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## Chlorine isotopic compositions of deep saline fluids in Ibusuki coastal geothermal region, Japan: using B–Cl isotopes to interpret fluid sources

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We report chlorine stable isotopic compositions ( $\delta^{37}\text{Cl}$ , expressed in ‰ relative to the standard mean ocean chloride) as well as  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of deep saline fluids taken at eight drill-holes reaching from 73 to 780 m below sea level in the Ibusuki coastal geothermal region, Japan. Analytical results show that the  $\delta^{37}\text{Cl}$  values narrowly range between  $-0.26$  and  $+0.21$  ‰ with an analytical precision of  $\pm 0.06$  ‰. Except for one sample, the samples examined are negative in  $\delta^{37}\text{Cl}$  value with varying Cl/B molar ratios from 117 to 1265. A correlation study between the Cl/B molar ratio and the  $\delta^{37}\text{Cl}/\delta^{11}\text{B}$  ratio indicates a hyperbola-type mixing of at least two Cl sources in the Ibusuki region. One of them depletes in  $^{37}\text{Cl}$  with a higher value of Cl/B molar ratio; and the other one enriches in  $^{37}\text{Cl}$  with a lower Cl/B molar ratio. The former is chemically identical to that of the deep brine, which is altered seawater through the seawater–hot rock interaction. The latter is chemically similar to gas condensate derived from the high-temperature (890 °C) vent of an island-arc volcano near the Ibusuki region.

**Keywords:** boron-11; chlorine-37; coastal geothermal region; deep brine; hydrogen-2; Ibusuki; isotope geochemistry; oxygen-18; sea water; subduction process; volatile

### 1. Introduction

The Ibusuki geothermal region is located in part of the Ata volcano [1] on the southern coast of Kyushu Island in Southwest Japan (Figure 1). Coastal waters in the region are typically high in salinity, possess Na–Ca–Cl-type chemistry, but are significantly different from seawater in  $\text{Mg}^{2+}/\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}/\text{Ca}^{2+}$ , and  $\text{Cl}^-/\text{B}$  molar ratios. It was reported that Ibusuki geothermal fluids as well as those of other geothermal springs in the southern part of Kyusyu, Japan, were influenced by meteoric water and magmatic volatiles [2]. According to [2], the latter originate from fluids formed by dehydration of amphibole and chlorite in the peridotite layer of the Philippine Sea plate when this plate subducts to more than 110 km in depth beneath the Eurasian plate.

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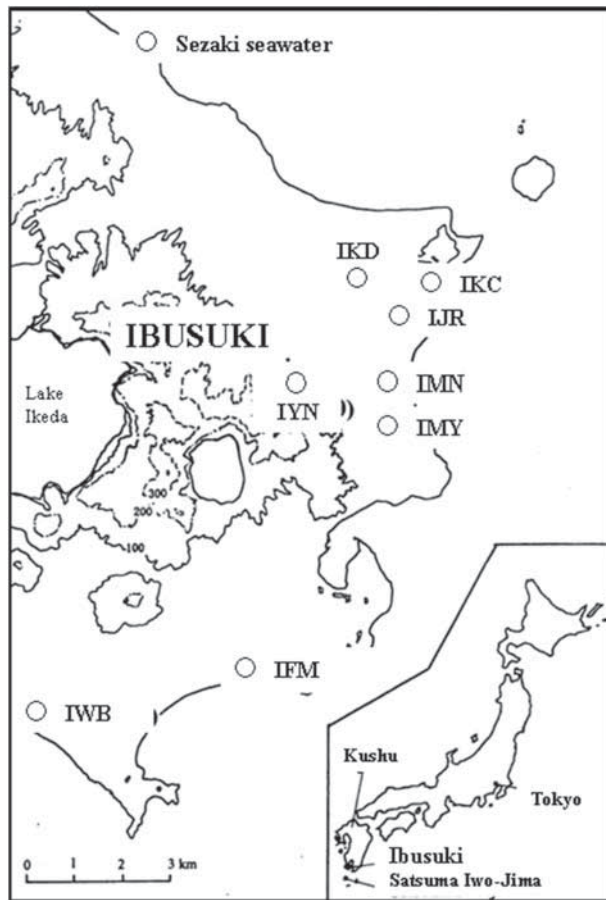


Figure 1. Location of the Ibusuki geothermal region on the Japanese Islands (inset), and sampling places of the geothermal fluids examined.

Note: The labels on the sampling places correspond to the water samples listed in Table 1.

A number of the chemical and isotopic studies investigating the origin of Ibusuki geothermal fluids have been reported. Hatae et al. [3] reported that hot spring waters in the region are characterised by high contents of salts and pH neutrality. Tarutani et al. [4] reported that the oxygen isotope compositions of the fluids they analysed were within the range of the seawater value. Studies on the hydrogen and oxygen isotopes indicated that these isotopic values of fluids in the region were in between those of ocean water and respective local meteoric waters as a result of seawater involvement in the Ibusuki hydrothermal systems [5,6]. A boron isotope study of the fluids pointed out that their boron was a mixture of marine and non-marine boron [7]. Those studies suggested, as a whole, that the Ibusuki fluids originate from seawater diluted by meteoric water. However, the Ibusuki fluids obtained from drill-holes of at most 780 m in depth were of saline fluid nature. Chemical and isotopic compositions of those fluids were altered by the fluid–rock interaction during migration in crust or were changed by addition of volatiles derived from magma in the region. If this were the case, the chlorine isotopic composition of the fluids could also be varied by the isotopic fractionation and/or dilution with magmatic volatiles. To determine the chlorine source of the Ibusuki geothermal fluids in the Ibusuki region. In this paper, we report results of such a chlorine isotopic analysis and discuss chlorine cycling through the subduction process in the region.

Chlorine has two stable isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , with a natural abundance ratio ( $^{37}\text{Cl}/^{35}\text{Cl}$ ) of about 0.32. The chlorine isotopic composition is expressed as  $\delta^{37}\text{Cl}$  (in ‰; vs. Standard Mean Ocean Chloride [SMOC]), and the natural variation was initially reported as small as 2 ‰ [8]. Chlorine is a conservative and hydrophilic element, and is mobile in lithosphere, aquasphere and atmosphere. Because of these properties of chlorine, the chlorine isotopic compositions have been employed as a potential indicator of the crustal recycling into mantle [9] or ocean [10], hydrothermal processes [11,12], water–rock interaction with rock alterations [13–18], origin of salinity in fluid inclusion [19,20], fluid histories of oceanic crust and sediments [21,22], fluid circulation through subduction processes [23–25], and magmatic fluid at a volcanic region [26]. It was recently reported that chlorine in mantle was isotopically homogeneous [27]. Another recent paper [28] stated that mid-ocean ridge basalt source mantles with lighter  $\delta^{37}\text{Cl}$  values suggested net Cl isotopic fractionation and/or the addition of a late volatile supply depleted in  $^{37}\text{Cl}$ . However, the studies on chromatographic Cl isotopic fractionations showed that the degree of fractionation was about 0.35 ‰ at 25 °C [29–31], which implied that the fractionation at higher temperatures could be negligible. Moreover, studies on Cl isotope fractionation between the vapour and liquid phases showed that the degree of the fractionation was nearly zero [15]. Those laboratory experiments suggested that  $\delta^{37}\text{Cl}$  values in deep drill-hole fluids could be preserved without suffering from any significant isotopic fractionation. So, the specific aim of the present study is to identify the chlorine sources originating from chloride dissolved in deep saline fluids in a coastal geothermal region.

## 2. Samples

Thirty-seven fluid samples were collected from different drill-holes with various depths (73–780 m below sea level) in the Ibusuki geothermal region (Figure 1) by scientists at Sophia University during the periods of 20–23 February and 6–9 September 1992. Concentrations of the major elements and the  $\delta^{11}\text{B}$  values were reported in [7]. Table 1 presents that the temperature varied from 42.2 to 102.2 °C and the pH value ranged between 3.68 and 7.59 with the majority being around 7. No correlation between the  $\delta^{11}\text{B}$  values and pH or between the  $\delta^{11}\text{B}$  values and the boron content was reported [7], which suggested that the boron isotope fractionation relating to the speciation of boron in the fluids was negligible.

For this study, eight fluid samples were selected out of the 37 samples. The samples chosen also geographically cover the most of major geothermal areas in the Ibusuki region, as shown in Figure 1. Based on the  $\delta^{11}\text{B}$ –Cl/B diagram (Figure 2), the selected eight fluids were considered representative ones in the region (*vide infra*).

## 3. Analyses

Chlorine, hydrogen and oxygen stable isotopic compositions of the fluid samples were measured in 1995 at Utrecht University.

Chlorine isotope-analytical technique was described in detail in [32]. A brief description is as follows: For each geothermal fluid sample, an aliquot containing about 0.5 mg chloride was prepared for chlorine isotopic measurement [7]. Silver nitrate solution was added to the aliquot to precipitate AgCl. This process was repeated on three aliquots of the same sample to obtain triplicate data for the sample. The chemical form of Cl in the AgCl precipitate was converted to  $\text{CH}_3\text{Cl}$  by the reaction with  $\text{CH}_3\text{I}$ . The formed  $\text{CH}_3\text{Cl}$  gas was then separated from  $\text{CH}_3\text{I}$  by gas chromatography, and the isolated  $\text{CH}_3\text{Cl}$  was used for the Cl isotopic analysis with a VG

Table 1. Analytical results on the stable isotope compositions of  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$  and  $\delta^{37}\text{Cl}$  and the molar ratios of the chemical constituents of the Ibusuki geothermal waters.

Name	code	dfs1 <sup>a,b</sup> (m)	Temp. <sup>b</sup> (°C)	pH <sup>b</sup>	Concentrations (mmol L <sup>-1</sup> ) <sup>b</sup>						Molar ratios					Isotope compositions (‰) <sup>d</sup>				
					Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	B	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup> /Ca <sup>2+</sup>	Mg <sup>2+</sup> /Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup> /Ca <sup>2+</sup>	Cl <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	Cl/B	R <sub>NaCl</sub> <sup>c</sup>	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{37}\text{Cl}$	$\delta^{11}\text{B}$ <sup>b</sup>
Fushime	IFM	290	91.6	7.59	225	18	0.4	1.37	339	1.6	13	0.02	0.09	212	247	0.58	-18	-2.7	-0.23	5
Katayama-3	IKC	73	52.6	7.22	261	14	23.6	0.40	305	12.8	19	1.69	0.91	24	763	0.57	-14	-2.4	-0.26	20
Kawajiri-2	IWB	780	56.0	6.56	487	14	5.1	0.44	544	28.1	35	0.36	2.01	19	1236	1.03	3	0.4	-0.18	39
Yamanonaka	IYN	100	81.8	6.77	233	16	8.6	2.29	268	0.8	15	0.54	0.05	335	117	0.50	-11	-0.7	-0.07	7
Juchodara	IJR	150	70.6	7.00	332	22	31.6	0.39	418	17.3	15	1.44	0.79	24	1072	0.76	-7	-1.6	-0.16	25
Katayama-4	IKD	248	48.9	3.68	91	13	1.9	0.79	113	5.1	7	0.15	0.39	22	143	0.21	-28	-4.1	0.21	2
Mukaiyoshi	IMY	135	102.1	7.29	254	23	3.9	1.15	302	3.1	11	0.17	0.13	97	263	0.56	-12	-1.3	-0.08	14
Minato	IMN	142	42.2	7.59	30	3	0.9	0.16	36.7	0.8	10	0.30	0.27	46	229	0.07	-34	-5.4	-0.09	10
Seawater <sup>e</sup>		0		8.03	461	10	57.6	0.38	536	25.7	46	5.76	2.57	21	1411	1.00	0	0.0	0.00	39

Notes: The first column shows the names of the wells where the geothermal fluids were taken by [7], and the second column indicates the abbreviation of the name. (a) The dfs1 stands for depth below sea level. (b) The data were referred to [7]. (c) This denotes the weight ratio of the total amount of NaCl in the fluid against that in seawater. (d) The values are normalised with the international standard samples: VSMOW for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , SMOC for  $\delta^{37}\text{Cl}$  and  $\delta^{11}\text{B}$  for NBS SRM 951. (e) The seawater sample was taken from the seacoast near Ibusuki.

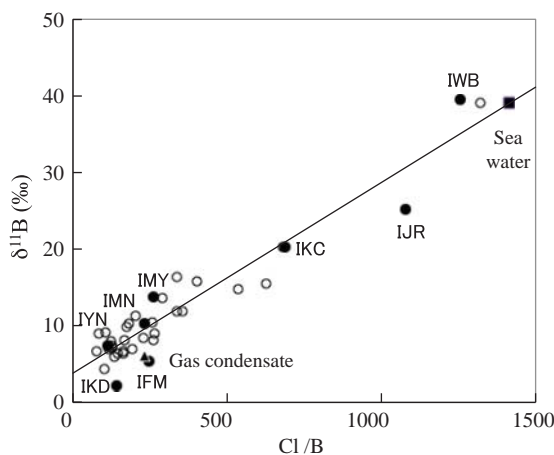


Figure 2. Correlation between  $\delta^{11}\text{B}$  and Cl/B molar ratio of the Ibusuki water samples.

Note: The solid circles tacked with the name are the eight samples employed in this study. Data of both the open and solid circles are reported in [7]. The solid line ( $\delta^{11}\text{B} = 0.0248 \times (\text{Cl}/\text{B}) + 3.28$ ) is the least squares-fitted line for the 39 samples' data [7] with the decision coefficient ( $R^2$ ) of 0.91. The line comfortably connected the plot of seawater (■) with that of the gas condensate (▲) sampled at Sausuma Iwo-jima nearby Ibusuki.

SIRA 24 EM dual inlet-double collector mass spectrometer. Multiple chlorine isotopic ratios ( $^{37}\text{Cl}/^{35}\text{Cl}$ ) obtained for a fluid sample were averaged and normalised to that of the SMOC taken from Atlantic Ocean water near Madeira an Utrecht Lab standard, and were expressed as  $\delta^{37}\text{Cl}$  (‰). The analytical error of all experimental processes was better than 0.06 ‰ ( $1\sigma$ ) [33].

Hydrogen and oxygen isotope analyses for the samples were performed with the same mass spectrometer. For the hydrogen isotope analysis, water in an aliquot of a sample was stoichiometrically converted to  $\text{H}_2$  under uranium catalysis [34], and for the oxygen isotope analysis, the established  $\text{H}_2\text{O}-\text{CO}_2$  equilibrium method was adopted [35]. The results were expressed as  $\delta^2\text{H}$  (‰) for hydrogen and  $\delta^{18}\text{O}$  (‰) for oxygen, respectively, after the normalisation to the international reference Vienna Standard Mean Ocean Water (VSMOW) [36] and the standard light Antarctic precipitation. The analytical uncertainties were normally better than 1.0 ‰ for  $\delta^2\text{H}$  and 0.05 ‰ for  $\delta^{18}\text{O}$ .

#### 4. Results

The  $\delta^{37}\text{Cl}$ ,  $\delta^2\text{H}$ , and  $\delta^{18}\text{O}$  values analysed in this study are reported in Table 1.

The  $\delta^{37}\text{Cl}$  values range between  $-0.26$  and  $+0.21$  ‰ with an average of  $-0.15$  ‰, and deviate negatively from the value of SMOC except for a sample named IKD ( $+0.21$  ‰). The variation in the  $\delta^{37}\text{Cl}$  value is beyond the confidence limit for the reproducibility of the present analytical technique. The degree of Ibusuki's  $\delta^{37}\text{Cl}$  variation of 0.47 ‰ is smaller than that of Icelandic geothermal waters, 2.01 ‰ [37], while it is larger than that of Japanese hot spring waters from the Kusatsu-Shirane volcanic region, 0.24 ‰ [38].

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values vary between  $+3$  ‰ and  $-34$  ‰ and between  $+0.4$  ‰ and  $-5.4$  ‰, respectively. The correlation between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  (the broken line in Figure 3) expressed by the least squares-fitted linear line, ( $\delta^2\text{H}) = 6.0 \times (\delta^{18}\text{O}) - 1.7$  ( $R^2 = 0.935$ ) agrees with the  $\delta^2\text{H}-\delta^{18}\text{O}$  line of a slope ( $\delta^2\text{H}/\delta^{18}\text{O}$ ) of 5.5. This agreement indicates that the geothermal fluids investigated here are mixtures of seawater with the SMOW values ( $\delta^2\text{H} = 0$  ‰,  $\delta^{18}\text{O} = 0$  ‰) and respective local meteoric waters ( $\delta^2\text{H} = -43.4$  ‰ to  $-24.2$  ‰,  $\delta^{18}\text{O} = -7.2$  ‰ to

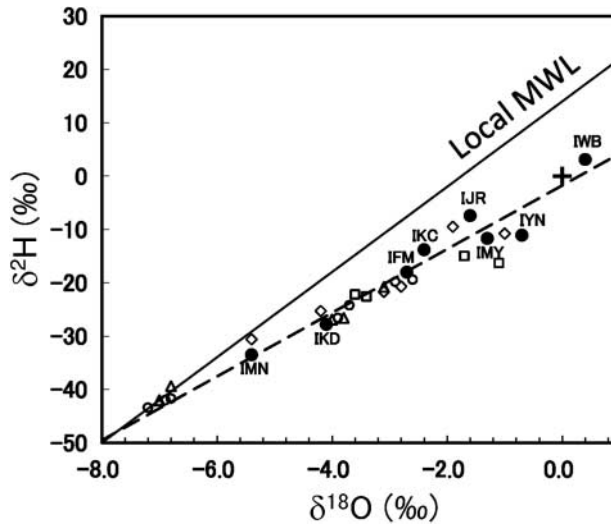


Figure 3. Correlation between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in the Ibusuki water samples.

Note: The solid line,  $(\delta^2\text{H}) = 8 \times (\delta^{18}\text{O}) + 14$ , is the local MWL drawn by using isotopic data of local ground waters presented in [6]. The broken line,  $(\delta^2\text{H}) = 5.97 \times (\delta^{18}\text{O}) - 1.74$ , shows the regression line for the data of the Ibusuki geothermal fluids obtained in this study. The decision coefficient ( $R^2$ ) was 0.93. The solid circles ( $\bullet$ ) tacked with the sample name abbreviated in Table 1 are the isotopic data obtained in this study. The bold cross (+) is the seawater value. The open circles ( $\circ$ ) are the data of the ground, lake and pond waters in the Ibusuki region reported in [5], and the open triangles ( $\Delta$ ) denote those of [6]. The open squares ( $\square$ ) and the open diamonds ( $\diamond$ ) are the data of Ibusuki hot spring waters reported in [5] and [6], respectively.

– 3.7 ‰) in the Ibusuki region [5]. The sample IMN is closely positioned at the crossover point of the local Meteoric Water Line (MWL; the solid line in Figure 3) and the Ibusuki hot water line.

## 5. Discussion

### 5.1. Correlation between two quantities

The value of the correlation coefficient ( $R$ ) between every pair of the concentrations of the major components and the stable isotopic compositions listed in Table 1 is summarised in Table 2.

Table 2. Correlation coefficients in the compositions of the major elements and stable isotopes.

	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	B	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^{37}\text{Cl}$	$\delta^{11}\text{B}$
$\text{Na}^+$	1.00	0.53	0.37	-0.02	0.98	0.82	0.98	0.91	-0.52	0.84
$\text{Ca}^{2+}$		1.00	0.37	0.37	0.61	0.15	0.60	0.63	-0.17	0.15
$\text{Mg}^{2+}$			1.00	-0.28	0.38	0.45	0.39	0.26	-0.39	0.43
B				1.00	0.02	-0.51	0.13	0.35	0.12	-0.49
$\text{Cl}^-$					1.00	0.76	0.96	0.88	-0.58	0.77
$\text{SO}_4^{2-}$						1.00	0.73	0.57	-0.33	0.94
$\delta^2\text{H}$							1.00	0.97	-0.48	0.78
$\delta^{18}\text{O}$								1.00	-0.37	0.62
$\delta^{37}\text{Cl}$									1.00	-0.50
$\delta^{11}\text{B}$										1.00

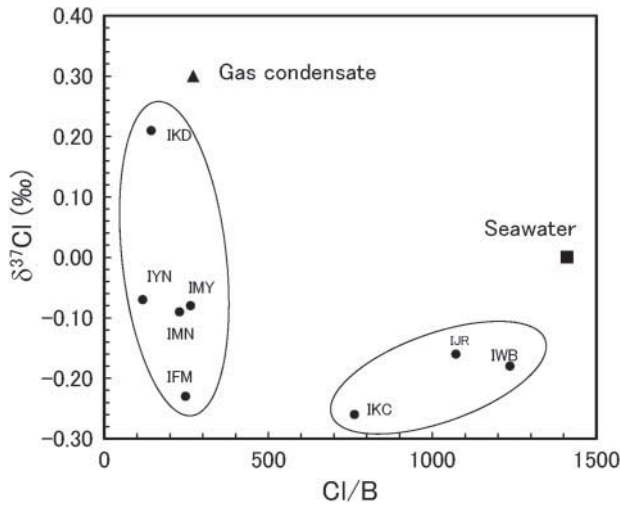


Figure 4. Correlation between Cl/B and  $\delta^{37}\text{Cl}$  in the Ibusuki water samples.

Note: The plots are divided into two groups encircled by the ovals (see text). The solid square (■) and the solid triangle (▲) indicate the plots of seawater and gas condensate, respectively.

The  $\delta^{37}\text{Cl}$  value is negatively correlated with that of the counterpart, except for B concentration. Although the absolute  $R$ -values for the  $\delta^{37}\text{Cl}$  are all less than 0.60, relatively good negative correlations are found in three pairs, that is,  $\delta^{37}\text{Cl}$  and  $\text{Na}^+$  concentration,  $\delta^{37}\text{Cl}$  and  $\text{Cl}^-$  concentration, and  $\delta^{37}\text{Cl}$  and  $\delta^{11}\text{B}$ . Since the  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations are positively correlated with each other (*vide infra*), it follows that the  $\delta^{37}\text{Cl}$  value increases with decreasing NaCl content and increasing  $\delta^{11}\text{B}$  value.

Besides the pairs including the  $\delta^{37}\text{Cl}$  value, fairly good correlations ( $R > +0.88$ ) are found in several pairs such as  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations,  $\text{Na}^+$  concentration and  $\delta^2\text{H}$ ,  $\text{Na}^+$  concentration and  $\delta^{18}\text{O}$ ,  $\text{Cl}^-$  concentration and  $\delta^2\text{H}$ ,  $\text{Cl}^-$  concentration and  $\delta^{18}\text{O}$ , and  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  pairs. Those positive correlations are explainable as the dilution effect of NaCl-type thermal water in the Ibusuki region by local meteoric water [5]. The  $\text{SO}_4^{2-}$  concentration decreases with decreasing  $\delta^{11}\text{B}$  value. It explains this finding that a seawater-hot rock interaction precipitates anhydrite (anhydrous calcium sulphate) from seawater [39]. The interaction preferentially takes  $^{10}\text{B}$  from seawater to hot rocks, causing the decreasing of the  $\delta^{11}\text{B}$  value in residual seawater [40].

The  $\delta^{37}\text{Cl}$  value is plotted against the  $\text{Cl}^-$  concentration normalised by B concentration in Figure 4. The plots are statistically classified into two groups; each of the two groups is enclosed by an oval. The members of one group show varying  $\delta^{37}\text{Cl}$  values, but have Cl/B values at around 230 that are similar to that of the gas condensate collected at Satsuma Iwo-Jima near Ibusuki (▲ in Figure 4). Another group is located close to the plot of seawater. Within this group, the  $\delta^{37}\text{Cl}$  value is positively correlated with the Cl/B ratio, which indicates that the  $\delta^{37}\text{Cl}$  value is gradually depleted from the value of seawater with decreasing Cl/B ratio.

The  $\delta^{11}\text{B}$  value is plotted against the  $\delta^{37}\text{Cl}$  value in Figure 5. The two quantities show a hyperbolic correlation, not a simple linear correlation with a negative slope. Samples IWB, IJR and IKC have Cl/B ratios of 763 or larger,  $\delta^{11}\text{B}$  values greater than +18 ‰ and  $\delta^{37}\text{Cl}$  values lower than -0.2 ‰. Samples IMN, IMY, IYN and IFM have Cl/B ratios of about 254,  $\delta^{11}\text{B}$  values around +10 ‰ and  $\delta^{37}\text{Cl}$  around -0.1 ‰. Sample IKD has a Cl/B ratio of 143, a  $\delta^{11}\text{B}$  value of +2 ‰ and a  $\delta^{37}\text{Cl}$  value of +0.21 ‰. This sample is located close to the gas condensate sample (▲) ( $\delta^{11}\text{B} = +6$  ‰ [41] and  $\delta^{37}\text{Cl} = +0.29$  ‰ [42]). As a whole, the Cl/B ratio gradually



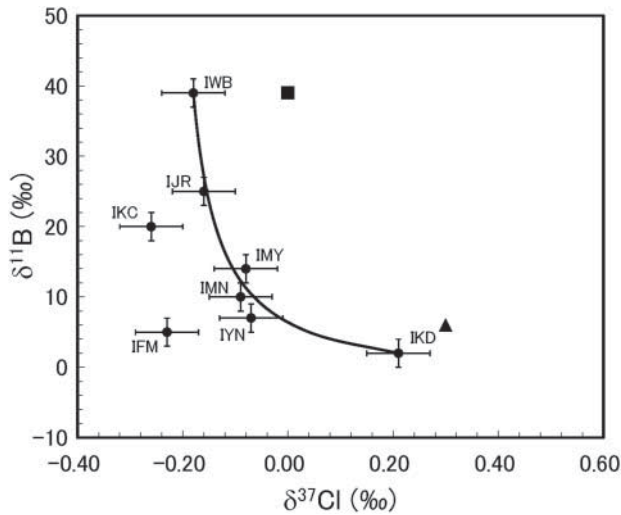


Figure 5. B–Cl isotope diagram.

Note: The labels on the plots correspond to the samples listed in Table 1. The number in the parenthesis next to the label was the Cl/B molar ratio. The error bars are equivalent to 1.0 ‰ for the  $\delta^{11}\text{B}$  values and 0.06 ‰ for the  $\delta^{37}\text{Cl}$  values. The  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  values of the gas condensate sample were ( $\blacktriangle$ ) reported as +6 ‰ [41] and +0.29 ‰ [42], respectively. The solid square ( $\blacksquare$ ) denotes the seawater point.

decreases from 1413 (IWB) to 127 (IKD). The data in Figure 5 indicate existence of relationship among the  $\delta^{11}\text{B}$  value, the  $\delta^{37}\text{Cl}$  value and the Cl/B ratio.

## 5.2. Binary mixtures of B and Cl with different isotopic ratios

Faure [43] described the plot of the isotopic ratios of an element against that of another element in a suite of binary mixtures defined a hyperbola given by Langmuir et al. [44]:

$$Ax + Bxy + Cy + D = 0, \quad (1)$$

where  $x$  and  $y$  are the isotopic ratios of the two elements, and  $A$ ,  $B$ ,  $C$  and  $D$  are coefficients. Denoting the two end members with the subscripts 1 and 2 and assuming that they have the isotopic ratios of  $x_1$  and  $y_1$ , and  $x_2$  and  $y_2$ , respectively, the coefficients of Equation (1) are given as:

$$A = a_2b_1y_2 - a_1b_2y_1, \quad (2)$$

$$B = a_1b_2 - a_2b_1, \quad (3)$$

$$C = a_2b_1x_1 - a_1b_2x_2, \quad (4)$$

and

$$D = a_1b_2x_2y_2 - a_2b_1x_1y_1. \quad (5)$$

In Equations (2)–(5),  $a_i$  is the amount of the isotope corresponding to the denominator of  $y_i$  and  $b_i$  is that of  $x_i$  ( $i = 1, 2$ ). We approximate that the amounts of  $^{10}\text{B}$  and  $^{35}\text{Cl}$  are proportional to the amounts of B and Cl, respectively. The shape of the hyperbola is controlled by the coefficient  $B$  of the cross-product term of Equation (1). If we define a factor  $K$  as a curvature of the mixing

hyperbola, then,  $K$  is expressed as,

$$K = \frac{(a_1 b_2)}{(a_2 b_1)} = \frac{(b_2/a_2)}{(b_1/a_1)}. \quad (6)$$

The greater the value of  $K$  is, the greater the curvature is.

In the present case, we plot  $^{11}\text{B}/^{10}\text{B}$  ( $y$ , the ordinate) vs.  $^{37}\text{Cl}/^{35}\text{Cl}$  ( $x$ , the abscissa) in Figure 5, so the coefficients  $A$ ,  $B$ ,  $C$  and  $D$  are rewritten as:

$$A = B_2 \times \text{Cl}_1 \times (^{11}\text{B}/^{10}\text{B})_2 - B_1 \times \text{Cl}_2 \times (^{11}\text{B}/^{10}\text{B})_1, \quad (7)$$

$$B = B_1 \times \text{Cl}_2 - B_2 \times \text{Cl}_1, \quad (8)$$

$$C = B_2 \times \text{Cl}_1 \times (^{37}\text{Cl}/^{35}\text{Cl})_1 - B_1 \times \text{Cl}_2 \times (^{37}\text{Cl}/^{35}\text{Cl})_2, \quad (9)$$

and

$$D = B_1 \times \text{Cl}_2 \times (^{11}\text{B}/^{10}\text{B})_2 \times (^{37}\text{Cl}/^{35}\text{Cl})_2 - B_2 \times \text{Cl}_1 \times (^{11}\text{B}/^{10}\text{B})_1 \times (^{37}\text{Cl}/^{35}\text{Cl})_1. \quad (10)$$

Here, the curvature is given by Equation (11):

$$K = \frac{(^{10}\text{B}_1 \cdot ^{35}\text{Cl}_2)}{(^{10}\text{B}_2 \cdot ^{35}\text{Cl}_1)} = \frac{(^{35}\text{Cl}_2/^{10}\text{B}_2)}{(^{35}\text{Cl}_1/^{10}\text{B}_1)} \approx \frac{(\text{Cl}_2/\text{B}_2)}{(\text{Cl}_1/\text{B}_1)}. \quad (11)$$

Since the amounts of  $^{10}\text{B}$  and  $^{35}\text{Cl}$  are expected to be proportional to those of  $\text{B}$  and  $\text{Cl}$ , respectively,  $K$  will be expressed as  $(\text{Cl}_2/\text{B}_2)/(\text{Cl}_1/\text{B}_1)$ . This means that the curvature is equivalent to the ratio of the  $\text{Cl}/\text{B}$  ratios of the two end members. Thus, good correlations among the  $\delta^{11}\text{B}$ ,  $\delta^{37}\text{Cl}$  and  $\text{Cl}/\text{B}$  values can be observed in Figure 5, in which, in addition to the fluid samples, the seawater (■) and gas condensate (▲) data are plotted. It can be said that the  $\text{Cl}/\text{B}$  ratio increases with decreasing  $\delta^{11}\text{B}$  value and with increasing  $\delta^{37}\text{Cl}$  value. The trend of the increase in the  $\text{Cl}/\text{B}$  ratio is observed from the sample IWB, the value of which is near that of seawater, to the sample IKD, the value of which is close to that of the high-temperature gas condensate. If we choose the samples IWB and IKD as the two end members to quantitatively show this trend, the value of  $K$  is then given as

$$K = \frac{(\text{Cl}_2/\text{B}_2)}{(\text{Cl}_1/\text{B}_1)} = \frac{143}{1236} = 0.116. \quad (12)$$

The obtained  $K$  value is much smaller than unity, which implies that the hyperbola expressing the mixing of the quantities  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  has a negative slope. Indeed, from the sample IWB to the sample IKD, the  $\text{Cl}/\text{B}$  ratio decreases with decreasing  $\delta^{11}\text{B}$  and increasing  $\delta^{37}\text{Cl}$ . This suggests that the decrease in the  $\text{Cl}/\text{B}$  ratio could be caused by the fact that the isotopic mole fraction of  $^{10}\text{B}$  increases more substantially than that of  $^{35}\text{Cl}$ . To say in other words, it suggests that the increase in the  $\text{Cl}/\text{B}$  ratio could be caused by the fact that the degree of decrease in the isotopic mole fraction of  $^{35}\text{Cl}$  is larger than that in the isotopic mole fraction of  $^{10}\text{B}$ .

### 5.3. Seawater-like deep saline fluid in the Ibusuki geothermal region

A previous study [5] discussed an influence of altered seawater on the Ibusuki geothermal fluid source and suggested that hydrothermal reactions between unaltered or diluted seawater and wall-rock minerals produced typical  $\text{Na}-\text{Ca}-\text{Cl}$  water types with low  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations. Among the samples in this study, the sample IWB taken from the deepest well ( $-750$  m) in the Ibusuki region is the closest to the seawater in the  $\delta^{11}\text{B}-\delta^{37}\text{Cl}$  diagram (Figure 5). The chemical composition of this sample is similar to the hydrothermally altered fluid described

in [5]. For instance, the molar ratios of  $\text{Mg}^{2+}/\text{Ca}^{2+}$ ,  $\text{Na}^+/\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}/\text{Ca}^{2+}$  are lower and the NaCl content is higher than those of seawater (the content of NaCl in the sample divided by that in seawater,  $R_{\text{NaCl}} = 1.03$ ), whereas the sodium and sulphate contents are as high as those of seawater (Table 1). These features, as mentioned before, are those commonly observed in residual saline water produced by the chemical reaction between seawater and hot rocks. The reaction causes precipitation of anhydrite from seawater that is saturated in the Na–Ca–Cl three-component system and decreases the amount of  $\text{SO}_4^{2-}$  in the liquid phase [39].

A previous study [39] on the hydrogen and oxygen isotopic analyses of Ibusuki geothermal samples identified water that showed  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values higher than those of mean ocean water (see seawater in Table 1), and as high as those of a deep brine. This suggested that the isotopically heavy water was a product of the seawater alteration [39]. In this study, the sample IWB is the only fluid having  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values higher than those of sea water (Table 1), suggesting that the IWB fluid is most likely altered seawater produced by seawater–hot rock interaction in the Ibusuki geothermal aquifer.

Figure 5 shows that the  $\delta^{37}\text{Cl}$  value of the IWB fluid is 0.18 ‰, which is smaller than that of the seawater, suggesting that the seawater–hot rock interaction preferentially depletes  $^{37}\text{Cl}$  into the fluid. If this kind of interaction occurred under high-temperature and high-pressure conditions, which are the ones expected for the present case, however, the accompanying chlorine isotope fractionation would be negligible. Thus, as far as the  $\delta^{37}\text{Cl}$  value is concerned, the IWB fluid is not simply the altered seawater by fluid–rock interaction nor a fluid formed by isotope dilution by a chlorine source depleted in  $^{37}\text{Cl}$ , although the source is unknown.

As for the  $\delta^{11}\text{B}$  value and boron content, the alteration reaction may deplete  $^{11}\text{B}$  and reduce the boron content of seawater, as it was seen in hydrothermal fluids at ocean ridges [40]. Contrary to this, the  $\delta^{11}\text{B}$  value and boron content of the present sample IWB (+39 ‰ and  $0.43 \text{ mmol L}^{-1}$ ) are as high as those of seawater (+38.9 ‰ and  $0.38 \text{ mmol L}^{-1}$ ), as reported in [7]. This may constrain the magnitude of seawater alteration by the water–rock interaction. It may suggest that in the case of Ibusuki, the  $\delta^{11}\text{B}$  value of the sample IWB may reflect that of the residual fluid produced by the alteration reaction with the negligible degree of the boron isotopic fractionation.

#### 5.4. Fluid bearing magmatic volatiles

The IKD fluid is the best candidate of the fluid influenced by magmatic volatiles among the Ibusuki fluids examined. This fluid is chemically distinctive, that is, it has a higher  $\delta^{37}\text{Cl}$  value (+0.21 ‰), a lower  $\delta^{11}\text{B}$  value (+2.1 ‰), and a lower Cl/B mole ratio than any other fluid samples examined (Table 2). It is interesting to note in Figure 5 that the plot of the sample IKD is very close to that of the high-temperature gas condensate ( $\blacktriangle$ ) with  $\delta^{11}\text{B} = +6 \text{ ‰}$  [41] and  $\delta^{37}\text{Cl} = +0.29 \text{ ‰}$  [42]. A study [41] on the  $\delta^{11}\text{B}$  values of gas samples taken from various temperature vents of Satsuma Iwo-jima revealed that lower temperature gas samples (< 400 °C) showed a large  $\delta^{11}\text{B}$  variation, compared to higher temperature gas samples (> 400 °C) that showed a nearly constant  $\delta^{11}\text{B}$  value. This finding was interpreted as showing that the  $\delta^{11}\text{B}$  value of the boron reservoir supplying boron to gases of various vents was better preserved in the latter than in the former. This is because isotope effects at higher temperature are normally negligible, and the high-temperature gas may thus have been less influenced by the shallow aquifer during volatilisation. If this is the case with the  $\delta^{37}\text{Cl}$  value in Ibusuki, the  $\delta^{37}\text{Cl}$  value of the highest temperature gas could have been preserved better and might represent that of the chlorine reservoir better than any other gases from lower temperature–fumarolic vents, as was pointed out by [42].

At a higher temperature, Cl isotopic exchange reactions between two phases in equilibrium become more negligible [45]. Experimentally obtained Cl isotope fractionation factors of equilibrium systems were at most 0.3 ‰ at room temperature [29,30,46]. If there are kinetic isotope

effects of chlorine during vapourisation of chlorine-bearing volatiles from the fluid phase at high temperatures, either isotopes of chlorine could be enriched in the volatile depending on its kind. If the volatile is HCl, for instance,  $^{37}\text{Cl}$  will be enriched in the vapour phase [16]. In fact, a large kinetic fractionation associated with Cl isotopes in volcanic systems during the gas-condensation process was recently reported; the Cl isotopes fractionating during interaction with water at high temperature ( $> 100\text{ }^\circ\text{C}$ ) caused  $\delta^{37}\text{Cl}$  values of the gases increasing from 0 up to 12 ‰ [47]. However, an experimental study on the Cl isotopic fractionation between coexisting vapour and liquid in the  $\text{H}_2\text{O}\text{--NaCl}$  system showed that the degree of the fractionation was nearly zero [15]. Results of those studies indicate that the liquid–vapour interactions may not affect the Cl isotopic composition of the water largely, suggesting that the  $\delta^{37}\text{Cl}$  value of a volatile preserves that of magma's value.

The difference in the  $\delta^{37}\text{Cl}$  value between the sample IKD, which was taken from a long drill-hole with 248 metres below sea level, and the highest temperature gas condensate is very small. This strongly indicates that the Cl isotopic fractionation between high-temperature gas and the sample IKD is negligible, and can be interpreted as showing that meteoric water functioned simply as a solvent to dissolve chloride, and consequently, the  $\delta^{37}\text{Cl}$  value of the sample IKD was little affected by any isotopic exchange.

The B isotope fractionation factor between the vapour and fluid phases was experimentally obtained, which showed that the heavier isotope ( $^{11}\text{B}$ ) is enriched into the vapour phase, whereas the lighter isotope is concentrated into the fluid phase [48]. Generally, isotope effects are temperature dependent; the higher the temperature is, the smaller the magnitude of the isotope effect is. Recent studies have shown that B isotope effects decreased with increasing pressure [31,49]. Therefore, the  $\delta^{11}\text{B}$  value in a high-temperature gas could represent those of magma as the boron reservoir. If a condensate of this gas formed the IKD-like geothermal fluid, the  $\delta^{11}\text{B}$  value of this fluid could represent that of the local magma.

The gas condensate marked with ▲ in Figures 2, 4, 5 and 6 was derived from a rhyolitic magma forming a volcanic island, Satsuma Iwo-jima, which is located on the Ryukyu Island arc. The Ibusuki geothermal area belongs to the Ata volcano, which is located on the same Island arc as Satsuma Iwo-jima belongs to. Both volcanos are situated on the same volcanic front line, which was formed by subduction of the Philippine Sea plate under the Eurasian plate. According to Nishimura [2], water is released as a result of dehydration of amphibole and chlorite in the dragged hydrated peridotite layer around 110 km just beneath the volcanic front. The released water migrates upwards and reaches the Ibusuki region. Matsubaya et al. [6] measured tritium contents in fumarolic steam, hot springs and ground waters in Satsuma Iwo-jima, and stated that contribution of the meteoric water or unaltered seawater to the fumarolic gas was not observed in the region. Assuming that the chloride in the sample IKD is originated from volatiles derived from magma of the Ata volcano where Ibusuki locates, the  $\delta^{37}\text{Cl}$  value of IKD will represent that of magmatic chloride. If Satsuma Iwo-jima has a similar history of chemical and isotopic alteration during upwards water migration, we may consider that the isotopic values of the gas condensates derived from the highest temperature (890 °C) vent of the Satsuma Iwo-jima are most likely the values of magmatic volatiles that influence the chlorine source of Ibusuki geothermal fluids. Among the samples examined, the IKD fluid is the only one that is acidic (pH = 3.68). The Cl/B ratio of the sample IKD is twice as high as the average of those of the gas condensates [41]. In addition, the  $R_{\text{NaCl}}$  value of IKD is 5–10 times lower than that of seawater. The IKD fluid is not similar to brine as the other samples are, but is like acidic water. Therefore, the sample IKD could be representative of the boron and chlorine reservoir in the Ibusuki geothermal system. In particular, the isotopic signatures of the sample IKD suggest that the reservoir would have been magmatic.

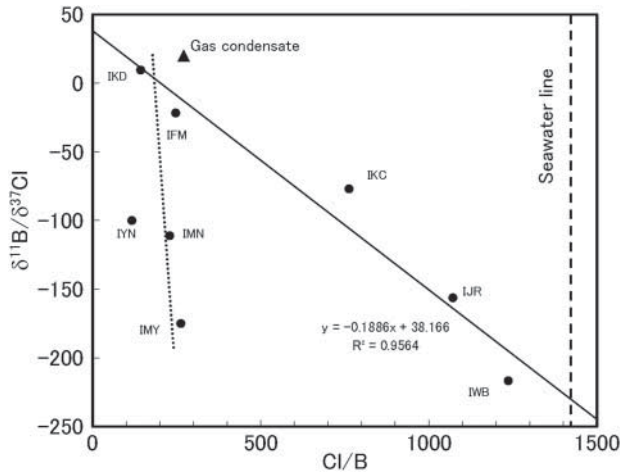


Figure 6. Relationship between  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  ratio and  $\text{Cl}/\text{B}$  molar ratio in the Ibusuki geothermal region. Note: The labels on the plots correspond to the samples listed in Table 1. The solid line represents the least squares-fitted line for five samples IKD, IFM, IKC, IJR and IWB (Group-1, G1). The dotted line represents the least squares-fitted line for five samples IKD, IFM, IYN, IMN and IMY (Group-2, G2). The vertical broken line indicates the  $\text{Cl}/\text{B}$  ratio of seawater. The triangle ( $\blacktriangle$ ) indicates the plot of the gas condensate from the highest temperature gas vent at Satsuma Iwo-jima (see text).

### 5.5. Relationship between $\delta^{11}\text{B}/\delta^{37}\text{Cl}$ ratio and $\text{Cl}/\text{B}$ molar ratio in the Ibusuki geothermal system

The relationship between the  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  ratio and the  $\text{Cl}/\text{B}$  molar ratio is shown in Figure 6. The samples are clearly divided into two groups: Group-1 (G1) includes samples IKD, IFM, IKC, IJR and IWB, whereas Group-2 (G2) includes samples IKD, IFM, IYN, IMN and IMY. The G1 members are closely located around the least squares-fitted line,  $(\delta^{11}\text{B}/\delta^{37}\text{Cl}) = -0.19 \times (\text{Cl}/\text{B}) + 38.17$  with the correlation coefficient of  $-0.96$ . The two end members of the group are the sample IKD, plotted near the high-temperature gas condensate and the sample IWB, whose chemical composition is that of altered seawater, discussed in Sections 5.2 and 5.3. This finding indicates that the  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  ratio decreases with increasing  $\text{Cl}/\text{B}$  molar ratio. The G2 members are located at around the  $\text{Cl}/\text{B}$  ratio of 200 and are independent of the  $\text{Cl}/\text{B}$  molar ratio. This implies that the G2 members are binary mixtures between two fluid sources of the similar  $\text{Cl}/\text{B}$  molar ratio but different  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  ratios, only if the samples IYN, IMN and IMY are not the outliers of the G1.

The relationship in Figure 6 is described as Equation (13).

$$\frac{(\delta^{11}\text{B}/\delta^{37}\text{Cl})}{(\text{Cl}/\text{B})} = \frac{\{\delta^{11}\text{B}/(1/\text{B})\}}{\{\delta^{37}\text{Cl}/(1/\text{Cl})\}} = p. \quad (13)$$

In the case of the G1, the value of the trend rate,  $p$ , is  $-0.19$ . Since the  $\delta^{37}\text{Cl}$  values of the G1 samples except for the sample IKD, an end member of the G1, are negative, we can derive the relation (Equation (14)) from Equation (13) as,

$$\frac{\delta^{11}\text{B}}{(1/\text{B})} > 0 \quad \text{and} \quad \frac{\delta^{37}\text{Cl}}{(1/\text{Cl})} < 0. \quad (14)$$

It shows that the  $\delta^{11}\text{B}$  value increased with increasing boron concentration and the  $\delta^{37}\text{Cl}$  value decreased with decreasing chlorine concentration in the fluids, implying the preferential increases in  $^{11}\text{B}$  and  $^{35}\text{Cl}$ . Figure 6 thus suggests that  $^{11}\text{B}$  increases and  $^{37}\text{Cl}$  decreases from the samples

IKD to IWB, with increasing Cl/B ratio because of the increase in chloride concentration and the decrease in the boron concentration.

In summary, the Ibusuki geothermal region has at least two fluid-mixing mechanisms: one is mixing between the magmatic volatiles and the altered seawater, and another is mixing between the magmatic volatiles and the local meteoric water.

## 6. Conclusions

In this study, eight geothermal fluids collected at various depths (73–780 m below sea level) in the Ibusuki coastal geothermal region were chemically and isotopically investigated to understand the geothermal system there.

The obtained  $\delta^{37}\text{Cl}$  values varied between  $-0.26$  and  $+0.21$  ‰. Only one sample showed a positive value. The average of the  $\delta^{37}\text{Cl}$  values of the remaining samples was  $-0.15$  ‰.

The  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  correlation,  $(\delta^2\text{H}) = 6.0 \times (\delta^{18}\text{O}) - 1.7$  ( $R^2 = 0.931$ ), agreed with the  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  line representing a mixture between seawater and respective local meteoric water in the Ibusuki region reported by [14]. The  $\delta^{37}\text{Cl}$  values plotted against Cl/B ratios apparently divided Ibusuki geothermal waters into two groups: the one located near the plot of the gas condensate sampled in a nearby area and the other near seawater.

A  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  – Cl/B diagram based on the  $\delta^{37}\text{Cl}$  data with the boron isotopic data ( $\delta^{11}\text{B}$ : ‰) by [7] indicates two mixing groups. One group mixes a fluid depleting in  $^{37}\text{Cl}$  with a higher value of Cl/B molar ratio with a fluid enriching in  $^{37}\text{Cl}$  with a lower Cl/B molar ratio and pH values (pH = 3.68), and the other group mixes two fluids of the similar Cl/B molar ratio but different  $\delta^{11}\text{B}/\delta^{37}\text{Cl}$  ratios. The former group identifies the sources as deep brine, which is altered seawater through the seawater–hot rock interaction, and magmatic volatile similar to gas condensate derived from the high-temperature (890 °C) vent of an island-arc volcano near the Ibusuki region. The latter group estimates possible existence of the third fluid source in Ibusuki, only if the samples in this group are not the outliers of the former.

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