Hydrochemistry and isotopic characteristics of non-volcanic hot springs around the Miocene Kofu granitic complex surrounding the Kofu Basin in the South Fossa Magna region, central Honshu, Japan

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Chemical and stable isotopic compositions (δD, δ^{18}O, and δ^{34}S) of non-volcanic hot spring waters around the Miocene Kofu granitic complex surrounding the Kofu basin in the South Fossa Magna region of central Honshu, Japan, were analyzed in order to investigate water–rock interactions and to determine the origin and sulfur isotopic characteristics of their trace amounts of SO_4^{2-} ion.

All water samples from the granitic rocks were classified as Na–Alkalinity (Alk) type, whereas water samples from the volcanic rocks were classified as Na–Alk, Na–SO_4, Na–SO_4·Cl·Alk, and Ca–SO_4 types. The water in the samples originated from meteoric water, and the average recharge altitude of the samples ranged from 947 m to 1397 m based on the altitude effect of δ^{18}O. The Na–Alk type waters from the granitic rocks were likely formed by the montmorillonization of plagioclase, cation exchange reaction of Na–montmorillonite, and calcite precipitation. Trace amounts of SO_4^{2-} ion of this type of water were derived from the oxidation of sulfide such as pyrite in granitic rocks or the roof sedimentary rocks of the Shimanto group, where H$^+$ caused by the sulfide oxidation was consumed in the process of plagioclase weathering. SO_4^{2-} ion content in the Na–Alk type water from the granitic rocks reflected the δ^{34}S values of granitic and sedimentary rocks of the Shimanto group. Water samples from the ilmenite series area have negative values ranging from –15.1 to –4.6‰, whereas waters from the magnetite series area have positive δ^{34}S values ranging from +1.7 to +8.0‰.

The hot spring water quality of the Na–Alk, Na–SO_4, Na–SO_4·Cl·Alk, and Ca–SO_4 types from the volcanic rocks area were estimated to be controlled by anhydrite dissolution, plagioclase weathering, cation exchange reaction of Na–montmorillonite, and precipitation of calcite during the fluid flow and mixing process. Different concentrations of SO_4^{2-} ions determined for these waters have a wide range of δ^{34}S values ranging from –4.1 to +13.6‰, which is likely attributed to the dissolution of ^{34}S-rich and ^{34}S-poor anhydrite. The ^{34}S-rich SO_4^{2-} ions were interpreted to be derived from sulfate in sulfuric acid, which arose from the disproportionation reaction of volcanic sulfur dioxide, whereas the ^{34}S-poor SO_4^{2-} ions were derived from the oxidation of ascending hydrogen sulfide in shallow ground waters during the active stage of past volcanism.

Keywords: Kofu granitic complex, non-volcanic hot spring, chemical property, water–rock interaction, δD·δ^{18}O·δ^{34}S value

INTRODUCTION

Many researchers have reported water quality characteristics of natural waters in granitic rocks of various localities. These include mineral waters from the Tanzawa Mountains (Oki *et al.*, 1964), hot spring waters of Dogo in Ehime Prefecture (Maki *et al.*, 1976), and mineral spring water from the Abukuma Plateau area (Suzuki, 1979). All of the aforementioned waters have low temperature and salinity with alkaline pH. According to Ichikuni *et al.* (1982), who described the chemistry of alkaline spring waters from the Abukuma Mountain area of Fukushima Prefecture based on water–rock equilibrium, the waters are formed by the reaction of rainwater with felsic rocks under a limited CO_2 supply. They determined that these alkaline waters are in equilibrium with

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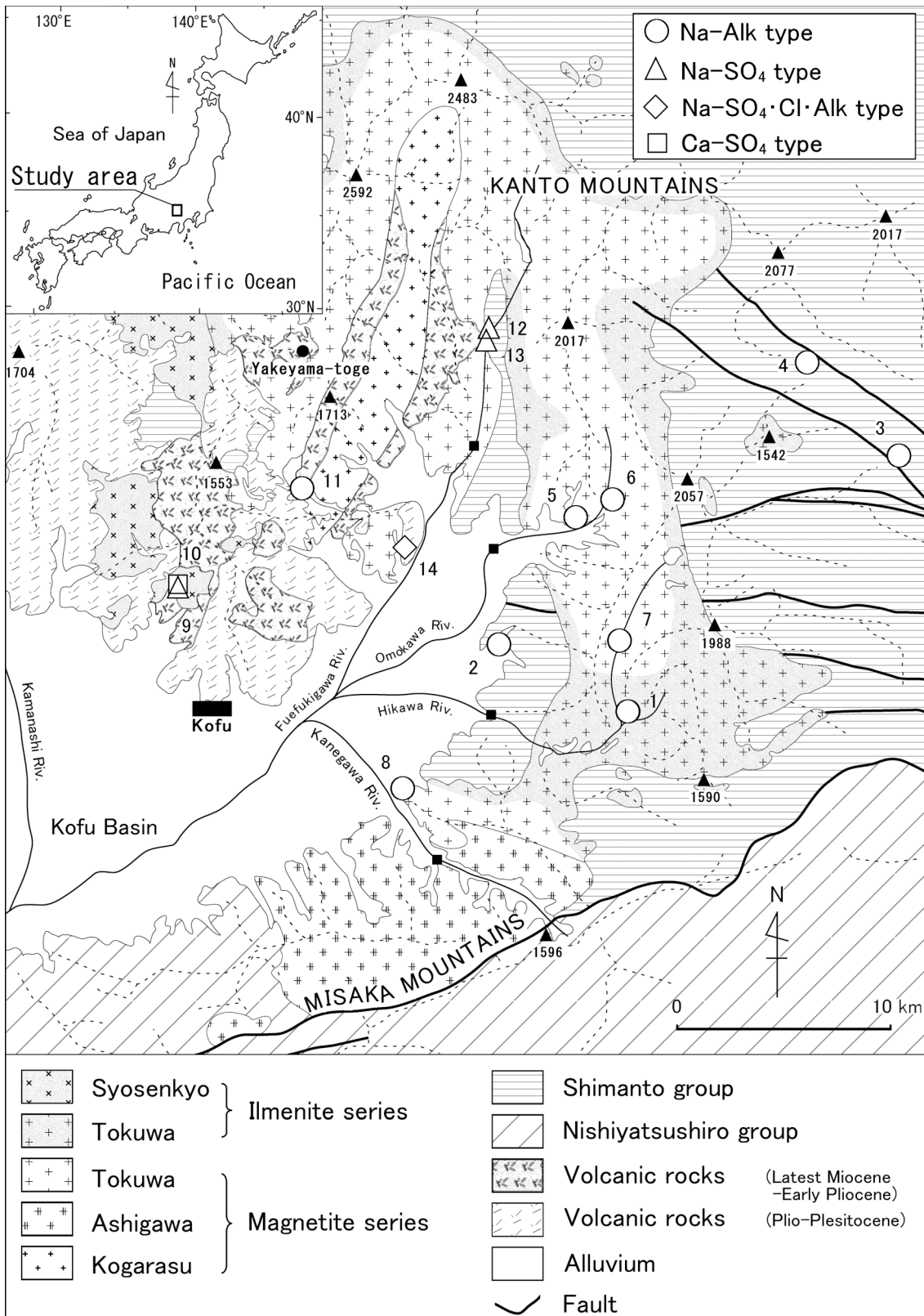
Fig. 1. Geological map and sample locations of the hot spring waters near the Miocene granitic complex surrounding the Kofu basin in the South Fossa Magna region (after Sato and Ishihara, 1983; Shimizu, 1986; Ozaki et al., 2002). Solid squares show sample locations of the Fuefukigawa, Omokawa, Hikawa, and Kanegawa rivers by Nakamura et al. (2008). Solid triangles with numbers show major mountains and heights above sea level (meters). Thin broken line shows major watershed boundaries.

kaolinite and Ca–motmorillonite. They also indicated an additional Ca–mineral in the equilibrium system, although its species was not clearly determined. In addition, they stated that such spring waters have not gathered enough attention because of their low temperature, concentration, and abundance. However, in recent years, the importance of the hydrochemical elucidation of those waters has increased due to hot spring use (e.g., Tanaka, 1989), the need to evaluate granitic rocks for radioactive waste disposal (e.g., Iwatsuki and Yoshida, 1999; Ajima *et al.*, 2006), or the prevention of anthropogenic contamination by N, P, and S in the water supply.

According to Sasaki (2004), who reviewed the geochemistry of groundwater in the granitoids of Japan, the geochemical features of groundwater in granitoids derived from meteoric water includes low salinity, Ca·Na–HCO_3 type with slightly acidic to neutral pH at shallow levels in addition to Na–HCO_3 type with slightly alkaline pH at deep levels. Water quality is controlled by water–rock interactions, such as the dissolution and precipitation of calcite, plagioclase weathering, and ion-exchange reactions of clay minerals. However, the origin of the SO_4^{2-} ion, which generally exists in trace amounts in granitic groundwater, has not been clearly described thus far.

The Miocene Kofu granitic complex surrounding the Kofu basin in the South Fossa Magna region of central Honshu is the most suitable site for discussing the hydrochemistry of groundwater in granitoids for the following reasons: We can easily discuss the relationships between the hydrochemical features of water and rock composition because the Kofu granitic complex consists of several different types of granitoids (e.g., Sato and Ishihara, 1983). Moreover, because a number of sources of alkaline water such as natural springs and drilled wells have been used for hot spring bathing purposes extensively around the complex, we can easily collect water samples. Although the water quality characteristics concerning these alkaline waters have been reported by many researchers (e.g., Takamatsu *et al.*, 1981; Kato *et al.*, 1987, 1988; Aikawa, 1995), the water–rock interaction that describes the origin of SO_4^{2-} ion and the isotopic compositions of δD, $\delta^{18}O$ and $\delta^{34}S$ have not been previously clarified.

In the present study, we analyzed the chemical and isotopic composition (δD, $\delta^{18}O$, and $\delta^{34}S$) of hot spring waters around the Miocene Kofu granitic complex area to investigate the water–rock interactions and determine the origin and sulfur isotopic characteristics of their trace amounts of SO_4^{2-} ion content.

OVERVIEW OF GEOLOGY

A simplified geological map and sample location of the hot spring waters around the Kofu granitic complex surrounding the Kofu basin in the South Fossa Magna region of central Honshu are shown in Fig. 1. The study area is located at the intersection of the Shimanto terrain and the Fossa Magna. The Shimanto group of the Cretaceous age and the granitic complex of the Miocene age have been unconformably covered by volcanic rocks of the Plio–Pleistocene age at the northern region of the Kofu basin (Mimura, 1971). The Nishiyatsushiro group consists mainly of submarine basalt to andesite volcaniclastic rock and lava, with mudstone, sandstone, and dacite volcaniclastics of middle Miocene age (Ozaki *et al.*, 2002; Matsuda, 2007). The Kofu granitic complex is divided into the following four units based on the timing of intrusion and composition (Sato and Ishihara, 1983): Syosenkyo-type monzogranite (14–11 Ma; Tsunoda *et al.*, 1992), Tokuwa-type granodiorite (10–9 Ma; Matsumoto *et al.*, 2007), Ashigawa-type tonalite (12 Ma; Sato, 1991; 11 Ma: Saito *et al.*, 1997), and Kogarasu-type granodiorite (4 Ma; Shibata *et al.*, 1984). The former two types intruded sedimentary rocks of the Shimanto group, whereas the latter two intruded the latest Miocene–early Pliocene volcanic rock formations. The Kogarasu type caused hydrothermal alterations to the latest Miocene–early Pliocene volcanic rocks in several areas (Takashima and Kosaka, 2000; Kanamaru and Takahashi, 2008).

According to Sato and Ishihara (1983) and Shimizu (1986), the Syosenkyo type and the marginal part of the Tokuwa type have low magnetic susceptibility corresponding to the ilmenite series due to solidification under reducing conditions caused by the contamination of magma with carbon-bearing sedimentary rocks of the Shimanto group. By contrast, the Ashigawa and Kogarasu types and the inner part of the Tokuwa type have high magnetic susceptibility that corresponds to the magnetite series.

SAMPLING AND ANALYTICAL PROCEDURES

We collected 14 samples of hot spring waters from natural discharge and drilled wells in the ilmenite and magnetite series of granitic rocks and volcanic rocks in the area (Fig. 1). Additionally, we collected drilling data such as well depth, temperature logging, and underground geology by interviewing the owner or facility manager. Most well water samples were collected after running for several minutes from the valve located at the well head; two water samples, Nos. 5 and 8, were collected from a holding tank. Temperature, electrical conductivity, and pH were directly measured using a standard, hand-held, calibrated meter (Horiba D-24). The total alkalinity (Alk) was determined by titration with sulfuric acid to a final pH of 4.8 (Hach AL-DT). Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-} were measured by ion chromatography (Shimadzu

Table 1. Chemical composition of hot spring waters around the Miocene granitic rocks surrounding the Kofu Basin in the South Fossa Magna region

No.	Locality	Date	E.L. m	Depth m	Temp. °C	pH	E.C. mS/m	Na⁺ mg/L	K⁺ mg/L	Ca²⁺ mg/L	Mg²⁺ mg/L	Total Fe mg/L	Al³⁺ mg/L	Cl⁻ mg/L	SO₄²⁻ mg/L	Alk mg/L	SiO₂ mg/L	δD ‰	δ¹⁸O ‰	δ³⁴S ‰
	Ilmenite-series granitic rocks area																			
1	Yamato	2009.5.25	980	1300	27.5	10.3	23.3	41.3	0.2	1.2	<0.1	<0.1	<0.1	4.3	10.9	76.0	38.6	−77.3	−11.0	−4.6
2	Katsunuma	2009.5.25	480	1500	39.1	9.2	27.3	55.3	0.7	3.4	<0.1	<0.1	<0.1	12.2	5.1	86.1	26.1	−82.6	−11.2	−15.1
3	Kosuge	2011.7.11	720	1500	31.0	9.7	35.0	66.7	1.2	4.5	1.3	<0.1	<0.1	5.7	5.9	126.8	29.4	−75.2	−11.3	−8.8
4	Tabayama	2011.7.11	625	1500	42.5	9.8	39.0	58.6	1.3	8.0	0.9	<0.1	<0.1	38.9	4.9	70.1	56.8	−76.5	−11.3	−8.0
	Magnetite-series granitic rocks area																			
5	Kamiodawara	2009.5.25	820	1500	27.0	10.1	19.2	33.4	0.1	1.4	<0.1	<0.1	<0.1	3.2	11.9	62.0	32.3	−77.8	−11.1	4.1
6	Kamihagihara	2012.11.08	905	0	25.7	9.8	14.5	23.4	0.5	2.5	0.1	<0.1	<0.1	4.0	14.8	40.1	27.2	−77.0	−11.7	6.0
7	Enzan	2012.11.08	1230	0	10.9	10.0	10.7	17.9	0.3	2.9	0.1	<0.1	<0.1	0.9	12.9	31.2	17.5	−79.5	−11.9	1.7
8	Ichinomiya	2012.10.31	450	n.d.	25.4	9.8	18.5	30.5	0.4	2.6	<0.1	<0.1	0.1	8.8	24.3	39.5	23.1	−71.6	−11.0	8.0
	Volcanic rocks area																			
9	Sekisuiji 1	2009.7.13	580	0	18.8	7.3	11.9	11.9	1.3	4.7	1.9	<0.1	<0.1	0.8	37.1	4.5	48.2	−72.4	−10.6	−4.1
10	Sekisuiji 2	2009.7.13	580	1500	22.8	8.4	106.3	25.7	1.6	234.7	0.0	<0.1	<0.1	0.8	605.9	17.6	17.7	−73.2	−10.7	13.6
11	Makidaira	2009.5.25	810	n.d.	34.6	9.9	20.2	52.6	0.4	5.6	<0.1	<0.1	0.1	12.9	18.0	48.0	25.7	−72.2	−10.8	9.5
12	Kawaura 1	2012.11.12	745	45	41.5	9.3	30.8	41.7	1.0	13.4	0.3	<0.1	<0.1	19.8	67.6	35.1	46.7	−77.7	−10.8	10.0
13	Kawaura 2	2012.11.12	700	1000	43.2	9.4	37.8	51.3	0.9	17.8	0.1	<0.1	<0.1	16.6	112.3	25.0	42.0	−75.0	−11.6	9.5
14	Makioka	2012.11.12	450	1000	40.4	9.7	31.9	54.5	0.3	3.2	<0.1	<0.1	0.1	28.0	43.7	47.0	33.6	−73.2	−10.6	5.7

EC: Electrical conductivity. Alk: Total alkalinity as CaCO₃. n.d.: No data.

LC-VP). Total Fe was measured by atomic absorption spectrophotometry (Shimadzu AA-6200), and Al^{3+} was measured by spectrophotometry using Eriochrome Cyanine R (Hach DR-2800); however, these parameters in all samples were below detection. The SiO_2 was analyzed by spectrophotometry using the molybdenum yellow method (Shimadzu UV-1650PC).

Isotopic compositions of hydrogen (D/H) and oxygen ($^{18}O/^{16}O$) were measured by a mass spectrometer connected on-line to a gas chromatograph (GV Instruments Isoprime-EA). For oxygen and hydrogen isotope analysis, water samples were decomposed in an oxygen-free environment by heating at 1050°C to produce H_2 analysis and at 1260°C to produce CO; the product gases were chromatographically separated and introduced into an ion source of the mass spectrometer. For the six samples collected in 2012, however, we used cavity ring-down spectroscopy coupled with a vaporizer (Picarro, L2120-i) to analyze the isotopic compositions of hydrogen and oxygen. Sulfur isotope ($^{34}S/^{32}S$) analysis of dissolved SO_4^{2-} was also performed using an Isoprime-EA mass spectrometer. The dissolved SO_4^{2-} in the water samples was collected as $BaSO_4$ and mixed with V_2O_5 as a combustion aid. The mixture was then heated to decompose into SO_2 gas, which was then introduced to the mass spectrometer. Hydrogen, oxygen, and sulfur isotopic compositions are reported as δD, $\delta^{18}O$, and $\delta^{34}S$ (‰) variations relative to a standard using the following notation:

$$\delta\ (\text{‰}) = [R_{\text{sample}}/R_{\text{standard}} - 1] \times 1000 \qquad (1)$$

where R is the isotopic ratios of D/H, $^{18}O/^{16}O$, and $^{34}S/^{32}S$. These standards include the Vienna Standard Mean Ocean Water (V-SMOW) for δD and $\delta^{18}O$ and Canyon Diablo Troilite (CDT) for $\delta^{34}S$. Analytical precisions are within values of ±1.0‰ for δD, ±0.1‰ for $\delta^{18}O$, and ±0.2‰ for $\delta^{34}S$.

RESULTS AND DISCUSSION

Chemical and isotopic compositions and relationship with bedrock

The analytical results are listed in Table 1, and a trilinear diagram for the water samples is presented in Fig. 2. In the granitic rocks area, temperatures of the samples ranged from 10.9 to 42.5°C, and the pH was between 9.2 and 10.3. All of the samples are Na–Alk type without exception. By contrast, temperatures of the samples from the volcanic rocks area ranged from 18.8 to 43.2°C, and the pH varied from 7.3 to 9.9. The waters were subdivided into Na–Alk type (No. 11), Na–SO_4 type (Nos. 9, 12, and 13), Na–SO_4·Cl·Alk type (No. 14), and Ca–SO_4 type (No. 10).

All water samples from the ilmenite series of granitic rocks had negative $\delta^{34}S$ values between –15.1‰ and –4.1‰, whereas the water samples from the magnetite series granitic area had positive $\delta^{34}S$ values between +1.7‰ and +8.0‰. Waters from the volcanic rocks area showed a wide range of $\delta^{34}S$ values from –4.1 to +13.6‰.

Sample Nos. 2, 3, and 4 were from a sedimentary rock formation of the Shimanto group (Fig. 1). However, based on an interview with the well owners, we believe that the waters originated from the underlying ilmenite series granitic rock that intersected the bases of these wells. These three samples gave off an obvious odor of hydrogen sulfide.

Origin of the hot spring waters

Except for the water sample from well No. 10, the electrical conductivities were low, between 10.7 mS/m and 39.0 mS/m. The δD and $\delta^{18}O$ values of the water samples ranged from –82.6‰ to –71.6‰ and from –11.9 to –10.6‰, respectively. These isotope values are similar to those of waters from rivers near the hot spring sites reported by Nakamura *et al.* (2008). The sampling points of river water are expressed as a closed square in Fig. 1, and the average altitude of the river watershed is shown in Table 2. These characteristics of electrical conductivity and δD and $\delta^{18}O$ values suggest that the hot spring waters are meteoric in origin.

The recharge altitude of the meteoric water can be estimated based on the altitude effect of the isotopic composition. Based on Nakamura (2008), the relationship between $\delta^{18}O$ values and the altitude of precipitation in the northeastern Kofu basin was represented by the following equation:

$$\text{Altitude (m)} = -500 \cdot \delta^{18}O - 4553. \qquad (2)$$

The average recharge altitudes of the sources of the hot spring waters were calculated as follows: 947 m for No. 1, taken from a hot spring site at an altitude of 980 m; 1047 m for No. 2 at 480 m; 1097 m for No. 3 at 720 m; 1097 m for No. 4 at 625 m; 997 m for No. 5 at 820 m; 1297 m for No. 6 at 905 m; 1397 m for No. 7 at 1230 m; 947 m for No. 8 at 450 m; 747 m for No. 9 at 580 m; 797 m for No. 10 at 580 m; 847 m for No. 11 at 810 m; 847 m for No. 12 at 745 m; 1247 m for No. 13 at 700 m; and 747 m for No. 14 at 450 m. Therefore, the hot spring waters were recharged at the same altitude or higher than those of the hot spring sites, as shown in Table 1.

The temperature–depth profile of well No. 1 shows a linear gradient typical of conduction (Fig. 3), indicating that the waters were trapped in pore space and stagnant rather than flowing upward. Under stagnant flow conditions and limited atmospheric CO_2 supply in the fine fractures of the granitic rocks at deep layer levels, the progress of water–rock interaction process was limited. These con-
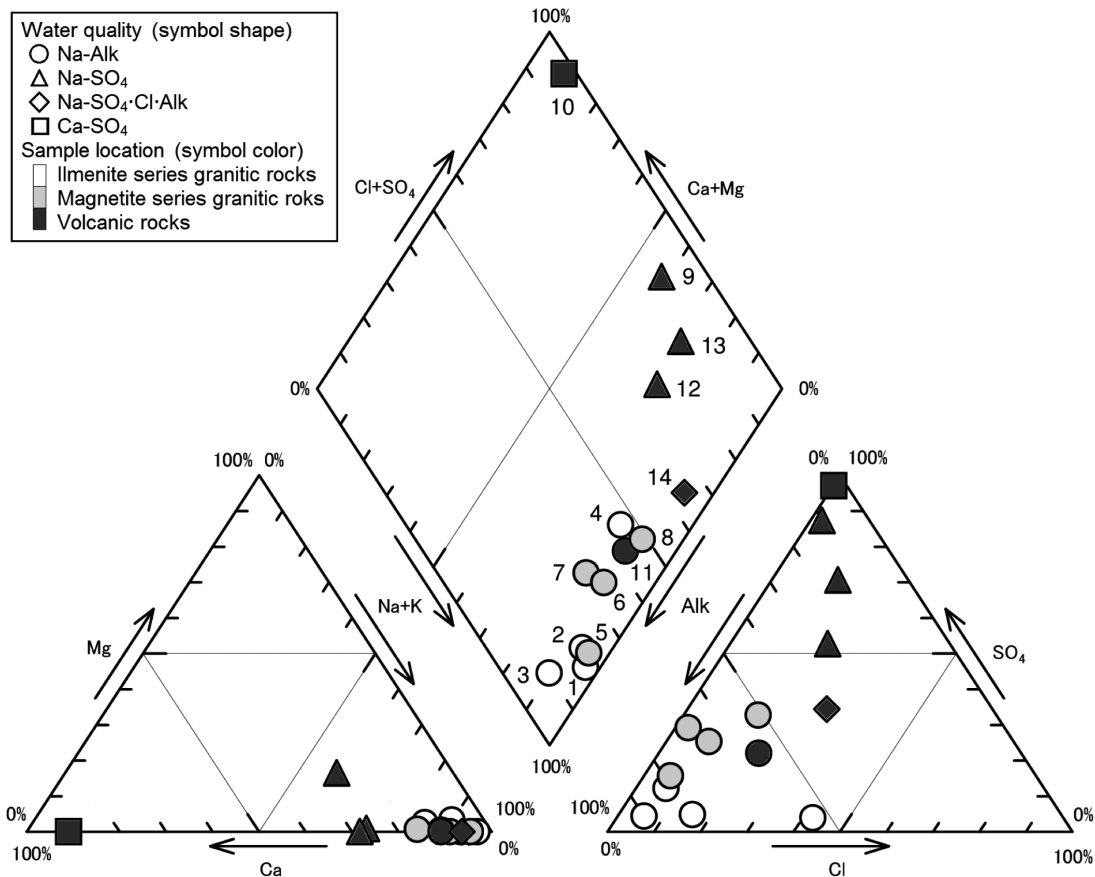
Fig. 2. Tri-linear diagram for hot spring waters. Numbers shows sample locations.

ditions are attributed to the low concentration of dissolved chemical constituents of the hot spring waters.

Formation mechanisms of hot spring water quality
(1) Weathering of plagioclase The hot spring waters had Na^+ and alkalinity as major chemical components but low concentrations of Mg^{2+}. Furthermore, particularly in the granitic rocks area, water samples exhibited a strong correlation between Na^+ and alkalinity (Fig. 4; $R^2 = 0.77$). These chemical properties suggest that the quality of hot spring waters in the granitic rocks area was influenced by the montmorillonization of plagioclase. Plagioclase is a solid-solution series between an albite and an anorthite end member and reacts with rainwater and atmospheric CO_2 by the following equations:

$$6CO_2 + 6H_2O \rightarrow 6H^+ + 6HCO_3^- \tag{3}$$

$$7NaAlSi_3O_8 + 6H^+ + 20H_2O$$
$$\rightarrow 3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 6Na^+ + 10H_4SiO_4 \tag{4}$$

$$7CaAl_2Si_2O_8 + 12H^+ + 8H_4SiO_4$$
$$\rightarrow 3Ca_{0.33}Al_{4.67}Si_{7.33}O_{20}(OH)_4 + 6Ca^{2+} + 16H_2O. \tag{5}$$
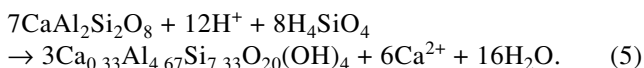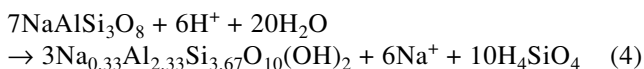
Table 2. Summary of isotopic compositions of precipitation and river water (annual average) with an average altitude of the watershed from Nakamura (2008)

Rivers	δD (‰)	$\delta^{18}O$ (‰)	Av. altitude (m)
Fuefukigawa River	−74.0	−10.7	1570
Omokawa River	−73.1	−10.4	1150
Hikawa River	−72.2	−10.4	1180
Kanegawa River	−71.5	−10.4	1110

This hypothesis is supported by the mineral equilibrium calculation results such that samples from the granitic rocks area are distributed in the montmorillonite regions in the stability diagram for the $Na_2O–Al_2O_2–SiO_2–H_2O$ and $CaO–Al_2O_2–SiO_2–H_2O$ system (Figs. 5a and b). Although the weathering rate of anorthite is faster than albite (Blum and Stillings, 1995), waters in the granitic rocks area had a dominant pattern of $Na^+ > Ca^{2+}$. This result can be attributed to an abundance of albite in intermediate-acid igneous rock (Kuroda and Suwa, 1983) and Ca^{2+} exchange with Na^+ of Na–montmorillonite. Moreover, because the waters in the granitic rocks area
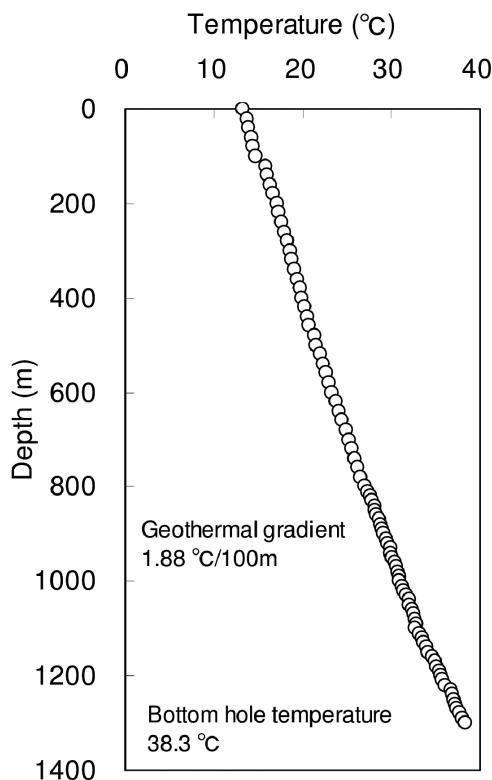
Fig. 3. Temperature logging data from Yamato hot spring (No. 1) well. Geothermal gradient was calculated by the following equation. $G = (T_b - T_a)/Depth$ (m) × 100, where G is the geothermal gradient, T_b is the bottom hole temperature, and T_a is the mean annual temperature (13.8°C) at Koshu city near the No. 1 well, as obtained from Japan Meteorological Agency (2013).

Fig. 4. Relationships between Na^+ and alkalinity concentrations in hot spring waters.

were supersaturated with respect to calcite (Fig. 6a), calcite precipitation may also have reduced Ca^{2+} concentrations in the waters.

(2) Oxidation of sulfides In the waters from the granitic rocks area, Nos. 1–8, the concentrations of SO_4^{2-} ion ranged from 4.9 mg/L to 24.3 mg/L. Based on the report on recent atmospheric deposition in Yamanashi Prefecture (Sasaki *et al.*, 2009), the annual average concentrations of SO_4^{2-} ion in the precipitation in 1988, 1989, 1990, and 2009 were calculated at 1.63, 1.52, 1.49, and 0.99 mg/L, respectively. Because the SO_4^{2-} ion concentration in the precipitation was low, the origin of the SO_4^{2-} ion in hot spring waters does not appear to originate from precipitation. By contrast, the average sulfur contents of ilmenite series and magnetite series granitic rocks in Japan are 630 mg/kg and 270 mg/kg, respectively (Sasaki and Ishihara, 1979). This sulfur content is likely rich enough to be the origin of the SO_4^{2-} ion in the hot spring waters. Although the sulfur in the granitic rocks is manifested in several different chemical forms such as sulfide
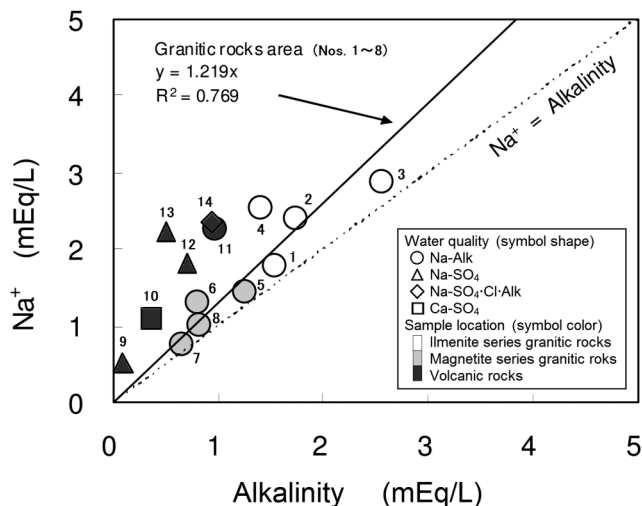
or sulfate minerals (Sasaki and Ishihara, 1979), sulfide minerals, particularly pyrite, are likely abundant in the study area (Tsunoda *et al.*, 1992; Shimizu *et al.*, 1995; Kanamaru and Takahashi, 2008; Takashima and Kosaka, 2000). Because pyrite is oxidized in oxygen-rich conditions close to the surface by the following reaction (Appelo and Postma, 2005), we consider that the trace amounts of SO_4^{2-} ion in the hot spring water may have originated from the oxidation of pyrite.

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+. (6)$$
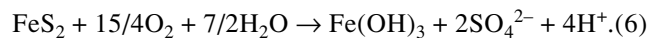
In consideration of the alkaline pH of the water samples, it is presumed that the H^+ released by the preceding pyrite oxidation was consumed by the interaction with plagioclase, as shown in Eqs. (4) and (5). Assuming reaction (4) and subsequent ion exchange reaction, the Na^+/Alk mEq ratio in the water was calculated to be up to 1.167, whereas the Na^+/Alk ratio in the sample water was slightly high at 1.219 (Fig. 4). We also consider that the reason for a high Na^+/Alk ratio in the water samples is partly attributed to montmorillonization of the plagioclase progressing without an alkalinity increase because the H^+ from the sulfide oxidation directly caused the plagioclase weathering (reactions (4) and (5)). The total equivalent amount of H^+ is the same as that of SO_4^{2-} in reaction (6), and the difference between Na^+ and SO_4^{2-} concentrations in mEq/L of the water samples is approximately equal to the alkalinity concentration in mEq/L (Fig. 7). This correlation can support the hypothesis that part of the plagioclase weathering was caused by the H^+ from sulfide oxidation. Nos. 2, 3, and 4 show conspicuous differences in the correlation of Fig. 7. We inferred that this ionic
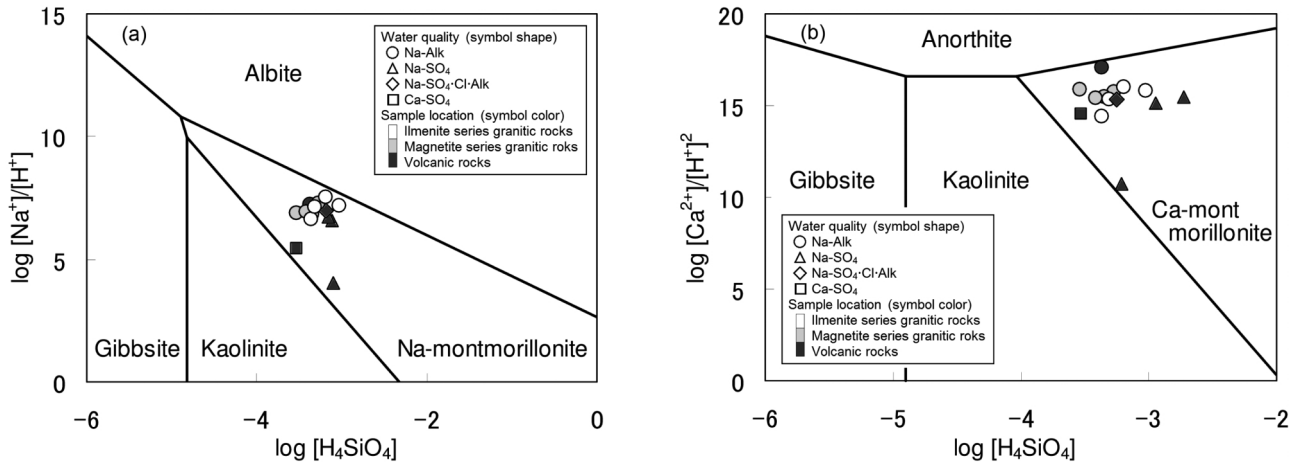
Fig. 5. Stability diagram of minerals in (a) $Na_2O–Al_2O_2–SiO_2–H_2O$ and (b) $CaO–Al_2O_2–SiO_2–H_2O$ system at 298 K and at 1 atm (Tardy, 1971).
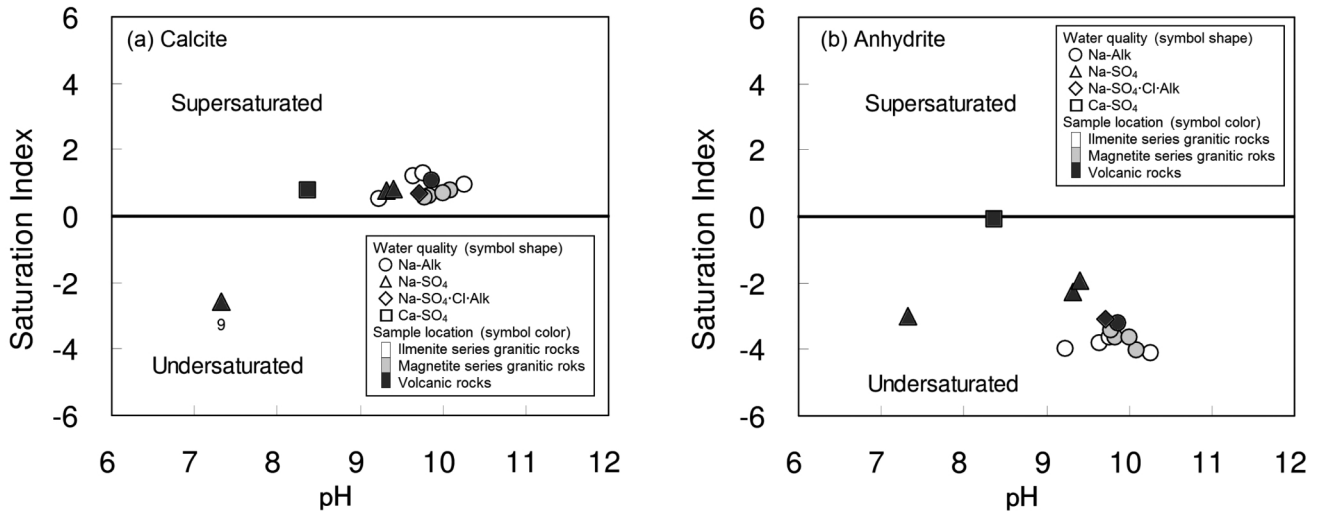

Fig. 6. Relationship between saturation index (SI) and pH in (a) calcite and (b) anhydrite. SI with respect to calcite ($SI_{calcite}$) and anhydrite ($SI_{anhydrite}$) were calculated by the following equation: $SI_{calcite} = log([Ca^{2+}]\cdot[CO_3^{2-}]/K_{sp})$, and $SI_{anhydrite} = log([Ca^{2+}]\cdot[SO_4^{2-}]/K_{sp})$; where concentrations of CO_3^{2-} were calculated using total alkalinity and pH. K_{sp} used in the calculation were $10^{-8.42}$ for calcite (from Stumm and Morgan, 1981) and $10^{-4.36}$ for anhydrite (from Krupp, 2005).

imbalance is likely due to SO_4^{2-} reduction to H_2S in the anaerobic underground because these samples had an obvious hydrogen sulfide odor.

The $\delta^{34}S$ values of SO_4^{2-} ions in the Na–Alk type waters in the ilmenite series ranged from –15.1 to –4.1‰, whereas the those for waters from the magnetite series area all ranged from +1.7 to +8.0‰. These sulfur isotopic characteristics are remarkably similar to the specific sulfur isotope trend of granitoids and sedimentary rocks of the Shimanto group in Japan reported by Sasaki and Ishihara (1979). In that study, the $\delta^{34}S$ of the ilmenite series granitoids were mostly negative, from –11 to +1‰,

whereas the magnetite series granitoids were positive, from +1‰ to +9‰. Sedimentary rocks of the Shimanto group also had negative $\delta^{34}S$ values, from –21.5 to –1.4‰. Additionally, Sasaki and Ishihara (1979) determined that the low $\delta^{34}S$ values of the ilmenite series granitoids are a result of the assimilation by the magma of sulfur from sedimentary rocks. This correspondence between the $\delta^{34}S$ values of water samples and geological distribution strongly supports the hypothesis that trace amounts of the SO_4^{2-} ion in the Na–Alk type waters in the granitic rocks originated from the oxidation of the pyrite. A low $\delta^{34}S$ value in the Katsunuma hot spring (–15.1‰; No. 2) was
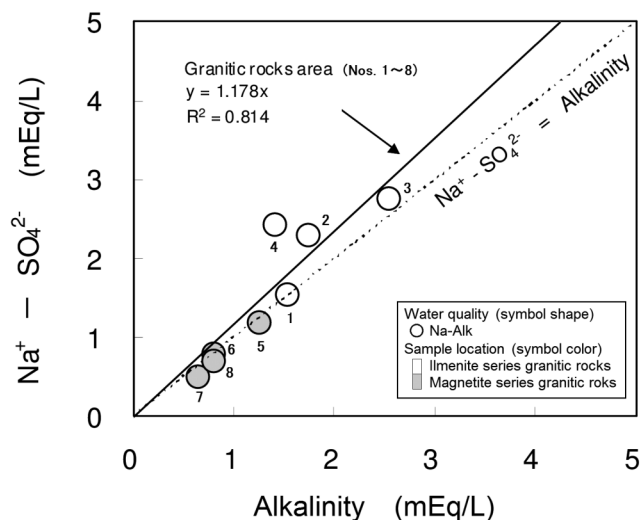
Fig. 7. *Difference between Na⁺ and SO₄²⁻ versus alkalinity concentration diagram for the hot springs from the granitic rocks area.*

Fig. 8. *Total amount of Na⁺ and Ca²⁺ versus total amount of alkalinity and SO₄²⁻ concentration diagram for the hot springs from the volcanic rocks area.*

thus likely affected by the roof sedimentary rocks of the Shimanto group.

(3) Dissolution of the anhydrite and cation exchange reaction of montmorillonite and precipitation of calcite The volcanic rocks north of the Kofu basin are hydrothermally altered (Takashima and Kosaka, 2000). This alteration was sub-divided into an alkaline alteration zone that occurs throughout the area and several acidic alteration zones that occur locally (Takashima and Kosaka, 2000). Acid alteration is well developed near Yakeyama-toge where a silica and alunite zone exists that contains natroalunite and alunite. Adjacent to this is a clay zone, next to this a mixed layer clay zone followed by a montmorillonite zone (Takashima and Kosaka, 2000).

Six water samples from the altered volcanic rocks area north of the Kofu basin, Nos. 9–14, had different concentrations of SO_4^{2-} ion. These waters were undersaturated with respect to anhydrite (Fig. 6b), and the sample from the Sekisuiji 2 hot spring, No. 10, had high concentrations of Ca^{2+} and SO_4^{2-} (Table 1; Ca^{2+}/SO_4^{2-} ratio of 0.9), suggesting the contribution of anhydrite dissolution. Anhydrite is a hydrothermal mineral commonly found in active geothermal fields around the world (Browne, 1978). In addition, anhydrite as an alteration mineral has been recognized in geothermal systems of Japan including Hatchobaru (Kiyosaki *et al.*, 2006), Fushime (Akaku *et al.*, 1991), Hakone (Matsumura and Fujimoto, 2008), and Kakkonda (Muramatsu *et al.*, 2000). Further details of alteration minerals and chemical equilibrium in Japanese geothermal systems have been reported by Chiba (1991). Considering these previous publications, it is reasonable to infer that the existence of
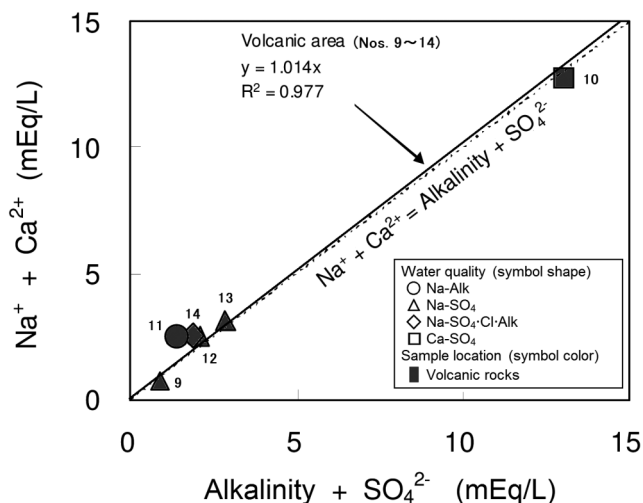
anhydrite was formed via past volcanic activities in underground volcanic rocks within the study area.

Because the water qualities of the six samples were distributed between Ca–SO₄ type and Na–Alk type water in the trilineardiagram (Fig. 2), it is presumed that the water qualities of the waters were controlled by the cation exchange reaction of Na–montmorillonite, which was caused by plagioclase weathering during the flow process after dissolution of the sulfate minerals; montmorillonite zones actually occur near the Yakeyama-toge (Takashima and Kosaka, 2000). As shown in the diagram, a strong correlation of the total amount of Na^+ and Ca^{2+} versus the total amount of alkalinity and SO_4^{2-} concentrations in mEq/L (Fig. 8; $R^2 = 0.98$) supports this hypothesis.

In addition, calcite precipitation may have occurred in the process of forming Na^+ and SO_4^{2-} rich water because mixing of Ca–SO₄ type and Na–Alk type waters caused an elevation of Ca^{2+} and alkalinity concentrations. In fact, most of these waters were supersaturated with respect to calcite (Fig. 6a), and several calcite depositions were recognized in the volcanic rocks near the Kogarasu granitic unit (Takashima and Kosaka, 2000; Kanamaru and Takahashi, 2008).

Based on aforementioned arguments, hot spring water compositions in the altered volcanic rocks area appear to be controlled by the dissolution of anhydrite, the montmorillonization of plagioclase, the cation exchange reaction of Na–montmorillonite, and the precipitation of calcite during the fluid flow and mixing process.

(4) Disproportionation reaction of sulfur dioxide during past volcanism Finally, we considered the possible rea-

sons for the wide dispersion of $\delta^{34}S$ values for the SO_4^{2-} ion from water derived from the volcanic rock area ranging from -4.1 to $+13.6‰$ (Table 1). Kiyosaki *et al*. (2006) reported that alunite minerals that have a wide range of $\delta^{34}S$ values in the Hatchobaru geothermal field; hypogene alunite has a heavy $\delta^{34}S$ of $+23.7‰$ at 1238 m underground, whereas the supergene alunite had a lower $\delta^{34}S$ value of $+0.5‰$ at 84.8 m underground. They described that this wide dispersion of $\delta^{34}S$ values for alunite minerals is related to a disproportionation reaction of volcanic gas as shown in Eq. (7), i.e., the hypogene alunite contained ^{34}S-rich sulfate derived from the disproportionation of volcanic SO_2 gas, whereas the supergene alunite contained ^{34}S-poor sulfate derived from the oxidation of ascending H_2S gas in shallow groundwater.

$$4SO_2 + 4H_2O \rightarrow 3H_2SO_4 + H_2S. \qquad (7)$$

In the Hatchobaru geothermal field, it was also recognized that anhydrite, which belongs to a sulfate mineral group similar to alunite minerals ($+12.0$ to $+23.7‰$), also exhibits similar dispersion in $\delta^{34}S$ values (Kiyosaki *et al*., 2002).

In another previous study, Muramatsu *et al*. (2014) interpreted that the origin of SO_4^{2-} ion with wide $\delta^{34}S$ values in hot spring-derived water from the Ikaho and Harunako areas near the Haruna volcano originated from the dissolution of anhydrite, which was produced from the disproportionation reaction between the fluids during an active stage of volcanism.

Considering these previous studies, the reasons for the wide dispersion of $\delta^{34}S$ values for SO_4^{2-} ions in the volcanic rocks area can be deduced as follows: The ^{34}S-rich SO_4^{2-} ions originated from the dissolution of anhydrite, which was produced from ^{34}S-rich sulfate in H_2SO_4 derived from the disproportionation reaction of volcanic SO_2, whereas the ^{34}S-poor SO_4^{2-} ions originated by the dissolution of anhydrite, which was produced from ^{34}S-poor sulfate derived from the oxidation of ascending H_2S in the shallow groundwaters, both during the active stage of past volcanism. Sekisuiji 1 (No. 9) and Sekisuiji 2 (No. 10) are mostly co-located, and their SO_4^{2-} contents showed a high $\delta^{34}S$ value of $+13.6‰$ deep underground (No. 10; 1500 m well depth) and a low $\delta^{34}S$ value of $-4.1‰$ in the shallow layer (No. 9; natural spring). These results are in agreement with the aforementioned explanation.

CONCLUSIONS

Chemical and stable isotopic compositions of non-volcanic hot spring waters near the Miocene Kofu granitic complex area surrounding the Kofu basin were analyzed in order to investigate the water–rock interac-

tions and to determine the origin and sulfur isotopic characteristics of the trace amounts of SO_4^{2-} ion. Three discernible conclusions can be drawn from this study.

(1) Hot spring water samples from granitic rocks were classified as a Na–Alk type without exception, whereas water samples from the volcanic rocks area were classified as Na–Alk, Na–SO_4, Na–SO_4·Cl·Alk, and Ca·SO_4 types. All of the water originated from meteoric water, and the average recharge altitudes of most samples were approximately the same or higher than the altitudes of the hot spring sites.

(2) The Na–Alk water from the granitic rocks area was likely formed by the montmorillonization of plagioclase, cation exchange reaction of Na–montmorillonite, and precipitation of calcite. SO_4^{2-} ions found in this type were trace amounts derived from the oxidation of sulfide, and H^+ released by this oxidation process was consumed through the interaction with plagioclase. Trace amounts of SO_4^{2-} ions in the Na–Alk type reflect the $\delta^{34}S$ values of granitic rocks and roof sedimentary rocks of the Shimanto group. All of the water samples from the ilmenite series area had negative values ranging from -15.1 to $-4.1‰$, whereas those from the magnetite series area had positive $\delta^{34}S$ values ranging from $+1.7$ to $+8.0‰$.

(3) Na–Alk, Na–SO_4, Na–SO_4·Cl·Alk, and Ca–SO_4 types from the volcanic rocks area to the north of Kofu basin were estimated to be controlled by the dissolution of anhydrite, montmorillonization of plagioclase, cation exchange reaction of Na–montmorillonite, and precipitation of calcite during the fluid flow and mixing process. These waters had a different concentration of SO_4^{2-} ion, which included a wide range of $\delta^{34}S$ values from -4.1 to $+13.6‰$. We inferred that the ^{34}S-rich SO_4^{2-} ions originated from the dissolution of anhydrite, which was produced from ^{34}S-rich sulfate in sulfuric acid derived from the disproportionation of volcanic sulfur dioxide. The ^{34}S-poor SO_4^{2-} ions originated from the dissolution of anhydrite, which was produced from ^{34}S-poor sulfate derived from the oxidation of ascending hydrogen sulfide in shallow ground water during the active stage of past volcanism.

In some cases, the sulfur isotope is used to determine the origin of aqueous sulfate ions. Such is the case for naturally derived aquifer materials and materials derived from anthropogenic pollution (e.g., Torssander *et al*., 2006; Sato *et al*., 2008; Noseck *et al*., 2009; Shikazono, 2011); this is not limited to the granitic and volcanic rock areas (e.g., Muramatsu *et al*., 2010a, b). However, environmental background data for the $\delta^{34}S$ values of aqueous sulfate are still not abundant. In a present study, we revealed that the dissolved sulfate ion in the granitic and volcanic rock areas had a wide range of $\delta^{34}S$ values depending on the formation process of the aquifer rock minerals. This result can be used as environmental back-

ground isotope data for the estimation of the origin of sulfate in water samples.

REFERENCES

Aikawa, K. (1995) Chemistry of hot springs in Yamanashi Prefecture—With special reference to the chemical components and distribution of hot springs. *J. Hot Spring Sci.* **45**, 188–210 (in Japanese).

Ajima, S., Todaka, N., Iwatsuki, T. and Furue, R. (2006) Hydrogeochemical modeling around the Mizunami underground research laboratory using multivariate analysis. *Jour. Japan Soc. Eng. Geol.* **47**, 120–130 (in Japanese with English abstract).

Akaku, K., Reed, M. H., Yagi, M., Kasai, K. and Tasuda, Y. (1991) Chemical and physical processes occurring in the Fushime geothermal system, Kyushu, Japan. *Geochem. J.* **25**, 315–333.

Appelo, C. A. J. and Postma, D. (2005) *Geochemistry, Groundwater and Pollution.* 2nd ed., Balkema, Leiden, 649 pp.

Blum, A. E. and Stillings, L. L. (1995) Feldspar dissolution kinetics. *Chemical Weathering Rates of Silicate Minerals. Reviews in Mineralogy* **31** (White, A. F. and Brantley, S. L., eds.), 291–352, Mineralogical Society of America, Washington, D.C.

Browne, P. R. L. (1978) Hydrothermal alteration in active geothermal fields. *Ann. Rev. Earth Planet. Sci.* **6**, 229–250.

Chiba, H. (1991) Attainment of solution and gas equilibrium in Japanese geothermal systems. *Geochem. J.* **25**, 335–355.

Ichikuni, M., Suzuki, R. and Tsurumi, M. (1982) Alkaline spring waters as a product of water–rock interaction. *Chikyukagaku (Geochemistry).* **16**, 25–29 (in Japanese with English abstract).

Iwatsuki, T. and Yoshida, H. (1999) Groundwater chemistry and fracture mineralogy in the basement granitic rock in the Tono uranium mine area, Gifu Prefecture, Japan—Groundwater composition, Eh evolution analysis by fracture filling mineral. *Geochem. J.* **33**, 19–32.

Japan Meteorological Agency (2013) http://www.jma.go.jp/jma/menu/report.html (last access date: 2013.8.1).

Kanamaru, T. and Takahashi, M. (2008) Whole-rock major element chemistry of the Higashi-Yamanashi Volcano- Plutonic Complex, central Japan. *Proc. Inst. Nat. Sci., Nihon Univ.* **43**, 155–165 (in Japanese with English abstract).

Kato, N., Aikawa, K., Tsukamoto, K., Imahashi, M., Takamatsu, N., Kamimura, K., Nakamura, M. and Akiyama, T. (1987) Geochemical studies on the alkaline springs around the Omo River in Enzan-City, Yamanashi Prefecture. *General Education Review, Toho Univ.* **19**, 23–32 (in Japanese).

Kato, N., Aikawa, K. and Tsukamoto, K. (1988) Geochemical studies on the hot and mineral springs around the Fuefuki River, Yamanashi Prefecture. *General Education Review, Toho Univ.* **20**, 19–26 (in Japanese).

Kiyosaki, J., Tanaka, K., Oikawa, K., Taguchi, S., Chiba, H., Tsunekawa, K. and Nagahama, N. (2002) Sulfur isotopic study of hydrothermal alteration minerals at the hatchobaru geothermal field (abstract). *2002 Ann. Meet. Geotherm. Res. Soc. Japan, Abstract and Program*, B09 (in Japanese).

Kiyosaki, J., Tanaka, K., Taguchi, S., Chiba, H., Takeuchi, K. and Motomura, Y. (2006) Hypogene acid alteration at the Hatchobaru geothermal field, Kyushu, Japan. *J. Geochem. Res. Soc. Japan* **28**, 287–297 (in Japanese with English abstract).

Krupp, R. E. (2005) Formation and chemical evolution of magnesium chloride brines by evaporite dissolution processes—Implications for evaporite geochemistry. *Geochim. Cosmochim. Acta* **69**, 4283–4299.

Kuroda, Y. and Suwa, K. (1983) *Polarizing Microscope and Rock Forming Minerals.* 2nd ed., Kyoritsu Shuppan, Tokyo, 368 pp. (in Japanese).

Maki, T., Takechi, T., Yamatake, S., Eguchi, S. and Shimaki, T. (1976) Geochemical consideration of the quality of spring waters in Dogo Spring Group, Shikoku, Japan. *J. Soc. Eng. Mineral Springs, Jpn.* **11**, 55–67 (in Japanese with English abstract).

Matsuda, T. (2007) Geology and geohistory of the Tertiary basement of Mt. Fuji. *Fuji Volcano* (Aramaki, S., Fujii, T., Nakada, S. and Miyaji, N., eds.), 45–57, Yamanashi Institute of Environmental Sciences, Fujiyoshida (in Japanese with English abstract).

Matsumoto, A., Ohta, Y., Hoshizumi, H., Takahashi, Y., Nishioka, Y., Miyake, Y., Tsunoda, K. and Shimizu, M. (2007) K–Ar age determinations of age unknown rocks in Japanese Islands—volcanic and plutonic rocks in the areas associated with Geological Map Project (during fiscal 2005). *Bull. Geol. Surv. Japan* **58**, 33–43 (in Japanese with English abstract).

Matsumura, M. and Fujimoto, K. (2008) Hydrothermal alteration of the basement inside of the caldera rim of the Hakone volcano. *Bull. Tokyo Gakugei Univ. Natur. Sci.* **60**, 111–119 (in Japanese with English abstract).

Mimura, K. (1971) The Plio–Pleistocene volcanic activity in the north of the Kofu basin, central Japan: Volcanic activity of the Mizugamori Volcanic rocks. *Chishitsugaku Zasshi* **77**, 375–388 (in Japanese with English abstract).

Muramatsu, Y., Komatsu, R., Sawaki, T., Sasaki, M. and Yanagiya, S. (2000) Geochemical study of fluid inclusions in anhydrite from the Kakkonda geothermal system, northeast Japan. *Geochem. J.* **34**, 175–193.

Muramatsu, Y., Oshiro, E. and Chiba, H. (2010a) Chemical evolution of river water infiltrating the bottom sediment at the Sugao Wealth nourishing Marsh. *Jpn. J. Limnol.* **71**, 1–10 (in Japanese with English abstract).

Muramatsu, Y., Arai, H., Kondo, F., Oshiro, E. and Chiba, H. (2010b) Nitrogen and sulfur isotope analysis of anthropogenic nitrate pollution of groundwater in the Shimousa Group, Chiba Prefecture. *Jpn. J. Soil Sci. Plant Nutr.* **81**, 7–15 (in Japanese with English abstract).

Muramatsu, Y., Katayama, H., Chiba, H. and Okamura F. (2014) Chemical and stable isotope (δD, $\delta^{18}O$ and $\delta^{34}S$) compositions of hot springs from the Haruna Volcano of central Japan, and their geological and mineralogical interpretations.

J. Hot Spring Sci. **63**, 298–316 (in Japanese with English abstract).

Nakamura, T. (2008) Nitrogen dynamics on the hydrologic flowpath in alluvial fans. Ph.D. Thesis, Univ. Yamanashi, Japan, 142 pp. (in Japanese).

Nakamura, T., Osada, Y. and Kazama, F. (2008) Identifying the effects of groundwater recharge on nitrate concentration in the eastern Kofu Basin using ^{2}H, ^{18}O and ^{15}N. *Jour. Jpn. Soc. Water Environ*. **31**, 87–92 (in Japanese with English abstract).

Noseck, U., Rozanski, K., Dulinski, M., Havlová, V., Sracek, O., Brasser, T., Hercik, M. and Buckau, G. (2009) Carbon chemistry and groundwater dynamics at natural analogue site Ruprechtov, Czech Republic: Insights from environmental isotopes. *Appl. Geochem*. **24**, 1765–1776.

Oki, Y., Tajima, Y., Hirano, T., Ogino, K., Hirota, S., Takahashi, S., Kokaji, F., Moriya, M. and Sugimoto, M. (1964) Mineral waters from the Tanzawa Mountains. *Bull. Hot Spring Res. Inst. Kanagawa Pref*. **1**, 19–37 (in Japanese with English abstract).

Ozaki, M., Makimoto, H., Sugiyama, Y., Miura, K., Sakai, A., Kubo, K., Kato, H., Komazawa, M., Hiroshima, T. and Sudo, S. (2002) Geological Map of Japan 1:200,000, Kofu. Geol. Surv. Japan, AIST, Tsukuba (in Japanese with English abstract).

Saito, K., Kato, K. and Sugi, S. (1997) K–Ar dating studies of Ashigawa and Tokuwa granodiorite bodies and plutonic geochronology in the South Fossa Magna, central Japan. *The Island Arc* **6**, 158–167.

Sasaki, A. and Ishihara, S. (1979) Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contrib. Mineral. Petrol*. **68**, 107–115.

Sasaki, M. (2004) Geochemical features of groundwaters in granitoids. *Bull. Geol. Surv. Japan* **55**, 439–446 (in Japanese with English abstract).

Sasaki, Y., Tsuji, K. and Simizu, G. (2009) Recent atmospheric deposition in Yamanashi. *Ann. Rep. Yamanashi Inst. Public Health* **53**, 75–76 (in Japanese).

Sato, K. (1991) Miocene granitoid magmatism at the island-arc junction, central Japan. *Mod. Geol*. **15**, 367–399.

Sato, K. and Ishihara, S. (1983) Chemical composition and magnetic susceptibility of the Kofu granitic complex. *Bull. Geol. Surv. Japan* **34**, 413–427 (in Japanese with English abstract).

Sato, Y., Kometani, M. and Satake, H. (2008) Geochemistry of surface water in Tateyama Caldera, northern central Japan—its relation to large-scale landslides. *Proc. IAH Cong*. **36**, 1–10.

Shibata, K., Kato, Y. and Mimura, K. (1984) K–Ar ages of granites and related rocks from the northern Kofu area. *Bull. Geol. Surv. Japan* **35**, 19–24 (in Japanese with English abstract).

Shikazono, N. (2011) *Elucidation of Sources of Tamagawa Upstream, Midstream and Downstream Sediments and Water and Pollution*. The Tokyu Foundation for Better Environment, Tokyo, 110 pp. (in Japanese).

Shimizu, M. (1986) The Tokuwa batholith, central Japan: an example of occurrence of Ilmenite-Series and Magnetite-Series granitoids in a batholith. *Univ. Museum, Univ. Tokyo, Bull*. **28**, 143 pp.

Shimizu, M., Shikazono, N. and Tsunoda, K. (1995) Sulphur isotopic characteristics of hydrothermal mineral deposits in the southern Fossa Magna region, Japan: Implications for the tectonic and geologic evolution in the southern Fossa Magna region after middle Miocene age. *Mem. Fac. Lib. Arts Educ. Pt. 2 Mathem. Nat. Sci. Univ. Yamanashi* **46**, 40–48.

Stumm, W. and Morgan, J. J. (1981) *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*. 2nd ed., Wiley, New York, 780 pp.

Suzuki, R. (1979) Fluoride in alkaline mineral springs. *Chikyukagaku* (*Geochemistry*) **13**, 25–31 (in Japanese with English abstract).

Takamatsu, N., Shimodaira, K., Imahashi, M. and Yoshioka, R. (1981) A study on the chemical composition of ground waters from granitic areas. *Chikyukagaku* (*Geochemistry*) **15**, 69–76 (in Japanese with English abstract).

Takashima, K. and Kosaka, K. (2000) Activity of hydrothermal alterations and formation history of fracture systems around the Pliocene Yakeyama Toge Hydrothermal Alteration Zone, North of the Kofu Basin, central Japan. *Proc. Inst. Nat. Sci., Nihon Univ*. **35**, 91–106 (in Japanese with English abstract).

Tanaka, O. (1989) Hot spring zone in the Yamanashi Prefecture, Japan. *The Otsuki-Tandai Ronshu* **20**, 225–244 (in Japanese).

Tardy, Y. (1971) Characterization of the principal weathering types by the geochemistry of waters from some European and African crystalline massifs. *Chem. Geol*. **7**, 253–271.

Torssander, P., Mörth, C. M. and Kumpulainen, R. (2006) Chemistry and sulfur isotope investigation of industrial wastewater contamination into groundwater aquifers, Piteå County, N. Sweden. *J. Geochem. Explor*. **88**, 64–67.

Tsunoda, K., Nishido, H. and Shimizu, M. (1992) K–Ar ages of mineralization associated with granitic rocks around the Kofu basin, Yamanashi Prefecture, central Japan. *Shigen Chishitsu* (*Mining Geology*) **42**, 147–153 (in Japanese with English abstract).