BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2690—2695 (1966)

A Geochemical Study of Iodine in Volcanic Gases

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(Received May 20, 1966)

Volcanic gases from several active volcanoes in Japan have been analyzed for iodine and chlorine: Showashinzan (I=0.025−0.20 mg.I/kg.H_2O, Cl=238−1830 mg.Cl/kg.H_2O), Iwatesan (I=0.053−0.19, Cl=2720−3360), Issaikyoyama (I=0.030−0.087, Cl=104—213), Nasudake (I=0.16−3.9, Cl=188—9460), Yakedake (I=0.58−0.93, Cl=1250−1730), Kuju-Ioyama (I=0.13−1.3, Cl=266—8000), Kirishima-Ioyama (I=0.036—0.84, Cl=200−4200), and Miharayama (I=0.45−1.5, Cl=1640−2180). Each volcano has a characteristic I/Cl ratio. Analyses have also been made of hot-spring waters from the environs of Nasudake, Kuju-Ioyama, and Kirishima-Ioyama. It is indicated that the hot-spring waters are similar in I/Cl ratio to the volcanic gases from the same area.

In a previous paper,[1] the abundance and the behavior of halogens in the volcanic gases were investigated. As to the iodine, however, some uncertainties remained because of the paucity of analytical data. For this paper, the iodine and chlorine contents of volcanic gases from eight active volcanoes in Japan (Showashinzan, Iwatesan, Issaikyoyama, Nasudake, Yakedake, Kuju-Ioyama, Kirishima-Ioyama, and Miharayama) have been investigated.

The iodine and chlorine contents of some hot-spring waters around Nasudake, Kuju-Ioyama, and Kirishima-Ioyama have also been investigated in order to examine the similarity in I/Cl ratio between hot-spring waters and volcanic gases from the same area.

1) T. Sugiura, Y. Mizutani and S. Oana, *J. Earth Sci., Nagoya Univ.*, **11**, 272 (1963).

Experimental

The Sampling of Volcanic Gases.—Through a glass tubing inserted into the fumarole, volcanic gases were introduced into a cold trap, in which the water vapor in the gases was condensed; the halogens were completely dissolved in the condensed water.[1] The solution was then subjected to the following analyses.

The Determination of Iodine and Chlorine.—The methods for the determination of these elements are:

TABLE I. IODINE AND CHLORINE CONTENTS OF VOLCANIC GASES

Showashinzan				
Fumarole	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl \times 10^4$
A-1, 1958	759	856	0.097	1.1
A-1, 1960	722	926	0.064	0.69
A-6a, 1959	700	1040	0.10	1.0
A-6a, 1960	695	1040	0.13	1.2
A-1, 1962	662	1760	0.20	1.1
C-2, 1959	645	970	0.11	1.2
A-1, 1963	635	1830	0.12	0.66
C-2, 1960	605	1310	0.11	0.87
C-2, 1962	538	625	0.083	1.3
A-4a, 1958	470	1090	0.12	1.1
B-4a, 1959	464	250	0.040	1.6
A-4a, 1959	460	1130	0.13	1.2
B-5, 1960	446	538	0.061	1.2
C-4, 1959	430	1310	0.16	1.2
B-3, 1961	375	318	0.043	1.3
B-6, 1960	347	547	0.066	1.2
B-1a, 1959	328	285	0.033	1.2
B-4b, 1959	300	290	0.040	1.6
B-1b, 1960	260	264	0.025	0.92
C-3, 1958	222	328	0.052	1.6
B-6, 1961	200	1220	0.15	1.2
C-3, 1959	194	234	0.033	1.4
C-3, 1960	187	242	0.063	2.9
Iwatesan				
Sampling date	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl \times 10^4$
Oct. 13, 1964	206	2720	0.16	0.59
Oct. 13, 1964	206	3100	0.053	0.17
Oct. 13, 1964	206	3360	0.19	0.57
Issaikyoyama				
Sampling date	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl \times 10^4$
Jan. 11, 1956	213	213	0.087	4.1
Oct. 10, 1958	141	104	0.030	2.9
Nasudake				
Fumarole	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl \times 10^4$
M-1, 1960	489	429	0.56	13
M-1, 1959	480	600	0.71	12
M-2c, 1961	410	510	0.53	11
M-1, 1963	396	360	0.31	8.6
M-1, 1965	370	191	0.21	11
M-2b, 1960	352	480	0.57	12
M-4a, 1965	340	188	0.19	10
M-4b, 1965	261	460	0.29	6.3
O-1b, 1965	228	710	0.63	8.9
M-2a, 1960	195	9460	3.7	3.9
O-2a, 1965	165	196	0.20	10
UN-1, 1965	158	4280	1.5	3.5
U-1, 1961	132	1810	0.49	2.7
O-2b, 1965	125	188	0.16	8.5
O-1, 1959	119	3180	3.9	12
OE-1, 1965	119	410	0.40	9.8
M-3, 1960	97	8700	0.67	0.77
Yakedake				
Fumarole	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl \times 10^4$
Y-2, 1965	163	1730	0.58	3.4
Y-6, 1965	168	1250	0.93	7.4

TABIE I. (Continued)

	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	I/Cl × 10^4
Kuju-Ioyama				
Fumarole	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	I/Cl × 10^4
KH-1, 1960	508	1340	1.3	9.7
KH-1d, 1964	360	8000	1.1	1.4
KH-3a, 1964	350	6580	0.89	1.5
KX-2a, 1964	180	5700	0.67	1.2
KO-3, 1964	160	7160	0.91	1.3
KO-1, 1964	155	5000	0.58	1.2
KX-3, 1964	150	6480	1.2	1.9
KX-1b, 1964	140	7440	1.3	1.7
KX-2b, 1964	120	5160	0.60	1.2
KH-1g, 1964	96	266	0.13	5.0
Kirishima-Ioyama				
Fumarole	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	I/Cl × 10^4
EE-1, 1965	220	2160	0.61	2.9
ES-3, 1965	202	1920	0.55	2.8
ES-4, 1965	201	1680	0.52	3.1
ES-1, 1965	187	2020	0.80	3.9
EE-2, 1965	178	350	0.12	3.4
EE-3, 1965	132	200	0.036	1.8
EW-1, 1965	128	4000	0.14	0.35
EE-4, 1965	121	4200	0.84	2.0
Miharayama*				
Sampling date	Temp., °C	Cl mg./kg.H_2O	I mg./kg.H_2O	I/Cl × 10^4
May 2, 1959	388	1640	0.45	2.2
May 12, 1959		1840	1.3	7.1
May 26, 1959		2180	1.5	6.9
May 27, 1959	392	1920	1.5	7.8

* These samples were given by K. Noguchi at Tokyo Metropolitan University.

Cl Mercuric thiocyanate[2)]
I The catalytic oxidation of $FeSCN^{2+}$ [3)]

Most of the samples contained an appreciable amount of sulfide which interferes with both chlorine and iodine analyses. Accordingly, samples were heated with sodium carbonate and hydrogen peroxide in order to oxidize the sulfide to sulfate.[2)] The solution was then subjected to the above-mentioned analyses.

Continuous Observation of the Iodine and Chlorine Contents of Volcanic Gases.—Continuous observations over a short period (3—5 hr.) were made in order to examine the constancy in iodine and chlorine contents of volcanic gases from several fumaroles of Showashinzan and Nasudake. Samples were collected from a fumarole at about 20-min. intervals. In each sampling time, each about 15 min. long, about 100 ml. of condensed water was collected.

Results

The analytical results are listed in Tables I to III, while the sampling sites of the volcanic gases and hot-spring waters are shown geographically in Fig. 1.

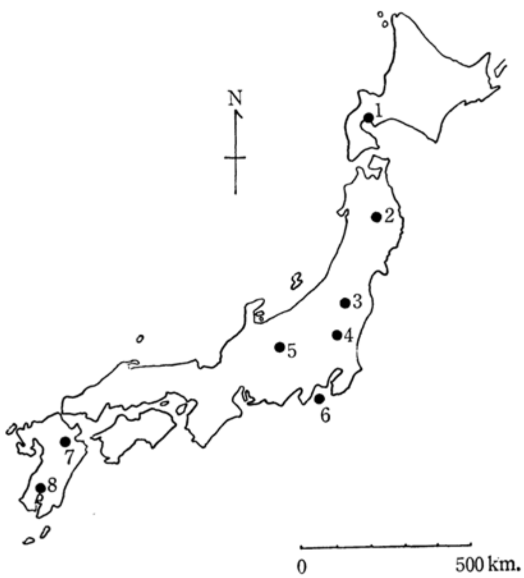

Fig. 1. Sampling site of volcanic gases and hot spring waters.

1. Showashinzan
2. Iwatesan
3. Issaikyoyama
4. Nasudake
5. Yakedake
6. Miharayama
7. Kuju-Ioyama
8. Kirishima-Ioyama

2) S. Utsumi, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **81**, 401 (1960).
3) S. Utsumi, M. Shiota, N. Yonehara and I. Iwasaki, ibid., **85**, 32 (1964).

TABLE II. IODINE AND CHLORINE CONTENTS OF HOT-SPRING WATERS IN THE ENVIRONS OF NASUDAKE

Locality	Temp., °C	Cl mg./l.	I mg./l.	I/Cl×10⁴
Oana	84	80	0.037	4.6
Yumoto-shika-yu	73	124	0.0080	0.65
Yumoto-gyonin-yu	60	104	0.0035	0.34
Benten-yu	52	48	0.010	2.1
Benten-yu	49	23	0.095	41
Benten-yu	45	22	0.010	4.5
Iimori	41	129	0.057	4.4
Takao-onsen	39	97	0.039	4.0
Kakko-onsen	37	107	0.015	1.2
Hot spring pool	28	53	0.0050	0.95

IODINE AND CHLORINE CONTENTS OF HOT-SPRING WATERS IN THE ENVIRONS OF KUJU-IOYAMA

Locality	Temp., °C	Cl mg./l.	I mg./l.	I/Cl×10⁴
Odake-onsen	92	1430	0.23	1.6
Suji-yu	60	286	0.050	1.7
Kora-yu	56	30	0.0036	1.2
Hizen-yu	55	263	0.035	1.3
Senshaku-yu	44	218	0.033	1.5
Hokkein-onsen	44	107	0.011	1.0
Ukenokuchi-onsen	41	224	0.013	0.51
Kan-no-jigoku		25	0.0026	1.0
Hossho-onsen		75	0.042	5.6

IODINE AND CHLORINE CONTENTS OF HOT-SPRING WATERS IN THE ENVIRONS OF KIRISHIMA-IOYAMA

Locality	Temp., °C	Cl mg./l.	I mg./l.	I/Cl×10⁴
Maruo bore	94	242	0.069	2.9
Ebino bore	93	4	0.000	< 1
Iodani-tessen	71	65	0.0078	1.1
Iodani-myobansen	66	63	0.0098	1.6
Ebino	56	152	0.010	0.66

Discussion and Conclusion

The following facts may be seen in Tables I to III:

1) The I/Cl ratio (in weight) of volcanic gases ranges from 10^{-3} to 10^{-5}. Most of the samples, however, have values from 10^{-3} to 10^{-4}. This value agrees with that given in the previous paper[1].

2) The I/Cl ratio of volcanic gases differs in different volcanoes, while the gases show a comparatively constant Br/Cl ratio.[1] The average I/Cl ratios are: Showashinzan (1.2×10^{-4}), Iwatesan (0.44×10^{-4}), Issaikyoyama (3.5×10^{-4}), Nasudake (temp. >300°C: 10.7×10^{-4}; temp.< 300°C: 6.7×10^{-4}), Yakedake (5.4×10^{-4}), Kuju-Ioyama (1.4×10^{-4}—two values were excluded from the average), Kirishima-Ioyama (temp.> 200°C: 3.0×10^{-4}; temp. <200°C: 2.3×10^{-4}), and Miharayama (6.0×10^{-4}).

3) The I/Cl value of volcanic hot-spring waters nearly agrees with that of the volcanic gases to which the hot-spring waters are believed to be related genetically.

4) The constancy in the I/Cl value is fairly good at each fumarole over a period of 2 to 3 hr. The results of continuous observations at the A-1 fumarole of Showashinzan show that the gases have a constant I/Cl value, while the iodine and chlorine contents vary widely. At Nasudake, it is observed that each of the fumaroles shows a constant I/Cl value with respect to the time change, though their values differ considerably from one fumarole to the other (Tables I and III).

The Behavior of Iodine in Volcanic Gases.— The gases of Kuju-Ioyama show a constant I/Cl value, though they show no clear relationship between the halogen content and the gas temperature. The gases of Showashinzan show a linear relationship between the iodine content and the gas temperature, as Fig. 2 shows. In addition, the gases have a conspicuously constant I/Cl ratio over a wide range of gas temperatures (187—759°C). This implies that the cause of the variation in iodine content is probably the same as that of the variation in chlorine.

It has already been reported by Mizutani[4] that the chlorine content of Showashinzan gases decreases linearly with a lowering of the temperature, and that the dilution effect of mixing water vapor into original gases is responsible for the variation in the chemical composition of the gases during

4) Y. Mizutani *J. Earth Sci., Nagoya Univ.*, **10**, 125 (1962).

Table III. Continuous observation of iodine and chlorine contents of volcanic gases

Nasudake
M-1, 1965 Temp. 370°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
2 : 15—2 : 25	195	0.24	12
2 : 30—2 : 40	188	0.20	11
2 : 45—2 : 55	198	0.21	11
3 : 00—3 : 10	185	0.20	11
3 : 15—3 : 25	195	0.20	10
3 : 30—3 : 40	195	0.22	11
3 : 45—3 : 55	188	0.22	12
4 : 00—4 : 10	190	0.20	11
4 : 15—4 : 25	195	0.23	12
4 : 30—4 : 40	185	0.21	11

Nasudake
M-4a, 1965 Temp. 340°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
9 : 20— 9 : 38	185	0.21	11
9 : 40— 9 : 53	180	0.19	11
9 : 55—10 : 08	188	0.15	8.0
10 : 10—10 : 23	180	0.16	8.9
10 : 25—10 : 39	193	0.15	7.8
10 : 41—10 : 54	205	0.25	12
10 : 57—11 : 12	188	0.20	11
11 : 14—11 : 30	185	0.20	11
11 : 34—11 : 50	188	0.21	11
11 : 53—12 : 08	190	0.22	12

Nasudake
M-4b, 1965 Temp. 261°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
9 : 20— 9 : 38	443	0.26	5.9
9 : 40— 9 : 53	458	0.38	8.3
9 : 55—10 : 08	458	0.24	5.2
10 : 10—10 : 23	465	0.24	5.2
10 : 25—10 : 39	470	0.23	4.9
10 : 41—10 : 54	448	0.30	6.7
10 : 57—11 : 12	463	0.32	6.9
11 : 14—11 : 30	468	0.34	7.3
11 : 34—11 : 50	463	0.26	5.6
11 : 53—12 : 08	465	0.33	7.1

Nasudake
O-2a, 1965 Temp. 165°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
11 : 13—11 : 26	195	0.22	11
11 : 30—11 : 47	200	0.21	11
11 : 51—12 : 04	198	0.20	10
12 : 07—12 : 22	198	0.20	10
12 : 26—12 : 44	202	0.20	10
13 : 24—13 : 37	193	0.19	10
13 : 41—13 : 54	195	0.20	10
13 : 58—14 : 13	195	0.19	10
14 : 16—14 : 29	193	0.18	9.3
14 : 32—14 : 48	190	0.19	10

Nasudake
O-2b, 1965 Temp. 125°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
11 : 13—11 : 26	180	0.16	8.9
11 : 30—11 : 47	200	0.15	7.5
11 : 51—12 : 04	193	0.20	10
12 : 07—12 : 22	185	0.13	7.0
12 : 26—12 : 44	203	0.16	7.9
13 : 24—13 : 37	135	0.14	10
13 : 41—13 : 54	210	0.16	7.6
13 : 58—14 : 13	173	0.14	8.1
14 : 16—14 : 29	213	0.19	8.9
14 : 32—14 : 08	190	0.16	8.4

Showashinzan
A-1, 1961 Temp. 703°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
15 : 00—15 : 10	1130	0.060	0.53
15 : 20—15 : 30	940	0.063	0.67
15 : 40—15 : 50	1250	0.075	0.60
16 : 00—16 : 10	1480	0.096	0.65
16 : 20—16: 30	1200	0.068	0.57
16 : 40—16 : 50	1340	0.083	0.62
17 : 00—17 : 10	1290	0.091	0.71
17 : 20—17 : 30	1190	0.086	0.72
17 : 40—17 : 50	1400	0.087	0.62
18 : 00—18 : 10	950	0.060	0.63

B-5, 1960 Temp. 446°C

Sampling time	Cl mg./kg.H_2O	I mg./kg.H_2O	$I/Cl\times10^4$
9 : 00	535	0.056	1.0
10 : 00	545	0.066	1.2
11 : 00	528	0.065	1.2
12 : 00	532	0.056	1.1
13 : 00	540	0.061	1.1
14 : 00	530	0.061	1.1

their effusion process. On the contrary, in the gases of Nasudake and Kirishima-Ioyama, iodine behaves differently from chlorine. In the cases of Nasudake, the I/Cl ratio of the gases varies widely with the gas temperature, as Fig. 3 shows. Gases with temperatures above 300°C show values of $(10—13)\times10^{-4}$, while gases with temperatures between 100°C and 300°C have values of $(0.8—12)\times10^{-4}$.

The gases of Kirishima-Ioyama are similar in this respect to those of Nasudake. The I/Cl value given for the gases with temperatures above 200°C shows $(2.8-3.1)\times10^{-4}$, while for the gases with temperatures below 200°C the value is $(0.35-3.9)\times10^{-4}$. The change in I/Cl ratio implies that the deposition and/or the addition of iodine and chlorine occurs in the gases as the temperature falls. Some evidence for the addition of some chemical components, including chlorine, to volcanic gases were suggested in the investigations

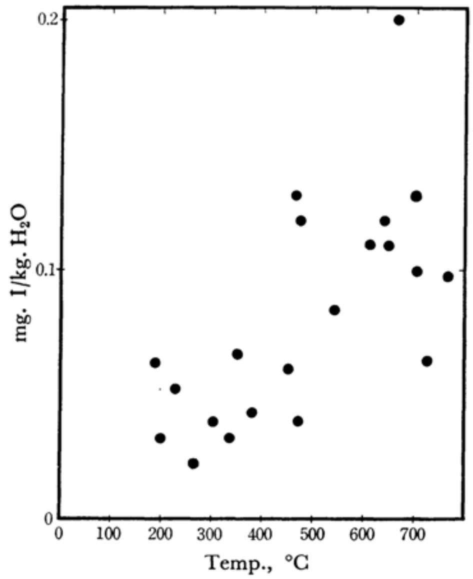

Fig. 2. Corelation between gas temperature and the iodine content of the gases of Showashinzan.

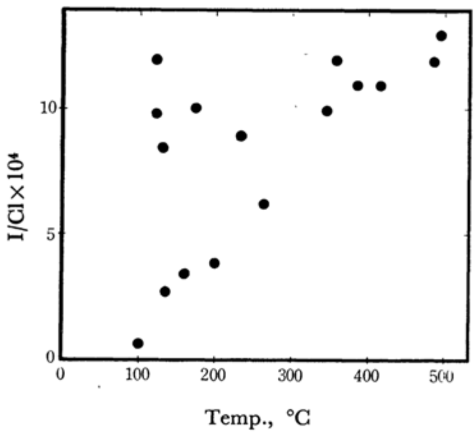

Fig. 3. Corelation between gas temperature and the I/Cl ratio of the gases of Nasudake.

by Mizutani et al.[5] and Suzuoki[6] of the chemical nature of the gases of Nasudake.

Both of these studies agree that the increase in chlorine in the gases is possibly caused by the contribution of the chlorine compounds which have accumulated in the subsurface during past effusion processes. Yoshida et al.[7] studied the halogen compounds sublimed from powdered volcanic rocks on heating; they showed that iodine behaves differently from chlorine during the volatilization and sublimation processes. Actually, volcanic sublimates, particularly alkali and ammonium chlorides, have lower I/Cl values ($10^{-5}-10^{-6}$),[7-9] than volcanic gases. If an appreciable quantity of halogens is supplied from such a deposit to the volcanic gases, the I/Cl value of the gases may be decreased, while the halogen content of the gases increases. It seems reasonable to explain the difference in I/Cl ratio with the decrease in the temperature as being caused by the increasing contribution of halogens from a secondary source, such as volcanic sublimates, though a problem remains as to the process of the discharge of halogens in deposits.

The authors express their gratitude to Dr. Nobuyuki Nakai for his helpful discussions.

5) Y. Mizutani, T. Sugiura and S. Oana, Read the abstract at the Meeting of the Volcanological Society of Japan, Oct., 1961.
6) T. Suzuoki, This Bulletin, **38**, 1946 (1965).
7) M. Yoshida, I. Makino, N. Yonehara and I. Iwasaki, This Bulletin, **38**, 1436 (1965).
8) Y. Mizutani, *J. Earth Sci., Nagoya Univ.*, **10**, 149 (1962).
9) K. Noguchi, T. Goto, S. Ueno and M. Ichikuni, *Bull. Volcanol. Soc. Japan (Kazan), 2nd Series*, **5**, 163 (1961).