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RELATIONS BETWEEN HALOGEN CONTENTS OF HOT SPRING WATER [I]

By

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Abstract

Bromine and iodine contents are compared with chlorine contents on many hot spring waters in the whole area of Beppu Spä. Interesting conditions are then appeared that various kinds of hot waters in Beppu are fundamentally formed by only one kind of underground hot water, composition of which is similar to that of boiling springs. Variations of other chemical characters may be supposed to be given chiefly in the secondary process of mixing with other groundwater or intruding sea water.

In Shirahama Hot Springs, chemical character of original hot water is obtained by extracting the contribution of chemical elements from mixing sea water. The result, in which contents of iodine and chlorine for original hot water thus obtained show the similar relation as in Beppu, gives the interest supposition for causing uniformity of relation between halogen contents in the course of producing liquid state under geothermal activity.

A few examples of halogen contents in other hot springs are also illustrated.

1. Introduction

It has been often reported that distribution of spring temperatures corresponded roughly with that of Cl^- contents in each hot spring area in Japan, and suppositions were presented that heat and cholorine of such thermal waters were chiefly supported by the mixture of underground hot water of high Cl^- content with usual groundwater. Yamashita [1965] found the similarities in chemical character of high temperature waters from boiling wells bored in hilly area of Beppu Hot Spring District and expressed that they seemed to be the original thermal water in Beppu and chloride in them seemed to be almost juvenile. On the other hand, we are able to find other thermal spring areas rich in Cl^- content and they are called sea water intrusion area. Especially, in southern coastal part of Beppu, processes of intruding sea water were ascertained in some detail. The authors [1965] determined the contents of Cl, Br and I of thermal water in this area and gave the possibility to distinguish the sources of chorine in sea water intrusion area from that in boiling spring waters.

2. Hot springs in northern region in Beppu Spä

Active geothermal areas in Beppu are separately distributed in two regions containing many steam wells along fault lines, which form southern and northern edges of Beppu Spä, and usual thermal springs are distributed in alluvial strata in downstream areas of these geothermal areas. Then, it is convenient to divide Beppu Hot Spring District in two parts, namely as southern and northern regions. Main part of southern region is composed of old city of Beppu and we may call it as Beppu area in the following section of this paper.

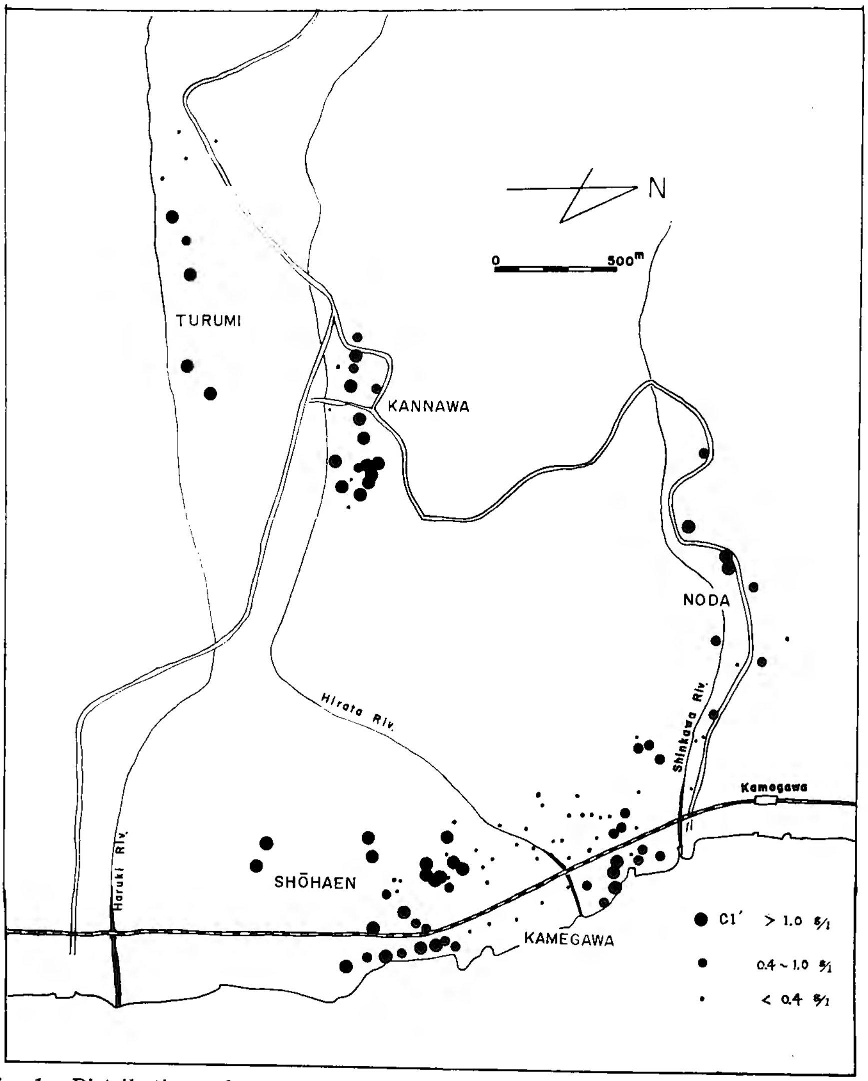

Fig. 1. Distributions of sampling wells and Cl^- contents in northern region of Beppu Spä.

In this region, artificial development of thermal springs were quite advanced and we can trace transitional states of discharging water from a number of bored wells with the heights of their positions, which are discribed as relatively dry steam in hilly area, boiling water rich in NaCl (for example V-2 in Table 1), usual thermal water, temperature of which ranges in 50°~70°C (B-69) and saline thermal water under sea water intrusion (B-1152). Such states suggest us relatively simple form for underground stream or mixing process of hot water with other kinds of ground water.

Table 1. Examples of chemical compositions of thermal water in southern region of Beppu (July 1963)

mg/l

No.	Temp. °C	pH	Cl	SO_4	HCO_3	Na	K	Ca	Mg
B-69	56.5	7.10	208.0	59.3	531.2	151.	18.3	75.0	43.5
B-1152	49.1	7.1	6757.9	457.1	507.4	2376.	301.0	1100.	408.6
V-2	98.0	9.0	740.3	79.1	182.3	546.	59.	6.4	3.5

However in northern region, it seems more complicated. There are boiling springs still near the coast or acid and alkaline hot springs are mingled in the same area. More detailed investigation must be requied to clarify the underground stream of hot water in this region. Chemical analysises of chief elements were carried out in July 1965 for 118 water samples from wells properly picked up in this whole region and, then, bromine and iodine contents are determined in 78 and 32 samples respectively.

Table 2. Examples of chemical compositions of thermal water in northern region of Beppu (July 1965)

mg/l

No.		Temp. °C	pH	Cl	SO_4	HCO_3	Na	K	Ca
Turumi	T- 1	99.5	8.85	20.	96.	197.3	127.	6.2	tr.
	T- 9	98.5	8.03	1540.	255.	46.0	906.	96.0	49.5
Kannawa	KN-2	99.5	3.94	2525.	349.	0.0	1535.	255.0	34.7
	KN-10	99.5	8.15	1135.	303.	24.9	705.	56.4	69.5
	KN-18	55.0	6.79	174.	200.	141.6	133.	28.5	59.7
Shohaen	S- 7	80.0	6.46	1596.	277.	106.2	1044.	91.8	60.7
	S-16	59.0	6.84	216.	90.	145.1	152.	23.5	37.7
	S-37	99.5	7.80	2272.	320.	6.9	1335.	191.5	79.4
Noda	N- 4	98.5	2.85	1289.	575.	0.0	686.	143.0	74.4
	N- 9	61.0	6.42	528.	186.	158.6	340.	56.2	69.7
Kamegawa	K- 3	58.4	6.90	1157.	182.	270.7	578.	71.0	153.3
	K-17	71.4	6.67	760.	210.	208.4	512.	72.0	125.9
	K-25	56.9	6.72	287.	137.	161.8	230.	32.2	33.7

This region is divided for convenience in five parts, namely as Turumi, Kannawa, Shohaen, Noda and Kamegawa. Positions of sampling wells are indicated in Fig. 1 by black points, sizes of which are classified by their Cl^- contents. Some examples of chief compositions in each part are shown in Table 2 and discharging states are described as follows.

In Turumi area, discharging state clearly differs with the height of position of well. Cl^- contents of boiling water become quite small and steam approaches dry in higher part (for example, T-1 in Table 2). It is infered that almost of discharging water are condensed water in the bore-holes. On the contrary, Cl^- contents of boiling water exceed 1g/1 in relatively lower part (T-9), compositions of which are nearly the same as usual boiling spring water pressented by Yamashita [1965].

In the central part of Kannawa area, there are some steam wells mingled with many boiling wells and some thermal wells of lower temperature are found around them (KN-18). Waters of high temperature are rich in Cl^- content and almost of them have pH values in a range of 7～8.5 (KN-10) in spite of some acid springs around them (KN-2). Almost of core samples of bore-holes are chiefly composed of Chlorite which tell us the heavy altering effect of hydrothermal activity.

Wells in central part of Shohaen area discharge hot water higher than 80°C and some of them are boiling (S-37) in spite of their positions near the coast. Their pH values are all in the range of 6.5～8 and they contain large concentrations of Cl^- and Na^+ as about equivalent ratios. Temperatures and Cl^- contents of spring waters become lower with approaching Kamegawa area in northern part (S-16). From a view-point of geological survey on core samples, there is thick lava stratum between 70 and 160 m depths composed of Hornblende Spherulitic Andesite. It is then considered that hot water flows through the artesian aquifer of sand and gravel stratum lower than this lava stratum, because the sharp increase of bore-hole temperature from 50 to 100°C is reported by Moriyama [1957].

In Noda area, large amount of natural flow of hot water or geyser bore-hole is still appeared. Boring depths are shallower than other areas and average in this area is 70 m. Almost of spring waters are acid but rich in Cl^- content (N-4). It seems to lose their acidities along the stream path toward Kamegawa area (N-9).

In the northern part of Kamegawa area, thermal water is supplied from Noda (K-17) and in the southern part, comes from Shohaen, both of which are seemed to be diluted by ground water. However, large concentration of Cl^- appeared in a part of coastal region near the mouth of Shinkawa River

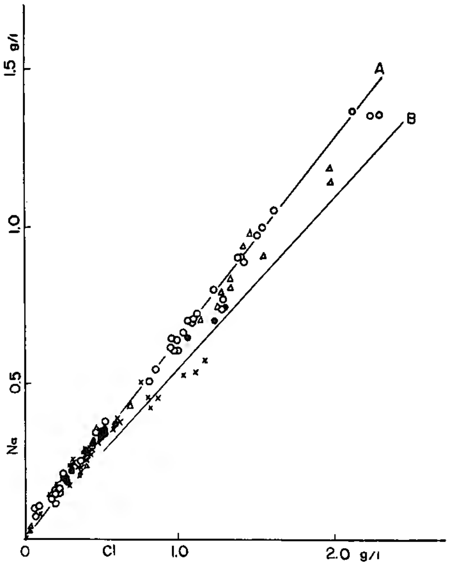

Fig. 2. Relation between Cl^- and Na^+ contents of hot spring waters in northern region of Beppu Spä.
○ Shohaen area ● Noda area
× Kamegawa area
△ Kannawa and Turumi area
Line A shows equivalent ratio.
Line B shows ratio in sea water.

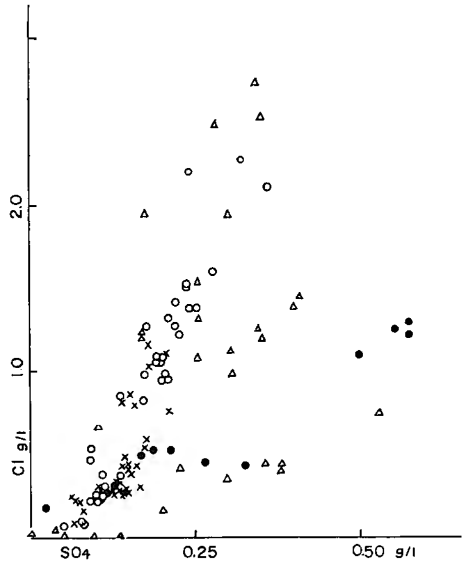

Fig. 3. Relation between Cl^- and SO_4^{--} contents of hot spring waters in northern region of Beppu Spä. Marks in figure are the same as in Fig. 2.

and it was considered to be an influence of sea water intrusion (K-3).

In order to summarize the chemical character of thermal water in these five areas, some diagrams representing relations between each chemical element are given in Figs. 2, 3 and 4.

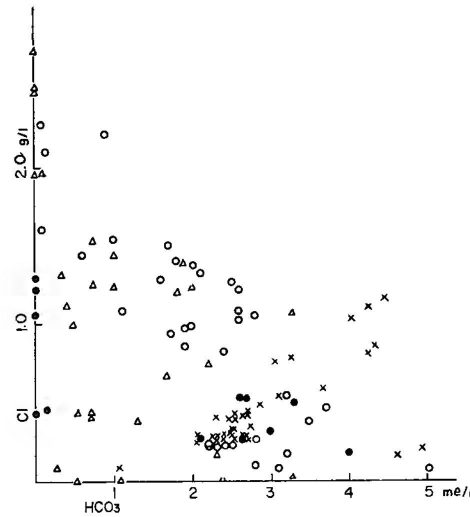

Fig. 4. Relation between Cl^- and HCO_3^- contents of hot spring waters in northern region of Beppu Spä. Marks in figure are the same as in Fig. 2.

In respect to the relation of Na^+ and Cl^-, almost of all samples distribute along line A in Fig. 2 designating the equivalent ratio of 0.65 but some in Kamegawa area approximates to line B showing the ratio of 0.55 in sea water. The formers are the general character of boiling springs and the latters are considered to be the effect of sea water intrusion.

From Fig. 3, nearly linear relation between Cl^- and SO_4^{--} contents is appeared in most of spring waters in this region but excesses of SO_4^{--} are notable for acid springs in a part of Noda and Kannawa areas compared with above linear relation. Such sulphuric acid waters were supposed owing to the dissolution of Alunite and other minerals formed in shallow region under hydrothermal activity into the neutral hot water of NaCl type.

It is clear that HCO_3^- is quite poor in boiling or acid springs and lower the temperatur, higher its content. Intereting tendency is shown in Fig 4, in

Table 3. Halogen contents in southern region of Beppu Spä

Beppu (1963)

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)	No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
H-6	190.4	0.44	0.047	B-199	1690.1	5.31	0.066
H-10	411.3	1.17	0.056	B-200	109.3	0.26	0.041
H-43	1244.5	3.90	0.052	B-203	133.9	0.39	0.049
H-45	3075.9	10.15	0.086	B-1010	167.5	0.44	0.044
H-46	7094.9	24.40	0.207	B-1011	2357.9	8.26	0.095
H-47	712.1	2.29	0.048	B-1012	214.5	0.61	0.060
H-68	357.1	1.35	0.080	B-1013	6135.3	21.06	0.164
H-69	1973.3	6.99	0.081	B-1014	8467.1	28.65	0.220
H-107	4990.6	17.66	0.110	B-1015	592.2	1.91	0.060
H-112	1787.8	5.79	0.060	B-1016	412.5	1.22	0.082
H-119	3462.4	11.29	0.078	B-1018	1783.5	6.17	0.072
H-123	2216.7	5.85	0.076	B-1022	1267.6	4.22	0.057
H-139	1905.1	6.22	0.058	B-1023	11798.3	36.38	0.158
H-149	8389.1	28.15	0.130	B-1043	163.0	0.36	0.047
B-4	652.2	2.22	0.058	B-1048	155.1	0.36	0.052
B-5	4601.6	16.20	0.082	B-1083	119.9	0.30	0.037
B-6	1866.8	6.43	0.053	B-1084	156.9	0.42	0.041
B-8	181.6	0.43	0.063	B-1088	174.5	0.46	0.047
B-55	179.8	0.43	0.048	B-1150	998.1	3.13	0.048
B-58	128.7	0.17	0.036	B-1151	1015.8	3.19	0.054
B-67	144.8	0.37	0.039	B-1152	6757.9	22.80	0.146
B-69	208.0	0.45	0.050	B-1154	1028.3	3.19	0.056
B-73	126.9	0.40	0.038	B-1155	969.8	2.93	0.081
B-76	167.6	0.43	0.044	V-1	537.6	1.30	0.071
B-80	167.6	0.41	0.041	V-2	740.3	2.18	0.116
B-186	704.7	2.26	0.065	V-3	884.8	2.26	0.140
B-190	859.8	3.29	0.055	sea water	17976.0	54.16	0.115
B-192	193.9	0.39	0.047	,,	17346.0	58.49	0.118
B-194	648.0	1.89	0.050	,,	16104.0	54.16	0.102
B-196	2159.3	7.48	0.078	,,	18051.0	61.40	0.103
B-197	139.3	0.29	0.038				

which HCO_3^- becomes rich with the increase of Cl^- content owing to advances of sea water mixing in a part of Kamegawa Hot Springs. This suggests the geochemical migration of carbon dioxide from acid hot springs to cold ground water and gives us the supposition that the sea water is intruding into shallow groundwater in first step and then mixing into the deeper thermal water.

Above analysises of chief elements present the expectation that thermal spring waters in northern part of Beppu Spä are originally formed by hot water of NaCl type usually appeared in boiling springs and variations of chemical character of them are due to the secondary process in relatively shallow region. Such a supposition is ascertained moreover by comparison of

Table 4. Halogen contents in northern region of Beppu Spä (1965)

Kannawa

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
1	439.7	1.30	
2	2524.8	6.96	0.290
4	992.9	2.90	
5	2744.6	7.62	0.2220
6	418.4	1.18	
7	397.2	1.05	
8	1405.6	4.18	
9	1262.4	3.17	
10	1134.7	3.13	
11	1446.3	4.13	0.1777
12	749.3	2.13	0.0836
13	1955.1	48.9	
14	1320.8	3.89	
16	1202.3	3.40	
17	1237.3	3.58	
19	1094.3	3.12	0.1305
20	352.0	0.99	
21	1315.4	3.84	0.1506

Noda

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
1	431.2	1.30	
2	1051.0	3.38	0.1278
3	1219.8	3.66	
4	1289.3	3.94	0.1506
5	448.2	1.44	
7	531.9	1.77	
9	527.6	1.65	0.0550
10	490.8	1.63	

Kamegawa

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
1	353.2	0.88	
2	483.7	1.33	
3	1157.4	3.61	0.0296
4	858.1	2.85	0.0431
5	808.5	2.89	
6	408.5	1.15	
8	1035.4	3.66	0.0398
10	425.5	1.20	
12	394.3	1.43	
13	439.7		0.0680
17	760.2	2.55	0.0805
21	292.2	0.86	0.0425
24	283.7	0.76	
26	272.3	0.75	
28	331.9	0.84	
31	210.3	0.58	
36	794.3	2.40	0.0930
37	594.6	1.96	0.0802
38	1102.1	3.74	0.0600
39	539.0	1.59	

Turumi

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
4	668.1	1.76	
5	1964.5	5.89	0.2414
6	2496.4	6.46	
7	1243.9	3.36	
9	1540.4	4.06	0.1988

Shohaen

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)	No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
1	1273.8	3.89	0.1887	23	369.4	0.98	
2	1214.5	3.77		24	1324.3	3.94	
3	1047.2	3.65	0.1391	26	1531.7	4.73	0.1743
4	813.7	2.33		28	2211.8	6.55	0.2379
5	1376.6	4.44	0.1760	29	1275.5	3.53	
6	533.2	1.52		30	1076.9	3.01	
7	1024.6	2.93	0.1193	31	1500.3	4.66	0.1827
8	1596.1	4.56	0.1827	32	972.3	2.70	
9	1080.4	3.19		33	1414.9	4.07	0.1633
11	939.2	2.72		34	853.8	2.80	0.1169
12	461.8	1.41		36	371.2	1.19	
13	245.7	0.68		38	2272.2	7.15	0.2301
21	981.0	2.86		39	2101.5	6.37	
22	1392.3	4.15	0.1662				

Mt. Kuzyu

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)
Ôtake-5	638.4	1.88	0.141
Ôtake-6	1270.4	3.16	0.203
Ôtake-8	634.0	1.74	0.137
Ôtake-9	1429.8	4.04	0.274
Takenoyu	1204.4	3.18	0.169

halogen contents.

3. Contents of Bromine and Iodine in Beppu Hot Springs

Results of analyses for halogen contents are shown in Table 3 for southern region and in Table 4 for northern region. Wells of

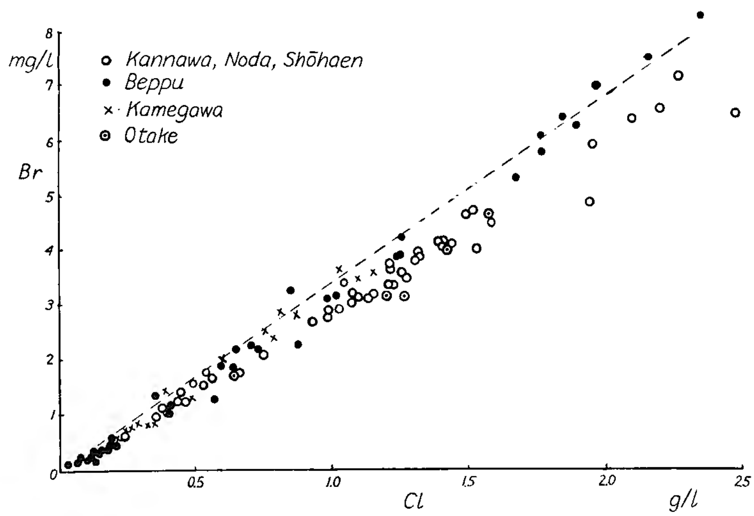

Fig. 5. Relation between Cl and Br of hot spring waters in Beppu Spä and Mt. Kuzyu.

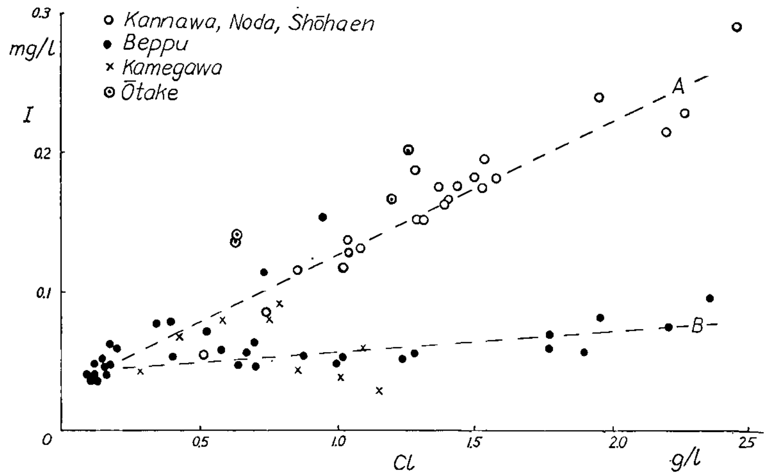

Fig. 6. Relation between Cl and I of hot spring waters in Beppu Spä and Mt. Kuzyu.

B and H numbers in Table 3 are situated in or around the sea water intrusion area and only three of V numbers are boiling springs. In Table 4, five areas of northern region are separately listed and results for some boiling springs of Ōtake and Takenoyu in Mt. Kuzyu about 30 km apart from Beppu are also illustrated.

It is noted in Fig. 5 that samples in sea water intrusion areas of Beppu and Kamegawa are distributed nearly along the line designating the ratio in sea water as 3.4×10^{-3} of Br/Cl though other samples show smaller ratios about in the range of $2.5\sim3\times10^{-3}$ and no difference is appeared between samples of boiling springs from Beppu Spä and Ōtake area.

Effect of difference in origins of cholorine is more clearly appeared in Fig. 6 showing the relation between iodine and chlorine. Samples under the mixing effect of sea water distribute nearly along line B and other samples, especially from boiling springs, stand on line A. Some excesses of iodine can be found for samples from Ōtake boiling springs but they are not so large to upset the supposition of simillarity in chemical character of boiling springs. Line B does not mean the simple mixing of original sea water, because extension of this line points out the iodine content of mixing sea water as about 0.35 mg/l which is seven times larger than that in original sea water. It must be expected that mixing sea water concentrate iodine in the course of intrusion through the soil (Kikkawa and Shiga [1965]).

Such results tell us that various kinds of hot spring water discharging from whole area of Beppu Spä originate from a kind of underground hot water having constant relation between halogen contents.

4. Shirahama Hot Springs

Shirahama Hot Springs are situated at the coast of Wakayama Prefecture, where hot waters of temperature from 50° to 86°C are discharged with large amount of CO_2 gas from seventeen bore-holes as in Fig 7. Country rocks of bore-holes are reported as Sandstone. Examples of chief chemical compositions analysed in August 1964 are listed in Table 5.

Chemical character of Shirahama Hot Springs are fairly represented by the relation between Cl^- and HCO_3^- contents as in Fig. 8. From the diagram, two groups can be distinguished, which may be called A and B groups. Group A distributes along a straight line connecting two points of H and S

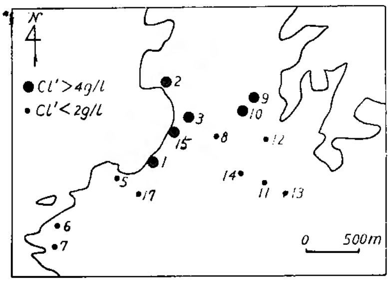

Fig. 7. Distribution of hot springs in Shirahama Spä.

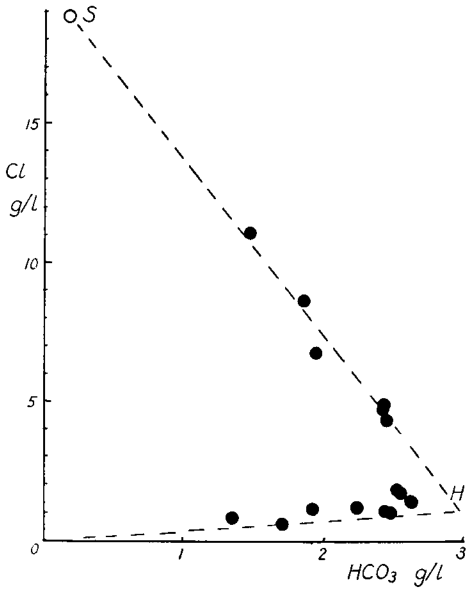

Fig. 8. Relation between Cl and HCO_3 in Shirahama Hot Springs.

Table 5. Examples of chemical composition of Shirahama Hot Springs

mg/l

No.	Temp. °C	pH	Cl	SO_4	HCO_3	Na	K	Ca	Mg
5	86.6	8.02	1801.5	106.6	2544.9	1760.	85.	16.2	49.8
12	48.3	7.40	1251.1	14.2	2222.8	1180.	63.	40.0	31.7
15	71.8	7.25	11010.4	1414.4	1395.7	6940.	180.	272.8	705.4

which shows the composition of sea water sampled at Shirahama Bay, and group B distributes nearly along OH line. Kikkawa [1954] reported that all of the spring waters belonged to group B till 1930 but, after that, some coastal springs changed their compositions as shown by group A under the effect of salt encroachment from the sea. Accordingly it may be said that spring waters included in group A were formed by a mixture of sea water and the hot water, now named H, and those in group B show the dilution of hot water H by ususal ground water.

Halogen contents are obtained in August 1964 and the results are written in Table 6, in which iodine contents are determined for water samples only belonged to group A.

Relation between Cl and I shown in Fig. 9 gives negative correspondency in which iodine content of thermal water is linearly decreased with mixing of sea water. When we assume a straight line representing this negative relation in Fig 9, value of 1.2 g/l on Cl axis may corresponds with 0.15 mg/l of iodine content which is considered as the composition of original hot water, named as H. On the other hand, 18.7 g/l on Cl axis being equivalent to sea water gives iodine content as 0.09 mg/l which approximates the value of sea water. It is noted that abovementioned relation between Cl and I of original hot water stands nearly on the straight line A in Fig. 9 which was introduced from the relation for boiling springs in Beppu Spä.

This result suggests us that the supposition of constant relation between halogen contents may be more generally applied to underground hot water in volcanic regions. Then, systematic researches on halogen contents of hot

Table 6. Halogen contents in Shirahama Hot Springs

Shirahama (1964)

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)	F (mg/l)
1	6737.9	23.84	0.128	2.05
2	8545.0	29.50		2.10
3	4766.2	16.24	0.133	2.60
5	1801.5	5.40	0.158	3.56
6	1149.0	3.47		4.25
7	851.1	2.57		4.58
8	1957.5	6.15	0.140	3.75
9	4936.4	16.74	0.150	3.40
10	4340.6	14.96	0.151	3.54
11	1035.5	2.86		3.95
12	1251.1	4.09		3.74
13	621.3	1.77		8.70
14	1007.1	3.06		5.86
15	11010.4	39.44	0.123	2.34
17	1018.5	2.79		4.36
19	1092.2	3.56		3.35
Sea water	18738.4	62.73	0.060	1.45
,,	18497.2	61.15		1.36

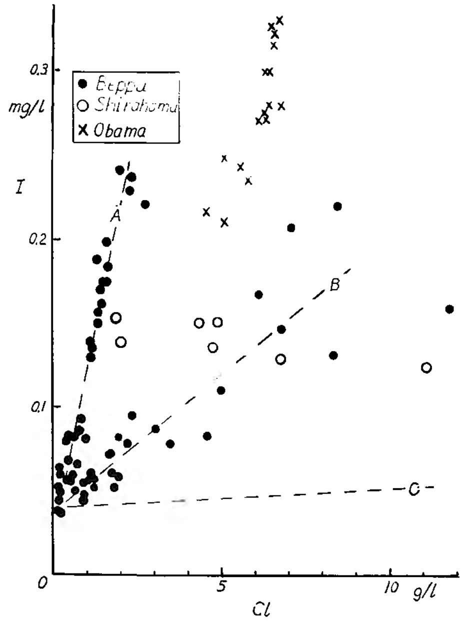

Fig. 9. Relation between Cl and I in some hot spring districts.
Lines A and B represent the relations in boiling springs and sea water intrusion area in Beppu. Line C shows the ratio of original sea water.

spring waters will probablly contribute to the study on production or storage of liquid under geothermal activity.

5. Obama Hot Springs

Obama Hot Springs are situated in the coastal part of Shimabara Peninsula in Nagasaki Prefecture. This Spä had suffered from sea water intrusion owing to the overdraft of hot water and Cl contents had rapiply increased to 11.5 g/l on average until 1954. After that, restrain of draft produced the effect upon driving out of sea water. Almost of 30 bore-holes discharge boiling water and Cl content has been decreased to 6.7 g/l at the highest.

Examples of chief chemical compositions and halogen contents in April 1964 are illustrated in Tables 7 and 8.

The relation given in Fig. 9 pressents doubtful indication that mixing sea water would encounter remarkable contribution of iodine on the course of intrusion if chief parts of such elements came from sea water. It cannot be concluded until now how many parts of such halogens would be contributed from sea water or from volcanic origin. Future study on variations of iodine contents with those of chlorine are required for this interesting problem.

Acknowledgements

The authors wish to express their hearty thanks to Professor S. Hayami

Table 7. Examples of chief chemical compositions of Obama Hot Springs
mg/l

No.	pH	Cl	SO_4	HCO_3	Na	K	Ca	Mg
3	8.15	5757.	549.0	193.6	3229.	302.	219.2	281.9
110	7.23	6749.7	703.2	226.5	3522.	330.	252.8	336.3

Table 8. Halogen contents in Obama Hot Springs

Obama (1964)

No.	Cl (mg/l)	Br (mg/l)	I (mg/l)	F (mg/l)
3	5757.1	20.02	0.235	0.43
7	6061.9	20.97	0.272	0.59
10	6522.8	22.76	0.323	0.63
12	6288.8	22.14	0.299	0.65
15	6331.4	22.07	0.329	0.69
17	6508.6	23.00	0.316	0.74
19	6466.1	22.80	0.326	0.70
23	6373.9	22.82	0.301	0.02
24	6345.6	22.19	0.300	0.67
26	4516.3	16.09	0.216	0.59
27	6430.6	22.55	0.279	0.73
30	6295.6	22.81	0.272	0.65
101	6274.7	22.18	0.255	0.74
110	6749.7	23.95	0.279	0.80
128	5594.0	19.78	0.243	0.65
129	5048.1	17.81	0.249	0.61
130	5069.4	17.86	0.210	0.52
Sea water	18653.8	63.91	0.088	1.40

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