

Fumarolic gases sampled at Ebino-Iwoyama and Shinmoedake volcanoes, Kirishima, Japan

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Introduction

New fumaroles have appeared at Mt Ebino-Iwoyama volcano Kirishima Japan in Dec 2015. After the appearance, volcanic earthquakes and tremor have been observed, suggesting the activation of volcanic activity. At Mt Shinmoedake volcano Kirishima Japan, a magmatic eruption happened in 2011. Until Jan 2017, the volcanic activity has decreased and the activity is almost dormant. In general, fumarolic gases contain magmatic components. In this study, we have sampled fumarolic gas at Ebino-Iwoyama and Shinmoedake volcanoes. The chemical and isotopic composition of fumarolic gases will give us the useful information for the evaluation of activity at the both volcanoes.

Fumarolic gas

We have sampled fumarolic gases at the fixed position on the summit area of both Ebino-Iwoyama and Shinmoedake volcanoes. The temperature of fumarolic gas, at the outlet of fumarole, was close to the boiling temperature of water under the local atmospheric pressure. The momentum of discharging fumarolic gases was low at the both volcanoes, producing no big sound.

Result and Discussion

(Ebino-Iwoyama volcano)

The CO₂/H₂O ratio of fumarolic gas had increased until May 2016 followed by a continuous drop after Jul 2016. In general, CO₂ gas originates in the degassing magma. The recent decrease of CO₂/H₂O ratio suggest the suppressed degassing activity of magma. The apparent equilibrium temperature (AET) can be calculated by use of the concentration of H₂O, H₂S, SO₂ and H₂ in fumarolic gas. The calculated AET was 232C in Dec 2015. It increased to 313C in Feb 2016, followed by a stabilized temperature. In Dec 2015, the 18O/16O ratio of H₂O in fumarolic gas was low. It increased significantly in Feb 2016 followed by a gradual increase. The changes in AET and 18O/16O ratio suggest an invasion by hot magmatic fluid within the shallow hydrothermal system beneath fumaroles.

(Shinmoedake volcano)

One conspicuous feature of fumarolic gas composition was the high CO₂ concentration extending to 5 to 7%. The concentration is much higher than the value of fumarolic gas sampled in 1991 and 1994, which was 1.4 to 1.9%. On the other hand, H₂S concentration was only 0.01 to 0.04%, much depleted relative to the gas in 1991 and 1994 such as 0.2 to 0.6%. The recent chemical composition of Shinmoedake volcano suggests the sustained degassing of CO₂ rich magma with the process removing H₂S gas working along the channel of volcanic fluid between magma and fumarole.

Keywords: Kirishima Ebino Iwoyama Shinmoedake, Volcanic gas, magma

A hydrothermal system of Kusatsu-Shirane volcano inferred from Cl concentrations and stable isotope ratios of Yugama crater lake water

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Kusatsu-Shirane volcano exhibits geothermal features such as hot springs that have almost the same $\text{SO}_4^{2-}/\text{Cl}^-$ ratio of water. These hot springs are derived from common parental fluid (Pf) which is produced by a mixing of magmatic high temperature volcanic gas and local meteoric water. The Pf is diluted by hot waters containing low concentration sulfate as waters flow under the ground surface (Yamamoto et al., 1997; Hirabayashi, 1999). A relation between Cl^- concentrations and stable isotope ratios of water requires an existence of vapor-liquid reservoir. The liquid phase of the reservoir is highly condensed in Cl^- produced by a boiling of the Pf. The vapor-liquid reservoir supplies hot water to Kagusa and Jyofu hot springs, located near the top of Kusatsu-Shirane volcano (Ohba et al., 2000).

Shirane pyroclastic cone, located at the summit of Kusatsu-Shirane volcano, has three crater lakes. The largest crater lake, locally called Yugama, has over 0.5 million m^3 of water with a temperature between 0 and 30 degree Celsius which is 10 degree Celsius higher than an ambient temperature. Phreatic eruptions have repeatedly occurred around the cone during the last 130 years. During the recent calm periods, subaqueous fumaroles of Yugama crater lake continue to supply hot water containing high concentration of H^+ , Cl^- and SO_4^{2-} to lake. Stable isotope ratios of lake water have values that are larger than that of the local meteoric water due to additions of magmatic fluids from the lake bottom.

We can easily collect lake water on the lake shore in order to monitor changes in concentrations of lake water. However, we cannot directly evaluate chemical features of fluid emitting from subaqueous fumaroles, because lake water experiences somewhat complex processes including isotopic fractionations during evaporation, condensation, seepage through the lake bottom and meteoric input.

In this study we have developed a numerical model which takes factors associated with variations of Cl^- and stable isotope ratios into account. Applying the model to observation data including water level, temperature, Cl^- concentrations and stable isotope ratios of hydrogen and oxygen, we estimate mass flux, enthalpy, Cl^- concentration and stable isotope ratios of water emitting from the lake bottom. During a calm period in 2012 - 2013, a relation between Cl^- concentrations and stable isotope ratios of water indicates that the hydrothermal reservoir beneath Yugama crater lake is a mixture of magmatic high temperature volcanic gas and the local meteoric waters.

Intense micro earthquake swarms and ground deformations occurred around Shirane pyroclastic cone in 2014, which are accompanied by changes in water temperature, Cl^- concentration and stable isotope ratios. Our model reveals an increase in supply of magmatic high temperature volcanic gas to the hydrothermal reservoir located beneath Yugama crater lake. However, the relation between Cl^- concentrations and stable isotope ratios of water cannot be explained by a mixing. We believe that enhanced boilings have occurred in the reservoir leading fractionations of stable isotope ratios.

In order to reveal the locality of the hydrothermal reservoir, which is an origin of water of Yugama crater

lake, hypocenters of micro earthquakes are precisely relocated by the DD technique. We identify two groups of hypocenters on the basis of its depth and time sequences. Attenuations of seismic waves indicate that the reservoir locates between the shallow and the deep groups of hypocenters, corresponding to an altitude of around 900 m a.s.l. The depth is consistent with the altitude of undersurface of an impermeable layer suggested by MT surveys (Ogawa, in prep.).

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Keywords: Kusatsu-Shirane volcano, Crater lake, Chloride ion, Stable isotope ratio of water, Micro earthquake

Volcanic fluids-rock interaction inferred from characteristics of altered minerals in volcanic products at Tokachidake volcano, central Hokkaido, Japan.

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Altered volcanic products from Tokachidake were mineralogically observed to interpret interaction between volcanic fluids and rock, by using XRD, Raman spectroscopy, and SEM-EDS. We collected samples from the 4.7 ka pyroclastic flow deposit (Gfl-0), lower and upper units of the 3.3 ka pyroclastic flow deposit (Gfl-1 and Gfl-2), and the 1926AD eruption deposits consisting of the lower debris avalanche deposit (Unit A), the middle hydrothermal surge deposit (Unit B), and the upper debris avalanche deposit (Unit C). Each product contains unaltered ash grains consisting of primary igneous minerals and volcanic glass, weakly-altered ash grains in which unaltered part coexists with altered minerals, and intensely-altered ash grains consisting only of altered minerals. Individual ash grains have one of three types of altered mineral assemblages: silica mineral (silica type), silica mineral-alunite±kaolin (alunite type), and silica mineral-kaolin (kaolin mineral type). Most ash grains in Gfl-0 have undergone alteration that produces the alunite type. The samples from Gfl-1 contain abundant kaolin mineral type ash, subordinate alunite type ash, and minor unaltered ash grains. Alteration types in the Gfl-2 deposit are similar to those of Gfl-1, but unaltered ash grains are more abundant in Gfl-1. Most of the ash grains in the 1926AD products underwent alteration which produced mainly silica and alunite types. These mineral assemblages in every product indicate only acidic alteration. The presence of unaltered parts in the most abundant weakly-altered ash indicates rock alteration by a brief, incomplete chemical reaction. For such brief and incomplete reaction, the followed two fluid-rock interactions can be available. One is water-rock interaction which acid hydrothermal water reacts with rocks. Another is vapor-rock interaction which volcanic vapor separated from magma reacts with rocks. Thus, the presence of weakly-altered ash suggests that rock alteration occurred by the brief, incomplete fluid-rock interactions was undergoing an acid-hydrothermal system and/or a volcanic vapor-dominated system developed under the crater when a magma intrudes and degasses. This concluded that the conditions of rock alteration at Tokachidake volcano can be controlled by a magma intrusion.

Keywords: Volcanic fluids, Fluid-Rock interaction, altered minerals

Geochemical simulation for hydrothermal activity

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The estimation of geochemical change in volcanic and geothermal process is important. And the geochemical calculator (simulator), for example, Solveq-Chiller, is useful tool to calculate of fluid change. Especially, in Hijiori EGS field, calcite precipitate with CO₂ gas release with pH increasing from hot water fluid due to rapidly super-saturated as calcite calculated by Solveq-Chiller.

And we calculated in the case of reaction between CO₂ gas and fluid, mass balance and case study of CO₂ gas injection simulation using Hijiori EGS system.

And the phase balance have to be considered in other volcanic and geothermal system and we will show other field examples.

Keywords: geochemical simulation, chemical composition, degas

Plumbing the depths of Yellowstone' s hydrothermal system: preliminary results from a helicopter magnetic and electromagnetic survey

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Although Yellowstone' s iconic hydrothermal systems are well mapped at the surface, their groundwater flow systems are almost completely unknown. In order to track the geophysical signatures of geysers, hot springs, mud pots, steam vents, and hydrothermal explosion craters at depths to hundreds of meters, we collected 4900 line-km of helicopter electromagnetic and magnetic (HEM) data. The data cover significant portions of the caldera including a majority of the known thermal areas. HEM data constrain electrical resistivity which is sensitive to groundwater salinity and temperature, phase distribution (liquid-vapor), and clay formed during chemical alteration of rocks. The magnetic data are sensitive to variations in the magnetization of lava flows, faults and hydrothermal alteration. The combination of electromagnetic and magnetic data is ideal for mapping zones of cold fresh water, hot saline water, steam, clay, and altered and unaltered rock. Preliminary inversion of the HEM data indicates low resistivity directly beneath Yellowstone Lake as well as beneath most of the area with mapped hydrothermally altered rocks; the majority of these areas are also associated with magnetic lows. In the northern part of Yellowstone Lake, low resistivity zones intersect with the lake bottom in close correspondence with mapped vents, fractures and hydrothermal explosion craters and are also associated with magnetic lows. Coincident resistivity and magnetic lows unassociated with mapped alteration occur, for example, along the southeast edge of the Mallard Lake dome and along the northeastern edge of Sour Creek Dome, suggesting the presence of buried alteration. Low resistivities unassociated with magnetic lows may relate to hot and/or saline groundwater, to which the magnetic data are insensitive. Resistivity and magnetic lows follow interpreted caldera boundaries in places, yet deviate in others. In the Norris-Mammoth Corridor, NNE-SSW trending linear resistivity and magnetic lows align with mapped faults. This pattern of coincident resistivity and magnetic lows may reflect fractures along which water is flowing. In addition, low resistivities underlie highly resistive and magnetic rhyolite flows, and in several cases, suggest interconnection between the different thermal areas.

Keywords: Yellowstone, geophysics, hydrothermal, electromagnetic, magnetic

Reactive transport modeling in peralkaline salic volcanic complex, caldera-hosted geothermal system; a case of Menengai volcano, Kenya

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Menengai geothermal area is one of high temperature caldera-hosted geothermal systems located in central part of Kenyan rift valley. The caldera together with local rift floor tectono-volcanic axes is considered essential in controlling the local movement of geothermal fluids in the area. Fluid-rock chemical interaction has gained more acceptance in recent years in geothermal application and there has been a growing particular attention in the coupled processes involved in reactive chemical transport in porous media. The current study attempts to develop a 1-D reactive transport model to assess fluid flow conduits and fluid interaction processes of Menengai geothermal field in Kenya. The model incorporates geothermal fluids, modeled from wellhead discharge chemistry to obtain the initial aquifer fluids feeding the reservoir. The resultant fluid was then injected into the model along an ascending porous media as the 'parent' fluid. Water chemical data from adjacent water borehole was included as the initial media fluid while pressure and temperature information are taken from well downhole measurements. The reservoir rocks are predominantly peralkaline, silica-oversaturated trachytes, with few lenses of tuffs, rhyolite, and basalt, thus, the initial mineral assemblage of the model taken to be of trachytic composition. The model was calibrated using observed field hydrothermal minerals. The simulation was performed using the parallelized version of TOUGHREACT v3 code that employs a sequential iteration approach that solves the solute transport and reaction equations separately. Flow and transport are based on space discretization by means of integral finite differences. An implicit time-weighting scheme is used for individual components of the model, consisting of flow, transport, and kinetic geochemical reaction. This study demonstrates the relationship between fluid flow, chemical reactions, and mass transport in a peralkaline salic volcanic complex, caldera-hosted geothermal system with a view of explaining the occurrence of hydrothermal minerals in up-flow zones in such systems.

Keywords: Menengai volcano, reactive transport, geochemical modeling, fluid-rock interaction, geothermal fluid

Review of volcanic-gas composition data in the JMA field survey reports, the 1960s –2001

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This presentation describes the intermediate results of volcanic gases in old documents reported by the Japan Meteorological Agency (JMA) in the 20th century.

JMA started the scheduled volcanic-gas field observation at active volcanoes in the 1960s. It had been run three times per year until 2001. This observation was to detect three kinds of volcanic gases, carbon dioxide (CO₂), sulfur dioxide (SO₂) and hydrogen sulfide (H₂S). Their concentrations were measured using with indicator tubes on site by the local meteorological observatory or the weather station. This measured result was send up to the district meteorological observatory and the headquarters of JMA as the internal report. However they were not compiled systematically, remained analogue documents. We are compiling gas data scanned these documents.

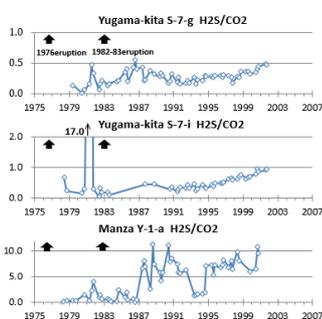
Composition ratios of volcanic gases have availability of estimating volcanic activity (e.g., Hirabayashi, 1993). However, observers have not given so attention to the composition ratios in the observation. In this survey, we reviewed time series of the composition ratio of several volcanoes.

In Mt. Kusatsushirane, it is known that the H₂S/(SO₂+H₂S) ratio increased and decreased rapidly just before the 1976 phreatic eruption (Ossaka, 1980). In addition to this, we dug up that the H₂S/CO₂ ratios at four fumaroles increased and decreased rapidly just before the 1982 - 1983 phreatic eruption in our survey.

Though the sampling and analysis on site at the day would not have satisfactory accuracy, precursory phenomena based on volcanic gas observation such as this encourage promoting the volcanic gas research for monitoring. We continue this survey to dig up other precursor changes of the gas component ratio.

In the presentation, we describe results of other volcanoes as well as Mt. Kusatsushirane.

Keywords: volcanic gas, composition ratio, Mt. Kusatsushirane, Japan Meteorological Agency



Measurements of gaseous elemental mercury discharge rates from soil around active craters

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Gaseous mercury emissions from ground surface at active volcanoes suggest thermal activities such as hydrothermal system. Mercury contained in geothermal hot water or hydrothermally altered rocks is released with an increase in temperature. Gaseous mercury separated from hydrothermal reservoirs is transported to the surface along relatively high permeable zone. Thus, a distribution of gaseous mercury emission rates from ground surface is one of a clue used to detect localities of geothermal reservoirs, fluid paths and permeable zones such as faults. Furthermore, changes in flux of gaseous mercury may reflect temperature changes in a hydrothermal reservoir although mercury flux from ground surface is affected by environmental factors including air temperature, soil moisture content and organic carbon.

Recently, portable apparatuses allowing to measure concentrations of gaseous elementary mercury (GEM) have been developed. We apply the NIC (R) EMP-2 portable GEM analyzer which is low power consumption and light weight. The GEM analyzer is easy to operate because special carrier gas is not required. Combining an Au amalgam method, the GEM analyzer automatically detect trace gaseous mercury of around 2.0 ng/m^3 . However, over 600 seconds are required to measure GEM concentrations of each site on the basis of a standard empirical procedure. To estimate GEM flux of each site, we have developed a simple numerical model of the empirical procedure. Our model suggests that a GEM concentration which is proportional to GEM flux at the site can be measured within 600 seconds. Measurement time changes depending on a ratio of a GEM concentration of ambient air to a GEM flux of a site.

We have measured GEM concentration at Owakudani geothermal area of Hakone volcano in order to reveal a distribution of GEM flux in September 2016. Owakudani is the most active thermal area at central cones of Hakone caldera in terms of emissions of a large amount of volatiles and hot springs. A phreatic eruption which produced a hundred tonne of highly altered materials occurred at Owakudani in 2015. To utilize hot springs of Hakone volcano safely, a hydrothermal system beneath central cones has been investigated in detail, and conceptual models have been proposed.

GEM concentrations obtained in this study show a correlation with ambient temperatures as known in previous reports. Applying an empirical method of a correction for temperatures, we obtain a GEM flux distribution based on GEM concentration around Owakudani. GEM fluxes decrease with a distance from the center of Owakudani. At a region more than 1.5-2 km from Owakudani, GEM concentrations show roughly constant values of around 4 ng/m^3 which indicates the value of background at Hakone Caldera.

These results suggest that GEM fluxes around Owakudani are enhanced by hydrothermal water. In the northeastward direction from Owakudani, values of GEM fluxes are slightly larger than these values measured at the same distance from Owakudani. Such a GEM anomaly may be caused by an underlying hydrothermal water, or depositions of mercury in volcanic gas which was drifted from fumaroles in Owakudani.

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Keywords: Gaseous elemental mercury, Hydrothermal system, Hakone volcano

Simplified determination method of fluoride ion in volcanic thermal water with an ion selective electrode

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Introduction

Water chemistry of active crater lakes and volcanic thermal water, especially concentrations of halide ions and sulfur species which are originated from magmatic volatiles, is a good indicator to predict volcanic activity. Among dissolved components, the fluoride ion is unique and notable. Hydrogen fluoride in magmatic volatiles has high reactivity with rocks through their underground pathways.¹⁾ Thus, fluoride ion is not detected in high concentration in volcanic thermal water at the ground surface when volcanic activity is not high, whereas it can be detected in significant concentration in active periods. For the accurate determination of fluoride ion content in volcanic thermal water, however, distillation treatment, a time-consuming process, is in general indispensable to separate fluoride ion from coexisting components which form complexes with it. In this study, we examined simplified determination methods of fluoride ions without distillation, i. e., those utilizing an ion selective electrode (ISE).

Experimental

Water of Yugama, an active crater lake of Kusatsu-Shirane volcano, Gunma, Japan, was served as a test sample. To determine the fluoride ion with an ISE in Yugama water without distillation, we examined several agents for masking metal ions which were to be added to a total ionic strength adjustment buffer (TISAB) for the ISE measurement. We tried both the calibration curve method and the Gran' s plot method. The latter is recommended in the literature for determination of fluoride ion by using an ISE in waste water containing aluminum ion.²⁾

Results and Discussion

The determined values varied depending on the kind of masking reagent added to the TISAB. Among the values, those obtained by using the TISAB containing CDTA (cyclohexanediaminetetraacetic acid)-sodium citrate³⁾ or tris(hydroxymethyl)aminomethane-sodium tartrate,⁴⁾ seemed to be reasonable because they were close to the one determined by ion chromatography after pretreatment in which distillation was incorporated according to the Standard Method of Analysis for Mineral Springs (the Ministry of the Environment, Japan). Concerning the comparison of the calibration curve and Gran' s plot methods, the former was found to be superior to the latter in reproducibility of data. In summary, we can determine fluoride ion in volcanic thermal water by using an ISE with an appropriate TISAB without sample pretreatment like distillation, and there is no need to choose the Gran' s plot method.

Reference

- 1) Kenji Nogami, Masato Iguchi, Kazuhiro Ishihara, Junichi Hirabayashi, Miki Daisuke: Study on behavior of a volatile ingredient of a volcanic eruption and volcanic ejecta, *Annals of Disas. Prev. Res. Inst., Kyoto Univ.*, No. 47 B, 2004
- 2) Takeshi Yamada, Etsu Yamada, Masanori Sato: Simplified determination of fluoride ion in wastewater by an ion selective electrode, *BUNSEKI KAGAKU*, 37, p. T61-T65, 1988
- 3) Peters MA, Ladd DM: Determination of fluoride in oxides with fluoride-ion activity electrode, *Talanta* 18, p. 655-664, 1971
- 4) Rakesh Ranjan, Amita Ranjan: Fluoride Toxicity in Animals, *SpringerBriefs in Animal Sciences*, Springer,

p. 101- 105, 2015

Keywords: ion selective electrode, fluoride ion, geothermal fluid, volcanic activity monitoring, crater lake

Geochemical characteristics of volcanic gases at Issaikyo, Azuma volcano, Japan

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Azuma volcano is one of the active volcanoes that consist of Higashi-Azuma, Naka-Azuma and Nishi-Azuma volcanic edifices, and there is fumarolic activity at Mt. Issaikyo of the Higashi-Azuma volcano (Hasegawa et al., 2011). In this presentation, analytical results of chemical and stable isotopic (δD and $\delta^{18}O$) compositions of volcanic gases discharged at Issaikyo will be presented.

Gas samples were collected from fumaroles within Ooana crater (W3b, W5 and W6b in order from east to west) on the south flank of Issaikyo, and a fumarole at about 300m south of Ooana crater (W10) on July and October in 2016 by using the techniques reported by Giggenbach and Goguel (1989) and Ozawa (1968). Analyses of gas samples were conducted by mainly using the methods described by Ozawa (1968), and δD and $\delta^{18}O$ values of the condensed water were measured by using cavity ring-down spectroscopy.

The outlet temperature of the gases at W3b, W5, W6b and W10 on October were 94.7°C, 101.8°C, 136.8°C and 95.4°C, respectively. Relative contents of N_2 , Ar, and He of gas samples were distributed in the mixing field of air, air saturated water (ASW) and andesitic gases (Fig.1). The δD and $\delta^{18}O$ values of condensed water of gas samples were relatively high in high-temperature samples and low in low-temperature samples. W3b and W10 gases sampled on October were plotted in the low $\delta^{18}O$ side of global meteoric water line (GMWL: $\delta D = 8 \cdot \delta^{18}O + 10$; Craig, 1961) in the δD vs. $\delta^{18}O$ diagram (Fig.2) and δD - $\delta^{18}O$ regression slope of all the samples was about 3.6, suggesting that the volcanic gases sampled in this study are affected by mixing of groundwater and vapor-liquid separation. Several further geochemical characteristics based on the analytical result will be described in this presentation.

Keywords: Azuma volcano, volcanic gas, chemical composition, δD · $\delta^{18}O$

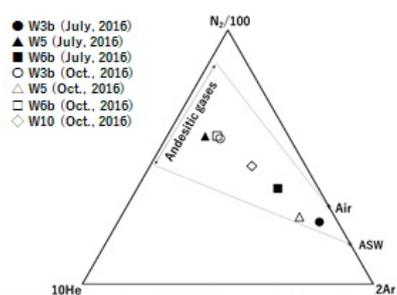


Fig. 1. Relative N_2 -He-Ar contents of samples.

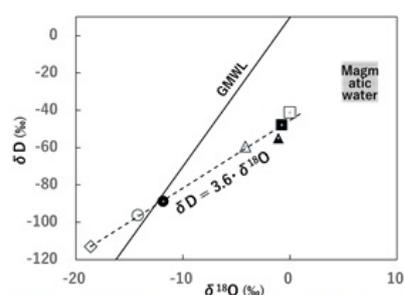


Fig. 2. δD vs. $\delta^{18}O$ diagram of condensed water of samples.

Simple estimation method for concentration of polythionate ions in Yugama, a crater lake of Kusatsu-Shirane volcano

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Introduction

The Kusatsu-Shirane volcano is an active volcano in Japan. It has three crater lakes at its summit. Yugama, the largest one of the three is an active crater lake. The water of Yugama contains aqueous sulfur oxyanions like polythionate ions. The concentration of polythionate ions in Yugama is a good indicator of the volcanic activity of the volcano since it fluctuates with the flux of SO₂ and H₂S supplied into the lake water from the subaqueous fumaroles.¹⁾ The precise determination method of polythionate ions is, however, bothersome because of their instability in aqueous circumstances, and requires the high technique of skilled analysts and some dedicated equipment. In this context, we have proposed a simple estimation method for contents of polythionate ions, which can be manipulated even by not-so-skilled analysts. The method was based on the concentration difference between SO₄²⁻ measured by ion chromatography and total SO₄²⁻ (*T*-SO₄²⁻) measured by the gravimetric analysis preceded by oxidation of sulfur species.²⁾ In this study, we examined a simpler and easier determination method of *T*-SO₄²⁻ using inductively coupled plasma atomic emission spectrometry (ICP-AES) instead of the conventional gravimetric method.

Experimental

Yugama water samples collected at a fixed sampling point (U-1) located at the southwestern shore of Yugama in 2016 were subjected to this study. We measured *T*-SO₄²⁻ concentration of a Yugama water sample repeatedly by the gravimetric method and the ICP-AES and examined the validity of the analytical data. The detailed analytical procedures are as follows:

- Gravimetric method. The sample was first boiled to remove dissolved H₂S, and bromine water was then added for oxidation of all dissolved sulfur oxyanions to SO₄²⁻. Next, an adequate amount of barium chloride solution was added to the resultant solution to precipitate SO₄²⁻ as barium sulfate. We determined the *T*-SO₄²⁻ concentration from the weight of the precipitated barium sulfate based on the conventional procedure of the gravimetric analysis.
- ICP-AES. The sample was adequately diluted after boiled, and its sulfur concentration was measured by the ICP-AES (SEIKO SPS3520UV-DD). The spectrometer used was equipped with a vacuum chamber for the detection and measurement of sulfur emission lines in the vacuum-ultraviolet region. The concentration of *T*-SO₄²⁻ was obtained from the measured sulfur concentration.

Results and discussion

The concentration of *T*-SO₄²⁻ in the Yugama water sample obtained by the gravimetric analysis and the ICP-AES are 5,349±34 mg/L (±: the 95 % confidence limit with *n*=3) and 5,260±82 mg/L (95 % confidence limit with *n*=5), respectively. The two analytical results were equal to each other within the experimental uncertainty, with the value by the ICP-AES showing a slightly larger error. Other than these measurements, the independent ICP-AES determination procedure for *T*-SO₄²⁻ was repeated three times and yielded 5,301±82 mg/L (95 % confidence limits, *n*=3). This value is also equal to the above mentioned values within the experimental uncertainty. In addition, the average *T*-SO₄²⁻ concentration in eight Yugama water samples collected between April and July in 2016 were determined by the two analytical methods. The determined values by the two methods agreed well with each other. All those

results revealed that the $T\text{-SO}_4^{2-}$ concentration was able to be determined more easily by the ICP-AES than by the gravimetric analysis, enabling the estimation of the concentration of polythionate ions in a rather short time.

- 1) B.TAKANO, K.WATANUKI: Monitoring of volcanic eruptions at Yugama crater lake by aqueous sulfur oxyanions, *Journal of Volcanology and Geothermal Research*,**40**,71-87(1990).
- 2)Y.KIKAWADA,H.HUKUHARA,S.NOMURA,Y.SHIROKAWA,A.INOUE,T.OI,J.OSAKA: Determination of Concentration of Total Sulfur Species and Estimation of Concentration of Poly-thionate Ions in Yugama, a Crater Lake of Kusatu-Shirane Volcano , *Bulletin of the Volcanological Society of Japan*,**51**,135-140(2006).

Keywords: Polythionate ions, Sulfur species, Crater lake, Aqueous fumaroles, Yugama

Changes in the contents of sulfur species in Yugama, an active crater lake of Kusatsu-Shirane volcano, connected with its recent volcanic activity

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The Kusatsu-Shirane volcano is one of the most famous active volcanoes in Japan. Yugama, an active crater lake located on the pyroclastic cone of the volcano, is filled with high acidity water due to the injection of hydrothermal fluids from subaqueous fumaroles. Yugama has been the center of recent volcanic activity. We have been monitoring the water chemistry of Yugama over the past five decades.

The volcano has been in an active period since the late 2000s, and the activity has increased further since March 2014. In 2014, an earthquake swarm was observed around Yugama crater with inflation at shallow depth beneath Yugama. The concentrations of chloride ion and dissolved sulfur species in the Yugama water started increasing sharply in September 2014, immediately after the end of the earthquake swarm. We estimated the total amount of polythionate ions in the Yugama water as the difference between the sulfate ion content determined by ion chromatography and total sulfur content determined by ICP-OES. Our analytical results reveal that polythionate ions, which had not been observed for few years, have appeared with remarkable amounts in the Yugama water in September 2014, and their total amount has drastically increased to 3000 mg/L on a sulfate basis within seven months. Resultantly, more than a half amount of dissolved sulfur in Yugama has existed as polythionate species since mid-2015. This high proportion of polythionate species to the total sulfur species in Yugama is comparable to that observed in the 1970s before the 1982-1983 phreatic eruptions at Yugama. The changes in ORP in the Yugama water in and after 2014 suggest that increasing of SO₂/H₂S ratio in the volcanic gasses from the subaqueous fumaroles induce a production of polythionate species. The chemistry of polythionates in the Yugama water may be more complex than we thought.

Keywords: Kusatsu-Shirane volcano, Yugama, crater lake, subaqueous fumarole, polythionate, sulfur oxyanion

The chemical composition and isotopic ratios of the volcanic gases from the Jigokudani Valley, Tateyama Volcano

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Tateyama Volcano located in the northern part of the Hida Mountains has an active geothermal field called the Jigokudani Valley (JV). The recent state of the hydrothermal system in the JV was clarified by the resistivity structure and the geochemical analyses of hot-spring waters (Seki et al., 2016), but comprehensive studies on volcanic gases have not been conducted for a long time. The last study was reported by Mizutani et al. (2000), in which the geochemical analyses were performed for the fumarolic gases sampled in 1991. The chemical and isotopic compositions of fumarolic gases are sensitive to changes in the volcanic activity because of the high mobility within a pathway from deep-seated magma to the ground surface. Therefore, it is necessary to examine the geochemistry of volcanic gases for a better understanding of the whole magma-hydrothermal system in addition to the hot-spring water analysis. Fumarolic gases in the JV were sampled at 7 sites in 2016, and the chemical compositions and the isotopic ratios of water and helium were analyzed in order to clarify the magmatic hydrothermal system of JV. The measured fumarolic temperatures showed from 91.6 to 113.6 °C, most of which are higher than the boiling point of water in this area. The isotopic ratios of waters from the fumarolic gases showed the values lighter than hot-spring waters. We found that the fumarolic gases containing HCl were discharged only in the highly active geothermal area of the JV, where the compositions of the hot-spring waters showed high Cl⁻ concentration (~20,000 ppm). In addition, the fumarolic gases showing high H₂S/SO₂ ratios were sampled in the areas where the hot-spring waters were mainly composed of SO₄²⁻ containing almost no Cl⁻, which indicates that SO₄²⁻ in the SO₄-type hot spring is derived from the oxidation of H₂S. ³He/⁴He ratios of the volcanic gases from JV were from 6.8 to 7.7 R_A, which indicates that He was derived from magmatic origin. The ³He/⁴He variation is predominantly controlled by the different degree of atmospheric contamination to the common magmatic He component, as the air-corrected ³He/⁴He ratios based on ⁴He/²⁰Ne ratios are almost constant (7.5 ± 0.2 R_A). In the presentation, we will report the further results of analysis of volcanic gases and the model of the hydrothermal system beneath the JV will be updated.

Keywords: Tateyama Volcano, Hydrothermal system, Fumarolic gases, Stable isotope ratio

Flux measurements of carbon dioxide at Beppu geothermal area using a portable non-dispersive infrared (NDIR) gas analyzer

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Degassing mechanisms play an important role for the Earth environment, since the current atmosphere and ocean have formed by release of volatile components from the solid Earth. The mechanisms may be catastrophic or continuous events; the former is a sudden release in a single event and the other is a process occurring throughout geological history of the Earth. A representative continuous degassing is volcanic activities. In the volcanic area, volatile components are released not only from the fumaroles but from the mountain body. Carbon dioxide (CO₂) is one of the volatile components, and its release is affected by the volcanic activity (Hernandez et al., 2001). Degassing mechanisms of soil gases are dependent on underground structures such as geological strata, faults and fissures. Active faults can be good passageways (Dogan et al., 2009). Here, we have measured CO₂ flux in the Beppu geothermal area, and reveal the degassing mechanisms of CO₂ related to volcanic activities.

Beppu geothermal area located on central Kyushu direction, Japan is situated in graben zone formed by tensional stress, and is generated by western active volcanoes of Mt. Tsurumi and Garan. These volcanoes supply geothermal fluids on the area. Allis and Yusa (1989) measured the temperature under 100 m depth in the area, and revealed two parts with high temperature. The high temperature areas are located along the faults of northern and southern parts. Mine (2006) measured CO₂ flux in the northern part and showed high values along the Kannawa fault. Here, we tried to measure CO₂ flux in the southern part around the Horita and Asamigawa faults.

We used a chamber method which is measurement of concentration rate of CO₂ in the vessel covered on the ground, and estimated CO₂ flux at about 200 sites. The obtained CO₂ fluxes range in 0.07-66.1 g/m²-day. High values of 2.71-66.1g/m²-day are observed on hot spring flows underground reported by Yusa and Ohsawa (2000), suggesting that CO₂ gases are released from hot spring flows underground and raise to ground surface.

References

Allis R.G. and Yusa Y. (1989) Fluid flow processes in the Beppu geothermal system, Japan. *Geothermics*, 18, 743-759.

Dogan T. et al., (2009) Adjacent releases of mantle helium and soil CO₂ from active faults: Observations from the Marmara region of the North Anatolian Fault zone, Turkey. *G3*, 10, Q11009.

Hernandez P. A. et al., (2001) Carbon Dioxide Degassing by Advective Flow from Usu Volcano, Japan.

Science, 292, 83-86.

Mine T. (2006) A study on the appreciation of geothermal activities, using soil-CO₂ flux profiles: A case study on Beppu Geothermal Area, Central Kyushu, Japan. 2006 Division of Earth and Planetary Sciences, Kyoto University Graduate School of Science, Geophysics Master thesis collection II, 1-88.

Yusa Y. and Ohsawa S. (2000) Age of Beppu Onsen. Oita Prefecture Hot Spring Investigation Study Report, 51, 1-8.

Keywords: Beppu, hot spring, carbon dioxide

Assessment of Geothermal Energy Potential from Low Enthalpy Fluid at Rural Areas in El Salvador by Using Open-Source Programming Language

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The geothermal resource assessment is the estimation of the amount of thermal energy that can be transformed from a geothermal reservoir and used economically by people as different kinds of applications. When a geothermal exploration starts, sometimes the provided data are either limited or missing. Therefore, in this study case, a simple technique called the volumetric method is used. The main purpose of this study is the use of the volumetric method to estimate ability to produce electrical energy from low enthalpy fluid in the northern part of El Salvador where there are hydrothermal manifestations or hot springs and the people who live there can use as an electrical source. The calculation of the geothermal energy stored in a volume is based on the range of reservoir parameters and carried out by using the stochastic Monte Carlo simulation. There are some kinds of licensed software for carrying out this task. However, for this case, the algorithm has been programmed by using Open-Source Programming Language, i.e. Python v2.7 and PyQt4. As an example, a theoretical conceptual model of a hot spring area located in the Municipality of Nombre de Jesús was chosen. After running the algorithm, it shows that the field could initially support a 16.1MWe power plant for 25 years and a possible expansion to 19.8MWe. However, it will be subject to further investigations for obtaining and validating the new data.

Keywords: El Salvador, low-enthalpy fluid, volumetric method, Open-Source Programming Language, Monte Carlo simulation

Geochemical study of the Uchinomaki hot spring within Aso caldera: time series change before and after the Kumamoto Earthquake

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The Uchinomaki hot spring is located in the north end of Asodani that is the northern part of Aso caldera floor. Some of the hot springs became disabled to pump up hot water after the 2016 Kumamoto earthquake, whereas spontaneous hot spring emanation from some other hot spring wells was recognized. Water emanation from open fissures developed in a rice paddy was also observed at three locations around the Uchinomaki hot spring area. As occasion of these drastic changes in water discharge, horizontal sliding of a kilometer-scale geologic block caused by vibrations from the earthquake was proposed based on a geophysical study (Tsuji et al., 2017). If it is the case, a reservoir of the Uchinomaki hot spring has not be affected by the earthquake and accompanying ground deformation. Actually, new wells drilled just beside abandoned ones have been successfully restore pumping hot spring waters. In order to provide supporting evidence for the geophysical study, we conducted chemical analysis of hot spring waters.

More than 30 water samples were collected from the Uchinomaki hot spring and adjacent areas. After measurement of temperature, pH, electric conductivity and oxidation-reduction potential, the water sample was filtered with a 0.45 um disk filter and stored. Chemical analysis was conducted by ICP-OES for cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+}), ion chromatography for anions (Cl^- , SO_4^{2-}), and alkalinity titration for carbonate (HCO_3^-). Isotopic composition of hydrogen and oxygen was determined by Wavelength-Scanned Cavity Ring-down Spectroscopy.

Time series change before and after the earthquake in hot spring water chemistry from the Uchinomaki area was not recognized. Their chemical composition was characterized by SO_4 -rich signature, which is commonly observed in groundwater within Aso caldera. Groundwater collected from the area on the southside of the Uchinomaki area is known as “Akamizu” from its high Fe concentration associated with high SO_4 concentration. In this study, the Uchinomaki hot spring waters showed Na+K-rich signature, whereas Akamizu groundwaters showed Ca-rich signature. The difference in cation composition would be attributed to that Uchinomaki hot spring and Akamizu groundwater have distinctive reservoirs.

The most vigorous emanation from a rice paddy was observed at the southwest side of the Uchinomaki hot spring area, which is in accordance with that the geophysical study demonstrates westward movement of the horizontal sliding. The emanated warm fluid showed Fe-rich and Ca-rich signature that is similar to chemical composition of the Akamizu groundwater. The horizontal landslide is likely not to have affected the fluid reservoirs but caused significant change of surface groundwater pathways in wide area around the Uchinomaki hot spring.

Keywords: Aso caldera floor, Hot spring reservoir, Horizontal slide

Repeated survey of ground temperature and hot springs around Iwo-yama, Kirishima Volcanic Group (2)

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Iwo-yama Volcano is located in the northwest of Karaguni-dake Volcano, central part of Kirishima Volcanic Group. This area had intense fumarolic activity before 1990s. After 1990s, fumarolic activity disappeared but hot spring activity has continued. However, volcanic tremors occurred frequently after 2014. And fumarolic activity appeared again at the summit of Iwo-yama in December 2015. The authors have carried out ground temperature observation and repeated measurements of electrical conductivity of hot spring waters; Western and Northeastern Flank of Iwo-yama and Ashiyu hot spring. Chemical composition was also analyzed. Ground temperature at 1m depth indicates the increase after October 2015, just before the reappearance of fumaroles, and after October 2016 (corresponds the increase of H₂S emission). Repeated measurements of electrical conductivity of spring water indicate EC of the W&NE springs are affected by rain water, but EC of Ashiyu water shows a significant change; 225 mS/m in 2008, 235-245 mS/m after the eruption of Shinmoe-dake in 2011, 256 mS/m in December 2015. According to the chemical analysis, SO₄ ion increased from 1060 mg/l to 1450 mg/l in Ashiyu, while the ratio of Cl/SO₄ changed from 0.12 to 0.07. On the other hand, Cl/SO₄ increased from 0.002 to 0.06 in the W Flank of Iwo-yama. This means SO₄ ion increased in Ashiyu after the beginning of volcanic tremor in August 2014, but in W Flank of Iwo-yama, both SO₄ ion and Cl ion increased. These evidences mean an increase of supply of volcanic gas beneath Iwo-Yama.

Keywords: Kirishima Volcanic Group, Geothermal activity, Volcanic activity

Geomagnetic evidence for the episodic fluid intrusion associated with the 2014 unrest of Kusatsu-Shirane volcano

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In Kusatsu-Shirane volcano, the elevated seismic activity, which accompanied a remarkable deformation and a change in the chemical compositions of volcanic gas, was observed from March 2014. In May 2014, a rapid change in the total geomagnetic intensity was observed, which was thought to be caused by demagnetization of the subsurface rocks around the Yugama crater. The amount of change was about one nano Tesla at the maximum, but the rate of change was rapid: the total intensity decreased only for about three weeks and did not show a significant change in the following two years. In this study, we attempted to infer temperature change accounting for this rapid geomagnetic variation within the volcanic edifice by a numerical simulation of hydrothermal fluid.

We used HYDROTHERM3.1.1 developed by the USGS for the simulation. The calculation was made within a cylindrical domain of 5km in height and 5km in radius. A high-temperature fluid was emplaced along the center axis as a source of temperature and flow fluctuations. A uniform permeability structure was assumed except for the low-permeable clay layer proposed by resistivity structure at the depth of 100 to 400m. Parameters such as permeability were adjusted so as to explain the average heat discharge at the surface, and the magnitude and time-scale of geomagnetic variation. We assumed that the hydrothermal fluid and the surrounding rocks were in an equilibrium state. The temperature dependence curve of the magnetization of rocks, which was used to transform temperature distribution into the magnetization distribution, was made from the experimental data for the volcanic rocks sampled in the summit area presented by Yamazaki et al. (1992).

Changes in the geomagnetic total intensity were calculated by the input of the high-temperature fluids at the depths. The geomagnetic variation occurred from the onset of fluid input and terminated when the fluid input was interrupted. Then, little change was calculated also after 100 days. The temperature distribution showed almost no change after 100 days, and the high temperature state was maintained beneath the clay layer. After numerous simulations were performed with changing several parameters, we found that the geomagnetic variation observed in May 2014 and the subsequent stagnant state of the total intensity could be explained by the temporary input of high-temperature fluid of higher than 400 degrees with a flux of 20 ton/sec for about three weeks. This possibly detected the discharge process of magmatic fluids caused by a breach of the sealing zone proposed by Ohba et al. (2008).

Keywords: hydrothermal system, Kusatsu-Shirane volcano, hydrothermal simulation, geomagnetic field variation

Gravity variation measurements and numerical modeling for the hydrothermal system of the Kuju volcano

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Laboratory of Geothermics, Kyushu University has conducted some observations including microearthquake observations, fumarolic heat discharge rate measurements and gravity variation measurements for the Kuju volcano where the phreatic eruption had occurred in 1995, and has constructed some numerical models of the hydrothermal system to explain mainly the geothermal condition variation including the temporal change of the fumarolic heat discharge rate after the 1995 eruption. This study tried to construct a new numerical model of the hydrothermal system to explain not only the geothermal condition variation but also the results of the gravity variation measurements.

We used a hydrothermal system simulator HYDROTHERM Ver. 2.2 (Hayba and Ingebritsen, 1994) for the numerical modeling. And gravity changes of the numerical model were calculated by the Okabe's formula (Okabe, 1979) using the density change of each block of the model caused by the geothermal water flow. The previous model of our laboratory indicates a similar trend of the gravity change with the observed result at each gravity measurement point but greater changes than the measured values. Then, we tried to improve the previous model.

In several improvements, size reduction of each block that constructs the previous model decreased the calculated gravity changes and brought the gravity changes close to the measured values although we had to stop the block size reduction in the middle of the study because of the specification limit of the computer we used. Therefore, we expect to be able to obtain a numerical model that explains not only the geothermal condition variation but also the gravity variation when we progress this improvement by using the computer system that can execute larger scale calculation.

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Hayba, D. O. and Ingebritsen, S. E. (1994) The Computer Model HYDROTHERM, a Three-Dimensional Finite-Difference Model to Simulate Ground-Water Flow and Heat Transport in the Temperature Range of 0 to 1,200°C. Water Resources Investigation Report, 94-4045, 85p

Okabe, M. (1979) Analytical expressions for gravity anomalies due to homogeneous polyhedral bodies and translations into magnetic anomalies. *Geophysics*, 44, p.730-741.

Keywords: Kuju volcano, gravity measurement, hydrothermal system, numerical modeling