Fluid formation mechanism of deep chloride hot spring waters from the central Kanto Plain, Central Japan

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Chemical and stable isotopic ($\delta^{18}O$, δD) compositions of the fourteen non-volcanic chloride hot spring waters in the Central Kanto Plain, Central Japan, were analyzed to clarify the diagenetic evolutions of pore water in the Kazusa and Annaka-Awa Groups. The chloride spring waters originate through mixing of fossil sea waters with local meteoric water. The fossil sea waters with lower contents of Mg^{2+} and SO_4^{2-} and higher contents of Ca^{2+} and Na^+ than those of the present sea water, are consists of two kinds of different $\delta^{18}O$ value. B and K^+ contents in the water from the Annaka-Awa Groups are higher and lower than those of the Kazusa Group, respectively.
These chemical and $\delta^{18}O$ compositions can be reasonably explained by the following diagenetic processes; Sulphate reduction process, calcite cementation, reaction of volcanic material to form smectite, ion exchange of smectite, and smectite-illite transformation. The oxygen isotope negative shift of the fossil sea water reserved in Kazusa Group reflects pervasive reaction of volcanic material to form smectite. Meanwhile, the oxygen isotope has positive shift of the fossil sea water reserved in the Annaka and Awa Groups, resulting from smectite-illite transformation.

Keywords: Central Kanto Plain, chloride hot spring water, diagenetic evolution

Helium isotopes in groundwaters in the southeast part of the Gunma Prefecture, Japan.

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Three distinct regions in the Kanto plain, central Japan, are recognized as the region existing lumps of groundwaters with high Cl- concentrations: (1) central parts of the Kanto plain (eastern part of Saitama Prefecture), (2) south-east parts of the Gunma Prefecture along the middle reaches of the Tone river north of the Area (1), (3) floodplains and diluvial uplands along the lower reaches of the Tone river (Ibaraki and Chiba Prefectures).
The high-chloride groundwaters from the central parts of the Kanto plain are characterized by the following features; (a) helium isotopic ratios (^{3}He/^{4}He) are relatively homogeneous with an end member of 0.8-1.1 x 10^{-6}, (b) ^{4}He concentrations show positive correlation with chloride concentration (Morikawa et al., 2006). Morikawa et al (2014) investigated the noble gases in the deeper groundwaters (hot springs) in the central parts of the Kanto plain and the high-chloride groundwaters from southeast part of the Gunma Prefecture to elucidate the origin of water and chloride component. Low ^{3}He/^{4}He ratios in the hot springs indicate that there is almost no interconnectivity between the high chloride groundwater and hot spring water around these regions. In contrast, the groundwaters from observation wells for land subsidence in the southeast parts of the Gunma Prefecture are somewhat similar to those in the groundwaters in the central part of the Kanto Plain. However, the correlation between chloride and helium concentrations was relatively weak with relatively large ^{3}He/^{4}He variation.
In this study, we further conducted complementary investigation for the groundwaters in the southeast part of Gunma Prefecture. The results revealed that groundwater with high chloride-^{4}He concentrations were also observed along the left bank of the Tone river. This region, however, is limited in an area of about 15 km from west-northwest to east-southwest and 5 km from north to south. The groundwaters from the outside of this region contained relatively low ^{4}He concentration with weak chloride-^{4}He correlation. This observation implies that high He concentration with moderately high ^{3}He/^{4}He components in groundwaters are originated in the south-east portion, near the Tone river, of Gunma prefecture and may relevant to a geological structure in deeper region of this region.
References: Morikawa et al. (2006) JPGU 2006, H121-004, Morikawa et al. (2014) JPGU 2014, AHW25-12

Keywords: Helium, Groundwater, Tone River, Kanto Plain, Chloride Ion, Noble Gas

Isotopic and chemical characteristics of well waters around Mt. Fuji

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In this study, 14 water samples were collected from wells of various depths from 4 to 1,500m and from natural springs around Mt. Fuji, and were subjected to chemical and isotopic analysis of hydrogen and oxygen (δD and $\delta^{18}O$).
The δD and $\delta^{18}O$ values of the water samples ranged from -86.4 to -49.6‰ and from −11.6 to -7.6‰, respectively, and negative correlation was recognized between isotope ratio and altitude of sampling point. Relationship between δD and $\delta^{18}O$ for sample waters was $\delta D = 8\cdot\delta^{18}O + 12$, and is very close to the local and global meteoric water lines ($\delta D = 8\cdot\delta^{18}O + 15.1$ from Yasuhara et al., 2007 and $\delta D = 8\cdot\delta^{18}O + 10$ from Craig, 1961, respectively). Altitude effect of δD and $\delta^{18}O$ in sample waters (altitude of sampling point was used in calculation) were calculated at -3.5‰ and -0.43‰ per 100m altitude, respectively. These isotopic gradients are mostly the same as published values for rain and snow (-3.0‰/100m for δD and -0.4‰/100m for $\delta^{18}O$; Waseda and Nakai, 1983). Based on the trilinear diagram, water samples were basically classified as Ca−HCO_3 type at shallow depths (0~15m depth), mixed cation−HCO_3 type at intermediate depths (less than about 200m), Ca·Na−SO_4·Cl and Na·Ca−SO_4·HCO_3 types or similar to them at more deep depth. Water qualities of deep wells appeared to be derived from submarine sediments and volcanic rocks which compose the basement of Mt. Fuji region because the water qualities of deep wells are similar to that of thermal water in the green tuff region of Japan (Sakai and Matsubaya, 1974).

Keywords: Mt. Fuji, well water, hot spring water, stable isotope ratio (δD·δ18O), water quality

Stable water isotope characteristics of the newly discovered lake bottom springs from Lake Kawaguchi, in the northern foot of Mount Fuji

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The existence of lake bottom springs have been suggested in Lake Kawaguchi, one of the Fuji Five Lakes at the northern foot of Mount Fuji, Japan, based on the patchy distribution of lake ice during winter. However, the knowledge on the distribution and the source of the springs is still limited. In this study, we conducted water quality survey using a CTD profiler from February to July in 2015 to explore the location of lake bottom springs, and measured stable water isotope ratios of lake bottom waters to examine potential source of the spring waters in Lake Kawaguchi. We found upwelling of relatively warm waters with low electrical conductivity (EC) at the east of the Unoshima Island (a small island located at the center of the lake) during winter, whereas the temperatures and the EC at the same location were significantly lower than the surrounding area during summer. These water quality anomalies suggest that the springs were likely distributed at the bottom of the lake within a radius of 25 meter at the east of the Unoshima Island. Stable (oxygen and hydrogen) isotope ratios of the lake bottom waters were ~2 per mil and ~10 per mil lower around the springs, respectively, suggesting the influence of groundwater from the surrounding mountains.

Keywords: Fuji Five Lakes, springs, stable water isotopes

Groundwater age determination by using ^{85}Kr in groundwater at the Kakitagawa spring water in Mt. Fuji spring discharge area

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Groundwater age dating study around Mt. Fuji area have been conducted by several researches (Ochiai, 1970; Yoshioka et al., 1993; Mahara et al., 1993; Asai and Tsujimura, 2010; Tosaki et al., 2011; Ohta et al., 2012). Various methods were adopted in Mt. Fuji spring discharge area such as ^{3}H, noble gases, CFCs, ^{36}Cl/Cl and ^{228}Ra/^{226}Ra activity. All results show relatively young age (0 to several decades) in the Mt. Fuji groundwater, except for CFCs method which affected local anthropogenic source (Asai and Tsujimura, 2010). However, the result in each method contains the “uncertainty” of its age. Unlike these methods, Krypton 85 (^{85}Kr) has high resolution for the age estimation, hence we conducted age determination at the Kakitagawa spring water located in the southeastern part of Mt. Fuji. Krypton 85 (^{85}Kr) is a man-made trace gas from reprocessing plant origin whose atmospheric concentrations have been increasing over the past few decades. As it is soluble in water, it can be used as groundwater age indicators over timescales ranging from a few years to a few decades. ^{85}Kr specific activities in groundwater was 1.022 ±0.028 Bq/m^3, and the estimated age were 5.2 ±0.4 years. This young age is corresponding to the previous studies, additionally the range of the estimated age by ^{85}Kr was much smaller compare to other methods. Furthermore, ^{85}Kr method shows the strong advantage against the anthropogenic contamination.

Keywords: Krypton-85, Groundwater age dating, Kakitagawa spring water

Investigation of salinization processes in a confined aquifer system; Application of sulfur and chlorine stable isotopes

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A combination of sulfur and chlorine stable isotopes (d^{34}S and d^{37}Cl) has been used to investigate salinization processes in a confined aquifer system in southwestern Nobi Plain (SWNP), central Japan. Deduced from the SO_4/Cl ratios and d^{34}S values, a tongue of brackish confined groundwater ($Cl^- > 1000$ mg/L), which extends from the shoreline of Ise Bay inland, mostly has two salinity sources; One is modern seawater, another is paleo seawater having no SO_4^{2-} due to sulfate reduction process. The Cl isotopic compositions are negatively correlated with paleo seawater Cl^- concentrations, while they are not correlated with either total Cl^- concentrations or d^{34}S values. Furthermore, Cl^- concentrations from modern seawater are positively correlated with d^{37}Cl values. In addition to these observations, diffusion model calculations suggest that paleo seawater Cl^- has diffused in argillaceous freshwater sediments whereas modern seawater Cl^- has not been affected by preferential diffusion of Cl isotopes because it has migrated by advection via both an unconfined aquifer and non-pumping wells.

Keywords: paleo seawater, diffusion process, confined aquifer

Origin of saline hot spring and flow system of inland hot spring
- Case study on the Yuda hot spring in Yamaguchi City -

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The Yuda hot spring in the Yamaguchi City is characterized by the high content of Na^+ and Cl^-. We carried out that geochemical and isotopic analysis of hot spring water, a geological survey and geophysical exploration to investigate the origin and flow system of the Yuda hot spring.
Deep hot spring water from bedrock characterized by NaCl type. Shallow hot spring water from overlying sediments is characterized by NaCl type and $NaHCO_3$ type. δD and $\delta^{18}O$ of all the hot spring water suggest that the Yuda hot spring water is originated inform a meteoric water. Li/Cl ratio of all deep hot spring waters are about 0.001 that is larger than that of the modern seawaters. $\delta^{13}C$ of DIC shows that the mantle-derived carbon is mixed in the Yuda hot spring waters. These characteristics correspond to the deep-seated fluid. However, the He isotope ratio ($^3He/^4He$) of 0.202 Ra (Yasukawa and Tanaka ,2008) and the Li isotope ratio of +10.84 ‰(Nishio personal communication) suggest that there is no supply of deep-seated fluid at present. As a result of the geochemical studies of the Yuda hot spring water, of the Yuda hot spring waters are thought to be ascended as follows:
1) Deep-seated fluid ascended from deep underground was mixed with meteoric groundwater.
2) The fluid remained at deep underground at once.
3) Isotopic characteristics of these fluids were affected by fluid-rock interaction.
4) Modern geochemical feature of Yuda hot springs were formed.
The resistivity profile obtained by CSAMT method (Controlled Source Audio frequency Magneto-Telluric) could not detect any low resistivity zones. As a result of the core logging, it is assumed that the hot spring water may ascend through the cracky intrusive rock with less than 1 m wide. As a result of the numerical analysis about the relationship between the width of flow path and the estimated resistivity, the flow space with 1 m in width is too small to be detected by CSAMT method.
It is concluded that the meteoric water discharged to deep underground by the local groundwater flow is heated by the geothermal gradient and ascend in a short time through the cracked zones developed in the intrusive rocks. Cl^- is possible to be derived from the deep underground as a deep-seated fluid in the past.

Keywords: Deep-seated fluid, saline hot spring, Yuda hot spring

Analyzing origin of rainwater and shallow groundwater in seasonal wetlands of north-central Namibia

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This study discussed on origin of rain- and subsurface-water (or shallow groundwater) in seasonal wetlands of north-central Namibia, which is locally called as the Cuvelai system seasonal wetlands (CSSWs). In order to do this, stable water isotopes (SWIs) of hydrogen and oxygen in rain-water, surface-water and subsurface-water were analysed. Especially rain-water samples were taken from all rainfall events in a whole wet season from October 2013 to April 2014. Then the isotopic ratio of SWIs in each rain-water sample was analyzed and used to derive annual mean value of the isotopic ratio of SWIs in precipitation weighted by each rainfall amount. This annual mean value was revealed to be a good indicator in order to detect how subsurface-water in CSSWs formed in the region through the use of delta diagram. Consequently the SWIs analysis in rain-, surface-, and subsurface-water revealed that shallow groundwater of small wetlands in the region was very likely to be recharged from surface-water, source of which was local rain-water and was temporary pooled in the lowest part of each small wetland. This was supported from the tritium counting of the current rain- and subsurface-water in the region. In order to confirm the origin of rain-water, atmospheric water budget analysis was also conducted using an atmospheric reanalysis data. From this analysis, it was found that around three-fourths of rain-water was derived from recycled water in local-regional scales.

Keywords: atmospheric water budget, stable water isotopes (SWIs), water-food security

Spatial and temporal variations of stable isotopes in precipitation across Cameroon: The first Cameroon Meteoric Water Line

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Stable hydrogen and oxygen isotopes in precipitation are valuable tools in groundwater recharge studies and the study of atmospheric moisture sources/circulation. Despite their significance, the isotopic data on rainfall is limited in most regions of Cameroon. Accordingly, the stable isotopes in over 290 monthly rain samples from 2012 to 2015 in 15 locations/stations across Cameroon are being investigated. The rain sampling stations have been grouped into four regions as a function of distance from the Atlantic Ocean and elevation. These are the coastal (<100 km from the sea), inland (>100 km from the sea), highland (>244 km from the sea and >1000 m asl) and further inland (>600 km from the sea) regions. The primary objective is to produce local/regional meteoric water lines (L/RMWLs) over Cameroon and subsequently the Cameroon Meteoric Water Line (CMWL). Other goals are to describe the temporal and spatial variations in stable isotopes of the rainfall and their relationship to annual precipitation cycle and determine the main controls on isotopic variations. Present results reveal a very wide range in $\delta^{18}O$ and δD from -9.43‰ and -65.61‰ at high elevations in Kumbo (1715 m) to 3.86‰ and 38.61‰ in the Ndop plain, respectively. The significant variation suggests various controls on the isotopic composition of the rain. Rain stations (Mutengene, Douala, Lobe, Mundemba and Kumba) in the coastal region gives $\delta D = 7.87\delta^{18}O + 13.20$ ($R^2 = 0.96$, n = 90) as the RMWL. The relationship: $\delta D = 8.21\delta^{18}O + 14.40$ ($R^2 = 0.95$, n = 51) defines the RMWL for the inland stations (Mamfe, Yaounde and Bertoua). At the Bamenda Highland stations (Bamenda, the Ndop plain, Ndawara Tea Estate, Wum, Kumbo and Nkambe), the RMWL is defined by $\delta D = 8.07\delta^{18}O + 14.50$ ($R^2 = 0.98$, n = 139). Two stations (Ngaoundere and Garoua) further inland in northern Cameroon give a RMWL: $\delta D = 6.72\delta^{18}O + 5.21$ ($R^2 = 0.99$, n = 10) with a relatively lower slope and d-intercept. The low slope and d-intercept reflect partial evaporation of the falling rain drops under semi-arid conditions in northern Cameroon. Overall, the first CMWL is $\delta D = 8.08\delta^{18}O + 14.19$ ($R^2 = 0.97$, n = 290). The similarity of the slope to the Global Meteoric Water Line indicates equilibrium conditions during rain formation with a minor effect of evaporation during the fall of raindrops to the ground on a national scale. Additional inland sources of moisture other than the Atlantic Ocean explain the high d-intercept in rainfall across the country. High d-excess values (>>10‰) in coastal precipitation within the rainforest region of Cameroon reflect recycled moisture from the rainforest. Meanwhile, the high d-excess values in the high altitude rains in the Bamenda highlands suggest the interplay of altitude effect and inland recycled moisture from inland water bodies. Across the country, the stable isotopes show an inverse relationship between elevation and rainfall depths suggesting altitude and amount effects, respectively. However, there is no discernible decrease in the isotope values from the coastal to inland stations as would be expected; hence, a lack of continental effect. Enriched isotopic signatures clearly mark low convective activities at each site during the pre- and post-monsoon rains. Intense convection during the monsoon peak coincides with the most depleted isotope values in the precipitation. Thus, the generated rainfall isotopic data is useful as a marker of annual changes in rainfall patterns. Given the dependence of most Cameroonians on rainfed agriculture, such information from the isotopes offers an important monitoring tool for changes in rainfall patterns for subsequent remediation measures. The data is not only useful for groundwater recharge studies in Cameroon but also for climatological research at a regional level (Central Africa).

Keywords: Stable isotope variations, Precipitation, Cameroon Meteoric Water Line, Deuterium excess, Moisture recycling, Amount effect

Stable isotopic compositions of river waters in the core area of the Shirakami Mountains, Japan

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The Shirakami Mountains is the general name given to an extensive mountainous region of 130,000 hectares ranging from the southwest of Aomori to the northwest of Akita prefecture. Within this area are 16,971 hectares of land, enclosing virgin beech forests in Japan, which were registered as a world heritage region in December 1993. However, environmental impact by acid rain at the Shirakami Mountains is becoming an issue these days. Acid rain deposits nitrates that can lead to increases in nitrogen in forests. So we continued research about the chemical and isotopic compositions of river and spring waters in the Shirakami Mountains area, to clarify origin and geochemical characteristics since 2011. However, little is known about stable isotopic composition of natural water in the core area. Therefore, we sampled natural water in a central area and analyzed chemical and isotopic compositions.

The result of the investigation was that delta-18O and delta-D of the core area's water samples showed -9.1 to -9.9 per mil and -55.7 to -59.4 per mil, respectively. Stable isotope composition of the samples roughly resemble those of meteoric water (delta-D = 8delta-18O+20), thereby indicating that these are local meteoric water. In addition, the range of Deuterium excess (d-excess) of samples is from 16.9 to 19.9 per mil. These characteristics of isotopic composition are similar to result of SW-part of Shirakami area.

Keywords: The Shirakami Mountains, oxygen and hydrogen isotopes

On stable isotope ratios of water in the Fuefuki River, Yamanashi Prefecture, Japan

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This study is carried out to make clear the changes in stable isotope ratios of water of the Fuefuki River. The Fuefuki River is originating from the Kanto mountainous district located in the northeastern part of Yamanashi Prefecture, and it flows along the south-eastern edge of the Kofu basin.
The results of the analysis are as follows.
At the upper reaches of the Fuefujki River, the values δD are influenced by ”the altitude effect of rainfall”, and at the down reaches area, the valuesδD are gradually become larger, i.e. heavier than the water of the upper reaches. δD of the water in the bottom of Kofu basin, downstream area of the Fuefuki River, is more heavier than that of upper reach of the river, However, between St.3 andSt.4, and between St.6 and St.7, the values of δD at the downstream points are smaller.
These changes is not possible to explain by altitude effect, and the authors pointed out that there are two type of inflow to the Fuefuki River, one is tributary stream with high mountain basin area, and the other is groundwater discharge to the Fuefuki River near the outlet area of the Kofu basin.

Keywords: Fuefuki River, stable isotopes, rivers recharge

Investigation of the groundwater source estimation in Kofu Basin for hydrological model

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The end member mixing analysis using hydrological tracers have been applied to identify the groundwater recharge sources in local area, such as scale of alluvial fan. However, it is difficult to apply to large scale, due to the wide values of temporal and special for the hydrological tracers. Objective of this study is investigating the groundwater recharge identification using hydrological tracers to adapt for the hydrological model for basin scale.

Groundwater samples were collected once a year from November 2010 to October 2012. Altogether 12 river water samples were collected in 2003, 2004 and 2006 from main rivers in Kofu basin. Rain water samples were collected once a month since 2008. All groundwater samples (n=50) are classified into three types based on recharge sources. Among them 20% of groundwater are mainly recharged by river water. Other 50% samples are river water mixed with local precipitation and 25% are river water mixed with mountain groundwater.

Keywords: Geoundwater, Kofu Basin, Water Stable Isotopes

Behavior of the age dating tracers in Satoyama-spring

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For accumulation of basic data about the age dating tracers, weekly sampling was carried out on Satoyama-spring in Nagoya city for one year. Based on the analysis results (stable isotopes, CFCs, SF_6, dissolved ion), we discuss the factor controlling the temporal variation of age dating tracers.

Keywords: age daring tracer, Satoyama-spring, stable isotope, CFCs, SF6

A study on caldera lake-groundwater system based on a multiple isotope approach

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Lake Masyu (212 m deep; 19.6 km^2 in area; water surface at 352 m a.m.s.l.), eastern Hokkaido, Japan, is a seepage caldera lake with no surface outflow and inflow. The caldera lake-groundwater system was investigated to elucidate the effect of lake-water seepage from Lake Masyu on the hydrology and hydrogeochemistry of Masyu volcano and its adjacent areas. Previous studies on the lake indicated that, on the basis of a conventional water balance method, there is a large amount of seepage of some 65,000 km^3/day to the surrounding volcanic aquifers.
The analyses of ^{2}H, ^{18}O,^{13}C, ^{3}He and water chemistry for samples from rivers, springs, and bores in 2009 and 2010 are reevaluated in detail to quantify the lake-water contribution to river and spring discharges and to the downgradient groundwater field. The water samples from Leke Masyu are markedly enriched in heavy isotopes and fall on a line with a slope of 5.0 in the δD vs.δ^{18}O diagram, which is characteristic of open-water bodies subject to evaporation. The lake water is also enriched in carbon isotope and in the range between 4 and 5‰ δ^{13}C. The mixing proportion of lake water was calculated on the basis of δD and δ^{18}O by applying a simple two end-member mixing model. As a result, the lake-water contribution proved to be significant for the huge springs on the southeastern flank (Nishibetsu-Gawa Headwater Springs) and those on the southwestern flank (Biruwa Springs), consisting of 30% of their discharges. Taking into account their total daily discharge of 140,000m^3 measured in July 2009, some 65% of the lake-water seepage from Lake Masyu, that is 42,000 m^3/day, is estimated to concentrate in these springs. In contrast, the Kaminoko-Ike Spring on the northern flank with a discharge of some 15,000m^3/day, water of which has long been considered to be of Lake Masyu origin, isotopically showed no evidence of lake water. It is also the case in the other medium-sized springs located on the northern and eastern flanks. The analyses of stable carbon isotope, high isotopic values of -9 to -7‰ δ^{13}C for Nishibetsu-Gawa Headwater Springs and of -9 to -8‰ δ^{13}C for Biruwa Springs, and a low value of -21‰ δ^{13}C for Kaminoko-Ike Spring, are consistent with these estimates. It is also the case with ^{3}He: Nishibetsu-Gawa Headwater Springs and Biruwa Springs had a high content of ^{3}He of magmatic origin, whereas there was no ^{3}He of magmatic origin in Kaminoko-Ike Spring. Rivers that originate in the flanks of Masyu volcano showed little or no isotopic evidence of lake water. An overall estimate, therefore, is that approximately 23,000 m^3/day of seepage from Lake Masyu is still unaccounted for. The hydraulic connection of volcanic aquifers to Lake Masyu is likely to account for this. The isotopic analyses show some hot springs and groundwaters from the 100-350m deep bores in the southern and southwestern flanks contain substantial proportions of lake water, indicating seepage water from Lake Masyu plays an important role in forming hydrothermal and groundwater system. A schematic diagram for the caldera lake-groundwater system in and around Masyu volcano is depicted on the basis of these data.

Keywords: groundwater system, caldera lake, lake-water seepage , spring, multiple isotope approach

Origin of mercury in the groundwater in Hirakata City, northeastern Osaka Prefecture

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Thirty one groundwaters contained excess mercury of standardvalue(0.5ppb) among the 4513 groundwaters monitored by Osaka Prefecture. Most of those were found in the northeastern part of Osaka(Hirakata and Shijo-nawate cities) and along the active Ikoma Fault system(Osaka Prefecture,2009). The mercury was plausibly geogenic, however, the source was not clear. This study was planned to reveal the origin of mercury using its stable isotopes.
The groundwater was sampled from 15 shallow dug wells and tube wells <10m depth in July 2015-in November in Hirakata city. The water level was 1~2m from the ground. After analyzing major chemistry and total mercury concentration, the groundwater highly containing mercury were selected to determine the mercury isotope ratios. The total mercury concentration was measured by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), the methyl mercury concentration was measured by Gas Chromatography- Atomic Fluorescence Spectrometry(GC-AFS), and the mercury isotope ratio was measured by Multi-Collector Inductively Coupled Plasma Spectrometry(MC-ICP/MS) attached with hydride generation system.
Major chemistry of the studied groundwaters were Ca^{2+}-HCO_3^- and Na-Cl- SO_4+NO_3types. Mercury concentrations were less than the standard value, while the maximum concentration was 133ppt. The mercury concentrations of groundwater from the same wells varied largely, relationship to season and /or precipitation. For one of the case, the groundwaters containing the lower mercury(90ppt) with the higher SO_4^{2-} than that containing higher mercury(133ppt). For the other case, the higher mercury containing groundwater(86ppt) containing higher Ca^{2+} and HCO_3^- than the low-mercury groundwater(59ppt). When the groundwaters taken from two wells, within 20m distance contained 55ppt mercury(well depth >5m) and 2.0ppt(2~3m depth). These observations suggest that the mercury in the groundwater >5m depth in diluted by infiltrating water from the surface around the wells. Therefore, mercury was not contaminated from the source on the ground surface. The most of mercury was in inorganic form, and mono-methyl mercury was less than 1% except one groundwater containing extremely low-mercury. Thus, the mercury does not relate to human activities or bio-chemical reaction.
The mercury isotope ratio is effective to specify origin. The mercury isotope ratio is influenced by bio-chemical fractionation, and many researchs have been done for the bioaccumulation processes (e.g. Blum 2013). While, less studies have reported for the behavior of mercury in the crust using stable isotopes. Although only two groundwaters were analyzed, the present study in the first report on the mercury isotope ratio of shallow groundwaters but not hydrothermal water. δ^{202}Hg of groundwater was -0.65‰~-0.85‰. Many mercury mines are known in the Kii Peninsula and Shikoku Island. Takeuchi(2011) reported that δ^{202}Hg of sinnabars from Niu-mine was -0.68±0.12(‰), Yamato mercury mine was -0.19±0.36(‰), and Mizui mine was -0.51±0.47(‰). The isotope ratios of syudied groundwaters were close to those values, indicating the similar origins of those mercuries. When cinnabar is precipitated from hydrothermal one liquid, isotope fractionation occur to concentrate heavier mercury in the cinnabar. If so, slightly smallen δ^{202}Hg of the studied groundwaters than those of the cinnabars from the Kii Peninsula and Shikoku would suggests more pristine isotope composition of the fluid from the deep crust. Mercury isotope study will be useful to trace the fluids from the deep in relation to the regional tectonics.

Keywords: mercury, groundwater, isotope

Systematic estimation and correction of Ba induced interference in ICP-MS for direct and quick analysis of REEs in geothermal waters

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High barium concentration and Ba/REE ratios are commonly observed in geothermal waters such as Arima-type brines, making it difficult to precisely determine REE characteristics, e.g., Eu, Ce anomalies and REE patterns of this kind of high matrix (major solutes) and ultra-low REE waters. We systematically evaluated Ba induced molecular ions in ICP-MS operated at solution mode and established a new correction method for direct determination of REE in high salinity geothermal waters.

Ba has seven isotopes from ^{130}Ba to ^{138}Ba with natural abundance of 0.1% to 71.7%, each of them will produce molecular ions in forms of oxide, hydroxide, hydride and argide in argon plasma. These molecular ions cover a mass range from 139 (^{138}BaH) to 178 (^{138}BaAr), theoretically overlapping with most of REE isotopes in complicated combinations. For example, both BaO and BaOH overlap the masses of light to middle REE isotopes, especially Eu. Conventional correction method simply considers that bulk interfering on Eu is contributed by BaO, and may result in large uncertainty or erroneous of REE anomalies and patterns. In this work we separately evaluated production rates of Ba oxide, hydroxide, hydride and argide for each of Ba isotopes in solution mode ICP-MS. Our data show that BaOH and BaO are major interfering species over Nd, Sm, Eu and Gd peaks. BaH and ^{138}Ba peak tailing seriously overlap with La and Ce signals. Argides are ignorable. Heavy REEs and Pr are free from a significant overlapping with any of the Ba induced interference. All the interference can be quantitatively estimated and reliably corrected for REE analysis.

We demonstrated the correction strategy by analysis of reference riverine water (SLRS-4) doped with Ba to Ba/Eu=125,000 similar to Arima-type brines. Determined REE data of Ba-doped SLRS-4 agrees very well with certified values. The method was also applied to determine REE compositions of various spring waters including Arima-type brine of the Arima area in southwest Japan (Nakamura et al, 2015). In this case, Ba induced interferences contributed to La, Ce, Nd, Sm, Eu and Gd raw signals for 92%, 24%, 48%, 78%, 96% and 75%, respectively. The intra REE interferences, e.g., PrO, NdO and SmO overlapping over middle and heavy REE signals, were less than 2.7% (mostly <1%), thus ignorable for discussion.

Keywords: Ba-induced interference, REE, geothermal waters, ICP-MS

Characteristics of event-based oxygen isotopic composition in precipitation at western part of Kanagawa prefecture

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Stable isotopes in precipitation are useful tool for understanding the hydrological cycle. Precipitation samples for every events have been collected at Hot Springs Research Institute located in the eastern foot of Mt. Hakone, and those oxygen isotopic compositions are analyzed 79samples collected from Dec. 1, 2012 to Nov. 30, 2013.Annual volume-weighted mean value oxygen isotopic composition in 2013 was -7.62 per mill, and seasonal ones are -11.10 per mill in winter, -5.76 per mill in spring, -8.52 per mill in the Baiu, -6.63 per mill in summer, -7.02 per mill in the Shurin, -5.81 per mill in autumn. Weighted mean value in winter and the Baiu is lower than annual one, while that in other seasons is higher. Thus, a clear seasonal variation is found in 2013. The purpose of this study is to estimate the factor which has lower isotopic composition in winter and the Baiu.Lower isotopic composition in winter resulted from the precipitation by low pressure. When depesouthern coast low pressure passed, the tendency which indicates one compared with the very low isotope ratio was seen. The influence of temperature effect is considered as a decline factor in winter. The intensity of rainfall brought by the Baiu front is large. Therefore, it is considered that amount effect was reflected increased.A clear correlation (R^2=0.83) was seen between the precipitation and compared with the oxygen isotope, and the phenomenon which represent rain amount effect was confirmed. However, event of precipitation more than 100 mm amount of precipitation 3 times in case of a typhoon in the Shurin, and the low isotopic ratio is high -5.2 per mill, -6.5 per mill and -9.3 per mill of respectively. Though there was a lot of precipitation, the isotope didn't shows low value. Thus the typhoon isotopic ratio is complicated.

Keywords: Mt. Hakone, oxygen isotope, amount effect , precipitation event