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

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Chemical and stable isotopic ( $\delta^{18}$ 0,  $\delta$ D) 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<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> and higher contents of Ca<sup>2+</sup> and Na<sup>+</sup> than those of the present sea water, are consists of two kinds of different  $\delta^{18}$ O value. B and K<sup>+</sup> 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<sup>-6</sup>, (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 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-<sup>4</sup>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 <sup>4</sup>He concentration with weak chloride-<sup>4</sup>He correlation. This observation implies that high He concentration with moderately high <sup>3</sup>He/<sup>4</sup>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 ( $\delta D$  and  $\delta^{18}O$ ).

The  $\delta D$  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  $\delta D$  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  $\delta D$  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  $\delta D$  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<sub>3</sub> type at shallow depths ( $0\sim15m$  depth), mixed cation-HCO<sub>3</sub> type at intermediate depths (less than about 200m), Ca·Na-SO<sub>4</sub>·Cl and Na·Ca-SO<sub>4</sub>·HCO<sub>3</sub> 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·δ180), 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 <sup>3</sup> H, noble gases, CFCs, <sup>36</sup>Cl/Cl and <sup>228</sup>Ra/<sup>226</sup>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 (<sup>85</sup>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 (<sup>85</sup>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. <sup>85</sup>Kr specific activities in groundwater was 1.022 ±0.028 Bq/m<sup>3</sup>, 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 <sup>85</sup>Kr was much smaller compare to other methods. Furthermore, <sup>85</sup>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  $(d^{34}S \text{ and } d^{37}Cl)$  has been used to investigate salinization processes in a confined aquifer system in southwestern Nobi Plain (SWNP), central Japan. Deduced from the SO<sub>4</sub>/Cl ratios and  $d^{34}S$  values, a tongue of brackish confined groundwater (Cl <sup>-</sup> > 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<sub>4</sub><sup>2-</sup> due to sulfate reduction process. The Cl isotopic compositions are negatively correlated with paleo seawater Cl<sup>-</sup> concentrations, while they are not correlated with either total Cl<sup>-</sup> concentrations or  $d^{34}S$  values. Furthermore, Cl<sup>-</sup> 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<sup>-</sup> has diffused in argillaceous freshwater sediments whereas modern seawater Cl<sup>-</sup> 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<sup>+</sup> and Cl<sup>-</sup>. 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<sub>3</sub> type.  $\delta D$  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 ( ${}^{3}\text{He}/{}^{4}\text{He}$ ) 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<sup>-</sup> 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  $\delta$ D 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<sup>2</sup> = 0.96, n = 90) as the RMWL. The relationship:  $\delta D = 8.21\delta^{18}O + 14.40$  (R<sup>2</sup> = 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<sup>2</sup> = 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-180 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-180+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