

原 著

Geochemical and Isotopic Characteristics of the Mineral Spring and Natural Spring Waters in the Setogawa Group of the Western Yamanashi Prefecture, Japan

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山梨県西部の瀬戸川層群における鉱泉および湧水の
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要 旨

山梨県西部の瀬戸川層群北部に位置する雨畑地域における鉱泉・湧水を対象に、主要溶存成分および水素・酸素・硫黄 ($\delta D \cdot \delta^{18}O \cdot \delta^{34}S$) 安定同位体分析を実施し、湧水地点から採取した岩石片の顕微鏡観察を実施した。得られた結果を基に、当該鉱泉水および湧水の起源と水質形成機構を検討した。

試料水はいずれも降水起源であり、主要成分の溶存割合は湧水で $Ca^{2+} > Na^+ > Mg^{2+}$ および $HCO_3^- > SO_4^{2-} > Cl^-$ 、鉱泉水で $Ca^{2+} > Mg^{2+} > Na^+$ および $HCO_3^- > SO_4^{2-} > Cl^-$ である。これらの成分のうち、最も主要な Ca^{2+} および HCO_3^- は瀬戸川層群に含まれる石灰質の溶解作用、 SO_4^{2-} は表層での黄鉄鉱の酸化反応に規制されており、 SO_4^{2-} が持つ $\delta^{34}S$ 値は瀬戸川層群の硫化物が持つ $\delta^{34}S$ 値を反映して特徴的に低い。この SO_4^{2-} は地下の嫌気環境における硫酸還元菌の作用によって H_2S を生じていると思われ、鉱泉地では硫化水素臭を伴っている。黄鉄鉱の酸化によってもたらされた H^+ は石灰質の溶解を引き起こして中和される。

キーワード：山梨県西部、瀬戸川層群、鉱泉水、水-鉱物相互作用、水質形成機構、安定同位体比 ($\delta D \cdot \delta^{18}O \cdot \delta^{34}S$)

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Abstract

Chemical and stable isotopic compositions (δD , $\delta^{18}O$, $\delta^{34}S$) of the water samples from a well drilled for mineral spring source and from a natural spring in the Amehata area located northern Setogawa Group of the western Yamanashi Prefecture, additionally disseminated minerals of a rock sample from the natural spring site, were investigated to determine the origin of the water and formation mechanisms of the water quality.

The sampled waters were meteoric in origin and the ionic dominance pattern observed was $Ca^{2+} > Na^+ > Mg^{2+}$ and $HCO_3^- > SO_4^{2-} > Cl^-$ for natural spring, and $Ca^{2+} > Mg^{2+} > Na^+$ and $HCO_3^- > SO_4^{2-} > Cl^-$ for mineral spring water. The primary dominant ionic contents of Ca^{2+} and HCO_3^- were derived from dissolution of calcareous material, and SO_4^{2-} was derived from pyrite oxidation at the aerobic surface layer. The SO_4^{2-} reflected highly negative $\delta^{34}S$ values of the sulfides in the Setogawa Group, and it may be reduced to H_2S by sulfate-reducing bacteria in the anaerobic underground. H^+ released by pyrite oxidation triggered this dissolution of calcareous material and was neutralized through the reaction.

Key words : Western Yamanashi Prefecture, Setogawa Group, Mineral spring, Water-rock interaction, Water formation mechanism, Stable isotope ratio ($\delta D \cdot \delta^{18}O \cdot \delta^{34}S$)

1. Introduction

Although the Kofu basin in Yamanashi Prefecture has been considered poor in hot spring sources in the past (Tanaka, 1989), a number of wells for hot spring bathing purposes have been drilled extensively in the last several decades. Many researchers have reported on water quality characteristics and distribution of hot spring waters in Yamanashi Prefecture (e.g., Akiyama, 1972 ; Sugihara and Shimaguchi, 1978 ; Aikawa, 1995), however, the origins of the water and formation mechanisms, such as details of the water-rock interactions that control water quality, have not been satisfactorily defined. Stable isotope data can be used to estimate the origin of water and dissolved chemical species of hot spring waters (e.g., Muramatsu *et al.*, 2012, 2013, 2014), but reports on the hydrogen, oxygen and sulfur isotopic compositions of hot spring waters in Yamanashi Prefecture are very few (Muramatsu *et al.*, 2011 ; Yaguchi *et al.*, 2014).

As Nishimura (2006) discussed the mechanism of well interference between existing and newly drilled hot springs of the Nishiyama hot spring area at the western part of Yamanashi Prefecture based on geological evidences, geological interpretation of water formation mechanism is indispensable for protection and sustainable development of hot springs. In Yamanashi Prefecture, about 70% of the drinking water comes from groundwater, thus many researchers have extensively investigated the groundwater of Yamanashi Prefecture (e.g., Yanai and Tsugane, 1957 ; Sakamoto *et al.*, 1990 ; Kobayashi and Koshimizu, 1999 ; Nakamura *et al.*, 2008 ; Kobayashi and Horiuchi, 2008 ; Kobayashi *et al.*, 2009 ; Kobayashi *et al.*, 2010). We also reviewed these reports for reference, however, most previous works were conducted principally in the Kofu Basin and focused on the distribution of anthropogenic pollutants and on the temporal change of groundwater quality. These were conducted in order to investigate the anthropogenic influence of groundwater quality in a densely populated area. Thus, interrelationships between geology and groundwater quality in Yamanashi Prefecture has not yet been clarified.

Amehata area is located in the northern Setogawa Group of the western part of Yamanashi

Prefecture. This area has one of the highest amounts of rainfall in Japan (mean annual rainfall is more than 2,100 mm ; Ministry of Land, Infrastructure and Transport Government of Japan (2014), and has been designated as one of several watershed conservation areas by the Yamanashi prefectural ordinance (Yamanashi Prefectural Government, 2012). Further, mineralogical and sulfur isotopic properties of Koei vein deposit in the Amehata have been reported by Shimizu *et al.* (1995). Thus, this area is considered a suitable site to discuss the relationships between water quality and geological characteristics without anthropogenic influence. The water supplies of this area, such as well and spring discharge, have been used for mineral spring bathing and other domestic purposes, but the origin of the water and their chemical components have not been described previously.

In this study, water samples were collected from a well drilled for mineral spring source and from a natural spring located in the Amehata area and subjected to chemical and isotopic analysis of hydrogen, oxygen, and sulfur. A phyllitic rock sample was also taken from a natural spring site for microscopic observation to check for the presence of any disseminated minerals. Based on the analytical results, we discussed the origin of the water and water-rock interactions, which determine the quality of the water.

2. Overview of Geology

A simplified geological map and sample locations are shown in Fig. 1. The Setogawa Belt of the Shimanto Belt is an Early to Middle Miocene accretionary complex situated at the easternmost part of the Akaishi Mountains in Central Japan. It is bordered by the Itoigawa-Shizuoka Tectonic Line (ISTL) at its eastern end and the Sasayama Tectonic Line to the west (Sugiyama, 1995). The Belt is comprised of three Groups (the Setogawa, Oigawa, and Ryuso Groups, from west to east), which are separated by the Fujishiro and Jumaiyama Faults branching from the ISTL (Sugiyama, 1995). The Setogawa Group forms a major part of the Setogawa Belt, which is mainly composed of slaty to phyllitic shale and sandstone (Sugiyama, 1995 ; Yagi *et al.*, 1996 ; Ozaki *et al.*, 2002). The Oigawa Group is mainly composed of shale and interbedded sandstone and shale. Furthermore, the Ryuso Group is mainly composed of rhyolite volcanic rock and lava (Sugiyama, 1995 ; Ozaki *et al.*, 2002). Several ore deposits are recognized in the Setogawa group (Shimizu *et al.*, 1995 ; Sugiyama 1995 ; Yakushi and Enjoji, 2004).

3. Sampling and Analytical Procedures

Two water samples were taken from a well drilled for mineral spring source and a natural spring in the Amehata area, northern Setogawa Group in the western Yamanashi Prefecture (Fig. 1). Additionally, phyllitic rock samples were collected from the natural spring site. Well depth and chemical analysis data for the Amehata mineral spring source were obtained by interviewing the facility manager. Temperature, electrical conductivity, and pH were directly measured using a standard, hand-held, calibrated meter (HORIBA D-24). Total alkalinity was also directly determined by using titration with sulfuric acid to a final pH of 4.8 (HACH AL-DT), and the total alkalinity is expressed as HCO_3^- . The amount of free CO_2 was calculated based on the

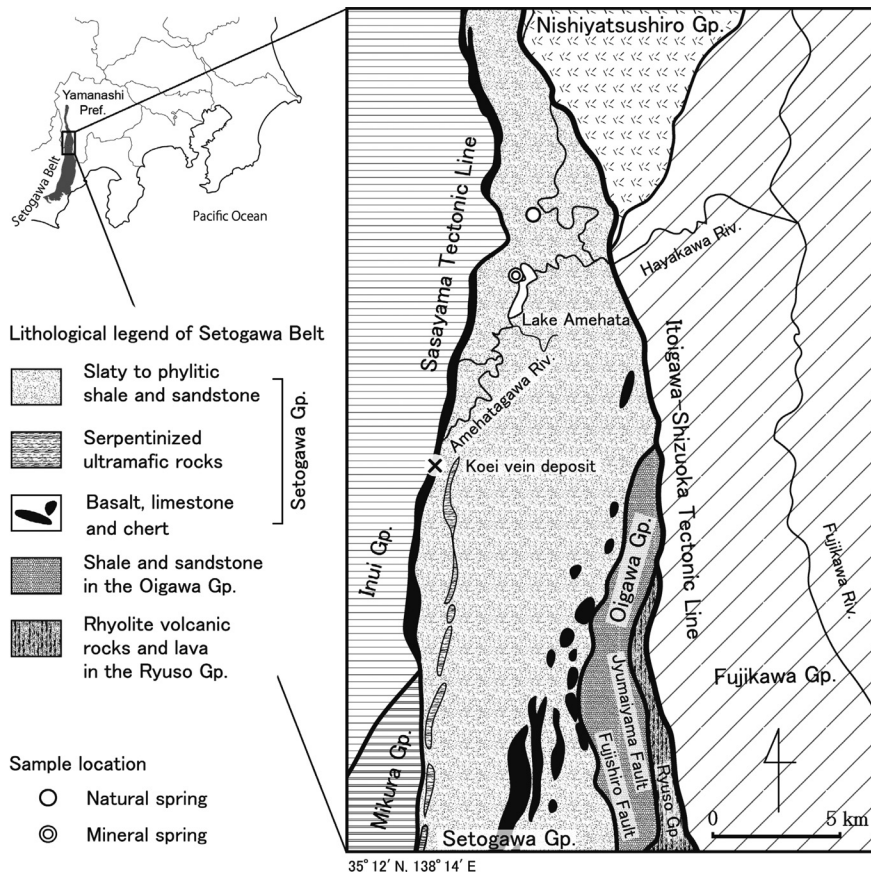


Fig. 1 Simplified geological map and sample locations of water samples in the northern Setogawa Group of the western Yamanashi Prefecture (modified after Sugiyama, 1995 ; Ozaki *et al.*, 2002).

alkalinity and pH values. Main compositions such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} were measured using ion chromatography (SHIMADZU LC-VP). $\Sigma\text{Fe}^{2+ \cdot 3+}$ was measured by atomic absorption spectrophotometry (SHIMADZU AA-6200). The SiO_2 was analyzed by spectrophotometry using molybdenum yellow method (SHIMADZU UV-1650PC). Concentration of boron was measured by carmine method (HACH DR-2800) and expressed as HBO_2 . The rock sample was observed using a digital microscope (KEYENCE VHX-2000) after polishing.

Isotopic compositions of hydrogen (D/H) and oxygen ($^{18}\text{O}/^{16}\text{O}$) were reported in terms of δD and $\delta^{18}\text{O}$ (‰), relative to the Vienna Standard Mean Ocean Water (V-SMOW) standard. These were also measured by a mass spectrometer connected on-line to a gas chromatograph (GV Instruments Isoprime-EA). After decomposing a sample by heating at 1,050°C for H_2 analysis and 1,260°C for CO analysis in an oxygen-free environment, the product gases were chromatographically separated and introduced into an ion source for analysis with a mass spectrometer. Sulfur isotope ($^{34}\text{S}/^{32}\text{S}$) 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

BaSO₄ and mixed with V₂O₅ as a combustion aid. The mixture was then heated in order to decompose it into a SO₂ gas, and obtained SO₂ gas was then analyzed by a mass spectrometer. Sulfur isotopic compositions were reported as δ³⁴S (‰) variations relative to the Canyon Diablo Troilite (CDT) standard. Analytical precisions are ±1.0‰ for δD, ±0.1‰ for δ¹⁸O, and ±0.2‰ for δ³⁴S values, respectively.

4. Results and Discussion

4.1 Chemical and isotopic compositions of the water samples

The analytical results of mineral spring and natural spring waters are listed in Table 1. The extremely low concentration of NO₃⁻ in water samples, which is one measure used in the water pollution index, suggests that there are little or no anthropogenic effects. Natural spring water showed slightly alkaline pH and ionic dominance patterns of Ca²⁺>Na⁺>Mg²⁺ and HCO₃⁻>SO₄²⁻>Cl⁻. The mineral spring water gave off a pervasive hydrogen sulfide odor, and the chemical contents were 10 times thicker than those of natural spring water, but it had the approximately same ionic dominance as the natural spring, i.e., Ca²⁺>Mg²⁺>Na⁺ and HCO₃⁻>SO₄²⁻>Cl⁻.

Hot spring analysis certificate (Yamanashi Prefecture Food Hygiene Association, 2009) show slightly higher concentration of major cation and anions such as, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe^{2+·3+}, Cl⁻, HCO₃⁻, and SO₄²⁻ ions, than these of hot spring source water sampled in this study, but show the same ionic dominance pattern. As shown in Table 1, all these analytical data, including data in this study and the hot spring analysis certificate (Yamanashi Prefecture Food Hygiene Association, 2009), show slightly higher concentrations of boron in the water samples (0.1 to 0.7 mg/L as B) than that of

Table 1 Chemical composition and pH of water samples collected from the northern Setogawa Group in the western Yamanashi Prefecture.

Sample ID	Date	Depth m	Temp. °C	pH	E. C. mS/m	Na ⁺ mg/L	K ⁺ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Fe ^{2+·3+} mg/L	Cl ⁻ mg/L
Mineral spring	20/07/2010	62	15.2	7.6	54.4	5.6	1.3	89.7	14.3	0.7	1.0
Natural spring	20/07/2010	0	13.3	8.3	5.7	3.0	0.1	5.1	1.1	0.3	0.5
Mineral spring*	18/09/2009	62	14.7	7.5	59.5	14.6	1.4	106.7	19.3	2.1	2.0

Sample ID	NO ₃ ⁻ mg/L	SO ₄ ²⁻ mg/L	HS ⁻ mg/L	S ₂ O ₃ ²⁻ mg/L	HCO ₃ ⁻ mg/L	Free CO ₂ mg/L	Free H ₂ S mg/L	H ₂ SiO ₃ mg/L	HBO ₂ mg/L	δD ‰	δ ¹⁸ O ‰	δ ³⁴ S ‰
Mineral spring	<0.1	96.7	-	-	232.8	12.4	-	17.9	2.8	-61.2	-9.76	-14.4
Natural spring	0.1	10.6	-	-	15.3	0.2	-	15.4	1.6	-65.3	-9.74	-13.7
Mineral spring*	<0.1	115.8	0.5	2.0	275.0	15.4	0.5	18.7	0.4	N.D.	N.D.	N.D.

*Data from Yamanashi Prefecture Food Hygiene Association, (2009). Free CO₂ concentrations were calculated using an equilibrium constant from Garrels and Christ (1965). E.C.: Electrical conductivity. Depth: Total depth of the well. -: Not analysis. N.D.: No data.

rain and river water of central Honshu (0.009 ppm and 0.042 ppm as B, respectively ; Utsumi and Isozaki, 1967). This boron content indicates that the quality of water samples is influenced by the interactions between water and sedimentary rock of the sampling site of the waters because the boron content is generally high in sedimentary rock (Ishikawa and Nakamura, 1989). Yazaki *et al.* (1981) have pointed out that the groundwater in this area tends to have ionic dominance of $\text{Na}^+ > \text{Ca}^{2+}$ and $\text{Cl}^- > \text{HCO}_3^-$ with a slightly alkaline pH. However, these water quality characteristics were virtually focused on an investigation of waters associated with natural gas. Therefore, relationship between water chemistry and sedimentary rock of the Amehata area has not been clearly identified. Regarding the sample waters in the present work, water quality is similar to general water qualities of shallow groundwater (Ca-HCO₃ type) rather than the features determined by Yazaki *et al.* (1981).

The $\delta^{34}\text{S}$ values of the dissolved SO_4^{2-} in the samples were characteristically highly negative. This may be one of the features, which found in the water samples from Setogawa Group of Amehata area.

4.2 Origin of the water and formation mechanisms of water quality

The δD and $\delta^{18}\text{O}$ values of the water samples suggested that the waters were meteoric in origin because the δ values of the water samples (Table 1), were similar to the annual mean values of the spring waters in the Kofu basin, which are meteoric in origin ($\delta\text{D} = -66\%$, $\delta^{18}\text{O} = -9.7\%$; Nakamura *et al.*, 2007).

In general, the water quality of the groundwater derived from meteoric water is controlled by several water-rock interaction processes, such as the dissolution and precipitation of calcite, plagioclase weathering, and ion-exchange reactions of clay minerals. This is especially true at shallow layer levels where a dissolution of calcite as shown in reaction (1) is the most dominant factor affecting the chemical properties of groundwater because the calcite dissolution rate is exceedingly faster than that of plagioclase (Rimstidt, 1997).



In the Setogawa Group, calcareous rocks, which contain several species of fossils, such as foraminiferal, nanno, molluscan and radiolarian fossils, have been occasionally recognized (e.g., Honjo and Minoura, 1968 ; Iwasaki and Ono, 1977 ; Ibaraki 1983, 1984 ; Sugiyama, 1995). Thus the calcareous content of the rocks seems to be the source of the Ca^{2+} and HCO_3^- in the water samples. However, the average concentrations of the Ca^{2+} and HCO_3^- in the natural waters (including spring water, groundwater, and river water) from every region of Japan are 14.7 mg/L and 50.7 mg/L, respectively (Yabusaki and Shimano, 2009). Based on this, the $\text{Ca}^{2+}/\text{HCO}_3^-$ meq ratio is calculated at 0.88. Conversely, the $\text{Ca}^{2+}/\text{HCO}_3^-$ ratio of the water sampled in the present study is slightly high, reaching 1.17 for mineral spring and 1.01 for natural spring water.

Next, we considered the origin of the SO_4^{2-} in the water samples. According to Shimizu *et al.* (1995), the Koei vein deposit (Fig. 1) in the Amehata area consists of an abundance of sulfide minerals, such as pyrite, pyrrhotite, chalcopyrite, and sphalerite. Furthermore, those sulfides have highly negative $\delta^{34}\text{S}$ values at -14.6% . Those $\delta^{34}\text{S}$ values are remarkably similar to the values of the SO_4^{2-} in the water samples (-14.4% for mineral spring ; -13.7% for natural spring), suggesting that the origin of the SO_4^{2-} was from an oxidation of the sulfide minerals. As

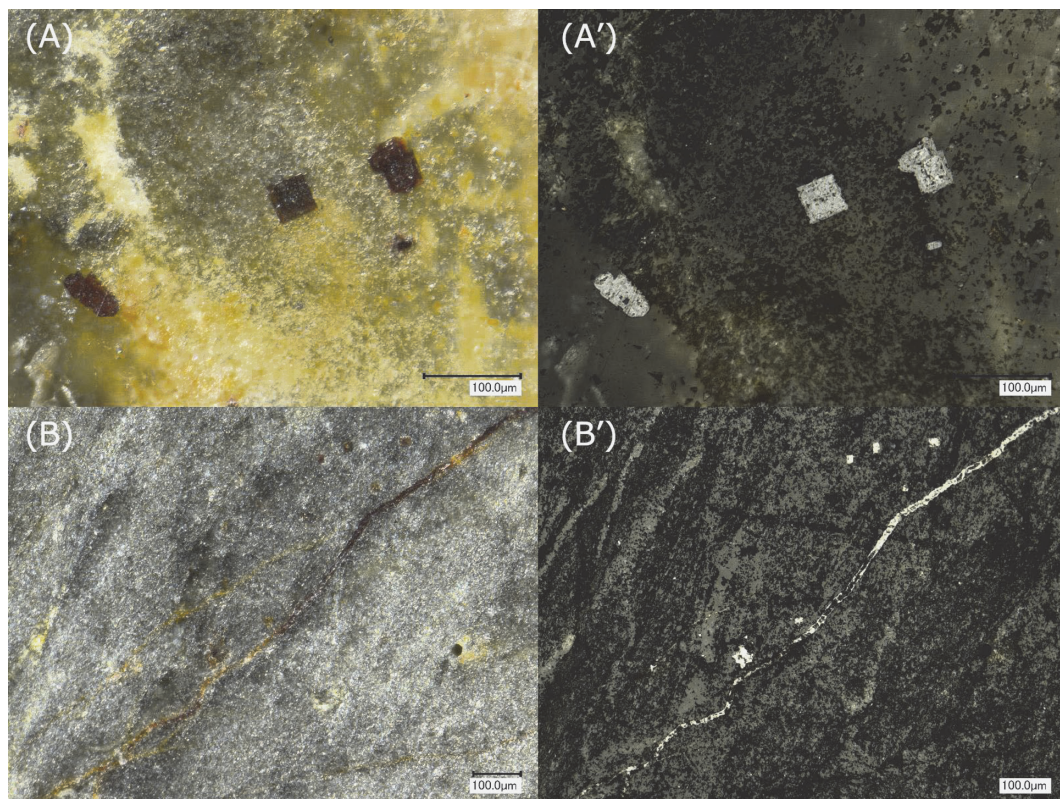
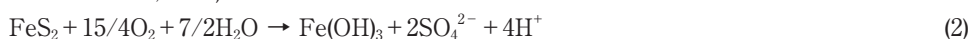


Fig. 2 Micrographs of finely-disseminated and oxidized pyrite in the polished rock sample. Cube type : (A) stereo microphotograph, (A') reflected light microphotograph. Veinlet type ; (B) stereo microphotograph, (B') reflected light microphotograph. Oxidation of the pyrite progressed to the inside.

a result of this microscopic observation of the phyllitic rock sample collected from the natural spring site, a finely-disseminated pyrite was recognized and the oxidation of it was seen to progress to the inside (Fig. 2). Therefore the SO_4^{2-} in the water samples were derived from the oxidation of pyrite at the oxygen-rich conditions close to the surface by the following reaction (Appelo and Postma, 2005) :



According to hot spring analysis certificate (Yamanashi Prefecture Food Hygiene Association, 2009), the mineral spring water contains dissolved $\text{S}_2\text{O}_3^{2-}$, HS^- and H_2S as specific chemical components of the Japanese Hot Spring Law. Because the slaty rock around Amehata area is rich in organic matter (Yazaki *et al.*, 1981), we considered that H_2S was produced via the sulfate reduction of sulfate-reducing bacteria in the anaerobic underground environment. This is due to the fact that the decomposition of organic matter can lead to anaerobic conditions in groundwater. The $\text{S}_2\text{O}_3^{2-}$ is possibly an intermediate product of the re-oxidation process of H_2S to SO_4^{2-} .

While pyrite oxidation progressed at the oxygen-rich surface layer, water samples were not acidified. Since water samples contained free CO_2 (Table 1), H^+ derived from pyrite oxidation

was consumed through the dissolution of calcareous material with the following reaction :



We also considered that the reason for a high $\text{Ca}^{2+}/\text{HCO}_3^-$ ratio in the water samples was due mostly to some dissolution of calcareous material progressing without a HCO_3^- release, as shown in the reaction (3).

In this study, chemical and isotopic characteristics of mineral and spring waters of Amehata, a watershed conservation area of Yamanashi Prefecture, were interpreted based on geological attributes. To protect and sustainable use of hot springs in Yamanashi Prefecture, further geological and isotopic investigations should be extensively conducted.

5. Conclusion

Water samples from a well drilled for mineral spring source and from a natural spring in the Amehata area of northern Setogawa Group in the western Yamanashi Prefecture, as well as a rock samples taken from the natural spring site were investigated in order to determine the origin of the water and chemical reactions, which determine the quality of the water. A couple of discernible conclusions below can be drawn from this study :

(1) The ionic dominance pattern observed in the water samples were $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ for natural spring, and $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$ for mineral spring water. Based on the isotopic characteristics of δD and $\delta^{18}\text{O}$, sample waters were meteoric in origin.

(2) The Ca^{2+} and HCO_3^- in the water were derived from the dissolution of calcareous material in the Setogawa Group. The SO_4^{2-} that has highly negative values of $\delta^{34}\text{S}$ was derived from the oxidation of pyrite at the aerobic surface layer. The hydrogen sulfide odor of the mineral spring might be caused by the SO_4^{2-} reduction to H_2S by sulfate-reducing bacteria in the anaerobic underground. H^+ derived from the pyrite oxidation was then neutralized through dissolution of calcareous materials.

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