_2 content varies with the geological feature. That is, the percentage of SiO_2 content to the salinity is 47.0 in river water from igneous rock area, and 14.3 in that from sedimentary rock area. Average content of SiO_2 in river waters in Japan is 26.8%. Even the value 14.3% of river water from sedimentary rock area in Japan is larger than the average value 11.7% of the world. This high content of SiO_2 is one of the characteristics of river water in Japan.

The river water in Kyūshū island generally has the similar composition to that in Japan. However, it has some differences as are shown in Table 1. One of them is more content of SiO_2. The average content of SiO_2 in river waters in Kyūshū island is 35 ppm, which is 33% to the salinity. This value is caused by the high content of SiO_2 in river waters from Aso welded tuff which is widly distributed in the central part of Kyūshū island. For example, the SiO_2 content of the Chikugo river, the Oita river and the Ono river are 42.7%, 42.6% and 43.4% respectively. And the SiO_2 content in river water in the Aira volcanic area in southern part of Kyūshū island is almost the same value as above, that value is presented by Ōnishi (1963). These volcanic areas are constituted with the igneous rocks of the last period of the Quaternary. These comparatively young rocks are easily weathered and release the SiO_2, resulting the great content of SiO_2 in the river waters in Kyūshū island.

In Kyūshū island, owing to the large dissolution of igneous rocks, the salt content in river water also becomes large. Average value of salinity in river water in Kyūshū island is 106 ppm, which is highest in Japan. For example, the above mentioned rivers, the Ōita and the Ōno have 125 ppm and 145 ppm (presented by J. Kobayashi, 1961) respectively, and these values are the higher classes among the rivers in Kyūshū island.

There are many hot springs in Kyūshū island, viz. Bepp, Kujū, Aso, Unzen and Kirishima spas. Therefore it is supposed that there is some Cl comes from these spas and rise its content in river water. The fact, however, is opposite; its content is less. The river water in Kyūshū island has 6.3 ppm Cl (5.9% to the salinity) and Na : Cl atomic ratio is 2.30 on an average. In volcanic hot springs, Na : Cl ratio is 0.95, so that these hot springs are not chief source of Cl supplied to river water. The ratio in rain is about 0.9. Accordingly the dissolved Na supplied to river water from igneous rocks is twice as large as quantity from precipitation in Kyūshū island. This high content of chemical components from igneous rocks makes Cl content in the river water less in ratio. Moreover the large precipitation in Kyūshū island in comparison with other districts like wise reduces the rate of Cl content.

Generally, rivers in Kyūshū island have some distinct features as mentioned above.

Scine July 1964 the author has been investigating the chemical composition of the Ōno river as a typical river which flows Aso welded tuff area, and found out some variations in chemical composition in the main stream and its tributaries with geological features of the basin. There is neither a hot spring nor a mineral spring is in the Ono basin, except Akagawa hot spring which is a

Table 1. Average composition of dissolved solids in river waters.

Constituent	Average of the World*	Average of Japan**	Average of Kyushu Island**
Na	5.79	9.41	8.96
K	2.12	1.68	2.00
Ca	20.39	12.50	10.54
Mg	3.41	2.70	3.16
Cl	5.68	8.21	5.90
SO_4	12.14	14.99	13.91
CO_3	35.15	21.60	21.07
SiO_2	11.67	26.84	32.98
Other Constituent	3.65	2.07	1.48
Total	100.00	100.00	100.00
Salinity (ppm)	146	71	106

* F. W. Clarke (1924)

** J. Kobayashi (1961)

gypsum hydrosullfide hot spring. It is situated at the upper reach of the tributary Inaba. There is no factory in the basin of the Ōno except at its mouth, and population density in the basin is low. Therefore the contamination by hot springs, mineral springs and waste water from factories and houses can be ignored.

In addition, the Banjo river which flows from Paleozoic argillaceous sedimentary rocks has been investigated.

This paper aims at reporting about the relation between chemical composition of the river water and the geological feature of the basin, comparing resolving of rocks in Aso welded tuff area with that in sedimentary rock area.

2 Field data

Geological feature of the Ōno river basin and the station locations at which water samples were obtained are shown in Fig. 1.

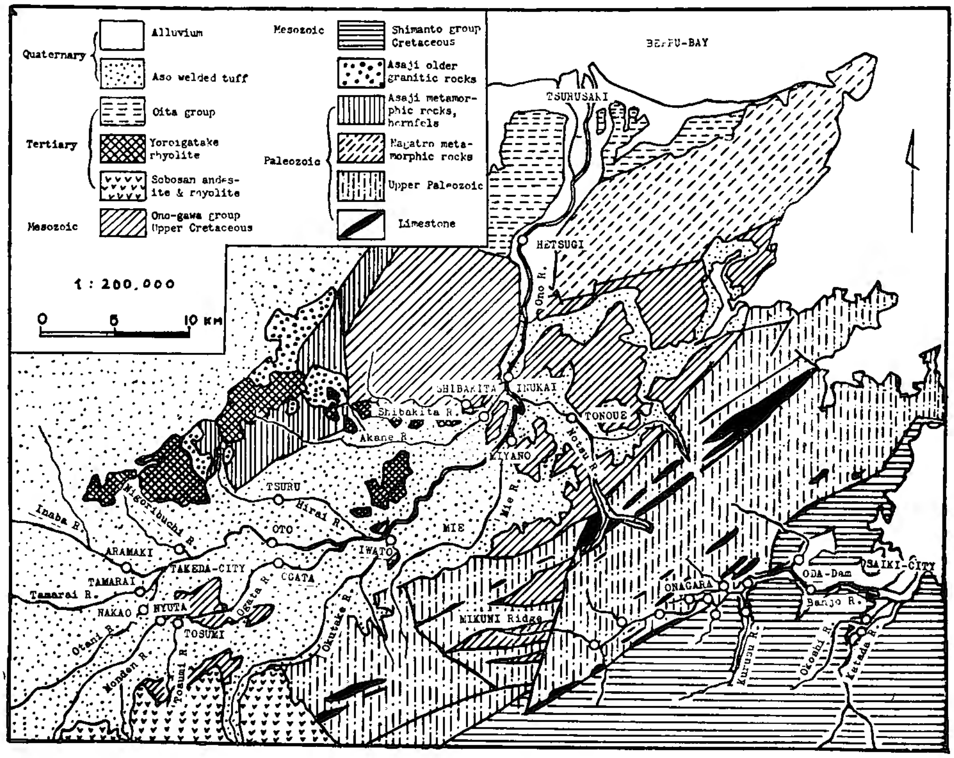

Fig. 1. Geological map of the basins of the Ōno and the Banjo. 16 station locations of the Ōno system and 13 station locations of the Banjo system at which water samples were obtained are shown.

Table 2. Chemical composition of river waters and spring waters.

Constituent	The Ōne River System										TAKEDA Spring		MIE Spring		The Banjo River System			
	A		B		C		D		E						"Argillaceous" (shale) water		"Shale with limestone" water	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Na	6.8	5.5	6.9	6.5	6.2	6.6	6.7	5.8	4.6	5.7	7.7	4.9	5.0	7.5	4.5	9.0	4.5	7.0
K	3.4	2.8	3.2	3.0	2.3	2.5	3.1	2.7	1.5	1.9	4.4	2.8	1.6	2.4	0.9	1.8	1.1	1.7
Ca	11.8	9.6	10.2	9.7	13.6	14.5	12.3	10.6	10.8	13.4	15.1	9.5	7.8	11.7	6.9	13.8	12.5	19.5
Mg	3.8	3.1	2.9	2.8	2.5	2.7	3.3	2.9	2.5	3.1	4.8	3.0	2.5	3.7	1.5	3.0	1.5	2.3
Cl	3.4	2.7	4.8	4.5	4.6	4.9	4.0	3.5	3.1	3.8	2.8	1.8	3.6	5.4	2.7	5.4	3.5	5.5
SO_4	10.1	8.2	9.7	9.2	11.1	11.9	11.4	9.9	18.5	22.9	9.8	6.2	8.5	12.7	5.7	11.4	5.8	9.0
CO_3	30.3	24.5	25.6	24.2	28.2	30.2	29.4	25.4	16.0	19.8	40.1	25.4	17.4	26.0	15.0	29.9	22.8	35.5
SiO_2	53.6	43.4	42.0	39.8	24.8	26.6	45.0	38.3	23.5	29.1	73.5	46.4	20.5	30.6	12.9	25.7	12.5	19.5
Other Constituent	0.3	0.2	0.3	0.3	0.1	0.1	0.4	0.3	0.2	0.3								
Salinity	123.5		105.6		93.4		115.6		80.7		158.2		66.9		50.1		64.2	

The Ōno River.

The sources of the Ōno river are Aso somma and Mt. Kujū. Tributaries of the Ōno, the Tamarai, the Inaba, the Nigoribuchi and the Ōtani join at Takeda-City and make the Ōno river, then flow northward to Beppu-Bay. Its length is 128.4 km and the catchment area is 1381 km^2.

Tributaries which flow into the Ōno from southern part of the basin are the Monden, the Tosumi, the Ogata, the Okutake and the Notsu, the lower reaches of them are the same Aso welded tuff, but the upper reaches are geologically different rocks. The Monden and the Tosumi flow from the Sobosan andesite and rhyolite zone (Miocene of Tertiary), and the Okutake, the Mie and the Notsu flow from the Paleozoic argillaceous sedimentary rock area.

Tributaries which flow into the Ōno from western part of the basin are the Hirai, the Akane and the Shibakita, among which the Hirai and the Akane flow from Yoroigatake rhyolite and Asaji metamorphic rocks which includes hornfels zone. But their main basins are also covered with the Aso welded tuff. The basin of Shibakita is formed of sedimentary rocks of the Upper Cretaceous called the Ōno-gawa group.

The locations at which water samples were obtained as follows: (from upper reaches downward) Nakao (the Ōtani), Tamarai (the Tamarai), Aramaki (the Inaba), Takeda (the Nigoribuchi), Nyuta (the Monden), Tosumi (the Tosumi), Ogata (the Ogata), Ōto (main stream), Tsuru (the Hirai), Iwato (the Okutake), Miyano (the Mie), Tonoue (the Notsu), Inukai (the Akane), Shibakita (the Shibakita), Inukai (main stream) and Hetsugi (main stream).

The Banjo River.

The Banjo river flows froms the Mikuni ridge then run eastward to Saiki Bay. Its length is 40 km. The upper basin of the river is composed of Paleozoic argillaceous sedimentary rocks, mainly argillaceous shale and limestone scattered, and the lower basin is Mesozonic Cretaceous Triassic sedimentary rocks called the Shimanto group.

The basin of the Katada and the Okoshi, which join into the Banjo at its mouth, are also covered with Shimanto group.

No water from hot springs nor mineral springs flows into the Banjo system except from the Onagara stalactite grotto at the middle reach. Waters from this grotto and other limestone area rich in calcium carbonate.

Water samples of this river were taken at 13 places. These places are shown in Fig. 1.

3 Results and discussion

3.1 Chemical Composition of Each River Water

Table 2 shows the average values of chemical composition of the waters of the Ōno river, the springs in Takeda and Mie, and the Banjo river respectively.

The values in columm A are the average composition of waters in the eight tributaries (the Ōtani, the Inaba, the Tamarai, the Nigoribuchi, the Monden, the Tosumi, the Ogata and the main stream at Ōto) which fow in the mountain distict and assemble near Takeda-City.

In the columm B, average values of three tributaries (the Hirai, the Mie and the Akane) are shown. These rivers flow at the middle reaches of the Ōno.

The values in columm C are average of the tributaries Notsu and Shibakita which flow sedimentary rock area.

In the columm D, average values of composition in the main stream at Hetsugi are shown. Hetsugi is the lowest location in the Ōno system; therefore the water at this place has synthetic composition of the Ōno.

Columm E shows the composition of the Okutake which flows from Sobosan andesite and Paleozoic argillaceous sedimentary rock area. Fe, Sn and Zn deposits are found at the upper reaches of the Okutake; therefore the contamination occurs by the pit water from these mines.

There are many springs near Takeda-City and southern part of Mie-Town, the former well out from Aso welded tuff and the latter from argillaceous sedimentary rocks. Average values of five springs at Takeda-City and two springs at Mie-Town are shown in Table 2.

For reference, Table 2 shows the average value of the composition of river waters of the Banjō. The river waters of the Banjō are divide into two groups by the geological feature, that is from the argillaceous sedimentary rock (shale) area and from the shale inserted with limestone area.

There are some differences of the contents of each component among the values presented in columm A, B and C as are shown in Table 2. These differences are chiefly caused by geological feature of the basin.

The drainage from Aso welded tuff has great salinity. In the Takeda spring water its value is maximum (158 ppm). The average value in river waters near Takeda-City (columm A) is 124 ppm and that near Mie-Town (columm B) is 106 ppm. On the other hand the values from sedimentary rocks are comparatively small. That is, the value of argillaceous sedimentary rock (shale) area of the Banjō is 50 ppm, that of shale with limestone area is 64 ppm and that in the Mie springs is 67 ppm. The value in columm C is comparatively high (93 ppm) since the lower reaches of these tributaries are covered with Aso welded tuff.

SiO_2 content is also varied with geological feature. In the Aso welded tuff area, the average content in the Takeda springs is highest (73.5 ppm) and is 46.4% to the salinity. In the river water from Aso welded tuff the SiO_2 content is over 40 ppm and 40~45% to the salinity on an average; on the other hand the river from sedimentary rock area has less SiO_2 content. For example, the river water of the Banjō from argillaceous sedimentary rocks with limestone area has 12.5 ppm of SiO_2 content and 19.5% to the salinity. And other Banjō river waters show 13~24 ppm of SiO_2 and 26~30% to the salinity. These values are much smaller than those of Aso welded tuff area.

In Aso welded tuff area, the river waters have higher SiO_2 content than the average of river waters in Kyūshū island, in which the SiO_2 percentage is 33.

The CO_3 content is 25% to the salinity of the water drained from Aso welded tuff and that from argillaceous sedimentary rocks (shale) is 30%. That from the argillaceous sedimentary rocks inserted with limestone area is 36%. These values at sedimentary rock area are moderate but the value at Aso welded tuff area is extremely high for the value at igneous rock area. This high content of CO_3 corresponds to the content of SiO_2; therefore it is found that the weathering and dissolution of Aso welded tuff is mainly caused by carbon dioxide in water.

The Cl and SO_4 content at argillaceous sedimentary rock (shale) area is larger than at Aso welded tuff area. The reason is considered as follows; the amount of dissolved components that come from the rocks is small and that from rain and dryfallouts is large. For, dissolution of rocks at argillaceous sedimentary rock area is not so much as at Aso welded tuff area.

The variation of Na content in river water corresponds to Cl, but K is reverse; therefore a great difference is found between Na : K atomic ratio in the river water from argillaceous sedimentary rock area and that from Aso welded tuff area. In the drainage from Aso welded tuff the ratio is 3, in that from argillaceous sedimentary rock area it is over 7, and in the tributaries of the Ōno which flow from sedimentary rock area it is approximately 5.

The Ca content is in direct proprtion to the CO_3 content as is shown in detail later on. The Ca content ratio at sedimentary rock area is larger than that at igneous rock area. However as to Mg content there is scarcely any differences by geological features; therefore the Mg : Ca atomic ratio is larger in the drainage from Aso welded tuff than that in the drainage from sedimentary rock area. The ratio in the former is 0.53 and in the latter is 0.30 on an average.

As for the CO_3 content only the tributary Okutake is different from ther rivers in the Ōno system. This difference is caused by the waste water from the mines at the upper reaches of the Okutake. This waste water causes the decrease of pH value of the river water (pH 4.4~5.0), and the decrease of CO_3 content cosequently. It also causes the predominant SO_4 content. But at Hetsugi no effect by this tributary is found because of the confluence of the tributalies Notsu and Shibakita which have opposite compositions to that of the Okutake.

3.2 Silica Content

Generally the dissolution of rocks is caused by carbon dioxide in ground water. According to K. Rankama (1949), the meteoric waters, i.e., those of atmospheric origin, contain carbon dioxide and small amounts of dissolved substances derived from the atmosphere. Upon entering the soil and rocks, they first incorporates soluble constituents, both inorganic and organic, from the soil. Additional carbon dioxide is also derived from humus and other organic substances, partly by the action of dissolved oxygen in the water. K. Rankama and Th. G. Sahama (1949) said, "Where there is abundant rainfall and much organic matter present in the soil, the ground water becomes notably charged with carbon dioxide. Therefore, in typical regions the amount of SiO_2 in the river waters becomes especially high". However the SiO_2 content in the river waters is not decided only by the CO_2 content of waters but also the properties of the adjacent rocks. In the Ōno river system, there are distinct differences in SiO_2 content among the Aso welded tuff area (last period of the Quaternary), argillaceous sedimentary rock area (Paleozoic) and sedimentary rock area called the Ono-gawa group (Upper Cretaceous).

Relation between HCO_3 and SiO_2 contents in each river is shown in Fig. 2. The data in Fig. 2 which are presented in various marks were obtained by analizing samples which were taken once a month.

As a representative river which flows Aso welded tuff area the Otani is shown in Fig. 2. Other rivers, the Tamarai, the Inaba, the Nigoribuchi, the Tosumi, the Monden and the Ogata have almost the same tendency in terms of these two components. All rivers near Takeda-City have the highest amount of SiO_2 in the Ōno system and their HCO_3 content is also high. In the water of these rivers HCO_3 content is in direct proportion to SiO_2 content, and HCO_3 : SiO_2 mole ratio is 1.1~1.3.

There are many springs near Takeda-City. These springs have typical composition of the ground water of Aso welded tuff area. By mixing these spring waters with surface water the rivers near Takeda-City are formed. Therefore the chemical composition of these river waters is similar to that of the spring waters. The composition of this spring waters is shown in Table

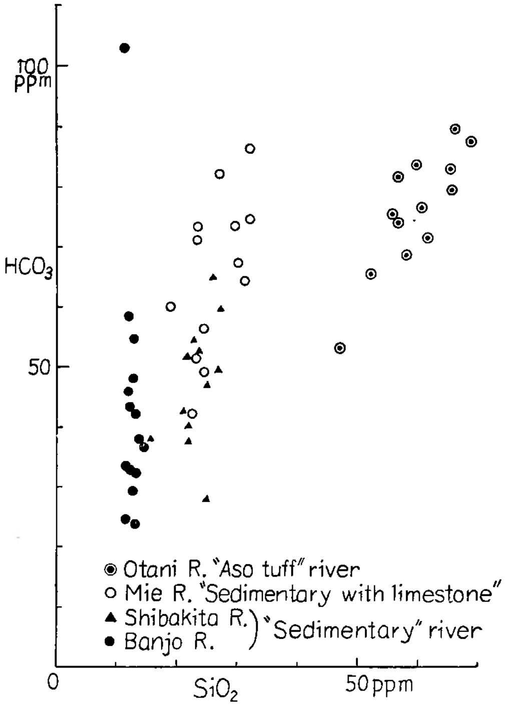

Fig. 2. Relation between HCO_3 and SiO_2 content in the river waters in Aso welded tuff area (the Otani river), in sedimentary rock area limestone scattered (tributary the Mie), in sedimentary rock area called Ono-gawa group (tributary the Shibakita) and in argillaceous sedimentary rock area (the Banjo river) respectively.

2. In the ground water near Takeda-City, $HCO_3 : SiO_2$ mole ratio is 1.09. This value is little smaller than that of the river waters near Takeda-City. The reason is considered as follows: when ground water pour into river, soluble silica in them is separate forming polymer and colloidal silica. In this district, the mole ratio of $HCO_3 : SiO_2$ of the Inaba is 0.90. This value is comparatively small. This is an effect of Akagawa hot spring and running water of Kuju plateau which has small content of HCO_3 and large content of SO_4.

Summary; in the river waters of Aso welded tuff area SiO_2 content is high (50~60 ppm), accordingly HCO_3 content is also high (50~70 ppm). The precentage of SiO_2 content to the salinity is 43.4 and that of HCO_3 is 24.5. Total is about 68. This shows the how largely Aso welded tuff is dissolved by the water charged with carbon dioxide.

On the other hand, there is no relation between HCO_3 and SiO_2 contents in the waters of the Banjō system. The basin of the Banjō is covered with argillaceous rocks (shale) and limestone is scattered here and there. Although the rivers which flow through limestone area have high content of HCO_3, but generally the river waters of the Banjō system have small salt content except the one that takes its water from the stalactite grottos. The average salinity of the Banjō system is only 50 ppm and the average HCO_3 content is not so much as that of Aso welded tuff area. The HCO_3 content of the tributary Komata is minimum (23.8 ppm) and the stalactite grotto water is maximum (103.6 ppm). Thus variation of HCO_3 content in the Banjō system is large. On the contrary SiO_2 contents range between 11.4 ppm and 14.6 ppm (the average value is 12.6 ppm) ; therefore its variation is very small.

The relation between HCO_3 content in waters and dissolution degree of rocks in igneous rock area is very different from that in sedimentary rock area. Therefore it is considered that dissolution mechanism of rock which is in comparatively young stage as Aso welded tuff is different from that of argillaceous sedimentary rocks. Aso welded tuff is more weathered by the water charged with cabon dioxide than argillaeous sedimentary rocks. Among igneous rocks in Japan, Aso welded tuff is most easily dissolved. On the contrary the argillaceous sedimentary rocks in the basin of the Banjō are not dissolved so much. This difference is caused by the origin and composition of rocks. Argillaceous sedimentary rocks are more minute in consititution than igneous rocks, so that they do not dissolve so much as the latter. Therefore it is supposed that main components in the river which flows through argillaceous sedimentary rock area come from rain and dryfallouts.

The tributaries Notsu, Okutake and Shibakita start from sedimentary rock area and flow through Aso welded tuff area ; therefore they have intermediate tendency between the waters from Aso welded tuff area and those from argillaceous sedimentary rock area in their composition as is shown in Fig. 2. $HCO_3 : SiO_2$ ratio of them, 2.0~2.5, are larger than those of the water from Aso welded tuf area. Only the Okutake has a small ratio (1.35) because it contains waste water from mines situated at the upper reach of its basin. The ratio of the water of Mie spring is 1.70. This spring water represent the ground water in argillaceous sedimentary rock area which is distributed in the southern part of Mie-Town.

3.3 Sodium and Potassium Contents

Average contents of Na and K in river waters of the world are 0.365 and 0.079 me/l respectively, and the sum is 0.444 me/l. In the river waters in Japan these values are 0.307 and 0.032 me/l, the sum 0.339 me/l. In Kyūshū island, they are 0.414 and 0.054, 0.468 me/l respectively. Cl content in river waters of the world, that in Japan and that in Kyūshū island are 0.234, 0.174

and 0.176 me/l respectively on an average. Therefore the values of (Na+K) −Cl of the world, of Japan and of Kyūshū island are 0.210, 0.165 and 0.292 me/l respectively. And the salinities in river waters of the world, of Japan and Kyūshū island are 146, 75 and 106 ppm respectively. From these values it can be said that the rate of alkali metal ion content in river waters in Kyūshū island is high. When we suppose that the most Cl in river water comes from atmospric precipitations (rain and dryfallouts) and that its content corresponds to the quantity of alkali metal elements, the (Na+K)−Cl value represents the quantity of these metal elements released from rocks. Therefore, the river water in Kyūshū island have high value of these metals from rocks.

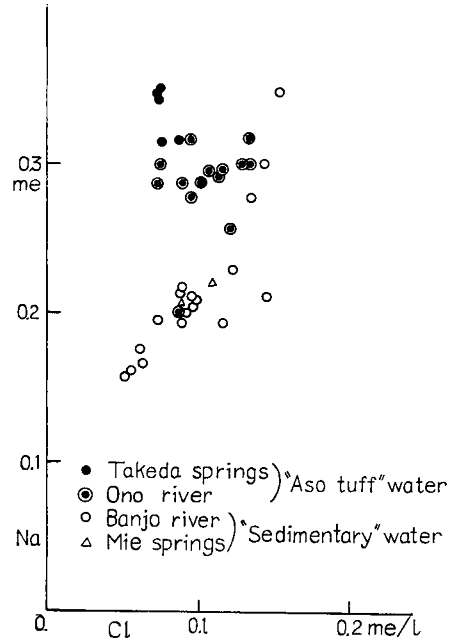

Fig. 3. Relation between Na and Cl content in the waters in Takeda springs, in the Ōno river, in the Banjō river and in Mie springs.

In the Ōno river system, Na contents in river waters draining from the reaches covered with Aso welded tuff have almost the same quantity, ranging from 6.4 to 7.3 ppm, and the average is 0.296 me/l (6.8 ppm). The K content is 0.088 me/l (3.4 ppm). The sum of Na and K contents is 0.384 me/l; and the Cl content is 0.097 me/l (3.4 ppm) on an average. Consequently the value of (Na+K)−Cl becomes 0.287 me/l. This value, for the salinity (124 ppm), is smaller than that of Kyūshū island. Percentage of Na and K to the salinity of river waters in Aso welded tuff area are 5.5 and 2.8 respectively; therefore the percentage of Na content is smaller than that of Kyūshū island and Japan (see Table 1). But the precentage of K content is reverse. Accordingly, the atmic ratio of Na : K becomes low in the river waters in the upper reach of the Ōno.

Na content in the Takada springs is 7.7 ppm and the salinity of the spring waters is 158 ppm on an average as are shown in Table 2, so that the percentage of Na content to its salinity is 4.9. K content of the springs is 4.4 ppm and is 2.8% to the salinity. The Na percentage of the spring waters is obviously smaller than that of Kyūshū island and Japan. The river waters from Aso welded tuff near Takada-City is chiefly composed of these Takeda springs as mentioned section 3.2; therefore the small rate of Na content in the river waters of Aso welded tuff near Takeda-City is caused by the mixing of these spring waters. The percentages of Cl content to the salinity in the river and spring waters which flow and well out near Takeda-City and 2.7 and 1.8 respectively. These are also smaller than those of Kyūshū island and Japan (average percentage of Cl content in Kyūshū island is 5.9 and that in Japan is 8.2). Accordingly, it is supposed that the Na in river and spring waters near Takeda-City is chiefly brought by dissolution of Aso welded tuff and only a small part of it is brought from rain and dryfallouts. On the centrary, the K content in the river waters in this district is larger than that in Kyūshū island and in Japan. The Na : K atomic ratio in rain and dryfallouts is exceedingly larger than that in rocks. Accordingly, as the quantities of Na and K which come into river water from adjacent rocks increase, the percentage of of K content becomes higher, but the Na : K atomic ratio lower. Therefore almost all the K in river water is brought by dissolution of rocks. As the dissolution of rocks becomes larger, the Na : K ratio in river waters lower. Relation between the Na and Cl contents in each river is shown in Fig. 3. There is no relation between the contents of Na and Cl in the waters in Aso welded tuff area. This shows that the Na has different origin from Cl in this area. Almost all the Cl in river waters is a cyclic element. Therefore most Na is a non cyclic element in this area; its origin in rocks.

On the other hand, the tributaries Okutake, Notsu and Shibakita which flow from sedimentary rock aea are the same in the relation between the content of Na and Cl in river waters with the Banjō which flow through argillaceous sedimentary rocks. In these rivers, Na content is generally smaller than in rivers of Aso welded tuff area, but it is in direct proportion to Cl content. Accordingly, it can be said that in these districts the dissolution of rocks is not so remarkable as in Aso welded tuff area, and considerable sum of cyclic

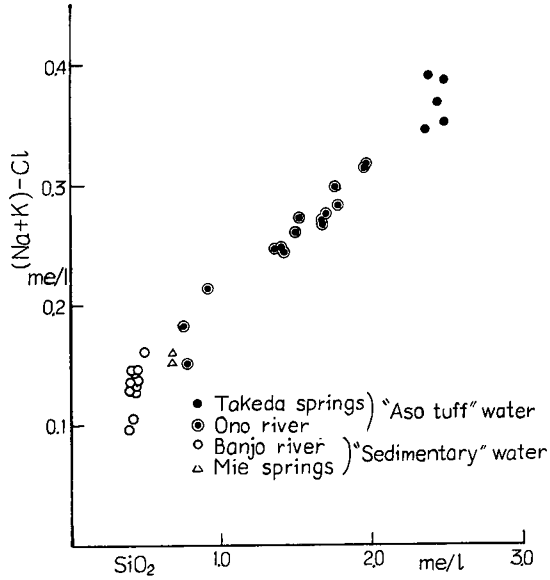

Fig. 4. Relation between the alkali metal content resolved from rocks and SiO_2 content in the waters of the springs and the rivers.

Na, which is brought by rain and dryfallouts, is included in the waters of these three tributiaries as in the Banjō.

As mentioned above, in case of that in Aso welded tuff area most Na is brought into river waters by dissolution of rocks and argillaceous sedimentary rock area Na is brought mainly by atmospheric precipitation. Cl is cyclic anion, and its equivalent cation, chiefly alkali metal, is also cyclic. Therefore (Na+K)−Cl represents the quantity of alkali metal which is dissolved from rocks. As shown in Fig. 4, there is direct proportion between (Na+K)−Cl and SiO_2 content in river waters in Aso welded tuff area, but in argillaceous sedimentary rock area such a relation can not be observed. It is evident, in Aso welded tuff area, that the large part of alkali metal content is brought into river waters by dissolution of igneous rocks. Dissolution of rocks is remarkable in Aso welded tuff area than in other area. This causes the high ratio of SiO_2 content to salinity in the river waters in this area than in argillaceous sedimentary rock area where SiO_2 resolution is small and most Na is brought by precipitation. Accordingly, in Aso welded tuff area, the alkali metal content ratio (Na %) to the salinity becomes lower.

Therefore, Na content in river waters in Aso welded tuff area should have direct proportion to SiO_2 content, whereas that in argillaceous sedimentary area is supposed to have no such a relation. This confirmed by the data in Fig. 4 which shows the relation between alkali metal and SiO_2 contents.

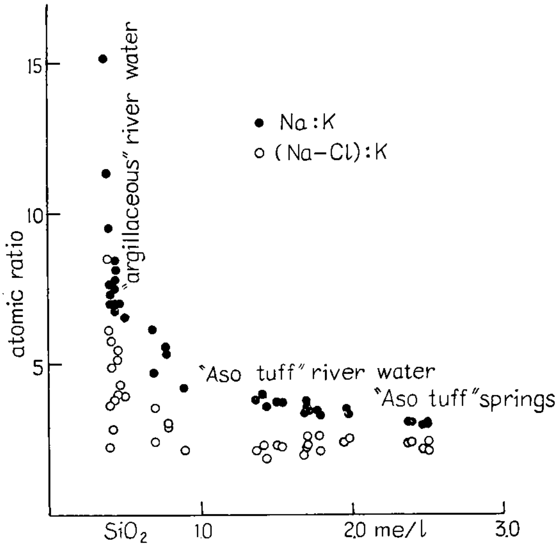

Fig. 5. Relation between Na : K atomic ratio and SiO_2 content in the river waters of the Ōno and the Banjō.

On the Na : K Atomic Ratio in River Waters

The atomic ratios of Na : K in igneous rocks and in sedimentary rocks recalculated by the author from the values given by F. W. Clarke and H. S. Washington (1922) are 1.87 and 0.61 respectively. And the ratios in river waters in igneous rock area and in sedimentary rock area are recalculated by the author from the rain corrected values given by E. J. Conway (1942) are 3.03 and 2.08 respectively. The average Na : K ratio in the river waters of the world recalculated without correction of rain is 4.6. In Kyūshū island and in Japan, that ratios are 7.64 and 9.60 respectively, which are larger than that of the world. This is caused by the fact, as mentioned in the introduction, that large amount of Na is brought into the river waters from rain in Kyūshū island and in Japan.

On the other hand, this ratio in the river waters from Aso welded tuff and Takeda springs are 3.33 and 2.98 respectively. These values show large content of K in contrast with Na content. The (Na – Cl) : K ratios of the rivers in this area and in Takeda springs are the same (2.27). It is considered that the (Na – Cl) value represents the quantity of Na dissolved from Aso welded tuff; therefore this 2.27 shows the ratio of Na to K quantities brought into these waters by dissolution of rocks. Incidentally, this value (2.27) gets nearer to the value in igneous rocks (1.87) mentioned above.

Generally, in the alkali metal released from igneous rocks to river waters

K has a tendency to separate from the water adsorbed by clay. Consequentry the ratio of Na : K in river waters becomes larger than in igneous rocks. As mentioned above, the ratio in igneous rocks is 1.87 and that in river waters rise to 3.03. Now, the value in the drainage from Aso welded tuff area is 2.72, which is nearer to that of igneous rocks. This fact shows that the seperation of K from the water is on smaller scale than in other areas. Perhaps this is because Aso welded tuff area near Takeda-City is in the upper reach of the Ōno system, which results in less suspensoid in waters and short distance of the running.

Relation between Na : K atomic ratio and SiO_2 content is shown in Fig. 5. At Aso welded tuff area in the Ōno system, the ratio is approximately 3 and slightly increases with the decrease of SiO_2 content. But in tributaries which flow from sedimentary rock area the ratio rises approximately to 5. In the Banjō system which flows through argillaceous sedimentary rock area the ratio rises still higher. In the Takeda springs the ratio is minimum (3), whereas the SiO_2 content is maximum (approximately 2.4 me/l). On the other hand, in the Banjō the ratio variates above 6 and the SiO_2 content is minimum (approximately 0.4 me/l).

As mentioned above, in Aso welded tuff area the relation between the Na : K ratio and the SiO_2 content is quite differet from that in sedimentary rock area.

Relation between (Na − Cl) : K ratio and SiO_2 content is also shown in Fig. 5 with different marks. The (Na − Cl) : K ratio (approximately 2.5) is constant independently of the SiO_2 content in the drainage from Aso welded tuff area. In other words, the quantityies of Na and K which are derived from Aso welded tuff by dissolution and not from rain and dryfallouts have a constant ratio between them in river waters. But in actually, the ratio of Na : K slightly rises with the decrease of SiO_2 content in river water of Aso welded tuff area. This is caused by dilution of surface water which includes the cyclic Na. On the other hand, in the river water flowing from argillaceous sedimentary rock area the SiO_2 content is smaller and the ratio of Na : K is varied independently of SiO_2 content.

By these fact, too, it is confirmed that dissolution mechanisum of rocks in Aso welded tuff is different from that in argillaceous sedimentary rock.

3.4 Calcium and Magnecium Contents

The average content of Ca and Mg in river waters near Takeda-City are 9.6% and 3.1% respectively. This value of Ca is slightly smaller than the average of Japan but is almost the same as that of Kyūshū island. In Takeda springs the content of Ca and Mg are 9.5% and 3.0% respectively. These

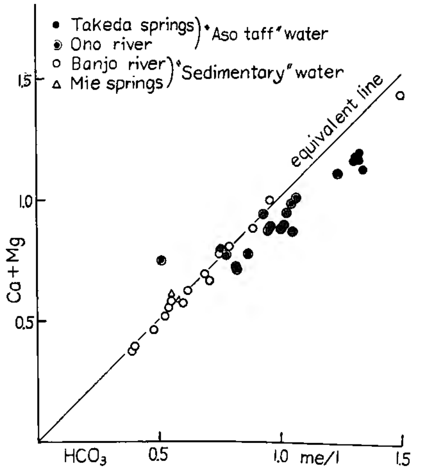

Fig. 6. Relation between the alkaline-earths and HCO_3 content in the waters of the Ōno and the Banjo system.

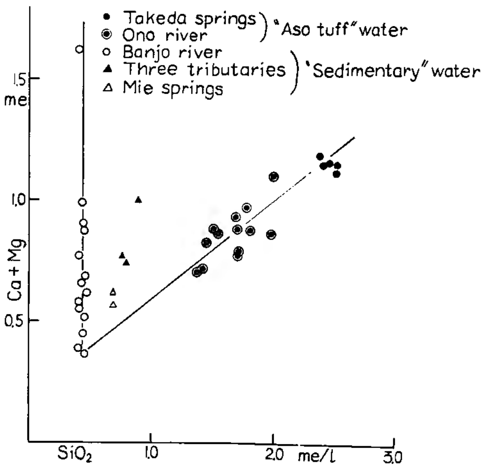

Fig. 7. Relation between the alkaline-earths and SiO_2 content in the waters of the Ōno system (which include Takada springs and three tributaries, the Okutake, the Mie and the Shibakita), Mie springs and the Banjo system.

values are almost the same as in the river waters in Aso welded tuff area around Takeda-City. Therefore, it can be said when these spring waters flow into and diluted with river waters, Ca does not deposit as $CaCO_3$.

On the other hand, in the Banjō system, Ca and Mg contents are 13.8% and 3.0% respectively in the argillaceous sedimentary rock area, and in shale area in which limestone is scattered, their contents are 19.5% and 2.3% respectively. The Ca content in the latter area, is twice as much as the content in river waters drained from Aso welded tuff area.

Ca+Mg content in either river water system, the Ōno or the Banjō, does not corespond to the Cl content. It indicates that most Ca and Mg in these river waters are not cyclic; therefore the origin of these elements are not in the ocean but in rocks. This fact suggests that Ca+Mg content varies with the content of what is the cause or the result of rock resolution. It is supposed, therefore, that the Ca+Mg content is in direct proportion to HCO_3 content in river waters. This relation is shown in Fig. 6.

In both river system, the Ōno and the Banjō, Ca+Mg is in direct proportion to HCO_3 content. In the Banjō, the Ca+Mg content is equivalent to HCO_3 content. But in the Ōno, the data slightly deviate from the equivalent line to HCO_3 content axis. This indicates that in the Ōno system there are some Na and or K cations, which correspond to HCO_3 content, in addition to Ca and

Mg (see section 3.2). From this fact it can be said that the most Na in the river waters of the Banjō is brought by rain and dryfallouts and Ca and Mg are brought by dissolution of rocks. Furthermore it is considered that the rocks chemically decomposed in weathering are mainly limestone, and decomposition of argillaceous sedimentary rocks is small.

These facts can be explained by Fig. 7 in which the relation between Ca+Mg content and SiO_2 content is shown. In the waters in Aso welded tuff area, the Ca+Mg content is in direct proportion to SiO_2 content, but in argillaceous sedimentary rock area (the Banjō system) this relation is not be seen, and all most all the data show that SiO_2 content in the Banjō is very small (approximatlely 0.4 me/l). As mentioned above, in the Banjō, the dissolution of argillaceous sedimentary rock (shale) is little; therefore the tributaries which flow through shale area in which limestone is not scattered, have small amounts of Ca+Mg, and their data are distributed near the intersecting point of two lines, which are the line of the Ōno river system and the Banjō.

Three tributaries of the Ōno river system which start from sedimentary rock area and flow through Aso welded tuff area are distributed at intermediate part between the Ōno river line and the Banjō river line.

Fig. 8 is devised to find out the alkali metal content that comes from rocks into river waters. It shows the relation between Ca+Mg content and $\Sigma K-Cl$ value. ΣK represents the sum of Na, K, Ca and Mg content. It can be considered that $\Sigma K-Cl$ represents the quantity of main cations (Na, K, Ca and Mg) which come into river water from rocks by chemical decomposition. If the Na content is equivalent to the Cl content, as in most cases they are equi-

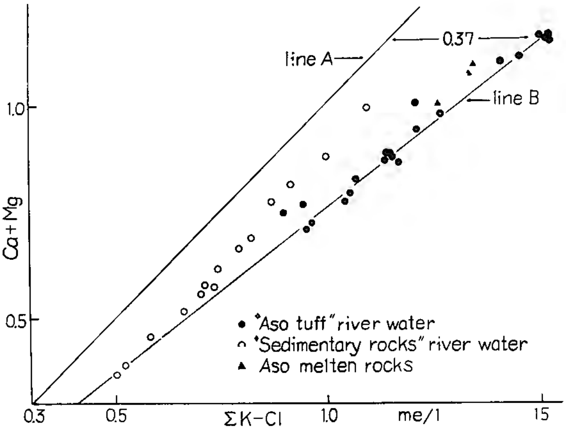

Fig. 8. Relation between the Ca+Mg content and total cations resolved from rocks in river waters of the Ōno ("Aso tuff" water) and the Banjo ("sedimentry rock" water).

valent to each other in rain, the data in Fig. 8 should be located on the equivalent line A. But, in fact, all these data are distributed deviating more or less to $\Sigma K-Cl$ axis. This is because non cyclic Na comes into river water by chemical decomposition of rocks. The more the content of Na which comes from rocks increases in river water, the more these data deviate from the line A.

The Takeda springs represent the chemical composition of the ground water in Aso welded tuff area. Mixing with surface water this ground water makes up the river waters in this area. In Fig. 8, the average deviation from the line A is 0.37 me when $\Sigma K-Cl=1.52$ me/l in Takeda springs. And in Takeda springs, the Na+K content is 0.45 me/l (see Table 2). Accordingly the quantity of Na+K which is supplied to the spring waters from rain and dryfallouts becomes 0.08 me/l. Therefore 82% of the Na+K content is supplied by dissolution of Aso welded tuff. Strictly speaking, this value should be calculated directly from rain which precipitates to this area, but in most cases the Na: Cl atomic ratio in rain is unity. In Fig. 8, the line B which links the origin and the Takeda springs indicates that 82% of Na+K content is supplied from rocks. Most of the data of the Ōno system come close to line B. But the data of the tributaries Okutake, Notsu and Shibakita are ditributed between line A and B. These tributaries start from sedimentary rocks. The Banjō shows the same tendency as these three tributaries. For example, the water from Onagara stalactie grotto deviates 0.22 me from the line A. Its Na+K content is 0.37 me; therefore 58.5% of Na+K content comes from rocks. Even in the grotto water that drains from adjacent rocks, the Na+K content of rock origin is smaller than that in the river waters from Aso welded tuff. In the water at Oda-dam at the lower reach of the Banjō, the percentage of Na+K which is supplied by dissolution of rocks goes down to 40. In Fig. 8 three data of analysis of Aso melten rock are shown with different marks. They are slightly deviated from line B to line A. This indicates that, in chemical dissolution of rocks, the alkali metals resolve more easily than alkaline-earths metals.

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