地 震 研 究 所 彙 報
Bull. Earthq. Res. Inst.
Univ. Tokyo
Vol. 83 (2008) pp. 217-225

# Chemical Characteristics of Hot Spring Water and Geological Environment in the Northernmost Area of the Itoigawa Shizuoka Tectonic Line

Ayaka Homma[1)]* and Hiroaki Tsukahara[2)]

[1)] Graduate School of Science and Technology, Shinshu University
[2)] Department of Environmental Sciences, Faculty of Science, Shinshu University

**Abstract**

Hot springs around the northernmost part of the Itoigawa Shizuoka Tectonic Line (ISTL) are investigated. The Otari and the Hakuba villages, Nagano Prefecture are the study area. The area is divided into two areas by the ISTL, the Hida Gaien belt area (western part) and the Fossa Magna area (eastern part): the former is consists of weakly metamorphosed formations containing melange belt with ultramafic rocks and the latter is of sedimentary rocks of mainly sandy mudstone. Physical and chemical measurements for the hot spring waters are expected to provide a relation between geological structure and characteristics of hot spring water, and also to provide information about correct trace of the ISTL in the area covered with sediments.

The percentage of ($Mg^{2+}+Ca^{2+}$) in total cation (in eq/l) is found to be a good indicator for drawing a line between the Hida Gaien belt area and the Fossa Magna area. In the case of the study area, the percentage for the drawing is 15%: lager values for the Hida Gaien belt area and smaller ones for the Fossa Magna area. Therefore, hot springs in the boundary zone are classified by the percentage. Furthermore, an unusual concentration in $SO_4^{2-}$ ion in the Fossa Magna area is observed. That is, the concentrations of $SO_4^{2-}$ ion in the hot spring waters are smaller than those of the river waters. The unusual concentration reveals that the origin of $SO_4^{2-}$ ion in the hot spring water is pyrite ($FeS_2$) in the formation. In the Renge hot spring group, very high concentrations of $SO_4^{2-}$ and $Mg^{2+}$ are observed, which are explained in terms of interaction among $SO_2$ gas from a volcano, ultra mafic rocks and underground water. That is, underground water reacting with high temperature $SO_2$ becomes strong acid hot water with large amount of $SO_4^{2-}$. The hot water reacts with ultra mafic rocks around the hot water reservoir, and the hot water has high concentration of $Mg^{2+}$.

**Key words**: Hot spring geochemistry, Hida Gaien belt, Fossa Magna, Itoigawa Shizuoka Tectonic Line

## 1. Introduction

The study area is situated at the northeastern part of Nagano Prefecture (Fig. 1). As shown on Fig. 2, the site is around the northernmost part of Itoigawa Shizuoka Tectonic Line (ISTL), and is divided by ISTL into two areas, the Fossa Magna area and the Hida Gaien belt area. ISTL is one of the largest inland active tectonic lines in the Japan Islands. However, the trace of ISTL is not always seen on the surface. ISTL forms complex structure here (*e.g.*, Nakano *et al.*, 2002). We expect that hot spring water provides individual information to geological evidence about the situation of ISTL under the sediments.

Iijima and Miyajima (1968) studied characteristics of hot spring in the Fossa Magna area in Nagano Prefecture and pointed out that the chemical components of hot waters were roughly related to the geologic settings of the hot springs. Abe *et al.* (1978) studied on chemical properties of hot spring waters

*e-mail: s07a608@shinshu-u.ac.jp (3-1-1 Asahi, Matsumoto 390-8621, Japan)

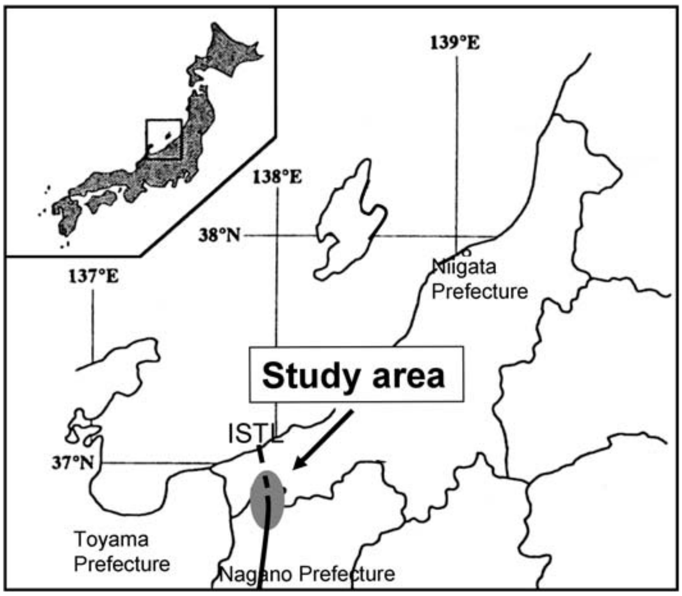


Fig. 1. Index map showing the location of study area.

along the Himekawa river which is flowing along the ISTL and described the characteristics of each hot spring water, but did not discuss about the relation between the geological structure and chemical composition of hot spring water. There is almost no systematic study on hot springs in relation to geological structure in the ISTL area.

We investigate the hot springs which are welling up in the area of the northernmost part of ISTL. There are many hot springs in both areas. We have extended the coverage of our study area wider than that of Abe *et al.* (1978) in order to survey two areas, the Fossa Magna area and the Hida Gaien belt area. River water near the hot spring is also analyzed for comparison with hot spring water quantity, and the river water measurements have given us a new viewpoint about origin of $SO_4^{2-}$ in hot spring water.

Movement of an active fault sometimes effects chemical change in ground water or hot spring water : for example, $Cl^-$ concentration increased in ground water before the 1995 Hyogo-ken Nanbu Earthquake (Tsunogai and Wakita, 1995), which began half a year before the earthquake. As mentioned above, the ISTL constitutes one of the largest active faults. The basic description about the hot spring water chemistry in this study area is expected to be useful for detecting precursory anomaly.

## 2. Geological settings of the study area

Geologically quite different two areas, the Fossa Magna area and the Hida Gaien belt area are contacted with each other by ISTL in the study area. As shown in Fig. 2, the Fossa Magna area situates in the eastern part, and the Hida Gaien belt is the western part.

The Fossa Magna area is covered by Neogene formations, mainly sedimentary rocks of sandy mudstone. On the contrary, the Hida Gaien belt is an ancient accretionary prism complex, and is composed of weakly metamorphosed formation of Devonian to Permian formations containing melange belt with ultramafic rocks.

There are some Quaternary volcanoes in the Hida Gaien belt area: the Shirouma-Oike volcano group which is mainly composed of Mt. Norikuradake and Mt. Kazahukidake. These volcanoes have erupted andesitic lavas and pyroclastic flow materials. Further, small scale granitic intrusions are exposed in this area.

Hot springs are sporadically distributed in the two areas. We wish to get keys in the characteristics of the hot springs that may be used to infer the difference between the two areas. We expect that the physical and chemical measurements for hot spring waters reveal the relation between geological structure and characteristics of hot spring water. Then we emphasize on getting information from border

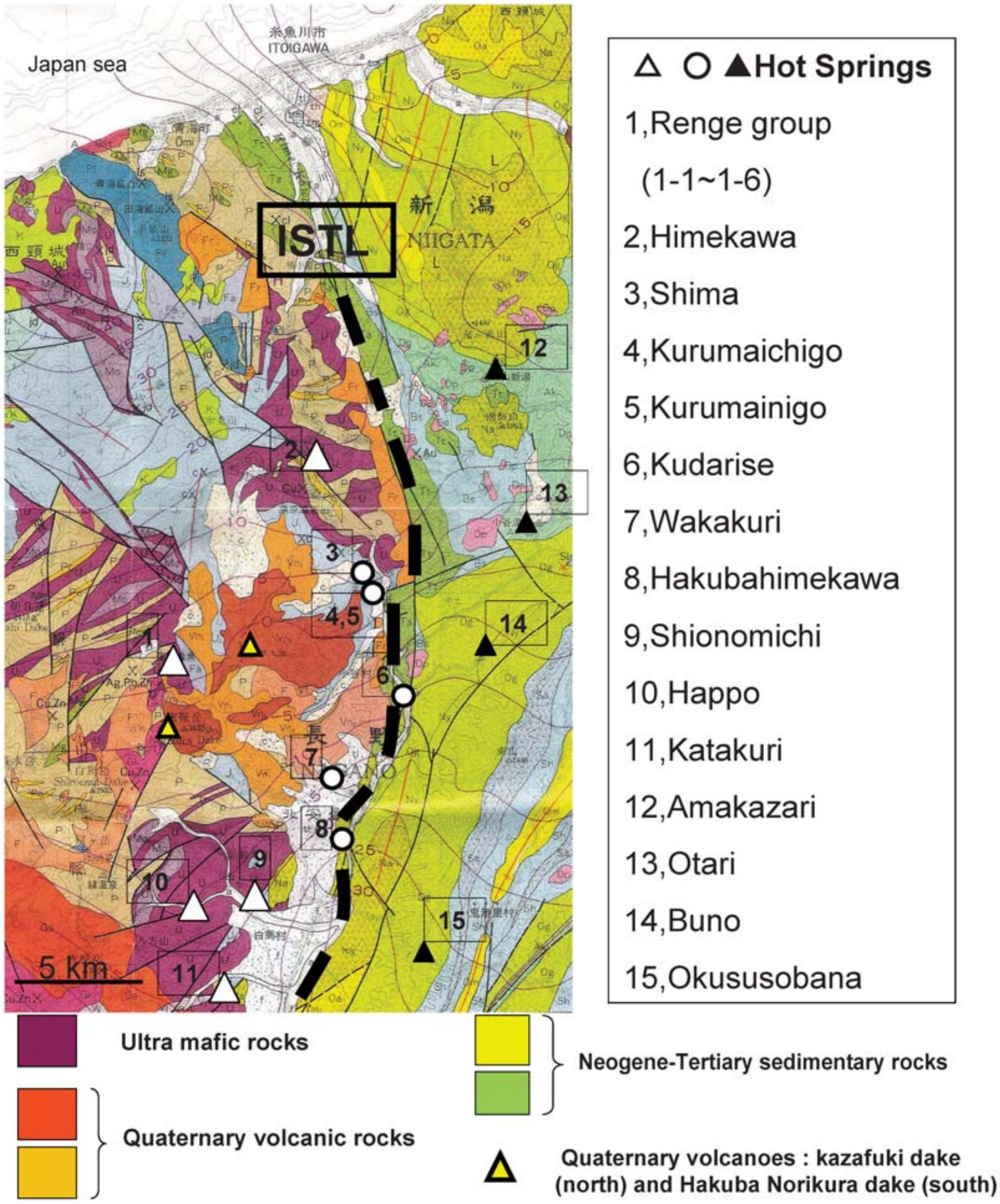


Fig. 2. Locations of hot springs and geological map (geological map from Harayama *et al.,* 1995). The east side of ISTL is the Fossa magna area of sandy mudstone, the west side the Hida Gaien belt of ancient accretionary prism complex with ultramafic rocks. Dashed line of the ISTL is schematically drawn along the geologic boundary. Three symbols, white triangles, black triangles, and white circles, indicate the hot spring locations, the Hida Gaien belt area, the Fossa Magna area, and the border area between the two areas, respectively.

area. We define a zonal area with 2.5 km distance from ISTL shown in the geological map of Harayama *et al.,* (1995, Fig. 2) as the border area hereinafter.

**3. Sampling and method for chemical analysis**

Most of hot springs in the study area is investigated. The measurement points, 21 points are shown in Fig. 2. We also measure the river water streaming nearby the hot spring to compare the data with those obtained from hot springs.

Water temperature, electrical conductivity (EC), and pH are measured at the sampling points. Water samples are collected in plastic bottles for chemical analysis in a laboratory. An ion chromatograph

(Jasco CO-1560 and PU-1580) is used for major ion components: $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, and $SO_4^{2-}$. The quantity of $HCO_3^-$ is estimated from ion balance calculation, that is, total cation minus two anions ($SO_4^{2-}+Cl^-$) in a unit of equivalent/litter, because the above mentioned ion components measured with the ion chromatograph include whole major components in the water except $HCO_3^-$.

We use the water sample obtained in late autumn to early winter, from October to December, because we want to obtain the data for stream water without mixing with melted snow. But we cannot get a sample at the Renge hot spring group in winter season because of closing. Therefore, we obtain the specimen in the summer only from the Renge group.

## 4. Results and Discussion

### (1) Chemical composition and geological structure

All of the measured data are put into tabular form in Table 1 for hot springs and in Table 2 for river waters.

It is well known that the equilibrium concentration of the individual aqueous carbonate species, $H_2CO_3$, $HCO_3^-$ and $CO_3^{2-}$, can be expressed as a function of pH. The $H_2CO_3$ is predominant in the water less than pH 6. Therefore, such high concentration of $HCO_3^-$ in the hot waters of Shima and Buno which have pH=5.8 and 5.88 (see No.5 and 14 in Table 1) seems to be unusual. However, the ratio $HCO_3^-$ to $H_2CO_3$ is not zero in hot water of pH=5.8 at 40℃ but about 1/3 (*e.g.,* Stumm and Morgan,1996). Therefore, when a lot of carbonate is dissolved in the hot spring water, not a little $HCO_3^-$ is also present in the water with $H_2CO_3$. In fact, alkalinity was determined in the laboratory by titration with hydrochloric acid, and it was confirmed that almost the same amount of $HCO_3^-$ as estimated values shown in the table existed in both Shima and Buno hot waters.

The each ion concentration in hot spring water is plotted on the Piper diagram (Fig. 3) for classification of the hot spring water on the basis of chemical composition. Three symbols in Fig. 3, white triangles, black triangles, and white circles, indicate the hot spring location, the Hida Gaien belt area, the Fossa Magna area, and the border zone between the two areas, respectively.

The key diagram in the Piper diagram, the central diamond diagram in Fig. 3, shows that the region larger than 15% of ($Ca^{2+}+Mg^{2+}$) in total cation, or smaller than 85% of ($Na^++K^+$) in total cation is occupied mostly by the Hida Gaien belt hot spring data shown by white triangles. It is expected from the key diagram that the percentage of ($Ca^{2+}+Mg^{2+}$) in total cation is applicable to judgment whether the hot spring water is influenced by the Fossa Magna formation or by the Hida Gaien belt formation.

For better understanding above phenomenon, we represent the ratio of ($Ca^{2+}+Mg^{2+}$) and ($Na^++K^+$) in total cation in percentage on Fig. 4. Gray bars in the figure shows percentage of ($Ca^{2+}+Mg^{2+}$) in total cation, and white bars are for the percentage of ($Na^++K^+$) in total cation. It is clear that almost all of the data obtained from the hot springs in the area of the Fossa Magna have percentages smaller than 15% of ($Ca^{2+}+Mg^{2+}$) in total cation.

When the 15% is the boundary value between the two areas, the hot springs in the boundary zone can be classified into two groups, *i.e.,* the Fossa Magna group and the Hida Gaien belt group, according to the percentage, and we may conclude that Katakuri and Kurumaichigo belong to the Hida Gaien belt group, and Wakakuri and Kurumanigo belong to Fossa Magna group. The hot springs Shima and Kudarise lie between the two groups.

The major cations of $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$ are generally originated from mother rocks of the hot spring. Silicic or acidic rocks such as sandstone and granitic rocks contain little amount of $Ca^{2+}$ and $Mg^{2+}$, and contains large amount of $Na^+$ and $K^+$. On the contrary, mafic or basic rocks are reversed. The Fossa Magna area is mainly covered by sedimentary rocks of sandy mudstone, and the Hida Gaien belt is composed of weakly metamorphosed complex with ultramafic rocks. Therefore, it is consistent that $Ca^{2+}$ and $Mg^{2+}$ contents are relatively small in the hot spring waters in the Fossa Magna area.

### (2) Origin of $SO_4^{2-}$

Figure 5 shows $SO_4^{2-}$ concentrations of hot spring and river waters in three areas, the Hida Gaien belt area, the Fossa Magna area, and the border zone between the two areas. White bars and black bars indicate hot spring data and river data, respectively. River data are obtained from water streaming nearby the hot spring. When multiple data have been obtained from one hot spring, averaged data is

Table 1. Measured data of hot springs

| No.[1] | Hot spring | Depth(m) | Sampling date | Temp (℃) | pH | EC (mS/m) | $Na^+$ (mg/l) | $K^+$(mg/l) | $Ca^{2+}$(mg/l) | $Mg^{2+}$(mg/l) | $Cl^-$(mg/l) | $SO_4^{2-}$(mg/l) | $HCO_3^-$(mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-1 | Renge Sangokuichi | 0 | 20060730 | 30.7 | 2.70 | 146.0 | 3.28 | 6.45 | 9.25 | 23.20 | 1.38 | 589.00 | 0.0 |
| 1-2 | Renge Yakushi | | 20060730 | 39.7 | 2.65 | 132.0 | 1.04 | 2.56 | 5.07 | 15.20 | 1.46 | 394.00 | 0.0 |
| 1-3 | Renge Senki | | 20060730 | 56.1 | 3.10 | 62.3 | 2.33 | 2.17 | 5.75 | 14.20 | 1.37 | 216.00 | 0.0 |
| 1-4 | Renge Gensen | | 20060730 | 89.1 | 3.00 | 65.8 | 1.68 | 2.62 | 2.60 | 5.05 | 0.87 | 227.00 | 0.0 |
| 1-5 | Renge Yakushinoura | | 20060730 | unknown | unknown | unknown | 2.10 | 2.70 | 5.50 | 14.40 | 3.63 | 379.00 | 0.0 |
| 1-6 | Renge Kogane | | 20060730 | 40.8 | 6.69 | 150.0 | 11.10 | 2.60 | 13.30 | 211.00 | 1.84 | 112.00 | 964.0 |
| 2 | Himekawa | 0 | 20060730 | 56.0 | 6.82 | 211.0 | 343.00 | 6.91 | 77.90 | 6.82 | 191.00 | 9.54 | 964.0 |
| | | | 20061121 | 48.5 | 7.85 | 216.0 | 318.00 | 28.40 | 51.00 | 19.00 | 172.00 | 0.68 | 842.0 |
| 3 | Kurumaichigo | 350 | 20060517 | 39.8 | 6.36 | 142.0 | 268.00 | 9.15 | 74.30 | 11.50 | 212.00 | 147.00 | 457.0 |
| | | | 20060525 | 40.0 | 6.25 | 137.0 | 206.00 | 5.11 | 57.30 | 8.91 | 106.00 | 57.10 | 517.0 |
| | | | 20061126 | 37.4 | 6.67 | 140.0 | 231.00 | 4.19 | 62.30 | 7.10 | 142.00 | 14.60 | 582.0 |
| 4 | Kurumanigo | 750 | 20060503 | 64.1 | 6.42 | 396.0 | 969.00 | 19.30 | 63.00 | 21.20 | 693.00 | 253.00 | 1390.0 |
| | | | 20060525 | 73.5 | 6.92 | 413.0 | 851.00 | 15.50 | 27.10 | 8.72 | 422.00 | 116.00 | 1540.0 |
| | | | 20061126 | 68.4 | 6.95 | 389.0 | 846.00 | 14.10 | 33.80 | 5.24 | 83.20 | 55.50 | 2190.0 |
| 5 | Shima | 10 | 20060503 | 39.1 | 5.80 | 98.7 | 394.00 | 9.62 | 91.70 | 8.06 | 197.00 | 9.88 | 1030.0 |
| | | | 20060525 | 40.1 | 6.15 | 189.0 | 742.00 | 5.68 | 4.16 | 7.36 | 297.00 | 29.40 | 1480.0 |
| | | | 20061126 | 39.4 | 6.07 | 196.0 | 277.00 | 6.79 | 7.78 | 2.87 | 40.80 | 28.40 | 677.0 |
| 6 | Kudarise | 100 | 20060605 | 30.1 | 6.90 | 297.0 | 652.00 | 7.04 | 2.72 | 77.10 | 332.00 | 33.80 | 1530.0 |
| | | | 20061201 | 31.0 | 7.01 | 303.0 | 742.00 | 5.68 | 4.16 | 7.36 | 297.00 | 29.40 | 1470.0 |
| 7 | Wakakuri | 1100 | 20060605 | 58.7 | 7.28 | 146.0 | 277.00 | 6.79 | 7.78 | 2.87 | 40.80 | 28.40 | 677.0 |
| | | | 20061201 | 57.8 | 7.33 | 164.0 | 338.00 | 4.75 | 1.15 | 1.42 | 41.30 | 26.40 | 812.0 |
| 8 | Katakuri | 1000 | 20010824 | 30.6 | 8.22 | 52.0 | 108.00 | 1.94 | 16.20 | 2.97 | 19.70 | 78.00 | 220.0 |
| | | | 20011209 | 29.9 | 7.07 | 61.9 | 137.00 | 1.46 | 17.40 | 3.63 | 25.50 | 115.00 | 248.0 |
| 9 | Hakubahimekawa | unknown | 20011209 | 50.1 | 7.40 | 451.0 | 725.00 | 75.30 | 166.00 | 44.50 | 1570.00 | 0.00 | 73.7 |
| 10 | Shionomichi | 1050 | 20010824 | 43.6 | 6.99 | 1500.0 | 3651.00 | 190.00 | 9.75 | 383.00 | 5450.00 | 5.09 | 2550.0 |
| | | | 20011209 | 44.6 | 6.94 | 1400.0 | 3704.00 | 159.00 | 134.00 | 405.00 | 5430.00 | 5.41 | 3170.0 |
| 11 | Happo | 1000 | 20010824 | 51.7 | 11.00 | 62.8 | 48.90 | 6.51 | 3.18 | 0.01 | 8.85 | 0.34 | 134.0 |
| | | | 20011209 | 51.9 | 11.10 | 62.1 | 47.50 | 5.15 | 20.80 | 0.00 | 8.10 | 0.16 | 183.0 |
| 12 | Amakazari | 0 | 20060823 | 46.6 | 6.45 | 291.0 | 584.00 | 24.70 | 46.40 | 13.70 | 362.00 | 0.00 | 1180.0 |
| | | | 20061126 | 42.0 | 7.13 | 284.0 | 599.00 | 17.70 | 19.80 | 7.92 | 351.00 | 1.98 | 1110.0 |
| 13 | Otari | 150 | 20060605 | 56.3 | 6.84 | 380.0 | 971.00 | 13.50 | 16.50 | 8.53 | 121.00 | 0.54 | 2480.0 |
| 14 | Buno | 0 | 20060517 | 30.3 | 6.27 | 1130.0 | 2990.00 | 74.60 | 49.10 | 242.00 | 3210.00 | 0.82 | 3880.0 |
| | | | 20060811 | 31.5 | 5.88 | 1270.0 | 2800.00 | 58.30 | 68.30 | 26.40 | 3290.00 | 0.23 | 2200.0 |
| 15 | Okususobana | 0 | 20061107 | 11.4 | 8.10 | 20.0 | 35.10 | 0.80 | 9.14 | 3.02 | 1.43 | 8.54 | 124.0 |

[1]Locality numbers are the same as those shown in Figure 2.
Data are given to three significant figures.

Table 2. River Water

| Area | River | Sampling date | Temp (℃) | pH | EC (mS/m) | $Na^+$ (mg/l) | $K^+$(mg/l) | $Ca^{2+}$(mg/l) | $Mg^{2+}$(mg/l) | $Cl^-$(mg/l) | $SO_4^{2-}$(mg/l) | $HCO_3^-$(mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hida Gaien area | Otokoro | 20061121 | 8.9 | 8.0 | 12.5 | 2.01 | 0.45 | 9.12 | 7.29 | 1.69 | 6.64 | 59.7 |
| | Simanoura | 20061121 | 9.2 | 6.6 | 7.88 | 3.10 | 0.94 | 5.66 | 1.67 | 2.36 | 9.97 | 18.8 |
| | Warabi | 20061101 | 8.4 | 6.5 | 6.84 | 2.02 | 0.64 | 6.25 | 1.00 | 1.29 | 13.8 | 10.9 |
| | Oyasawa | 20061101 | 8.7 | 6.3 | 7.08 | 1.91 | 0.49 | 7.08 | 1.12 | 0.91 | 10.7 | 18.1 |
| | Kusunoki | 20061016 | 10.4 | 6.6 | 6.61 | 2.15 | 0.39 | 5.83 | 1.55 | 0.86 | 2.65 | 27.3 |
| | Matsu | 20061016 | 6.9 | 7.2 | 4.68 | 0.59 | 0.41 | 3.81 | 0.63 | 0.54 | 5.01 | 9.80 |
| | Hira | 20061016 | 9.4 | 6.6 | 6.02 | 0.93 | 0.31 | 4.56 | 2.27 | 0.65 | 3.20 | 23.3 |
| | Inu | 20061016 | 10.5 | 6.8 | 5.84 | 1.01 | 0.30 | 5.51 | 1.62 | 0.61 | 3.45 | 22.9 |
| Fossa magna area | Nechi | 20061126 | 7.9 | 7.0 | 16.8 | 8.92 | 0.50 | 15.5 | 3.63 | 4.20 | 27.2 | 48.5 |
| | Usui | 20061121 | 7.1 | 6.2 | 6.32 | 3.36 | 0.52 | 5.35 | 1.44 | 2.36 | 4.67 | 23.5 |
| | Nakatani | 20061101 | 10.6 | 7.9 | 24.4 | 8.13 | 0.58 | 35.4 | 6.68 | 1.48 | 35.3 | 62.1 |
| | Tsuchitani | 20061101 | 11.2 | 7.6 | 28.1 | 34.1 | 1.37 | 15.1 | 4.80 | 3.85 | 47.8 | 96.3 |
| | Nichido | 20061101 | 11.0 | 7.5 | 28.8 | 26.7 | 1.35 | 19.9 | 5.58 | 16.4 | 44.6 | 77.8 |
| | Yokone | 20061101 | 9.9 | 7.3 | 22.1 | 14.8 | 0.89 | 21.4 | 5.51 | 3.22 | 36.2 | 82.9 |
| | Nodaira | 20061016 | 12.8 | 6.9 | 17.9 | 10.1 | 1.17 | 14.2 | 5.34 | 2.68 | 35.7 | 49.2 |
| | Tanichi | 20061016 | 11.5 | 7.1 | 12.8 | 9.66 | 0.80 | 8.54 | 2.95 | 1.28 | 20.8 | 39.5 |

$HCO_3^-$ is a value calculated under an assumption of ion balance (see text).
Data are given to three significant figures.

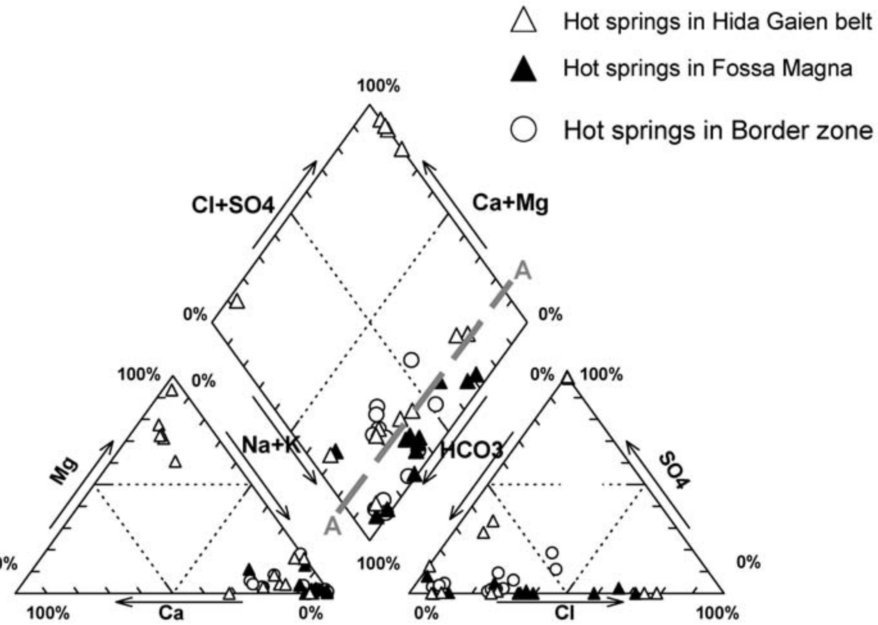


Fig. 3. Measured data represented in the Piper diagram. Dashed line A is drawn at 15% of $(Ca^{2+}+Mg^{2+})$/total cation in eq/l.

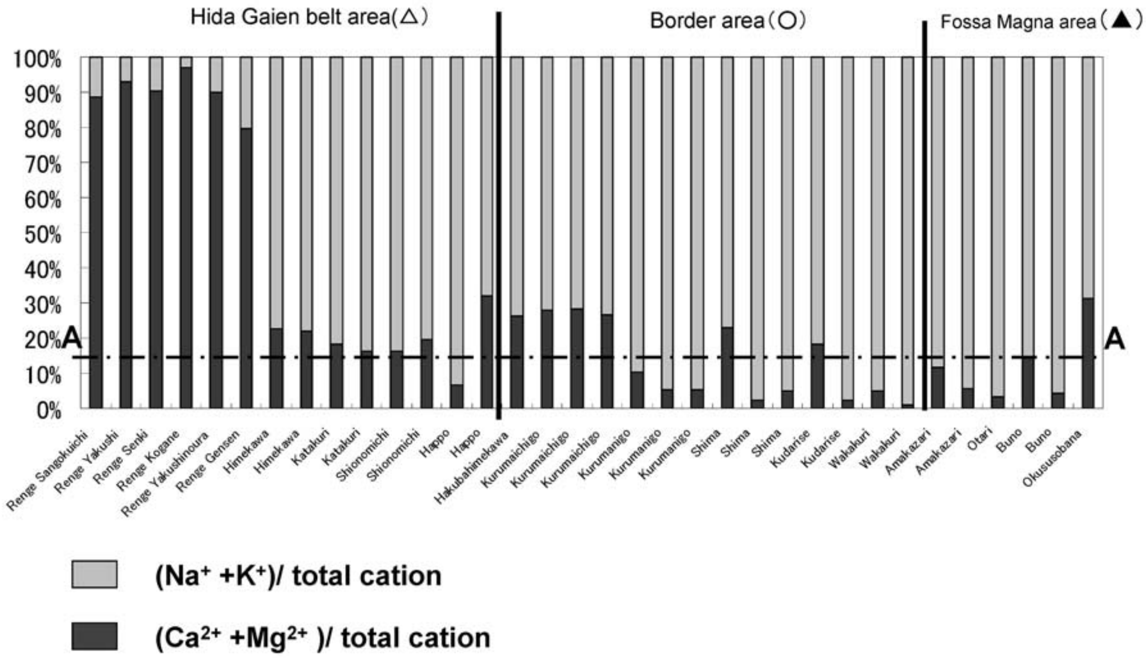


Fig. 4. The ratios of $(Ca^{2+}+Mg^{2+})$ and $(Na^{+}+K^{+})$ to total cation in eq/l. Dashed line A is drawn at 15% of $(Ca^{2+}+Mg^{2+})$/total cation.

used for Fig. 5.

The bar graph of the Fossa Magna area is obviously different from those of two other areas. That is, the $SO_4^{2-}$ concentrations in hot springs are smaller than those in rivers. Generally, ion concentrations in hot spring waters are higher than those in the nearby river water because hot spring water dissolve ions from rocks much more than river water. In fact, in the Fossa Magna area, concentrations of ions except $SO_4^{2-}$ in hot water (see Table 1) are higher than those in river water (see Table 2).

On the contrary, in the Hida Gaien belt area and

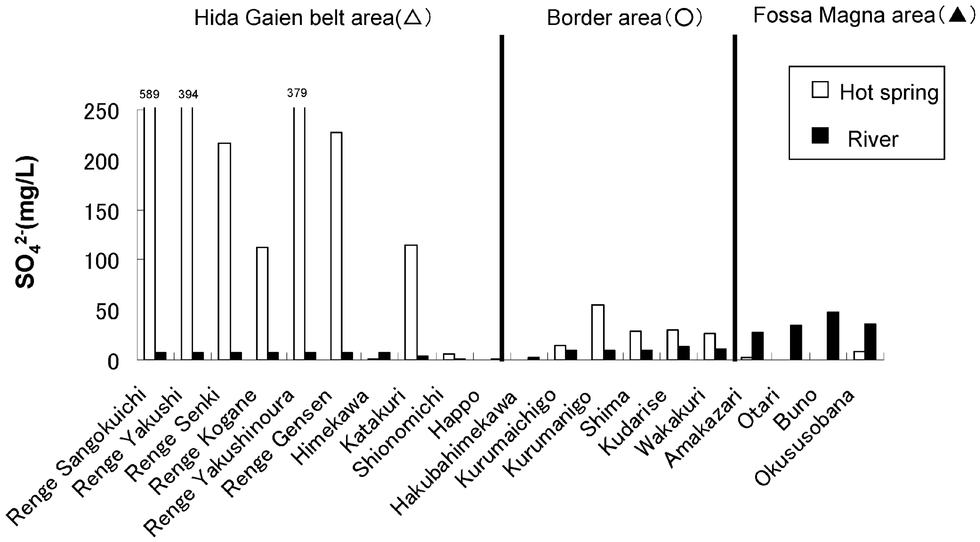


Fig. 5. The $SO_4^{2-}$ concentration of the hot springs and river waters.

the border area, the concentrations of all ions including $SO_4^{2-}$ in hot springs are larger than those in rivers. This is normal state.

Why does the reverse of what we expect appear in $SO_4^{2-}$ concentration in the Fossa Magna area? There are mainly three source materials for $SO_4^{2-}$ ion underground: (1) fumarolic gas of $SO_2$, (2) rock forming mineral of gypsum ($CaSO_4 \cdot 2H_2O$), and (3) rock forming mineral of pyrite ($FeS_2$) (*e.g.,* Seki *et al.,* 2004). In the case of the Fossa Magna area in the study area, the source material should be above (2) and/or (3) since this area is not active volcano area. Gypsum is easily dissolved into $Ca^{2+}$ and $SO_4^{2-}$ in water. However, pyrite needs oxygen to form $SO_4^{2-}$ ion in water as follows:

$$FeS_2+4O_2+3H_2O \rightarrow Fe(OH)_3+2SO_4^{2-}+6H^+$$

River water has enough $O_2$ derived from air, but hot spring water from a depth has no oxygen. When some amounts of pyrite exists in the formation, $SO_4^{2-}$ is generated in the river water by the reaction between pyrite and oxygen, but is not generated in the oxygen free hot spring water. This is accounted for the difference of the $SO_4^{2-}$ concentration.

In fact, Koma *et al.* (1983) described that pyrite is commonly included in marine sedimentary rocks. The Fossa Magna area is filled with marine Neogene sedimentary rocks, and pyrite is included in the formation. Further, Chigira (1988) mentioned that the biggest change in the mineral composition of mudstone by weathering with water is disappearance of pyrite and chlorite at the oxidation front.

Consequently, it is concluded that the source material of $SO_4^{2-}$ in the river on the Fossa Magna area is not fumarolic gas or gypsum but pyrite.

On the other hand, the origin of $SO_4^{2-}$ in the hot springs of the Renge area in the Hida Gaien belt area is attributable to $SO_2$ gas because there is an active volcano, Hakuba-Oike, near the hot springs. In addition, if gypsum is the source of $SO_4^{2-}$, the hot water should contain much more $Ca^{2+}$.

### (3) High concentration of $Mg^{2+}$ and ultra mafic rocks

As shown in Table 1 and Fig. 3, $Mg^{2+}$ concentration and the ratio of $Mg^{2+}$ to total cation are extremely large in the Renge group hot spring waters. Usually, metal cation in groundwater comes from formations around the reservoir. Therefore, $Mg^{2+}$ ion must come from the surrounding rocks. It is known that the ultramafic rocks such as serpentinite contains a large amount of Mg, and is cropped out around the Renge hot spring group as shown in geological map of Fig. 2. Ultra mafic rocks are distributed over the Hida Gaien belt zone (Matsuhisa, 1968). As a natural consequence, it is possible that the Renge hot springs have high concentration of $Mg^{2+}$.

The highest concentration of $Mg^{2+}$ is observed at Renge Kogane in the Renge group as shown in Table 1. This phenomenon gives suggestion that the hot water at Renge Kogane reacts with rocks long time. On the other hand, the concentration of $SO_4^{2-}$ of the Renge Kogane is the smallest in the Kogane group. This means that the hot water has not mixed vigorously with $SO_2$ gas. Further, there are two distinctive features on the Renge Kogane, high concentration of $HCO_3^-$ and nearly neutral pH (pH=6.69). It can be interpreted that volcanic gas of $CO_2$ instead of $SO_2$ gas has mixed with water, which makes the unique hot water of the Renge Kogane.

## 5. Conclusions

Hot springs around the northernmost part of the Itoigawa Shizuoka Tectonic Line (ISTL) are investigated. The study area is divided into two areas by the ISTL, the Hida Gaien belt areas (western part) and the Fossa Magna area (eastern part). Following results are found.

(1) The percentage of ($Mg^{2+}+Ca^{2+}$) in total cation (in eq/l) is found to be a good indicator for drawing the trace of the ISTL. In the case of the study area, the percentage for drawing is 15%: lager value area is the Hida Gaien belt area and smaller value the Fossa Magna area.

(2) From the above conclusion, each hot spring situated in the boundary zone can be classified into two groups: the Hida Gaien belt group and the Fossa Magna group.

(3) An unusual phenomenon in the Fossa Magna area, the concentrations of $SO_4^{2-}$ ion in the hot spring waters are smaller than those of the river waters, reveals that the origin of $SO_4^{2-}$ ion in the hot spring water is pyrite ($FeS_2$) in the formation.

(4) The systematic variation in pH, $SO_4^{2-}$ and $Mg^{2+}$ in the Renge hot spring group is explained in terms of interaction among $SO_2$ and $CO_2$ gases from a volcano, ultra mafic rocks and underground water. Underground water reacting with high temperature $SO_2$ becomes strongly acidic hot water with large amount of $SO_4^{2-}$, and another ground water reacting with $CO_2$ becomes almost neutral hot water with large amount of $HCO_3^-$. The both hot waters react with ultra mafic rocks around the hot water reservoir and the concentration of $Mg^{2+}$ increases.

## Acknowledgements

We wish to thank Mr. Kenta Emori (received master's degree at Shinshu University in Mar. 2008) for helping chemical measurements. Thesis for master's degree of Shinshu University by T. Hayashi (1998) gives us important information about different concentration in chemical component between the rivers on either side of the ISTL. We are grateful to Dr. Shunich Nakai (ERI, Univ. Tokyo) for his review with thoughtful comments and suggestions. Further, we thank many owners and managers of hot springs for kind service.

### References

Abe, S., H. Sakai and N. Iijima, 1978, Studies of the hot springs in catchment area of Himekawa river of the northwest of Nagano Prefecture of central Japan, *J. Balneological Soc. Japan,* **29**, 58–67. (in Japanese with English abstract)

Chigira M., 1988, Chemical weathering of mudstone of the Pleistocene Haizume Formation, Niigata Prefecture, Central Japan, *J. Geol. Soc. Japan,* **94**, 419–431. (in Japanese with English abstract)

Harayama, S., F. Takizawa, H. Kato, M. Komazawa, T. Hiroshima and S. Sudo, 1995, *Geological Sheet Map 1: 200,000 "Toyama",* Geological Survey of Japan.

Iijima, N. and S. Miyajima, 1968, Geological and geochemical studies on the hot springs in the northern Fossa Magna, *J. Soc. Eng. Mineral Springs Japan,* **6**, 61–84. (in Japanese with English abstract)

Koma T., Suzuki Y., Kodama K., 1983, Forms of sulfur, carbon, chlorine, and iron compounds and their depositional environment, in the Kazusa Group, the Boso Peninsula, central Japan. *Bull. Geol. Surv. Japan,* **34**, 191–206. (in Japanese with English abstract)

Matsuhisa Y., 1968, The ultrabasic rock mass in the Happo-One area, Nagano Prefecture, Japan. *J. Mineral. Petrological Sci.,* **59**, 195–205.

Nakano, S., M. Takeuchi, T. Yoshiwara, H. Nagamori, Y. Kariya, K. Okumura, and Y. Taguchi, 2002, *Geological Sheet Map 1:50,000 "Shiroumadake",* Geological Survey of Japan, AIST.

Seki, Y., T. Nakajima, H. Kamioka, Y. Kanai, M. Manaka and K. Tsukimura, 2004, Discharged water from deep wells in the eastern Kanto region—the relationship between water quality and underground geology—, *J. Balneological Soc. Japan,* **54**, 1–24. (in Japanese with English abstract)

Stumm, W. and J.J. Morgan,1996, Aquatic Chemistry, 3rd ed., John-Wiley & Sons, pp.1022.

Tsunogai, U. and H. Wakita, 1995, Precursory chemical changes in ground water: Kobe earthquake, Japan, *Science,* **269**, 61–63.

(Received June 20, 2008)
(Accepted November 8, 2008)