Research strategy of multi-isotope studies on environmental research

*Ichiro Tayasu[1], Ki-Cheol Shin[1], Takanori Nakano[1]

1.Research Institute for Humanity and Nature

Environmental traceability method is based on material cycling, and thus considered to be applicable to the studies on various environmental issues. Especially, the method can be applicable to evaluate human impacts on ecosystem properties. In terrestrial ecosystems, heterogeneity of local environment in multiple elements and isotope ratios exists in geology, providing information to watershed ecosystems through water cycling, material cycling and movement of living organisms. The information can be used as an indicator of environmental traceability method.

The Research Institute for Humanity and Nature (RIHN) is operating a co-research framework, named “Isotope Environmental Research Collaboration”. The research pursues research development through multi-elemental analysis and multi-isotope analysis, considering the environmental traceability. To achieve the goal, various approaches are required including development of manuals for observation, standardization of analysis and construction of protocols for sharing data, etc.

It is recently considered that research collaboration with local people, local government, and local education is important to solve environmental issue. We propose the importance of research collaboration between universities and our role to enhance research collaboration based on RIHN initiative.

Keywords: Stable isotopes, Environmental traceability, Watershed

Estimation of air pollutant sources from the seasonal variation of Sr and Pb isotope ratios of aerosols

*Shota Kato[1], Atsushi Matsuki[2], Ki-Cheol Shin[3], Takanori Nakano[3]

1.Graduate School of Natural Science & Technology, Kanazawa University, 2.Institute of Nature and Environmental Technology, Kanazawa University, 3.Research Institute for Humanity and Nature

[Introduction] Transboundary air pollution remains as a major environmental concern in Japan since it is located downwind of the Asian continental outflow. Due to the prevailing high pressure system in the Pacific, it has been generally accepted that the air quality near the ground surface of central Japan is relatively unaffected by the polluted air-mass originating from the Asian continent. However, our recent observations and increasing number of studies have seen episodes of high aerosol concentrations even in summer periods, indicating the significance of the polluted air-mass not only spring and winter but also in summer. However, as there are a variety of aerosol sources (e.g. refuse incineration, volcanic eruption) within Japan, it is difficult to distinguish domestic aerosols from foreign ones. In order to identify the sources of air pollutants in Japan, we determined the Sr and Pb isotopic ratios and elemental compositions of aerosols collected at Noto peninsula, Japan, in different seasons.

[Samples and analytical procedure] The sampling site is NOTO Ground-based Research Observatory (NOTOGRO) at the tip of Noto peninsula (37°45’N, 137°36’E). All of the samples were collected weekly on the roof of a building (15 m a.g.l.) using a High-volume air sampler (AH-600F, SHIBATA) with a constant flow rate of 700 L/min. Only the coarse fraction exceeding 2.5 μm in diameter was collected on a 12.6 x16.6 cm^2 SiO_2 filter through an impactor. Filters were extracted with 5% HOAc (acetic acid) solution. Residual fraction after extraction with HOAc was digested in $HF\text{-}HCl\text{-}HNO_3$ solution. Isotopic ratios of Sr and Pb were measured using a Thermo Scientific Triton thermal ionization mass spectrometer (TIMS) and Thermo Scientific Neptune multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS), respectively.

[Results and discussion] The HOAc-leachate materials are characterized by low $^{87}Sr/^{86}Sr$ ratios and approach to a marine value of 0.70918, indicating the dominant contribution of sea salt aerosol. In contrast, the HOAc-residue materials have high $^{87}Sr/^{86}Sr$ ratios, and sample collected from 9 to 16 July show the highest $^{87}Sr/^{86}Sr$ ratios similar to surface soil silicates in the north China (0.71432 in average; Nakano et al., 2004). This result supports a view that the continental air-mass may reach to Japan even in summer season. About Pb isotope ratios of the HOAc-leachate materials, samples with low V/Mn showed similar Pb isotopic ratios reported in China. Major sources of V and Mn are from oil combustion and coal combustion, respectively. This result suggests that the air-mass over NOTOGRO in spring to early summer of 2015 are affected by the coal-derived aerosols in China.

Keywords: aerosol, Sr-Pb isotopes, transboundary air pollution

An attempt to estimate the source and accumulation of atmospheric deposition Sr and Pb isotope ratios in the bryophyte

*Tamihisa Ohta[1], Yoshitaka Oishi[2]

1.Research Institute for Humanity and Nature, 2.Hokkaido University

Recently, excessive input of heavy metals and other pollutions into the surface of environment have been developed through consumption of fossil fuels and yellow sand. Although there are many monitoring sites for atmospheric deposition in Japan, the studies that estimated the amounts of fall in forest ecosystem are very few due to difficulty of installation of sampler. In this study, we focused on relationship between atmospheric deposition and bryophyte. Since some kind of bryophyte obtains almost their nutrients from atmospheric deposition, and metallic elements are penetrated into their tissue. Therefore, we considered isotope ratios and heavy metal concentration of bryophyte tissue might provide a useful index of source and accumulation of atmospheric deposition. We collected bryophyte, soil and leaf in many part of Akita, Nagano Miyazaki prefecture, and analyzed heavy metal concentration and isotope ratios (Sr and Pb). Sr and Pb isotope ratios of the some bryophyte samples differed to the soil and leaf sample. This means bryophyte contain metals supplied from atmospheric deposition. In the future, we plant to analyze bryophyte collected another sites such as the Sea of Japan side. And because the uptake rates of heavy metal vary among bryophyte species, we have to select indicator species for estimate of atmospheric deposition.

Keywords: Fossil fuel, strontium isotope ratio , atmospheric deposition

Stream water chemistry and dynamics of sulfur derived from atmospheric deposition in a forested catchment in central Japan

*Hiroyuki Sase[1], Masamichi Takahashi[2], Kazuhide Matsuda[3], Keiichi Sato[1], Toko Tanikawa[2], Naoyuki Yamashita[1], Tsuyoshi Ohizumi[1], Takuya Ishida[4], Masato Kamisako[1], Ryo Kobayashi[1], Shigeki Uchiyama[1], Tatsuyoshi Saito[1], Masayuki Morohashi[1], Haruo Fukuhara[5], Shinji Kaneko[2], Takanobu Inoue[6], Toshiro Yamada[7], Chisato Takenaka[4], Ichiro Tayasu[8], Takanori Nakano[8], Tomoyuki Hakamata[9], Seiichi Ohta[10]

1.Asia Center for Air Pollution Research, 2.Forestry and Forest Product Research Institute, 3.Tokyo University of Agriculture and Technology, 4.Nagoya University, 5.Niigata University, 6.Toyohashi University of Technology, 7.Gifu University, 8.Research Institute for Humanity and Nature, 9.Hamamatsu Photonics, 10.Kyoto University

[Introduction]

Ijira catchment is located in the downwind side of the Chukyo Industrial Area in central Japan and has been historically experiencing large-scale depositions of sulfur and nitrogen from the atmosphere. The catchment was acidified and nitrogen-saturated in the mid-1990s, according to previous studies (Yamada et al. 2007; Nakahara et al. 2010). However, recovery from acidification and nitrogen saturation has been observed recently.

[Methods]

We used the following monitoring data from the Ministry of the Environment of Japan: long-term data of stream water chemistry since 1988, wet deposition (rainwater) monitoring data since 2000, the input-output budget since 2007, and isotopic data of sulfur and strontium in rainwater, soil solution and stream water since 2014. Moreover, sulfur isotopic data of tree rings in Cryptomeria Japonica from the Chukyo Area was also used for analysis of long-term trends on stream water chemistry and dynamics of sulfur derived from atmospheric deposition in the forested catchment.

[Results and discussion]

The stream water pH declined from 7.3 in 1994/1995 to 6.6 in 2003, and then promptly recovered to a value of approximately 7 thereafter. Simultaneously, the NO_3^- concentration increased until 2002/2003 and thereafter started declining in 2005. During the period of acidification with NO_3^- leaching, the SO_4^{2-} concentration reached the highest value in 1994 with a mean concentration of 210 $\mu mol_c\ L^{-1}$, and then gradually declined to 127 $\mu mol_c\ L^{-1}$ in 2013. In addition, the concentrations of dissolved organic carbon were high from the mid-1990s to the early-2000s. The mean annual SO_4^{2-} input from 2007 to 2012 was 0.9 ±0.1 $kmol_c\ ha^{-1}\ year^{-1}$, while the mean annual output from the stream for the corresponding period was 2.3 ±0.5 $kmol_c\ ha^{-1}\ year^{-1}$. Even after taking into account various uncertainties, the output of SO_4^{2-} exceeded the input. The mean sulfur isotopic ratios ($\delta^{34}S$) of SO_4^{2-} in rainwater and soil solution at 20 cm depth were 4.6‰ and 3.8‰, respectively, while that in the stream water was −13‰. Recent sulfur inputs appear to be retained in relatively shallow soil layers. The sulfur in shallow layers may have contributed to the high concentrations in the mid-1990s. Reports in the literature suggest the existence of geological sources with significantly low $\delta^{34}S$ values (from −14‰ to −8‰) near the study catchment. Therefore, it is possible that the SO_4^{2-} derived from geological sources contributes to the large discrepancy, although dendrochronology suggests certain effects of the atmospheric inputs with lower $\delta^{34}S$ (from −7‰ to +1‰) in the 1960s/1970s in the Chukyo Industrial Area.

[Acknowledgements]

This study was conducted based on the monitoring data from the Ministry of the Environment of Japan and the related research outputs. Strontium isotopic analysis was conducted by the support of Joint Research Grant for the Environmental Isotope Study of Research Institute for Humanity and Nature.

Authors thank officers, experts and scientists in the relevant organizations.

[References]
Nakahara et al. 2010. *Biogeochemistry* 97: 141-158.
Yamada et al. 2007. *Water, Air, and Soil Pollution: Focus* 7: 259-266.

Keywords: acidification, nitrogen saturation, sulfur, isotope

Application of Multiple-indicator to groundwater flow and chemistry study in the alluvial fan

*Yumi Yoshioka[1], Kimihito Nakamura[2], Nakano Takanori[3], Haruhiko Horino[4], Ki-Cheol Shin[3]

1.Tottori University, 2.Kyoto University, 3.Research Institute for Humanity and Nature, 4.Osaka Prefecture University

The Tedori River Alluvial fan between the Tedori and Sai Rivers in central Japan contains abundant groundwater resource and it supplies the region drinking and industrial water. The paddy and crop-rotated paddy fields occupy 45% of its total area (140km^2). To maintain sustainable groundwater use and prevent groundwater contamination, it is necessary to investigate the flow paths and sources of the groundwater. In this study, 83 water samples mainly from shallow groundwater, river water, and paddy water, were collected in the alluvial fan during the paddy irrigation period. We analyzed stable isotope ratios of H, O, and Sr and concentrations of major dissolved ions and trace elements.

The δ^2H and δ^{18}O values in the shallow groundwater are relatively low along the Tedori River and increased with the distance from the river; this trend would be caused by dilution effect by the river water. However, there is little contribution of the paddy water with high values reflecting the influences of the evaporation effect. Concentrations of Mg^{2+}, Ca^{2+}, Sr^{2+}, HCO_3^-, and SO_4^{2-} in the groundwater have a similar distribution trend: lower along the Tedori River and higher in the central area of the fan where paddies are relatively widespread. The $^{87}Sr/^{86}Sr$ ratios of the groundwater are related to near-surface geology. The groundwater in sediment from the Tedori River has relatively high $^{87}Sr/^{86}Sr$ ratios, whereas that from the Sai River in the north of the fan has low $^{87}Sr/^{86}Sr$ ratios. The river water of the Tedori River is also high ratio reflecting sediments in the upper river basin. The three stable isotopes indicate that the groundwater in the central and southern fans is recharged from the Tedori River, whereas recharge in the north is from the Sai River.

There are linear relationships between $^{87}Sr/^{86}Sr$ ratio and the reciprocal concentrations of Sr^{2+}, Mg^{2+}, and Ca^{2+}. These geochemical characteristics suggest that groundwater recharged from the Tedori River flows towards the central fan and then runs off the sea. It mixes with waters from precipitation and paddy water that have become enriched in these components during downward infiltration. The results obtained by application of multiple-indictor are consistent with our hydrological observation results: groundwater contour maps and river water balances, and groundwater flows reproduced by the three dimensional numerical simulation.

Keywords: Strontium isotope, Paddy field, Groundwater-river interaction

Characteristics of the distribution of $\delta^{18}O$, δD and d-excess values in groundwater and spring water at Fukushima and Niigata prefecture

*Shiho Yabusaki[1]

1.Faculty of Symbiotic Systems Science, Fukushima University

Stable isotopes of oxygen and hydrogen are useful to understanding the recharge are of groundwater and spring water. The object of this study is to grasp the detailed distribution of stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD) in groundwater and spring water at Fukushima and Niigata prefecture.

Stable isotopes of oxygen and hydrogen are relatively high near the coastal area and relatively low at inland area, thus the inland effect is confirmed. And isotopes are relatively low in high altitude area (e.g. mountainous area), the altitude effect and temperature effect are also recognized.

From the distribution map of d-excess values, it is obvious that the d-excess is relatively low at Pacific coastal regions (Fukushima prefecture) and relatively high at coasts of Japan Sea regions (Niigata prefecture). It is assumed that the difference of d-excess values is affected by origin of the water vapor. The d-excess values change near the Ou mountains, and not change near the Abukuma mountains. Elevation of the Ou mountains is higher than Abukuma mountains, hence the water vapor is prevented by the Ou mountains is considered.

Keywords: Fukushima, Niigata, groundwater, spring water, stable isotope, d-excess

Natural abundance of ^{15}N in Japanese forest soils

*Keisuke Koba[1], Bin Hiratsuka[2], Rieko Urakawa[3], Kazuya Nishina[6], Kazuo Isobe[7], Hideaki Shibata[4], Nobuhito Ohte[5]

1.Center for Ecological Research, Kyoto University, 2.Faculty of Agriculture, Tokyo University of Agriculture and Technology, 3.Asia Center for Air Pollution Research, 4.Field Science Center for Northern Biosphere, Hokkaido University, 5.Graduate School of Informatics, Kyoto University, 6.National Institute for Environmental Studies, 7.Graduate School of Agricultural and Life Sciences, The University of Tokyo

Natural abundance of ^{15}N of bulk soil N has been investigated in many studies with emphasis on soil N decomposition, N loss, and chronosequence of N dynamics in forests. $\delta^{15}N$ of bulk soil N generally increases with soil depths, which is considered as a consequence of the loss of ^{15}N-delpleted N via leaching and gaseous loss both coupled with N mineralization and nitrification as well as the incorporation of ^{15}N-enriched N into bulk soil N via microbial biomass. However, the details on how ^{15}N of bulk soil N can be discriminated during these processes are not clear.

We analyzed the $\delta^{15}N$ of bulk soil N collected in the GRENE (Green Network of Excellence) environmental information project and the ReSIN (Regional and comparative Soil Incubation study on Nitrogen dynamics in forest ecosystems) project (Urakawa et al. 2014, 2016). Mineral forest soils were collected in each watershed from five soil profiles with different soil depths down to 40 or 50cm depth. We used a modified EA-IRMS in TUAT with higher sensitivity to measure the $\delta^{15}N$ of bulk soil N with low N concentrations. We analyzed the soil samples (488 samples from 32 watersheds) with higher N concentration than ca. 0.1% (with less than 8mg sample weight to run) to reduce the risk of incomplete combustion.

$\delta^{15}N$ of bulk soil N ranged from -3.2 to +10.2 permill with N concentrations ranging from 0.1 to 1.3%. Isotopic fractionation factors for bulk soil N, estimated from the relationship between N concentrations and $\delta^{15}N$ values, ranged from 0.6 to 7.2 permill. The differences in mycorrhizal association of plants would influence the isotopic fractionation factor (Hobbie and Ouimette 2009), although we found no significant relationships between mycorrhizal associations (ECM, AM) and the isotopic fractionation factors. Climate factors such as MAT and MAP suggested as the factors affecting $\delta^{15}N$ of bulk soil N (Amundson et al. 2003) were not significantly correlated with $\delta^{15}N$ of bulk soil N. In the presentation we will discuss the possible factors influencing $\delta^{15}N$ of bulk soil N and isotopic fractionation factors in the forest watersheds.

Keywords: Stable isotopes, Forest soils, Nitrogen dynamics

Tracing Atmospherically Deposited Nitrate in Forest Ecosystem Using Triple Nitrate Isotopes

*Kazuaki Sumi[1], Masanori Katsuyama[1], Midori Yano[2], Keisuke Koba[2]

1.Kyoto University, Graduate School of Agriculture, 2.Kyoto University, Center for Ecological Research

Nitrogen saturation is one of the forest environmental issues as a result of increasing anthropogenic emission of reactive nitrogen. Forest which reached nitrogen saturation exports residual nitrogen as dissolved inorganic nitrogen (mainly nitrate: NO_3^-) and the amount of NO_3^- leaching is one of the signal of nitrogen saturation. However, the mechanism of nitrate export from forest ecosystem is not well understood because of complexity of forest internal nitrogen cycle. In fact, NO_3^- has two sources, atmospherically deposited nitrate ($NO_3^-{}_{atm}$) and microbial nitrate ($NO_3^-{}_{microb}$) in forest ecosystem. These two sources could not be separated so far, but triple nitrate isotope analysis techniques enabled distinguishing $NO_3^-{}_{atm}$ from $NO_3^-{}_{microb}$, and revealed that the fraction of $NO_3^-{}_{atm}$ (f_{atm}) in stream water is about 10% worldwide. To clarify the mechanism of export of atmospherically deposited nitrate ($NO_3^-{}_{atm}$) to stream from forest catchment, we explored which factors of forest ecosystem influence f_{atm} in stream water.

We measured $\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$, $\Delta^{17}O-NO_3^-$, and NO_3^- concentration along with forest hydrological pathways, through fall, soil water, ground water and stream water at Kiryu Experimental Watersheds (KEW) in central Japan.

We calculated the value of f_{atm} of four stream water, and mean value was about 10% except for one of the stream water which flows steep slope catchment. These results are consistent with the reports for stream. In soil, the concentration of NO_3^- and the values of f_{atm} were decreased along with the soil depth suggesting that $NO_3^-{}_{atm}$ was consumed immediately at surface soil. In contrast, the values of f_{atm} were not fluctuated in ground water which suggests that the value of f_{atm} in stream water is almost determined at soil.

Keywords: forest ecosystem, nitrate isotopes, oxygen isotope anomaly

Effects of rapid environmental changes on groundwater dissolved organic carbon dynamics in Tropical peat swamp

*Masayuki Itoh[1], Hiroshi Nishimura[1], Takashi Hirano[2], Gunawan Haris[3], Kitso Kusin[4], Osamu Kozan[1], Yotaro Tanaka[1], Masanori Katsuyama[1]

1.Kyoto University, 2.Hokkaido University, 3.Riau University, 4.Palangkaraya University

Tropical peatland forests in Southeast Asia are considered to be one of the most important parts of larger ecosystems due to the huge amount of carbon stock and biodiversity they contain. Yet, recent rapid and intensive deforestation to procure timber and land for commercial plants or crops (Oil palm etc.) must have induced fundamental changes in the material cycling. We focused on the effects of human impacts such as deforestation, plantation, and manmade fires on groundwater dissolved organic carbon (DOC) dynamics in the natural forest, secondary forest, and degraded peatland (shown in Photo; originally there was peat swamp forest) area in East part of Sumatra Island and Central Kalimantan, Indonesia. We measured dissolved organic and inorganic matters in peatland groundwater both in wet and dry seasons. We compared the results of both bare land site after the deforestation and the fires and oil palm site planted after the fire. Both DOC quantity and quality differences are investigated between different land use types.

Keywords: Tropical peat swamp, Southeast Asia, Land use change

Absorption of radiocesium by fungi -estimation of soil hyphal distribution using stable isotopes-

*Takuya Hayashi[1], Naoki Okada[1]

1.Kyoto University Graduate School of Global Environmental Studies

Many studies after the Chernobyl nuclear accident in 1986 have reported that fungal fruit bodies accumulated higher ^{137}Cs concentration than other organic materials in forest ecosystem. Some of the studies pointed out soil hyphal distribution as one of the main factors determining ^{137}Cs concentration in fungi, but the viewpoint has not yet been examined well. We therefore have attempted multi stable isotopes (^{13}C, ^{15}N and ^{34}S) to examine the relationship between hyphal vertical distribution and ^{137}Cs concentration in fruit bodies.

Study site was a broad-leaved forest dominated by konara oak, mixed with fir, located at 20 km southwest from the Fukushima Daiichi Nuclear Power Plant, in Kawauchi Village, Fukushima Prefecture. Fruit bodies and soil core samples (down to 30 cm below the soil surface) were collected. After oven-dried, the fruit bodies were ground into powder, and isotope ratio (d^{13}C, d^{15}N and d^{34}S) and ^{137}Cs concentrations of samples were measured. Each soil core was separated into 2-cm long, sieved after air-dried, and isotope ratio and ^{137}Cs concentrations were measured. For ^{34}S measurement, sulfur was extracted from samples with Parr bomb and collected as precipitation of $BaSO_4$. Litter and humus layers were also collected, treated and analyzed as other samples.

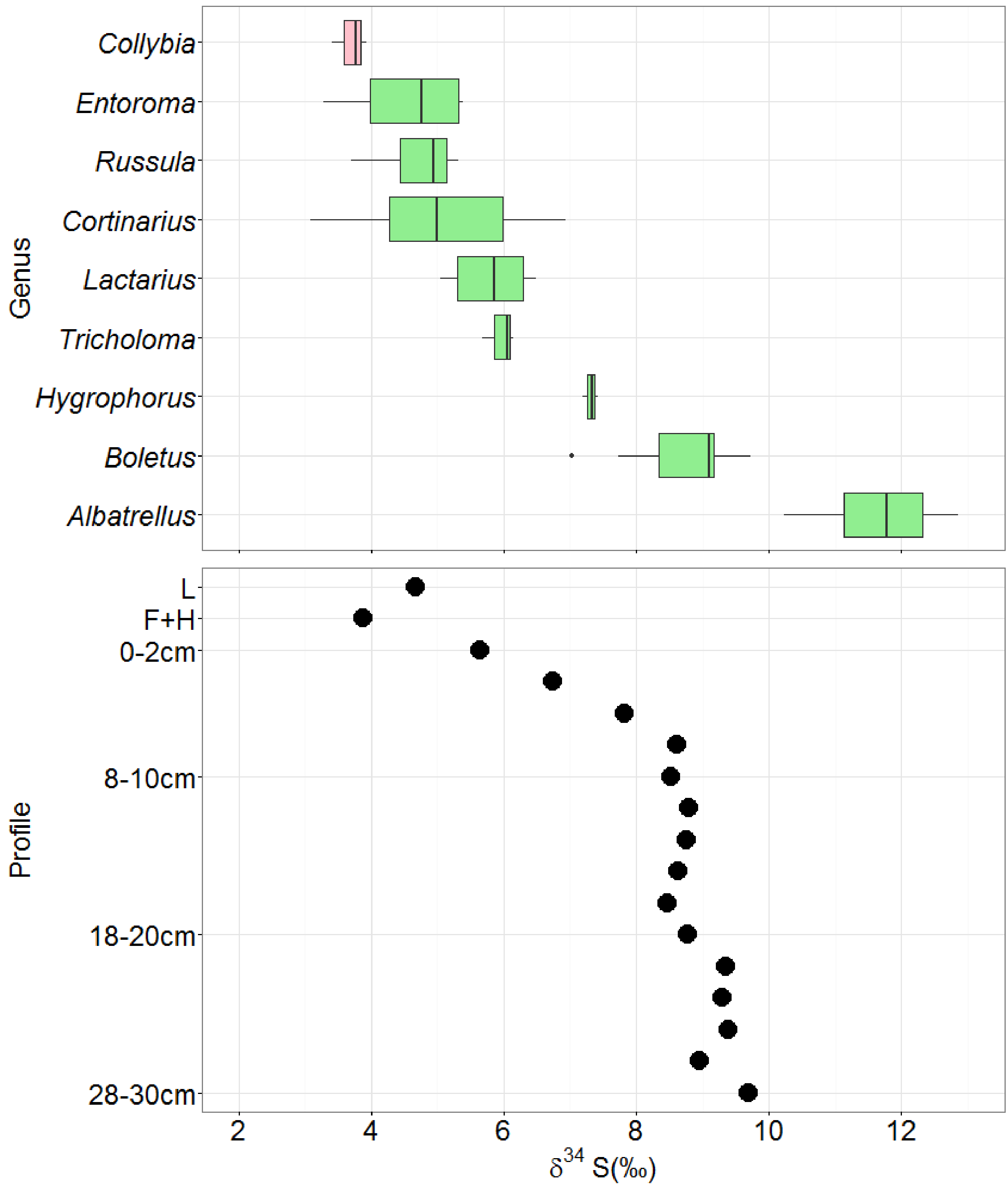
^{137}Cs concentration in saprophytic fungi was lower than that of ectomycorrhizal (ECM) fungi in average, but there was wide variation among genera and within genus in ECM fungi. Saprophytic fungi did not accumulate so much ^{137}Cs despite the high ^{137}Cs concentration in litter and humus layers. The vertical profiles of d^{13}C, d^{15}N and d^{34}S had a common trend; d values decreased with the depth. Saprophytic fungi showed most negative delta values for N and S isotopes, but most positive for C isotopes in the fungus groups. Genus-specific d values were observed for N and S isotopes, which variation was comparable to those observed for soil vertical profiles (figure).

Results of isotopes analysis suggested hyphal distributions of saprophytic and ECM fungi were completely different and that there was considerable difference in ECM fungi. Saprophytic fungi had d^{13}C and d^{15}N values close to those in organic layers after being adjusted based on the suggestions from previous studies about isotope fractionation. d^{34}S values in saprophytic fungi also were close to those in organic layers. The results of 3 isotopes indicated the hyphae of saprophytic fungi were restricted almost to soil organic layers. On the contrary, hyphal distribution of ECM had wide variations in mineral soil as indicated by genus-specific variations of d^{15}N and d^{34}S.

We did not observe significant relationships between hyphal distribution and ^{137}Cs concentration in fruit bodies. Saprophytic fungi showed lower ^{137}Cs concentration than ectomycorrhizal fungi regardless of shallow distribution of hyphae; and some genera of ECM fungi had similar values though they had different stable isotope ratios. These data are not consistent with the view that emphasized the relationship between hyphal distribution and ^{137}Cs concentration in fruit bodies. The view of soil-depth dependent ^{137}Cs accumulation by fungi needs to be re-examined.

Sulfur isotope seemed to be useful for estimating hyphal vertical distributions. Since the vertical profile of d^{34}S was similar to those of d^{13}C and d^{15}N, multi isotope approach will provide an effective tool for investigating biological processes in soil ecosystems. For further application to fungi study, isotope fractionation of sulfur and d^{34}S of available sulfur by fungi has to be studied.

Keywords: radioicesium, hyphae, stable isotope



δ^{34}S in fruit bodies and soil profile

Reconstruction of dog diet in Jomon period using carbon and nitrogen isotope analysis

*Takashi Gakuhari[1], Minoru Yoneda[2]

1.Kanazawa University, 2.The University of Tokyo

Dog is the earliest domesticated animal among other livestock. Dog’s role as companion animal and support for hunting is different from those of other livestock (e.g. goat, sheep, cattle and horse) which are mainly exploited for foods or labor as food. Because dog diet is similar to human diet in traditional subsistence, reconstructing dog diet is important to evaluate ancient human subsistence over time and space. A number of previous study show that isotope signature (carbon and nitrogen) obtained from ancient dog remains resemble to contemporary human remains.

Recently, a number of dog remain, especially for Jomon period, was excavated and identified in Japanese archipelago. However, the study of evaluating the isotope signature of Jomon dog is very little. Gakuhari et al. (2015) demonstrated the date of two buried dogs in Jomon period using directly radiocarbon dating of dog bones, so that two buried dog were dated to ca. 7300 calBP. In addition, the carbon and nitrogen isotope analysis of bone collagen indicated that the dietary characteristic of two buried dogs is similar to those of human remains from same site.

Here, we report new data of radiocarbon dating and stable isotope analysis from other dog bones in Kamikuroiwa rockshelter site and Higashimyo shellmound. We discuss the dietary characteristic of Jomon dog in Western Japan.

As results, other dogs in Kamikuroiwa rockshelter and 11 dogs in Higashimyo shellmoud showed very close ages to two buried dogs in Kamikuroiwa rockshelter, and assigned to the last Initial Jomon and the initial Early Jomon period. Although these results were not consisted with the previous archaeological interpretation, they are important because these dogs were one of the oldest evidence of certain Canis domestication in East Asia. In addition, based on carbon and nitrogen isotope analysis, we found that Kamikuroiwa and Higashimyo dogs could be discriminated to three populations with different isotopic patterns. This new finding is important to reconstruct ancient feeding culture of dog and human subsistence for Jomon period.

Keywords: Jomon dog, nitorgen

Food web analysis using stable carbon and nitrogen isotopic ratios: from the shallow to deep water in Toyama Bay

*Tomoki Otsuka[1], JING ZHANG[1], Inamura Osamu[2]

1.University of Toyama, 2.Uozu Aquarium

The isotopic ratios of stable carbon and nitrogen are useful to clarify the influence that the environmental changes (e.g. climate changes) on marine food web. The main aim of this study was to explore the food web in Toyama Bay, which has different water mass structure in the water shallower than approximately 200m and the water deeper than that. The aquatic sample of fishes and zooplankton inhabiting in the water shallower than 200m and in the water deeper than 200m, sinking particles, sedimentary organic matter and POM (particulate organic matter) were collected in Toyama Bay. We also collected sample of zooplankton and POM in Yamato basin, Central Japan Sea, and analyzed the stable carbon and nitrogen isotopic ratios of these sample. From the analysis results, we reached following findings. Aquatic creatures of both the shallow water and the deep water in Toyama Bay are located on a food web starting from POM and it is considered that phytoplankton produced near the sea surface is the primary producer. The δ^{13}C values of zooplankton collected in Toyama Bay were higher than those from Yamato basin. It is inferred that the growth rate of the phytoplankton in Toyama Bay is faster. The δ^{15}N values of the fish inhabiting in the deep water are higher than the fish inhabiting in the shallow water. In the deep water, there were scavengers and zooplankton whose δ^{15}N values are higher than those in the shallow water suggesting that they raised the trophic level. Furthermore, the δ^{15}N level of POM collected in Toyama Bay and Yamato basin were low with the average of 3.3 ‰, it is suggested that the δ^{15}N value of primary producers is low.

Keywords: Stable isotope, carbon and nitrogen, Food web

Geochemical diagnosis of groundwater flow system in the Ohno basin, Fukui prefecture

*Takanori Nakano[1], Kicheol Shin[1], Tamihisa Ohta[1], Yukiko Kusano[1], Ichiro Tayasu[1], Yoshihiro Yamada[2], Yoriko Yokoo[3], Maki Tsujimura[4], koichi ikeda[4], toshiaki kaeriyama[5], Akihiro Yamada[5], Kouhei Shitajima[5], Hiroyuki Ozawa[5]

1.Research Institute for Humanity and Nature, Inter-University Research Institute Corporation National Institutes for the Humanities, 2.Faculty of Agriculture, Kagawa University, 3.Faculty of Science and Engineering, Doshisha University, 4.Faculty of life and environmental Sciences, University of Tsukuba, 5.Municipal office of Ohno city

Shallow groundwater system is developed in the city area of the northwestern Ohno basin, Fukui prefecture. This groundwater, termed as city-GW, has been used for daily lives and industries, but the recharge area and flow system of city-GW remain unclear. For the sustainable use of city-GW, we determined multiple components for the surface water and well water collected by elementary pupils as environmental education.

The oxygen and hydrogen isotope ratios of the city-GW decrease from -8.1 ‰and -48 ‰to -9.1 ‰and -57 ‰toward the west. The city-GW is divided by an interval of 0.1 ‰in the d^{18}O value and 0.8 ‰in the d^{2}H value. As the groundwater level decreases from south to west, it is likely that each isotope envelope corresponds to the flow channel. This view is consistent with the spatial distribution of several dissolved ions such as Ca^{2+}; the high concentration of Ca^{2+} corresponds to the groundwater with a uniform d^{18}O-d^{2}H value (-8.9 - -8.8 ‰and -52 - -51.2 ‰). It is likely that the city-GW is recharged mainly from the southern alluvial fan where agriculture is active. This is consistent with the high concentrations of As and Mo in southeastern city-GW, suggesting the contribution of fertilizer.

The western city-GW is enriched in NO_3, indicating the source of N to be human activities such as sewerage. Several components (K, SO4) in the western city-GW is further subdivided into the north and the south by Mt. Kameyama, which is composed of granite. This result suggests that the geochemical nature of aquifer sediments in the north are different from that in the south by this mountain. This view is compatible with the analysis for the fluctuation record of water level at 14 monitoring sites in the city-GW area. We consider that Mt. Kamayama plays a role as a barrier for the southerly flow of the city-GW. Thus, the water quality mapping is effective for elucidating the flow system of groundwater.

Keywords: groundwater, Ohno basin, flow channel, stable isotope

Influence of volcanic ash in soils on Ca cycling in forest ecosystems - Using Sr isotopes to determine the contribution of volcanic ash to Sr and Ca in stream waters and plants in a granite watershed -

*Masami Koshikawa[1], Mirai Watanabe[1], Ki-Cheol Shin[2], Takanori Nakano[2]

1.National Institute for Environmental Studies, 2.Research Institute for Humanity and Nature

Ca in soil serves as a neutralizer of acids and is an essential nutrient for plants. The supply of Ca from weathering of rocks and its subsequent cycling is a key factor that controls the tolerance of forest ecosystems to acid deposition. In studies of the Ca cycle, stable isotopes of Sr have been used to trace Ca, because the chemical and biological behaviors of Sr resemble those of Ca. The Sr isotope method has been successfully applied, not only to investigate Ca cycling in acid-impacted ecosystems, but also to evaluate soil development processes and water-rock interactions in groundwaters and surface waters.

Volcanic ash, composed of small grains and with a large specific surface area, is present as a tephra layer in soils in Japan; this ash releases base cations rapidly owing to relatively quick weathering. However, it is difficult to estimate the distribution of volcanic ash on steep slopes, because it blends into soil and cannot be visually identified easily. Sr isotopes may be used to detect volcanic ash blended with soil and volcanic ash-derived Sr in plants and stream waters, because the stable Sr isotope ratio of volcanic ash is, in most cases, different from the ratio of the parent materials.

The aim of this study was to examine the role of volcanic ash in the Ca cycle in Japanese forest ecosystems. Soils, plants, and stream waters from a ridge, slope, and a valley were collected in a granite watershed on Mt. Tsukuba, central Japan. Rocks and atmospheric precipitation were also collected to represent Ca sources in the watershed. The $^{87}Sr/^{86}Sr$ ratios and element compositions of samples were determined to support identification of the origins of Sr and Ca in plants and stream waters.

The $^{87}Sr/^{86}Sr$ ratios were determined using a thermal ionization mass spectrometer (TIMS) (Triton; Thermo Fisher Scientific) at the Research Institute for Humanity and Nature. Acid digests of soils and plants, and filtrates of stream waters and bulk precipitation, were transferred to Teflon vials, heated until dry, dissolved in 2 M HCl, purified by cation exchange (Na et al. 1995), and subjected to TIMS analysis.

The $^{87}Sr/^{86}Sr$ ratios of soils on steep slopes and the valley floor ranged from 0.7110 to 0.7139, which indicates that the major source of Sr was the granite substrate ($^{87}Sr/^{86}Sr$ ratio 0.7120–0.7131). Soils on a ridge had lower $^{87}Sr/^{86}Sr$ ratios (0.7068–0.7072), indicating that they were mainly composed of volcanic ash materials released around 30,000 years ago from Mt. Akagi (0.7069). The $^{87}Sr/^{86}Sr$ ratio decreased and the concentrations of Sr (and Ca) increased in stream water with increased elevation from the valley bottom to the ridge, indicating that volcanic ash was the dominant source of both cations in the upstream area. The contributions of volcanic ash-derived Sr to upstream and downstream water were 50 % and 0–1 %, respectively. The $^{87}Sr/^{86}Sr$ ratios of plants were between those of the soils in which the plants were growing and those of atmospheric precipitation (0.7100). More than 74 % of the Sr in plants on the ridge, but less than 17 % in plants in the valley bottom, was volcanic ash-derived. The origin of Sr (and thus Ca) in stream waters and plants varied depending on the volcanic ash content in soils, which was significantly influenced by the site elevation. These results confirm that information about the Sr isotopic composition is useful for determining the sources and contributions of Sr and Ca in stream waters and plants, even in complex systems containing volcanic ash and bedrock weathered products.

Keywords: Ca sources, Sr isotopes, Atmospheric precipitation, Soil, Plants, Stream water

Provenance analysis of aluminosilicate detritus in marine environment by Sr-Nd isotopes: terrigenous input from the Amur River to the Sea of Okhotsk and the western subarctic Pacific

*Yoshihiro Asahara[1], Tomoki Yasuda[1], Ryo Ichikawa[1], Takeshi Nakatsuka[2], Hideki Minami[3], Seiya Nagao[4], Jun Nishioka[5]

1.Graduate School of Environmental Studies, Nagoya University, 2.Research Institute for Humanity and Nature, 3.School of Biological Sciences, Tokai University, 4.Institute of Nature and Environmental Technology, Kanazawa University, 5.Institute of Low Temperature Science, Hokkaido University

Provenance analysis of terrigenous material in marine sediment and suspended matter provides information about a paleo- and modern environment such as atmospheric and ocean circulations and climate change on continent. It also figures out a relationship between terrigenous input and biological productivity in ocean. Radiogenic isotopes such as strontium ($^{87}Sr/^{86}Sr$) and neodymium ($^{143}Nd/^{144}Nd$) in detrital (aluminosilicate) fraction of marine sediments and suspended particles are valuable indicators for identifying the geographical provenance of the terrigenous material (e.g. Dasch, 1969; Grousset et al., 1988; Asahara et al., 1999; Asahara et al., 2012). Because the isotope ratios in detritus, especially Nd isotope, are not significantly altered by the process of weathering, transportation and deposition.

Primary productivity is high in the Sea of Okhotsk (OS), most likely because of terrigenous input from the Amur River that includes dissolved matter and suspended matter. And the western subarctic Pacific (WSP) is one of High Nutrient Low Chlorophyll (HNLC) regions, and the most important source of iron in the WSP has been thought to be terrigenous matter from the Amur River together with the Asian dust (e.g. Nishioka et al., 2007). To reveal the transport and deposition processes of the fluvial materials in the OS, the Sr and Nd isotopes of the detritus in the surface sediments and suspended matter were investigated.

The regional variations of the isotopes indicate that the detritus has three main sources: Amur River detritus, with a high $^{87}Sr/^{86}Sr$ ratio (0.711–0.715) and relatively low ε_{Nd} value (–8 to –7); volcanic detritus derived from the Okhotsk-Chukotka volcanic belt to the north of the OS, with a low $^{87}Sr/^{86}Sr$ ratio (0.703) and high ε_{Nd} value (+7 to +8); and detritus from the sedimentary rocks north of Sakhalin Island, with a high $^{87}Sr/^{86}Sr$ ratio (0.709–0.710) and low ε_{Nd} value (–10 to –9). The results indicate that the Amur River detritus is dispersed across the northwestern continental shelf and further transported southward along the east coast of Sakhalin while flowing out of the shelf. The Amur River detritus flowing out of the shelf is mixed with the Okhotsk-Chukotoka volcanic material transported from the northern area of the OS by the Okhotsk Sea intermediate water (OSIW). The transport processes of the Amur River detritus in this area are supported by previous studies of turbidity that indicated that the dense shelf water (DSW) entrains resuspended sedimentary particles on the northwestern continental shelf and transports them to the OSIW. It is possible that the OSIW entrains the Amur River material, which then circulates in the OS and partly flows out to the WSP.

[Reference]

Yasuda, T., Asahara, Y., Ichikawa, R., Nakatsuka, T., Minami, H., Nagao, S. (2014) Distribution and transport processes of lithogenic material fromthe Amur River revealed by the Sr and Nd isotope ratios of sediments from the Sea of Okhotsk. Progress in Oceanography 126, 155-167.

Keywords: strontium isotope, neodymium isotope, marine sediment, the Sea of Okhotsk, Amur River

Spatial variation of neodymium and strontium isotope ratios of shellfish soft bodies in the coastal sea of eastern Tohoku District

*Saitoh Yu[1], Takanori Nakano[1], Ki-Cheol Shin[1], Katsuyuki Yamashita[2], Hiroshi Amakawa[4], Chikage Yoshimizu[1], Jun Matsubayashi[1], Yoshikazu Kato[1], Hiroyuki Togashi[3], Yosuke Amano[3], Yutaka Kurita[3], Noboru Okuda[1], Ichiro Tayasu[1]

1.Research Institute for Humanity and Nature, 2.Graduate School of Natural Science and Technology, Okayama University, 3.Tohoku National Fisheries Research Institute,Fisheries Research Agency, 4.Japan Agency for Marine-Earth Science and Technology

Sr isotope ratio ($^{87}Sr/^{86}Sr$) has been used as a geographical index of water and vegetation and a tracer of animal migration in terrestrial ecosystem. However, it has little power in marine ecosystem because of extremely homogeneous $^{87}Sr/^{86}Sr$ ratio in seawater. In contrast, the Nd isotope ratio ($^{143}Nd/^{144}Nd$) has a potential to become effective tracer of marine organisms because the $^{143}Nd/^{144}Nd$ ratio of seawater is known to show a variation in the area and depth in the ocean (Amakawa et al., 2004). Nonetheless, there is little report on the Nd isotope ratio for marine and even terrestrial organisms, largely due to the extremely low content of Nd in organisms, and the resultant poor awareness of the element in ecological fields.

In order to explore the potential of Nd isotope as a biogeographical tracer in marine ecosystem, we determined the isotope ratios of Nd and Sr in soft bodies of shellfishes, mainly oysters and mussels in the coastal sea of eastern Tohoku district. Our results show that the $^{143}Nd/^{144}Nd$ ratio of the shellfish has a wide variation (0.5123-0.5128), whereas the $^{87}Sr/^{86}Sr$ ratio lies in the narrow range (0.70912-0.70921), which is almost equivalent to the value of seawater. Although the shellfish has lower $^{143}Nd/^{144}Nd$ ratio than the exchangeable fraction of river sediments in the watershed of the coast, both ratios show a strong positive relationship ($r^2 = 0.75$). Further, the shellfishes have higher $^{143}Nd/^{144}Nd$ ratios than seawater in the northern Pacific, and the exchangeable $^{143}Nd/^{144}Nd$ ratio of river sediments has a weak negative relationship with the $^{87}Sr/^{86}Sr$ ratio of the associated river water ($r^2 = 0.37$). These results demonstrate that the shellfish contains Nd derived from the watershed rocks of the adjoining river and Nd from oceanic water. It is concluded that the Nd isotope ratio has promise as a geographical index of habitat and foraging site of marine organisms and an effective tracer of marine animal migration at least in coastal sea zones.

Keywords: Nd isotope ratio of organisms, soft bodies of shellfish, marine ecosystem

Geochemistry of Mesopotamian clay tablets and strontium cycle in West Asia

*Ryo Anma[1], Ki-Cheol Shin[2], Takanori Nakano[2], Yoriko Yokoo[3], Kosuke Asai[3]

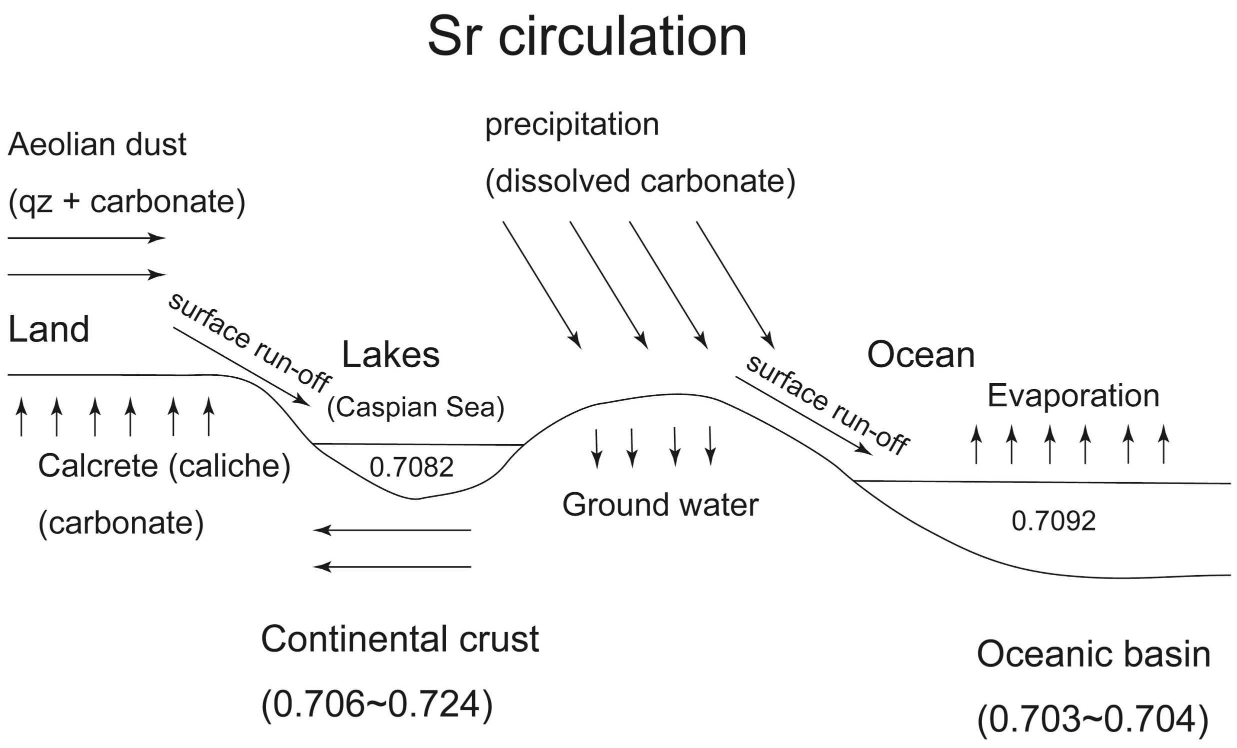
1.Faculty of Life and Environmental Science, University of Tsukuba, 2.Research Institute for Humanity and Nature, 3.Doshisha University

In this study, we present bulk chemical compositions and Sr-Nd isotopic ratios of cuneiform clay tablets ubiquitously excavated from Mesopotamia aiming to pin the place of origin by comparing characteristic physical feature of tablet clay and sediments from Meosopotamia. The obtained data were further compared with the compositions of meteoric water and river water in West Asia to discuss circulation of strontium and other elements, that involves interaction between rock/sediments, water and atmosphere.

Bulk chemical analyses on tablet clay samples revealed that they contain ~1% Na_2O, whereas CaO contents reached up to ~10%, implying that secondary Ca-carbonates were accumulated in pore spaces in original sediments during diagenesis or during preservation of the clay tablets. Ca-carbonate fills the pore-space under the optical microscope and was also detected by XRD analyses. The Ca-carbonate may have added artificially as a cementing material to achieve and maintain appropriate material properties for writing. TiO_2 (0.6%), Ni and Cr contents (> 100 ppm) are high as a felsic magmatic rock and imply some influence of mafic rocks, such as ophiolites. Samples from Nuzi (upstream of Tigris) has higher Ti/Fe ratio compared to Euphrates samples.

All the clay tablet samples show a weak Eu-anomaly and LREE enriched pattern, but they have different REE concentrations. Bulk Sr-Nd isotopic ratios were plot in a narrow range: 0.70835 to 0.70895 for ^{87}Sr /^{86}Sr isotopic ratio, 0.51237 to 0.51243 for ^{143}Nd /^{144}Nd. To evaluate the influence of Ca-carbonates in the tablet, we leached clay samples using acetic acid. Sr isotopic ratios of the leachate were approximately 0.7080 and plot in much narrower range. The obtained Sr isotopic ratio is similar to that of average Turkish meteoric water and Caspian Sea water (0.7082), but significantly lower than marine Sr isotopic ratios (0.7092). Iranian meteoric water has slightly higher value than Turkish meteoric water, but still lower than the marine Sr isotopic ratio. Sr isotopic ratio in the meteoric water is generally controlled by composition of aerosol (loess), especially soluble material such as carbonates. Our results indicate that Ca-carbonate cements (caliche or calcrete) formed at the surface condition have a great influence on the strontium circulation in the atmosphere of West Asia.

Keywords: Mesopotamia, Strontium cycle, clay tablet, cement, meteoric water, sediments


Sr circulation
Aeolian dust
(qz + carbonate)
precipitation
(dissolved carbonate)
Land
surface run-off
Lakes
(Caspian Sea)
0.7082
Calcrete (caliche)
(carbonate)
Ground water
Ocean
surface run-off
Evaporation
0.7092
Continental crust
(0.706~0.724)
Oceanic basin
(0.703~0.704)

Usefulness of strontium isotope composition for determining the geographical origin of Japanese horseradish (*Wasabia japonica*) (II)

*Takafumi Kamitani[1], Sachiko Nakamura[1], Akira Ito[1], Sayaka Ogo[1], Takuya Nishijima[2], Ki-Cheol Shin[3], Yasuhide Muranaka[1]

1.Shizuoka Institute of Environment and Hygiene, 2.Shizuoka Prefectural Research Institute of Agriculture and Forestry, 3.Research Institute for Humanity and Nature

Originally, the use of strontium isotope ratios (^{87}Sr/^{86}Sr) was restricted to geology and petrology, but they have been used as a particularly effective tracer of geographical food origin, as plants reflect the strontium isotope composition of the regionally based rock, soil, and water.

Japanese horseradish (*Wasabia japonica*) is cultivated in springs and streams located at the top of rivers, where dissolved element and isotopic compositions would reflect the geological characteristics with the exception of effects of atmospheric deposition and human activity. This study aims to evaluate the usefulness of ^{87}Sr/^{86}Sr for determining the geographical origin of Japanese horseradish.

We collected 97 horseradish samples and 95 water samples from 34 locations of major production areas in Japan: Shizuoka, Iwate, Nagano, Tokyo, and Shimane. These samples were subjected to trace elements and ^{87}Sr/^{86}Sr analyses. The ^{87}Sr/^{86}Sr values differed, based on the geological characteristics of their site locations, and the value of horseradish sample was well accorded with that of water sample in the same location. The horseradishes collected from Izu and Fuji regions in Shizuoka, where young volcanic rocks such as Quaternary basalts are distributed, had low ^{87}Sr/^{86}Sr (below 0.7040), whereas those from Nagano and Tokyo, where older rocks such as Mesozoic granites and accretionary complex are distributed, showed higher ratios (over 0.7095). We conclude that ^{87}Sr/^{86}Sr value of the horseradish allowed us to distinguish the production area clearly.

Keywords: discrimination of the geographic origin, Japanese horseradish (Wasabia japonica), trace element, strontium isotopic ratio, Shizuoka Prefecture