

## Environmental map project for Future Asia study

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As the third Earth Summit was held at Rio in June 2012, international cooperative research is indispensable for the solution of global environmental issues. ICSU (International Council for Science) has been implemented international cooperative programs on global environments of WCRP, DIVERSITAS, IGBP, and IHDP in 1980s to 1990s and started a new program as Future Earth (FE) in 2012 by integrating them. In the FE, Japan is expected to play a central role as a research hub in Asia. RIHN established Japan office as GEC (Global Environmental Change)-JAPAN and has stated to prepare for studies of Future Asia (FA).

FE-FA study aims to unify natural environmental studies on the atmosphere, hydrosphere, pedosphere, and biosphere and human-social studies as a transdisciplinary science. RIHN (Research Institute for Humanity and Nature) has been implemented domain-based projects on the human-nature interactions after its establishment in 2001, and started design-based projects for sustainable society after 2011 to meet this tendency on international environmental researches. In the realm of FA, a number of detailed information regarding human-environmental interactions and the wide recognition and use of this information in society is indispensable. Material behavior study is in a stage of exploring a new field to meet this FE-FA study.

All natural and artificial materials are composed of elements. As most elements are composed of stable isotopes (SI), which have a potential as a finger-print of element, elemental and SI data can be utilized as the basic information of transdisciplinary science. Isotope Ecology based on carbon and nitrogen isotopes has been developed in IGBP and DIVERSITAS researches. Isotope Hydrology based on hydrogen and oxygen isotopes has also been contributed to WCRP and IGBP researches. In the FE-FA studies, water, food, and health, which are sustainable basis of human body in addition to air and biota, are considered to be important. Accordingly, in order to foster the FA study, it is required to use biological elements and their SI used in ecological and hydrological studies as well as metal elements and their SI used in solid-earth sciences such as geology. RIHN hosts advanced SI instruments of both elements and aims to explore isotope environmental study based on the multiple information of both SIs.

For Future Asia, RIHN, as an inter-university organization, proposes a basic project to build the data base and map of elements and SIs of environmental materials by linking with universities and research institutes over Japan to Asia. This project aims to foster the resource development of researchers and users of SI, the promotion of RIHN's SI instruments, and the integration of SI methods for environmental study. A combined map of SI with other GIS information can enhance the reliability of environmental diagnosis based on precautionary principle. In case of Saijo city of Ehime prefecture, the environmental map was made with citizens to enhance their capacity building and is used for preparation of the groundwater law for its sustainable use. SI maps are called as ISOSCAPE in EU and USA and are utilized for food security and considered as a nation resource like DNA database. This map information is also utilized in paleo-environmental, archeological and other studies. We would like to discuss the potential of isotope environmental study toward FA study.

Keywords: future asia, environmental map, precautionary principle, isotope environmental study, human resource development, cooperation

## Platform of environmental isotope monitoring with science in society

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During Rio+20 on June 2012, many discussions for solving global environmental problems including ministerial level conferences have been made, however the conflict between developed and developing countries still exists, and the agreement between science and society have not reached yet. International Council of Science Union (ICSU), International Social Science Union (ISSC) and others have launched a new 10 years program Future Earth during the Rio+20 to take a step forward. The concepts of Future Earth are (1) co-design/co-production which means scientists will work together from the beginning with all stakeholders to share the problems and process of the solutions, (2) importance of regional aspect between global and local, (3) young scientists involvement, and (4) transdisciplinarity.

Global Environmental Change (GEC) Research in Japan made a platform to share information and knowledge for integration of GEC researches on 2011. A series of international meetings related to Future Earth program have been made in RIHN including 5th Belmont forum and Future Asia Symposium. Therefore it is now ready to extend the GEC-Japan platform to GEC-Japan/Asia platform for Future Earth in Asia.

Environmental isotope study is important for global environmental researches because it is a powerful tool and method to visualize the linkages between many environmental issues such as water, food, health etc. Integration of the problems is the first step and the key for human well-being and sustainable society, and the environmental isotope study with co-design and co-production may be one of the key transdisciplinarity ways for integration of our knowledge.

Keywords: future earth, co-design/co-production, environmental isotope

## On the information of ecosystem and biodiversity obtained from isotope ratios of living organisms

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Conservation of biodiversity is a key issue in a changing world. However, it is well known that biodiversity assessment itself requires much effort. Several levels are recognized in describing biodiversity: e.g. genetic, species, landscape and ecosystem level. Various indicators are proposed to describe the state of biodiversity.

Inland water ecosystems have been dramatically altered by recent human activities. Human impact including land use change has great influence on the ecosystems. Stable isotope ratios of nutrient in a river are indicators of nutrient status of a watershed. Stable isotope ratios of living organisms are one of the indicators to study a functional position (trophic position, dependency of food sources, nutrient status of the environment, etc.) of the organism, and thus provide useful information about the relationships between the organisms. Furthermore, stable isotope ratios of stored specimen contain information of the past environment; for example, trophic state of each watershed.

Various techniques are being applied to the monitoring of biodiversity and the isotopic signatures are potential tools. Nitrogen isotope ratios of individual amino acids are promising tools for determining trophic level of each organism, but application to ecosystem level study is limited. I present some results obtained from the project Stable isotope indicators for evaluating ecosystem functions of biodiversity of The Environment Research and Technology Development Fund D1102.

Keywords: isotope ratio, information, ecosystem, biodiversity

## Isotope ecology of human diet

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A method for precise estimation of trophic position was recently developed using analysis of the nitrogen isotopic composition of amino acids (McClelland and Montoya, 2002; Chikaraishi et al., 2009). This method is based on the empirical observations that difference in the  $\delta^{15}\text{N}$  values of glutamic acid and phenylalanine in a given organism is a simple function of trophic position of the organism. The method has an advantage over the commonly used bulk isotope method in that it is not influenced by the temporal variations in  $\delta^{15}\text{N}$  value of primary producer or substrate. The method has been proven useful for estimating the food sources of both aquatic and terrestrial organisms (Popp et al., 2007; Chikaraishi et al., 2009, 2010; Styring et al., 2010). Because isotopic relationship among amino acids is different between aquatic and terrestrial organisms, diets of omnivores like human cannot be uniquely solved even in this methodology.

Nevertheless, we have applied the nitrogen isotopic analysis of amino acids to the modern human nail. Our results suggested that diets of modern human are much less relied on marine organisms relative to coastal ancient human, as expected (Naito et al., 2012). Reflecting denitrification in the modern over-fertilized soil, phenylalanine from modern human is somewhat enriched in  $^{15}\text{N}$  relative to that from ancient human (Naito et al., 2010). We are currently measuring terrestrial protein source of modern human diet (e.g., beef, chicken, pork, etc.) for better constraining the interpretation of the isotopic signature. Among modern human, phenylalanine from modern Japanese is somewhat depleted in  $^{15}\text{N}$  while glutamic acid is enriched in  $^{15}\text{N}$  relative to European people on average, reflecting more fish in their diets. In this presentation, I will overview the analytical results of modern human nail and try to nail down the human energy source from the natural energy flow.

Keywords: Human, Diet, Amino acid, Nitrogen isotopic composition

## Analysis of stream food webs using stable nitrogen isotope ratios of amino acids

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Food web studies are a central theme in ecology that relate to material and energy dynamics in an ecosystem. In the stream ecosystem, which connects terrestrial and aquatic ecosystems, stable carbon isotope ratios are sometimes too variable to estimate food sources for organisms. Though stable nitrogen isotope ratios are used to estimate trophic levels (TLs) of organisms, the isotopic enrichment factor per TL is known to be different across various kinds of organisms. For the purpose of better understanding of food web structure in stream ecosystems, a novel technique is indispensable.

Recently, stable nitrogen isotope measurement of individual amino acids (SIAA) has been developed and enabled researches to estimate TLs of organisms in a simple food chain system. In the amino acid metabolism, glutamic acid experiences deamination and transamination, which consequences great isotopic enrichment per TL. On the other hand, phenylalanine conserves its amine during metabolism, resulting in little isotopic enrichment per TL. Therefore, the TLs of organisms in a simple food chain can be determined by following equation (Chikaraishi et al. 2009):

$$TL = (\delta^{15}N_{Glu} - \delta^{15}N_{Phe} + \beta) / 7.6 + 1$$

where  $\delta^{15}N_{Glu}$  and  $\delta^{15}N_{Phe}$  are stable nitrogen isotope ratios of glutamic acid and phenylalanine of an organism, respectively, and  $\beta$  is the nitrogen isotopic difference between phenylalanine and glutamic acid of a primary producer. Since aquatic and terrestrial primary producers have a distinctive  $\beta$  value, a mixing ratio of resources that are derived from both aquatic and terrestrial food chains should be considered to estimate the TLs of organisms in complex food webs. So far, it is still unknown whether the SIAA technique is applicable to understand complex food web structure or not.

In this study, we aimed to analyze stream food webs using the SIAA. In November 2011 and May 2012, we collected stream macroinvertebrates and fishes, together with their potential food sources (periphyton: aquatic primary producer; C3 plant litter: terrestrial primary producer) from upper and lower sites of the two streams, which have contrastive riparian landscapes. Amino acids of organisms and food sources were purified by HCl hydrolysis, followed by Npivaloyl/isopropyl derivation. The SIAA were determined by isotope ratio mass spectrometry coupled to a gas chromatograph via combustion and reduction furnaces.

Stable nitrogen isotope ratios of glutamic acid and phenylalanine identified that the TLs of primary producers (periphyton and C3 plant litter) and primary consumers (e.g., mayfly and caddisfly larva) were 1 and 2, respectively. On the other hand, the TLs (assuming only aquatic food chain) of secondary and tertiary consumers (e.g., stonefly and dragonfly larva and fishes) were lower than those expected by their feeding habits. Since aquatic and terrestrial primary producers have a distinctive  $\beta$  value, we calculated a mixing ratio of both aquatic and terrestrial resources for individual organisms prior to the TL calculation. The estimated TLs (assuming source mixing) of secondary and tertiary consumers roughly corresponded to their feeding habits, suggesting that their diets were derived from both aquatic and terrestrial food chains.

Our result suggests that the SIAA technique is applicable to analyze stream food webs, and perhaps other complex food webs as well. In the presentation, we will add further discussions on the TLs of secondary and tertiary consumers in stream food webs, as well as comparisons of the results among sites, streams, and seasons.

### References

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Keywords: periphyton, terrestrial C3 litter, aquatic insect, fish, food source, trophic level

## Tracing the Geographical Origin of Food Using Stable Isotope Analysis

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The types and amounts of available foods have been expanding globally, and consumers can now obtain products from all over the world. However, in recent years consumers have experienced numerous negative incidents such as unsafe levels of residual pesticide in exported fruits and vegetables, which has prompted greater awareness of geographical origin and chemical levels in food. Such concerned consumers prefer to buy foods directly from farmers even if the products are more expensive than exported equivalents. The increased demand for reliable food in the interest of better health and nutrition has greatly influenced industry practices. A valid traceability system to ensure the safety and high quality of food has been proposed. Regulations on food safety standards focus on quality control, process verification, labeling, and traceability. In accordance with law, packaging must be labeled to indicate product information such as cultivar, cultivation area, and year of production. However, it remains very likely that packages continue to be incorrectly labeled, either accidentally or intentionally. Thus, there is a need for a simple analytical method for checking the authenticity of food products.

Multi- stable isotope analysis has also become an important tool for determining the provenance of foods. Stable isotope analysis has become particularly useful in addressing authenticity problems. This method has been widely used to trace the origin of organic materials in various fields, such as geochemistry, biochemistry, archaeology, and petroleum chemistry. Generally, the isotopic compositions of plant materials reflect the isotopic compositions of source materials (e.g., CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>4</sub>, and NO<sub>2</sub>) and their assimilation processes as well as growth environments. For example, the carbon isotopic compositions of plants depends on fractionation during diffusion of CO<sub>2</sub> into the leaves and the subsequent photosynthetic metabolism and water use efficiency, suggesting that carbon isotope discrimination is associated with well-watered conditions. The nitrogen isotopic composition of plant materials mainly depends on soil nutrition. The oxygen isotopic composition mainly reflects that of local groundwater such as precipitation and meltwater. The sulfur isotope ratios are influenced by several factors such as fertilizers, sea spray, volcanic emissions, or lithology. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio in soils and the plants growing thereon depend on the geological age of the underlying rocks. Therefore, the Sr isotopic ratios of plants can provide site-specific signatures depending on the geologic history of the area. On this basis, isotopic compositions have been used to investigate the authenticity of food materials. For example, the adulteration of honey and juice can be identified by differences in the carbon isotopic compositions between authentic and adulterated products. Moreover, the geographical origin of food materials such as meat, dairy products, wine and cereal crops can be traced by using natural variations of the isotopic compositions. We review the applications to the discrimination of geographical origins of foods.

Keywords: foods, geographical origin, stable isotope analysis

## Determination of the Geographic Origins of Grains with Strontium and Lead Isotope Ratios and Multielement Concentrations

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### Introduction

The importance of food authenticity is increasing due to expanding global trade and economy. Nowadays geographical identification of food materials are labeled in many countries because the information is very important to consumer. Geographical identification can be useful not only to help consumers in their selection of foodstuffs but also for branding strategy purposes. However, such identification has sometimes been fraudulently labeled for financial gain. Therefore, techniques to prevent consumers or producers from suffering financial damage are required.

The techniques determining the geographical origin of raw materials of food or foodstuff itself have previously been developed. However, conventional methods have defects that an enormous database for each target food item is required, and cannot avoid some level of discrimination error. So, we examined to develop a more reliable technique, which improves these defects, utilizing isotopic ratios of Sr and Pb. As features of these isotopic ratios, plant-available Sr and Pb in soil are absorbed by plants without isotope fractionation. Thus, the geographical origin of a crop can be estimated from these isotopic ratios in soil and vice versa. Since crops grown under the same soil and water conditions at the same area have the same isotopic ratios of these elements, a large database is not required for each target item, which makes it possible to determine the geographical origin of a new crop. Furthermore, since Sr and Pb isotope ratios feature small variations in the same production area less than factors used in other techniques, this technique possesses high reliability.

We applied the method determining Sr and Pb isotopic ratios in cereal grains<sup>1),2)</sup>, including polished rice of very low Pb concentration, to determination of their production countries. Multielement concentrations were also used for this purpose to achieve sufficient origin determination.<sup>3)</sup>

### Samples

Cereal grain samples were rice (*Oryza sativa*), barley (*Hordeum vulgare*), wheat (*Triticum aestivum*), and buckwheat (*Fagopyrum esculentum*)<sup>1),2)</sup>

Sample was digested by acid using a sample digestion system (SCP Science) and dissolved in 0.05 M HNO<sub>3</sub>. Strontium and Pb in the solution were separated and concentrated by extraction chromatography with Sr resin (Eichrom Technologies). <sup>87</sup>Sr/<sup>86</sup>Sr and Pb isotopic ratios in the sample solutions were determined with a double focusing inductively coupled plasma mass spectrometer (ICP-MS) (Element2, Thermo Fisher Scientific). Uncertainties of this method were around 0.06% for <sup>87</sup>Sr/<sup>86</sup>Sr and 0.2% for Pb isotopic ratios (<sup>204</sup>Pb/<sup>206</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb, <sup>208</sup>Pb/<sup>206</sup>Pb) as 1s. Multielement concentrations were also determined with the same instrument.

### Results

Many of <sup>87</sup>Sr/<sup>86</sup>Sr values of grains grown in Japan were within 0.703-0.710 with some outlier samples and tended to be lower values than other countries intended in this study. The grains in northeastern region, around Izu Peninsula, and Oita prefecture in Japan tended to have lower values than other regions in Japan. The grains grown around Lake Biwa tended to have higher values than other regions. Different grain species grown in the same area had almost the same <sup>87</sup>Sr/<sup>86</sup>Sr values. We made a <sup>87</sup>Sr/<sup>86</sup>Sr map of grains, which will be applicable to other agricultural products, using obtained data. Lead isotope compositions of Japanese grains were within a small area. Each country showed a specific isotopic composition. Some grain samples grown in certain countries could be determined the countries by only the isotopic compositions, but other grain samples could be determined the countries by using multielement concentration data as well.

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Keywords: St, Pb, isotope ratio, geographic origin, grain, ICP-MS

## stable-isotope geochemical map of metallic elements with rapid chemical purification technique

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Isotope ratios of light elements (O, C, N, H, and S) have been applied to various geochemical and ecological samples to understand their cycles in the geosphere. Samples are usually prepared in gaseous form to determine their precise isotope ratios by gas source MS. In contrast, precise determination of isotope ratios of other poly-isotopic elements, so called as metallic elements, had been difficult by conventional solid source MS, especially for the detection of their mass-dependent isotopic fractionation.

However, rapid and precise determination of isotope ratios is nowadays possible for metallic elements with ICP mass spectrometry (ICP-MS) with a multiple collector array. The most important advantage of this MS against conventional MS is its robustness to remaining matrix elements, and large sample throughput can be achieved with rapid chemical purification techniques for analytes. This new approach can be applied to understand the origin of metallic elements in the geosphere as isotope geochemical map. Potential applications of their isotope ratios will be outlined in this presentation as well as their purification techniques.

Keywords: ICP-MS, isotope ratio, heavy elements, geochemical map



## Strontium isotope map of terrestrial water of the Japanese Archipelago based on the geological model

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Strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) of terrestrial water exhibit regional variations in relation to geology of catchments. Since these variations can be reflected to the values of plants and animals, strontium isotope ratios are useful in many fields, such as geochemistry, ecology, environmental science, and archaeology. We made strontium isotope maps generated from bedrock and water model based on a geological map using a GIS. Strontium isotope map of bedrock was calculated using a strontium isotope evolution model of crust, which is a function of abundances of rubidium and strontium, and the age of the rocks. Bedrock model gave large geographical variations of the strontium values (0.704-0.724). Strontium isotope ratios of water were calculated using concentrations of strontium in rocks, estimated weathering rates, and flux and flow direction of waters. The results of water model correlated well with the values of bottled waters that were collected from the Japanese Archipelago (170 samples: 0.704-0.712). This indicates that strontium isotope ratios of terrestrial waters can be estimated from the bedrock and water model.

Keywords: strontium isotope ratio, rubidium, GIS, isoscape, georoc databas

## Water quality map in the southern part of Mt. Fuji for establishment of groundwater governance

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The local ecosystems in the area of Mt. Fuji have been supported and characterized by the large amount of groundwater. Human being has also received much benefit from the groundwater and spring not just for domestic and industrial use but for local traditional culture concerning water. The stable use of groundwater is important for the sustainable development of this area, and it is necessary for developing strategy for groundwater conservation and use to elucidate the mechanism of groundwater flow in the basin.

We summarized the quality of spring waters in the southern part of Mt. Fuji in map for the purpose of estimating the origin and recharge area of these springs. Study area is the foot of Mt. Fuji in Shizuoka Prefecture, including surrounding mountains (e.g. Mt. Ashitaka, Mt. Hakone, Tenshu Mountains). We collected 133 spring water samples from the study site in early winter (November to December 2009). We are also monitoring the quality of 35 spring water and 17 precipitating water samples. Samples were analyzed for major ions, trace elements and hydrogen, oxygen, and strontium isotopes. Geographic Information System was used to make the water quality map, which also contains information of e.g. geology, vegetation, land use and social conditions, in the study area.

The concentrations of Cl and Na of the monthly precipitation were higher during winter, whereas lower during summer and autumn. The isotopic composition of oxygen ( $d^{18}O$ ) and hydrogen ( $dD$ ) of the monthly precipitation did not vary seasonally, but  $d^{18}O$  and  $dD$  values became lower at high altitude. The deuterium-excess values ( $d$ -values) of precipitation were higher at winter period and lower at summer period. In Mt. Fuji area, the snowfall in winter as well as the rainfall in summer is supposed to be formed by water vapor from the Pacific Ocean, so the seasonal fluctuation pattern of  $d^{18}O$  and  $dD$  values would result from the seasonal difference in forming process of water vapor at the Pacific.

Relatively low  $d^{18}O$  values were observed in the foot of Mt. Fuji except for spring waters in the southwestern foot. Low  $d^{18}O$  values indicate that the groundwater was recharged at high altitude, which is estimated between 1,000 and 1,800 meters above sea level. The  $d$ -values tended to increase ( $>14$ ) at the springs which showed low  $d^{18}O$  values, probably because the winter precipitation amount including snow is large in the recharge area.

The concentrations of oxyanion-forming elements (e.g. V, P, As) are negatively correlated with  $d^{18}O$  values. The high concentrations are interpreted as resulting from the elution of the elements by long-term interaction between rock and groundwater recharged at high altitude of Mt. Fuji. Conversely, high concentrations of  $NO_3$  were observed at the springs in the southern foot of Mt. Ashitaka and the southwestern foot of Mt. Fuji, where high  $d^{18}O$  values were observed. We consider the high concentrations of  $NO_3$  to be of agricultural origin, because tea plantation predominates in the area. The spring waters in the basaltic rock area (Mt. Fuji, Mt. Ashitaka and Mt. Hakone) display low  $^{87}Sr/^{86}Sr$  values under 0.7040. In contrast, the  $^{87}Sr/^{86}Sr$  values of spring waters in sedimentary rock area (Tenshu Mountains) are much higher (over 0.7055). In the monitoring data of spring water in the south foot of Mt. Fuji, high concentration of major ions and high  $^{87}Sr/^{86}Sr$  values were observed between October and December, while low concentration of V and large quantity of spring water were observed in the same term, probably because of the difference in layers of original groundwater.

As described above, we can clarify the regional characteristics of spring water through the analysis of stable isotopes and dissolved elements. Mapping the information of water quality with GIS made it possible to analyze factors which contribute to the regional variations and, in addition, to form a basis for building a groundwater governance in the study area.

Keywords: Mt. Fuji, spring, water quality, GIS, groundwater recharge, groundwater governance

## History of Alaskan mountain glaciers analyzed by detrital Nd and Pb isotopes

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Changes in atmospheric CO<sub>2</sub>, ocean circulation, the extent of the cryosphere, or a combination of these boundary conditions are believed to have caused the Late Pliocene climate Transition (LPT, ~3.6 to 2.6 million years ago), characterized by development of more glaciated conditions. Yet, cryospheric evolution in northern high latitudes is not constrained well enough to properly understand the effect of high latitude cryosphere dynamics on LPT. Here, we present 4.1-million-year neodymium (Nd) and lead (Pb) isotope records of detrital sediments?tracers of sediment provenance?from the Bering Sea (Hole U1341B). We show that Bering Sea detrital sediments represented a mixture of sediments from the Aleutian and Alaskan sectors. During glacial and deglacial periods the contribution of Alaskan-origin clastics exceeds 50% due to melting of Alaskan glacier. We also found a stepwise increase (>~10%) in Alaskan-origin clastic supply beginning at ~4.1 Ma, implying that the northern high latitude cryosphere had started to grow 1 Ma before the major onset of Northern Hemisphere Glaciation. The early growth of Alaskan glaciers might be a result of combined effects of decreased atmospheric pCO<sub>2</sub> and enhanced moisture supply due to stagnation of Pacific meridional circulation induced by the Panamanian seaway closure during the early Pliocene.

## Applications of mercury isotope analysis for identifying Hg source and tracking Hg transformations in environment

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Mercury (Hg) concentration in environment has increased since the Industrial Revolution due to anthropogenic emissions such as coal burning and wastes from consumer products. Hg is a global threat to human and environmental health because it is environmentally persistent, tends to be bioaccumulated, and a highly toxic element. International community plans to reduce the Hg emission to environment by signing the Minamata Convention by the end of 2013, and many studies are still required in order to understand details of Hg biogeochemical cycle and develop a proxy for distinguish anthropogenic from natural sources. It has been recognized that Hg isotope analysis is an important new tool for identifying Hg source and tracking Hg transformations in the environment. Hg isotope ratios are varied in different Hg reservoirs and fractionated by a number of biogeochemical processes, including speciation, biomagnification, and redox cycling. For example,  $\delta^{202}\text{Hg}$  values of Hg-containing sulfides from Hg ores in Japan are mostly negative, and those from an active submarine hydrothermal region in Okinawa trough are mostly negative as well. On the other hand,  $\delta^{202}\text{Hg}$  values of tuna fishes are mostly positive, which indicates that there is a relatively large isotopic fractionation from a source to the fishes. Moreover, odd-even Hg isotope ratios in biological samples often indicate a mass independent fractionation (MIF) induced by photoreduction. Hg isotope analysis is, therefore, a promising analytical tool for distinguishing Hg in environment, helps us understand details of global Hg biogeochemical cycles, and enable us to track Hg in environment.

Keywords: Mercury, Environmental Pollutant, Mercury Isotope, CV-MC-ICP/MS

## Development of atmospheric pressure sampling device for direct elemental analysis using LA-ICP-Mass Spectrometry

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Combination of laser ablation sample introduction technique and ICP-mass spectrometry (LA-ICPMS) has been widely used for element and isotopic analyses for various geochemical and biochemical samples [1]. The laser ablation utilising shorter wavelength or shorter pulse duration can minimise the elemental fractionation during both the laser ablation and ionisation processes, and the resulting precision for elemental and isotopic ratio measurements has been successfully improved. One of the great advantages to use the LA-ICPMS technique is that the analysis can be made under the atmospheric pressure, and therefore, this technique can be applied for the elemental analysis of the wet samples including cell or tissue. However, it should be noted that the sample was located inside the cell to improve the transmission efficiency of the sample aerosol from the sample to ICP ion source. This suggests that the elemental analysis could not be achieved for the large-sized sample or continuously delivering samples. To overcome this, we have developed direct sampling technique using the laser ablation under the atmospheric pressure conditions using a gas exchange device (GED) [2,3]. Laser ablation was carried out under the atmospheric air, and the laser induced sample aerosols were extracted and collected with air using a diaphragm pump. The carrier gas was converted from the air (N<sub>2</sub> and O<sub>2</sub>) to Ar through the semipermeable filter, and the sample aerosol was introduced into the ICP in the same manner with the conventional laser ablation setup. To minimize the pulsation of the gas flow, which causes serious reduction in the analytical sensitivity of ICPMS, the glass capillary tubing (i.d. 0.4 mm) was adopted between the diaphragm pump and gas exchange tubing.

In this study, we have monitored the signal intensities of <sup>208</sup>Pb, <sup>232</sup>Th, <sup>238</sup>U in order to test the collection yield of the sample aerosols. Signal intensities of <sup>232</sup>Th<sup>16</sup>O and <sup>238</sup>U<sup>16</sup>O were also monitored to test the production ratio of oxide signals, which could reflect the amount of residual O<sub>2</sub> in Ar carrier gas through the gas exchange process. With the simple extraction setup using a cut-off tubing and diaphragm pump, the resulting signal intensities for Pb, Th and U were almost one order of magnitude lower than those achieved by the conventional laser ablation setup (i.e., cell configuration). This indicates that the laser induced sample particles could not be collected by the simple extraction using the cut-off tubing. Although He was flushed onto the ablation pit toward the collection tubing (push-pull setup) in order to improve the collection efficiency, the signal intensities for Pb, Th and U became rather lower than the simple extraction setup. This could be due to deterioration in the evacuation rate of the diaphragm pump because of lower viscosity of He. In contrast, the production ratios for ThO<sup>+</sup>/U<sup>+</sup> and UO<sup>+</sup>/O<sup>+</sup> became lower when the higher flow rate of He flushing was employed. The lowering of the oxide production could be explained by the possible dilution of O<sub>2</sub> in air by He flushing. Principles and advantage of the present laser sampling technique and versatility in elemental mapping analysis will be demonstrated in this presentation.

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Keywords: Atmospheric Pressure Sampling, Air Sampling, Gas Exchange Device, Laser Ablation, LA-ICPMS Technique

## Variability of stable isotopes in precipitation based on the result which observed at 6 sites for long period

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The stable isotopes of oxygen and hydrogen are useful to consider the water cycle and groundwater flow, because these isotopes do not react with a rock under the normal condition and isotopic ratios are constant with the time. Additionally, water (H<sub>2</sub>O) consists of Oxygen and Hydrogen, so stable isotopes of oxygen and hydrogen are used well for hydrological studies.

Because the stable isotopes of oxygen and hydrogen are affected by the elevation, latitude, distance from the coast and air temperature, these isotopic ratios are different in each site. And these isotopic ratios of same month are variable if the year is different. It is also thought that the global warming will influence the stable isotopic values. Therefore, to grasp the characteristics of long term variation of stable isotopes in precipitation is objective in this study.

The observation sites are Tsukuba City (from 1992 to 2006), Ogawa Town (from 1993), Utsunomiya City (from 1998), Kumagaya City (from 2007), Matsumoto City (from 2009) and Kyoto City (from 2009 to 2010). In the site of Matsumoto and Kyoto, precipitation samples have been collected at several points for confirming the altitude effect. The monthly precipitation samples have been collected at each site. The stable isotopes of oxygen and hydrogen were analyzed for all samples.

The seasonal variation of stable isotopes dose not appear clearly, however, the isotopic ratios are relatively low in autumn season which is affected by the typhoon and autumnal rain front, and also low in January and February. From the result of study of Yabusaki and Tase (2005), it is considered that the isotopic ratios are influenced by the air temperature in winter season and influenced by the precipitation amount from summer to autumn season. Because the isotopic ratios are relatively low in the observation site of Matsumoto City, the altitude effect and inland effect is confirmed. Thus the variation of stable isotopes is almost same in each observation site, so it is indicated that the source of water vapor which is origin of precipitation is same at the site of Kanto and Chubu district. The variation range of isotopic ratios in precipitation is relatively small from April in 1998 to January in 2000 and from September in 2007 to November in 2011. It may be affected by the precipitation amount or air temperature. The variation range of isotopic ratio is Utsunomiya City < Ogawa Town, Tsukuba City < Matsumoto City. Because the air temperature is relatively low and the snowfall is relatively large in Matsumoto City, it is thought that the variation of isotopic ratios is greatly. The seasonal variation of d-excess values, that is low in summer season and high in winter season, appears obviously. Therefore, it is assumed that the prevailing source of water vapor is Pacific side in summer season and Japan Sea side in winter season. According to the long term variation of the stable isotopes, air temperature and precipitation amount, the air temperature is rising gradually, however the isotopic ratios are decreasing gradually. As the reason of the decrease of isotope ratios, it is considered that the isotopic ratios are related to rainfall intensity.

Keywords: precipitation, stable isotopes, long term variation of stable isotopes

## Altitude effect of isotope ratio of oxygen and chemical constituents of precipitation collected on the Mt. Tateyama

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Observation of precipitations on the slope of mountain is one of a method to reveal the behaviors of water circulation and chemical constituents in the upper atmosphere.

Altitude profiles of oxygen isotope ratios and concentrations of chemical constituents in rain water were analyzed by using precipitation samples collect at nine stations on the Midagahara platform located at west side of Mt.Tateyama, one station at Shomyo valley and one station at Toyama city, Toyama Prefecture, Japan. Altitude of the highest sampling station (Murododaira) on the Midagahara Platform is 2450 m above sea level, and the lowest sampling station (Bijodaira) on that is 970 m above sea level.

The feature of the Midagahara Platform is that gentle slope with constant angle continues from Bijodaira as west end of the Midagahara Platform to Murododaira as east end of that. Distance between Bijodaira and Murododaira is about 13 km.

Altitude effects were observed in the precipitation amount. Precipitation amount were increased with increase in height above sea level of sampling stations. Isotope ratios of oxygen of precipitation water was decreased in linear functions with increase height above sea level of sampling stations. Decrease ratios of isotope ratio of oxygen were from -0.0013 per mill/m to -0.0025 per mill/m.

Concentrations of Na<sup>+</sup> in precipitation were decreased with increase in height above sea level of sampling stations. However, concentrations of Na<sup>+</sup> in precipitations became similar at sampling stations over 2000 m above sea level. Altitude effects were also observed in concentrations of NO<sub>3</sub><sup>-</sup> and nssSO<sub>4</sub><sup>2-</sup> in precipitations. However, decrease ratios of concentrations with increase altitude were higher in NO<sub>3</sub><sup>-</sup> concentrations than that of nssSO<sub>4</sub><sup>2-</sup> concentrations. Analysis of the difference of expressions of altitude effect might reveal the source of water vapor, chemical constituents in precipitation water.

Keywords: altitude effect, oxygen isotope ratio, sodium ion, nitrate ion, non sea-salt sulfate ion, Mt.Tateyama

## Origin of atmospheric lead around Omura Bay, Nagasaki, Japan

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Recently, air quality in Japan is suffering from pollution from other countries including China. Atmospheric heavy metals such as lead are revealed to originate from other countries (e.g., Mukai et al., 1999). North of the Kyushu Island, where Omura Bay is located, is an appropriate area to directly observe such cross-border air pollution. Aerosol particles were sampled with temporal high resolution from May 2011 to August 2012 on the eastern hill of Omura Bay. In order to assess the responsibility of the cross-border pollution for the anthropogenic metals in the air around this area, we measured the trace element concentration and Sr-Pb isotope ratios of 1M-HCl leachates and the residues of the aerosol samples. The residues can be considered as silicate mineral particles of natural origin, while the leachates represent soluble component of aerosol, such as mist, fume, and sea spray. The leachates contain 8-18 times the amount of Zn, Cd, and Pb that the silicates do. This suggests that these elements are of anthropogenic origin.

The <sup>87</sup>Sr/<sup>86</sup>Sr of silicate components is high in winter and spring (0.712-0.714), and is lowest in Summer (0.706). These high and low ratios are typical of Asian dust and Japanese local sediment, respectively. The seasonal change is considered to reflect the difference of dominant wind direction between winter and summer. <sup>87</sup>Sr/<sup>86</sup>Sr correlates with soluble Cd and Pb ( $r > 0.7$ ), but not with Zn ( $r = 0.28$ ). Anthropogenic Pb and Cd seem to increase their flux with the contribution of Asian dust to the mineral particles. However, the Pb isotope ratios of soluble component suggest that their origin is Japan in March and February (<sup>206</sup>Pb/<sup>207</sup>Pb: 1.16, <sup>208</sup>Pb/<sup>207</sup>Pb: 2.44), when much amount of Asian dust arrives, while the soluble Pb from September to December (<sup>206</sup>Pb/<sup>207</sup>Pb: 1.13-1.15, <sup>208</sup>Pb/<sup>207</sup>Pb: 2.42-2.43), when the contribution of Asian dust to silicate is not significant, is suggested to have originated from Beijing, far-east Russia, or Central Asia. This indicates that the cross-border air pollution occurs not in spring when is the acme of Asian dust but in autumn and winter. Coal combustion for heating and wintry atmospheric pressure pattern may have acted synergistically. The reasons why the soluble Pb in spring has local origin, and why the highest Pb flux occurs in spring are presumed that 1) the significantly high altitude of the transportation path of Asian dust refused the influence of Chinese urban air, and 2) the large amount of dust particles had adsorbed and concentrated the lead on their surface from sea sprays and Japanese air in crossing the Japan Sea and in settling long distance from the high altitude to Omura Bay.

In this study, we could not conclusively indicate the actual source of atmospheric lead. Lead isotope ratios are now widely used to estimate the origin of anthropogenic lead. However, citable <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb data of high precision are rare on the contrary to <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>207</sup>Pb, or <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb, perhaps because the study of atmospheric lead isotopes have been mainly conducted by using quadropole ICP-MS. Accumulation of <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb data of atmospheric lead sources is necessary for more accurate identification of the pollutant source.

Keywords: aerosol, anthropogenic lead, Sr-Pb isotope ratios, cross-border pollution



## Ongoing atmospheric monitoring activities at Noto peninsula

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Anthropogenic emissions are now perturbing biogeochemistry and climate, and it is particularly actualized in the parts of East Asia. The long-range transport of atmospheric pollutants is increasingly recognized in the downwind regions of rapidly growing industry and urban activities. There is a growing concern on the environmental consequences. Currently, there is an urgent need for high quality observational data to be collected and shared, in order to accurately estimate the health and climate impacts of the East Asian aerosols and trace gases, and eventually have the assessed impact reflected into the regional environmental policies.

Noto peninsula stems from the western coast of mainland Japan and extends approximately 150 km into the Japan Sea. Long-term record of polycyclic aromatic hydrocarbon (PAH) concentrations (Yang et al., 2007) has proven that geographical location of Noto peninsula is ideal for a baseline atmospheric monitoring station in East Asia, since it is surrounded by the sea and isolated from any neighboring major city or other pollution sources.

In order to reinforce the aerosol monitoring capabilities at Noto peninsula, the NOTOGRO (acronym for NOTO Ground-based Research Observatory) station was established in Suzu city (37.45°N, 137.36°E) at the tip of the peninsula. The instruments are housed in a room on the top level of a 3-storey building facing the eastern coast of Suzu city. The PM10 inlet located directly above the room provides sample air into the room for the aerosol in-situ measurements. The sample air is then shared by various instruments via an isokinetic flow splitter. The core instruments deployed at the station for long-term aerosol monitoring consist of those endorsed by the Global Atmospheric Watch Network (GAW/WMO) including e.g. aerosol chemical speciation monitor (ACSM). In addition to the aerosol in-situ measurements, atmospheric trace gas measurements (CO, O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>) as well as column aerosol optical depth measurements are being conducted at the station in collaboration with domestic partner institutions.

The growing long-term record has revealed, for example, periodic transport of atmospheric pollutants characterized by increased levels and variable fractions of elemental carbon, sulfate, and organics within fine particles, especially in spring and autumn. Air-mass trajectory calculations suggested distinct transport patterns depending on the seasons, and often associating the major pollution sources to be within the continent. However, such analysis remains rather inconclusive when identifying the exact emission source. Therefore, expectations are high for the finger-printing aspect of the related elements using isotope ratios for the more precise source apportionment.

Keywords: atmospheric aerosols, trans-boundary pollution, ground-based observation

## Preliminary study on hydrological and isotope environment of coastal area of Shirakami Mountains

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Shirakami Mountains, located around the boundary of Akita and Aomori prefectures, has amount of precipitation and full of nature, especially forest ecosystem. Central part of the mountains was registered with the World Heritage in 1993. On the other hand, acid rain has been observed for a long time. Study on the effect of acid rain to water environment and forest ecosystem is quite few. However, effect of acid rain is considered to be remarkable in the coastal area (Japan sea side), because source of acid rain is recharged from Asian countries (Ministry of Environment).

This study focuses on water and isotope environment of the coastal area of Shirakami Mountains and collected samples of surface water and spring. In this presentation, geochemical and isotopic characteristics of samples will be shown.

Keywords: Shirakami Mountains, water environment, environmental isotope

## Map of the river materials in the northern part of Shikoku Island, Japan

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In the Kagawa Prefecture of Japan, there is a little precipitation, and therefore, the pollution of river water is a serious issue. The rate at which environmental standards have been met with respect to the levels of biochemical oxygen demand (BOD) is below the national average. The same degree of organic matter concentration that is found in the eutrophic lake is also observed in the river downstream. When attempting to clarify how the river becomes polluted with organic matter, it is important to analyze the organic matter source and its load process. During the analysis, it is necessary to relate the origin of the river water and the water use in the basin.

In the present study, a material map of the river was prepared to construct a basic database. The formation mechanism that affects river water quality can be analyzed qualitatively and quantitatively by overlapping notice obtained from the distribution of various materials. In this speech, the current state of the river quality of Kagawa Prefecture is analyzed and the relationship between the river water quality and the watershed environment is considered from a chemical map of various materials, including the  $\Delta^{18}\text{O}$  and  $\Delta^{18}\text{D}$  of the river water.

Our analysis showed a negative correlation between precipitation and the water concentration rate (calculated by comparing  $\text{Cl}^-/\text{O}$  in the stream to  $\text{Cl}^-/\text{O}$  in precipitation) in the headwaters ( $r = -0.726$ ,  $a < 0.01$ ). In addition, it showed a positive correlation between major ion concentration and the water concentration rate ( $r = 0.797$ ,  $a < 0.001$ ). In the northern part of the Shikoku island, the major ion concentration in the headwaters showed a lower value with 0.47 meq/L in the Kamo river of Ehime Prefecture, where much precipitation exists, compared with ion concentrations in Kagawa Prefecture (average 0.94 meq/L) and Ehime Prefecture (average 0.75 meq/L, except for Kamo river). In the headwaters of the north region on the Shikoku Island, the amount of precipitation influenced the water concentration rate in the headwaters. As a result, it had a major impact on the major ion concentration of the stream water.

Chlorophyll *a* and the pheo-pigment concentrations became high in the middle and downstream. As determined from the multiple regression analysis, in the observation points where the irrigation pond density in the watershed was high, chlorophyll *a* and the pheo-pigment concentrations was high. This fact suggests that organic matter produced in the pond could be a factor in the increase in the amount of the organic matter in the river water.

The  $\Delta^{18}\text{O}$  of the upstream was low and rose by approximately 3 per-mil in the middle and downstream. On the other hand, the difference of the  $\Delta^{18}\text{O}$  of the rain in the headwaters and the plains is below 1 per-mil. It is difficult to determine if evaporation might be the cause of the high  $\Delta^{18}\text{O}$  in the middle and downstream, because the river length in the Kagawa Prefecture is short, only 20 to 50 km, and the river water travels from the upstream region to reach the sea in about a day at the average long-run water flow. In the Kagawa Prefecture, many ponds exist in the river watershed to make use of the water resource efficiently, and the  $\Delta^{18}\text{O}$  of those ponds were several per mil higher than the  $\Delta^{18}\text{O}$  of upstream water. In the river basin, upstream water was stored in the irrigation ponds, and the water of the irrigation ponds was distributed to paddy fields via the river. In water use of such repeated, it was considered that the  $\Delta^{18}\text{O}$  of the middle and downstream became high because the river water included much water through the irrigation pond.

In view of the  $\Delta^{18}\text{O}$  results and the statistical analysis, it can be interpreted that the inflow of organic matter from the eutrophic pond into the middle and downstream of the river was a factor of the organic pollution of the river in Kagawa Prefecture.

Keywords: Shikoku Island, River water, Water quality,  $\Delta^{18}\text{O}$ , Kagawa Prefecture

## Geochemical and isotopic map of Asahi and Yoshii Rivers, Okayama Prefecture

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The Asahi and Yoshii Rivers are the two of the three largest rivers in the Okayama Prefecture, flowing broadly from north to south in the central and eastern region of the prefecture. The water from the rivers supports both industrial and agricultural activities in the prefecture. Thus, a quantitative knowledge of their water sources and circulation process(es) through construction of detailed geochemical map is essential. Here we report the results of geochemical analyses of more than 200 samples collected from the two rivers and their tributaries during March 2011 to December 2012. All samples were filtered with 0.2 micrometer filter prior to the analyses for major dissolved constituents (F, Cl, NO<sub>3</sub>, SO<sub>4</sub>, Br, PO<sub>4</sub>, Ca, Mg, Na, K), trace elements and O-H-Sr-S isotopes.

The results obtained so far have revealed that there are systematic changes in the deuterium excess (DE), Sr isotope ratio and the concentrations of elements such as Ca, Mg, Sr and Ba from the upstream towards the downstream.

The DE is generally high in the upstream (>20) and gradually decreases towards the downstream (<12). The seasonal variation in the DE was less than 5 permil. The regional change in the DE is interpreted to be the result of difference in the air mass contributing to the meteoric water of different locations.

The Ca, Sr, Ba concentrations of the river water, on the other hand, is low in the northern region and increases towards the south. With the exception of few locations (e.g. southern region of the Kagamino City), Sr isotope ratio also increases towards the south. Because the change in the Sr isotope ratio is broadly correlated with changes in the age and types of rocks exposed in the river basin, the variation in the Ca, Sr, Ba concentrations may be closely related to the water-rock interactions.

We also observed a systematic increase in the NO<sub>3</sub> and SO<sub>4</sub> concentrations from the upstream to downstream. The S isotopic composition, on the other hand, was high in the north and low in the south. Since NO<sub>3</sub> and SO<sub>4</sub> concentrations tend to increase abruptly in the densely populated region, these variations may reflect a change in the degree of human influence such as breakdown of fertilizers used for agricultural activities.

Keywords: Geochemical map, Asahi River, Yoshii River, Okayama Prefecture, Trace element, Isotope

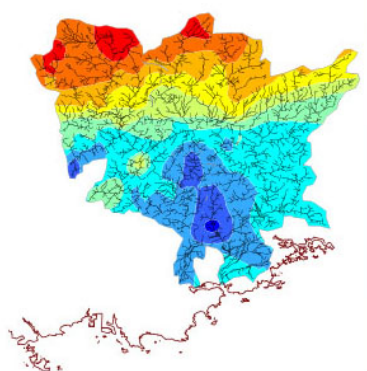


Figure 1. DE of waters from the Asahi and Yoshii rivers  
(RED=high BLUE=low)

## Water quality of Hiikawa and Kandogawa rivers in the eastern Shimane and its difference

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Here we evaluated water quality of the Hiikawa and Kandogawa Rivers running in the eastern part of Shimane Prefecture, SW Japan. River water was sampled between 2009 and 2011 and its major and trace element concentrations, Sr isotope ratio were measured together with basic information such as EC and pH. Our new findings are as follows:

(1) Concentration in  $\text{Na}^+$  and  $\text{Cl}^-$  are higher along the coastal region of Shimane Peninsula, decreasing to the Chugoku-mountain. This change is suggestive of the contribution from sea-salt grains transported by wind. The relatively high values on the Shimane Peninsula imply this peninsula has been acting as a topographic barrier. Their concentration is much smaller in the samples obtained from the Kandogawa River. This was probably due to the deep valley developed near the border of the plain and mountains, suppressing the transport of sea-salt grains into the upstream region of the river. On the contrary, the middle reach valley of the Hiikawa River is wider, which may allow the transport of sea-salt grains to the upper reach of the river.

(2) The higher concentrations of the  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  were obtained from the upstream region of the Hiikawa River. Very gentler topography even in the uppermost reach area of the Hiikawa River than that of the Kandogawa River may explain higher ion concentrations near the upstream end of the river.

(3) No major urban areas along the middle and upper reaches of the Kandogawa River may be the reason of smaller concentration in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  except for Mt. Sambe region where field for livestock farming is widely spread.

As the results, the dissolved ion concentrations are higher along the Hiikawa River and its major control factor may be due to topography, such as gentler topography along the Hiikawa River which allow penetration of sea-salt grains into the upstream region as well as promote reaction between rocks and water. The steeper topography, particularly seen in the middle reach of the Kandogawa River is due to andesitic volcanoclastics. The slight difference in geology between areas is reflected as differences in topography, leading to water quality difference between these two rivers.

Keywords: Water quality, Sr isotope ratio, Hexa diagram, Hiikawa River, Kandogawa River

## Geochemical and isotopic map of spring water and surface water in Yuza town of Yamagata prefecture

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Yuza town is located in the northern part of Shounai plain, which develops in the northwestern area of Yamagata prefecture. This town faces Japan Sea in the west and Mt Choukai in the north. Mt Choukai is 2236 m in height and is known to be rich in rain and snow, whose annual amount is estimated to reach 12000 mm per year. Owing to the large amount of precipitation, many springs occur in the foot of mountain, plain, coast, and seafloor. *Pungitius sinensis*, an endangered species, lives in the freshwater spring, and oyster on rock, a specialty of this town, distributes around the seafloor spring. Groundwater in Mt. Choukai and plain is used for drinking, agriculture, and salmon culture, supporting daily lives and industries. Preservation and sustainable use of groundwater is indispensable for Yuza town and other areas in the watershed of Mt. Choukai. Yuza town is examining to develop regulations for the preservation of groundwater and spring. We collected surface water and groundwater from the whole area of Yuza town. We also collected monthly rainwater at three sites with different elevation from 2010 to 2011. We determined the concentrations of dissolved components and stable isotope ratios of H, O, and Sr in the water. The result is summarized as follows.

The water quality of precipitation showed a large temporal variation. Winter precipitation is rich in Cl, Na, and Br due to the supply of sea-salt component from Japan Sea. It is also high in heavy metals such as Pb, Cd, and Zn, largely transported from the Asian continent by westerly winds. The seasonal variations of  $\delta H$  and  $\delta^{18}O$  values in precipitation are less distinct, but the  $\delta$ -value is high in winter and low in summer irrespective of sites. These components can be utilized as a powerful atmosphere-derived index.

The geochemical components and isotopic ratios of spring water and surface water did not show a temporal variation. But they showed a large geographical variation and the waters are classified into 8 areas. The  $\delta H$  and  $\delta^{18}O$  values of freshwater showed an altitude effect, but those of groundwater and artesian water in the central part of Yuza town are low compared to waters in the surroundings. The comparison of isotope ratio and quality in the water shows that the groundwater is recharged largely from Gakkou river and from nearby watersheds.

The concentration of Cl and Na in the coastal water also showed an altitude effect. It is notable that water in the northern rocky area is high in sea-salt components compared to the water in the southern sandy beach. This result indicates that sea-salt particles are productive in the rocky coast.

Snow-melt water in the high elevation area of Mt. Choukai and swamp water around summit plateau of Mt Yoshide are characterized by low  $\delta$ -values, showing a contribution of summer precipitation. The  $\delta$ -value of other waters shows a geographical variation and the water of the eastern area of Mt. Choukai has high  $\delta$ -value, suggesting large input of winter precipitation. This result is consistent with high amount of snow in the eastern Choukai.

Groundwater is low in heavy metals (Pb, Cd), which are high in the snow-melt and swamp water, indicating the contribution of precipitation. It is also notable that these water is characterized by high  $^{87}Sr/^{86}Sr$  ratios ( $>0.707$ ). Most waters in mountainous area and plain area, which are composed of andesite and their clastic sediments, have low  $^{87}Sr/^{86}Sr$  ratios (0.704-0.705), indicating andesite-derived Sr. Water with high  $^{87}Sr/^{86}Sr$  ratio indicates the dominant contribution of precipitation-derived Sr. It is considered that groundwater in mountain foot and plain is characterized by low contents of Pb and Cd, indicating that atmospherically-derived heavy metals are mostly adsorbed in the soil.

Groundwater in coastal hill has high contents of  $NO_3$ , Mg, B, and As, which are presumably derived from fertilizer. Water

Keywords: groundwater, geochemical map, strontium isotope, water isotope, nitric pollution, heavy metals

## Characteristic features of chemical compositions and isotopic ratios of river water in Akita Prefecture

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Chemical compositions and isotopic ratios of river water in Akita Prefecture were examined for samples collected in the base-flow period from October to December in 2011 at 125 sites. All water samples were filtered through disposable cellulose acetate filters with a pore size of 0.2 micrometer. Chemical analyses were performed at the Research Institute for Humanity and Nature. The concentrations of dissolved components in the water were determined by means of inductively plasma mass spectrometry (Agilent 7500cx) and an ion chromatograph (Dionex ICS3000), respectively. We determined H and O isotope ratios using Cavity Ringdown Spectrometer (Picarro L2120-i), and Sr isotope ratios by using a thermal ionization mass spectrometer (Thermo Fisher TRITON). The geographical distribution of water quality component was analyzed using Arc-GIS of EERI.

Geology of Akita Prefecture mainly consists of Neogene and Quaternary strata. Quaternary volcanic rocks cover the Neogene strata in the eastern part of Akita Prefecture along Ou Mountains. Sedimentary strata in Neogene tend to be distributed in the western part of the prefecture.

Acidic river waters are distributed in areas in the eastern part of Akita Prefecture in which there are Quaternary volcanoes and acidic hot springs with magmatic components. Acidic river waters characterized by occurrence of abundant mines are also distributed in the central part of the prefecture.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations are high in river water in areas along Ou Mountains consisting of Quaternary volcanic rocks and along the coast of the Sea of Japan (coast of Akita Prefecture). The high concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are due to effects of acidic thermal water and sea salt particles.  $\text{F}^-$  concentration is high in river flowing from Hachimantai and Kurikoma areas of Ou Mountains. The high  $\text{F}^-$  concentration is traced from Ou Mountains to the Sea of Japan for over 100 km along the Omono river system.  $\text{NO}_3^-$  concentration is high in river water in flat plains for agriculture in Akita Prefecture.

Na and K concentrations are high in rivers along the coast of Akita Prefecture, Kurikoma area in the southeastern part of the prefecture and Ohdate area in the northeastern part of the prefecture. The high Na and K concentrations in rivers along the coast of Akita Prefecture and Kurikoma area are caused by sea salt particles and acidic thermal water, respectively. River water having high Na and K concentrations in Ohdate area is characterized by high Mg,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations. These facts suggest that fossil seawater from hot springs was mixed with normal river water. The distribution of river water having a high Ca content overlaps with the distribution of river water having a high  $\text{SO}_4^{2-}$  content in the area of Quaternary volcanic rocks along Ou Mountains. The high Ca content is thought to be a result of water/rock interaction between volcanic rocks and  $\text{SO}_4^{2-}$ -bearing ground water formed by oxidation of sulfide minerals in volcanic rocks.

Hydrogen and oxygen isotopic ratios of river water in Akita Prefecture tend to be heavier in the coastal area of the prefecture and lighter in the eastern part of the prefecture along the Ou Mountains. Hydrogen and oxygen isotopic ratios of river water are also heavier in the area from Yokote to Daisen Cities with a northwest to southeast direction. The d-values of hydrogen and oxygen isotopic ratios are higher in river water in Hachimantai-Moriyoshi and Kurikoma areas, which have large annual snow accumulation.

The effects of sea salt particles, thermal water, mine drainage water, and water/rock interaction between Neogene and Quaternary strata and ground water control the chemical compositions of river water in Akita Prefecture.

Keywords: water quality, geochemical map, Akita, mine, hot spring, river water

## Sulfur isotope map of surface water in northeastern Kanto, central Japan

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I determined the concentration and isotope ratio of sulfur in Naka and Kuji river watersheds in northeastern Kanto, and analysed their geographical distribution in terms of the watershed geology. Sulfur isotope ratio ( $\delta^{34}\text{S}$ ) in the surface water in the granite watershed of Abukuma mountainous area ranged from 2 to 8 per mill. Similar value is observed in the stream water on the plateau of Quaternary sediments.

These values are different from the  $\delta^{34}\text{S}$  value of rock sulfur, but are close to that of rain water, indicating that the major source of sulfur is originated from meteoric water. This suggestion is consistent with the low concentration of sulfur in the provenant geology of Abukuma granite and its clastic sediments.

The  $\delta^{34}\text{S}$  value of surface water in the watershed of Mesozoic sedimentary rocks ranged from -2 to 6 per mill. This value is indistinguishable from the  $\delta^{34}\text{S}$  value of rock sulfur, suggesting the sulfur in the water is derived from sulfide and/or sulfate minerals in the rock through chemical weathering. This suggestion is consistent with that surface water in the sedimentary-rock watershed tends to be higher than that in the granite one.

Surface water, whose watershed geology is composed of sedimentary rocks of Miocene age, had variable  $\delta^{34}\text{S}$  values (-8 to 18 per mill). It is likely that water with low  $\delta^{34}\text{S}$  value is derived from the dissolution of  $^{34}\text{S}$ -depleted sulfides, which formed in anoxic marine environment by the activity of sulfur-reducing bacteria. In contrast, the source of sulfur with high  $^{34}\text{S}$  is unclear. It would be possible to attribute this  $^{34}\text{S}$ -enriched sulfur to sulfate in the Miocene seawater, which had high  $\delta^{34}\text{S}$  value (20-24 per mill). An alternate view is that the high  $^{34}\text{S}$  sulfate ion is derived from the remaining sulfate of groundwater which was subjected to sulfate reduction. Further study is needed to elucidate the formation of high  $^{34}\text{S}$ -enriched water.

Keywords: sulfur isotope, river water, Kanto



## Variations in Sr and Nd isotopic ratios in cryoconite on glaciers in Asia, Alaska, and Greenland

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Variations in Sr and Nd isotopic ratios of cryoconite on glaciers in Asia, Alaska, and Greenland

Recent shrinkages of glacial mass are not only due to global warming, but also possibly to accumulation of cryoconite on the glacial surface. Cryoconite is a biogenic surface dust consisting of organic matter mainly derived from living microbes on the glaciers, and mineral particles originated from basal till and/or wind-blown dust. Since cryoconite is dark color, it can reduce surface albedo of glaciers and accelerate their melting. Thus, it is important to understand their sources and formation process on the glaciers.

The characteristics of cryoconite vary among geographical locations. For example, there are small amounts of cryoconite on Arctic glaciers and their glacial surface is clean. In contrast, large amounts of cryoconite accumulate on Asian glaciers and their glacial surface appears very dirty. These differences in cryoconite are likely to affect on surface albedo and melting of each glacier. However, the formation process of cryoconite, especially origins of minerals and production process of organic matters are still not well understood.

Stable isotopic ratios of strontium (Sr) and neodymium (Nd) provide a means of identifying sources of substances and have been commonly used in loess or sediment studies. Furthermore, Sr isotope has been used as a tracer of Ca ion in studies of geochemical process, because its chemical characteristics are similar to Ca. Thus, Sr in organic matter including such organisms on the glacier may reveal their nutrient sources and ecology of them. In this study, we analyzed Sr and Nd isotopic ratios of four mineral and organic fractions in cryoconite on Asian and Polar glaciers. Based on the isotopic ratios, we identified origins of minerals in cryoconite and mineral sources used as nutrients by microbes on the glaciers.

Sr and Nd isotopic ratios in the mineral fractions, especially silicate minerals, which are major components of mineral particles, vary significantly among the glaciers. Cryoconite on Asian glaciers showed higher Sr and lower Nd ratios in the north and also showed little variation within a glacier. On the other hand, those on Alaskan glacier showed lower Sr and large spatial variation in Nd on a glacier. Cryoconite on Greenlandic glaciers showed further high Sr and low Nd than the other glaciers. This suggests that origins of silicate minerals in cryoconite are substantially different among the glaciers. Compared with the isotopic ratios of silicate minerals in moraine, desert, and loess reported over the regions, those in cryoconite on Asian, Alaskan, and Greenlandic glaciers were close to those in respective regions. This result indicates that silicate minerals in cryoconite were derived from surrounding the glaciers. The Sr isotopic ratios of organic matter in cryoconite also varied among the glaciers. They may reflect the minerals used by glacial microbes as nutrients.

Keywords: Sr-Nd isotope ratio, cryoconite, microbes on glaciers

## Strontium isotope constraints on the provenance of dissolved cations in rain at Kyotanabe and Nishinomiya, western Japan

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We determined the elemental and Sr isotope compositions of monthly wet precipitation at Kyotanabe and Nishinomiya to elucidate the seasonal and regional variation in the provenance of dissolved cations.

Concentrations of Ca and Sr of precipitation tended to become high in spring and low in autumn and winter. The pH values became high in spring. The Sr isotopic composition varied seasonally with high  $^{87}\text{Sr}/^{86}\text{Sr}$  in spring and low  $^{87}\text{Sr}/^{86}\text{Sr}$  during summer and winter season. Aian dust events are frequent in spring and the maximum  $^{87}\text{Sr}/^{86}\text{Sr}$  in the spring precipitation was close to the  $^{87}\text{Sr}/^{86}\text{Sr}$  for calcium carbonate in loess in China. Accordingly, the elevated  $^{87}\text{Sr}/^{86}\text{Sr}$ , Ca and Sr concentrations and pH values in the spring precipitation are attributed to the dissolution of calcium carbonate in Asian dust.

If Sr in rain during summer and winter season is assumed to be a mixture of non-Asian dust components (sea salt and soil mineral dust and anthropogenic emission around the sampling sites), then it is possible to calculate the relative contribution of Asian dust in rain. The Asian dust component is estimated to vary 16-60% and 4-36% in the spring precipitation at Kyotanabe and Nishinomiya, respectively.

We calculated the non-sea-salt (nss) proportion of Sr in rain on a Na basis. The nss-Sr proportion is estimated 23% and 15% in precipitation at Kyotanabe and Nishinomiya, respectively. The nss-  $\text{nssSO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations of precipitation at Nishinomiya were higher than those of precipitation at Kyotanabe. This result shows that the precipitation at Nishinomiya was affected by the anthropogenic materials.

We calculated the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the mixture of non-sea salt component in rain using the proportions of sea-salt-Sr and nss-Sr and the  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the mixture of non-sea salt component in rain at Kyotanabe and Nishinomiya were close to but slightly less than the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for exchangeable cations from the sediments of the Osaka group and Rokko granite, respectively. These results suggest that there are the contributions of local mineral dust and the anthropogenic emissions which has the lower  $^{87}\text{Sr}/^{86}\text{Sr}$  in rain at Kyotanabe and Nishinomiya.

Keywords: precipitation, Sr isotope, Asian dust

## Distribution of Sr isotope ratios in the vegetation of Siberian dwarf pine at Mt. Tateyama

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Chubu-Sangaku mountainous area in central Japan is composed of mountains whose elevation is over 2500 m above sea level (a.s.l.). In the soil of this high elevation area, biological activity is inactive due to low air temperature and long snow cover, resulting in the slow decay of biomass, immobilization of nutrient, and depressing the material circulation. Wet and dry depositions in these mountainous ecosystems play an important role as nutrient supply. Wet precipitation on the forest ecological system partly adheres on leaves and branches, and water returns to the atmosphere by evaporation. The chemical composition of throughfall changes from the precipitation by interaction with tree and grass. Some elements are absorbed from crown. Further high elevation area is sensitive to materials transported from regional air pollution. However, there are a few geochemical and material-circulation studies on the mountainous ecosystem with high elevation. We have been studied ecological and plant physiological studies on Mt. Tateyama, one representative Chubu-Sangaku mountainous area. The ecological system of Mt. Tateyama is important, since this mountain is strongly impacted from air-pollutants from the Asian continent as it faces the Sea of Japan, and is affected by global warming as the air temperature increases more than three times as the world average during recent 30 years.

Sr is known as a powerful hydrological and ecological tracer but it is utilized as a fingerprint to understand plant physiology. This isotope is unique as it can quantitatively discriminate atmosphere-derived Sr from bedrock-derived Sr. In order to elucidate the material circulation system on the forest ecosystem in Tateyama, we sampled a variety of water (rainfall, throughfall, fog water, snow, groundwater, and dale water) and Siberian dwarf pine in Joudodaira, and determined their Sr isotope ratios. Our result shows that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of groundwater (0.7068) and dale water (0.7070) are almost identical to that of soil and bed rock (0.7070), suggesting that Sr in the surface and ground water is largely derived bedrock through chemical weathering. This is consistent with that rainwater (0.7091) and fogwater (0.7090) have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. As this ratio is similar to seawater value (0.7092), Sr in precipitation is largely of sea-salt origin. It is notable that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of dirty materials in snow is variable from 0.7095 to 0.7198. This high ratio suggests an incorporation of Asian dust particle whose  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is around 0.720. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of throughfall is 0.7094, indicating a contribution Asian dust Sr. The most notable feature is that Siberian dwarf pine (*Pinus pumila*) has high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7099 in leaf and branch and 0.7097 in litter). Most alpine plants have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.707 of *Gaultheria miqueliana* and 0.708-0.7095 of others). This result demonstrates that Siberian dwarf pine is actively absorbing Asian dust particles.

Keywords: Asian dust, *Pinus pumila*, plant ecophysiology, Sr isotope, Alpine, Forest hydrology

## Evaluation of the sulfur dynamics change in Japanese forest soils using sulfur isotope ratios

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Anthropogenic sulfur emissions have been increased with human activities and affected sulfur dynamics in forest ecosystems. Since the stable sulfur isotope ratios ( $\delta^{34}\text{S}$ ) of various origins have specific values, the values of various environmental samples from forest ecosystems have been used for evaluation on the effect of increased sulfur deposition. In Japan, some studies showed that much more sulfate ions have been adsorbed in soils compared with North America and Europe [1, 2]. The effect of sulfur deposition may be larger in the soils with higher adsorption capability than a lower one, but little data is available.

To understand the effect of sulfur deposition on soils with high adsorption capability, we measured depth distributions of  $\delta^{34}\text{S}$  and the adsorption equilibrium of sulfate concentrations between soil particles and soil water, which are influenced by sulfur deposition.

The investigation was carried out at three study sites, Yokkaichi (YOK), Inabu (INA), and Ijira (IJR), in central Japan. These study sites have different history of sulfur deposition. YOK had been affected by quite high sulfur deposition on 1960's. IJR has relatively received high sulfur deposition recently. INA is located about 60 km NE of main urban area (Nagoya City). Two soil pits were excavated in each site and mineral soil samples were obtained at each depth.

The  $\delta^{34}\text{S}$  were measured for total sulfur and phosphate-extractable sulfur including mainly adsorbed and water soluble sulfate. The sulfate concentrations in adsorption equilibriums were obtained by adsorption isotherms.

Although the phosphate-extractable  $\delta^{34}\text{S}$  ( $\delta^{34}\text{S}_{\text{phos}}$ ) values showed the same range (2.4-6.6 per mil) in all sites, the depth distributions were different among the sites. The  $\delta^{34}\text{S}_{\text{phos}}$  values in INA and IJR were similar in depth of 20-80 cm or increased with depth. On the other hand, those in YOK had the lowest values (2.4 and 2.9 per mil in YOK-1 and YOK-2, respectively) in depths of 40-80 cm in each soil pits. In addition, the equilibrium sulfate concentration curve in YOK-1 was higher position in depth of 40-50 cm where showed the lowest  $\delta^{34}\text{S}_{\text{phos}}$  value. These results indicated that in YOK anthropogenic sulfur with lower  $\delta^{34}\text{S}$  values deposited in the past existed in a certain depth of forest soil, and sulfate adsorptions on soil had increased in the range of those depths.

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Keywords: sulfur isotope, sulfate ion adsorption, sulfur deposition

## Carbon-nitrogen-sulfur isotopic tracing method to understand different anaerobic bacterial processes in aquifer systems

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Denitrification is recognized as an important natural attenuation function for groundwater nitrate contamination. This study proposes a new concept for better understanding the major anaerobic bacterial reduction including denitrification occurring in aquifer systems by using C, N, and S stable isotopic combination as reaction net recorder. To verify the utility of C-N-S isotopic tracing method (named as CNS-IT method), we newly investigated delta 13C-DIC and delta 34S-SO<sub>4</sub> characteristics of the Kumamoto groundwater systems, which denitrification mechanism has already been well studied based on the delta 15N-NO<sub>3</sub> and delta 18O-NO<sub>3</sub> tracing study.

Significant sulfate reduction (with maximum increase of delta 34S-SO<sub>4</sub> of 55 permil) with progress of denitrification (with maximum increase of delta 15N-NO<sub>3</sub> of 38 permil) was observed as groundwater flows down gradient. In contrast, decline of delta 34S-SO<sub>4</sub> (with maximum decrease of delta 34S-SO<sub>4</sub> of 8 permil) with denitrification was found only sporadically. These observations imply the possibility that denitrification found over the study area was mainly driven by heterotrophic process as did for sulfate reduction, but autotrophic denitrification was occurred in just very limited space. Moreover, low delta 13C-DIC feature (-21 ~ -17 permil) of groundwater at recharge area suggested that water was already enriched in organic C source DIC at most upgradient area prior to denitrification occurred. This fact prevented us to evaluate the isotopic fractionation effect by denitrification on delta 13C-DIC. However, we rather found that the CNS-IT method could be more efficiently used for the evidence of occurrence of methanogens reaction (actually, we found maximum increase of delta 13C-DIC of 8 permil at the denitrification hotspot).

The case study in Kumamoto demonstrated the usefulness of CNS-IT method for comprehensive understand of major anaerobic bacterial processes, including distinguishment between heterotrophic vs. autotrophic denitrification, occurring in aquifer systems. In the presentation, we will attempt to propose practical utility of CNS-IT method by showing delta 15N-NO<sub>3</sub>, delta 13C-DIC, and delta 34S-SO<sub>4</sub> evolutionary patterns according to combinations of major anaerobic bacterial reactions.

Keywords: isotope ratios, groundwater, Kumamoto, denitrification, heterotrophic, autotrophic

## Paleoenvironment reconstruction from Sr,Nd isotopic ratio, Lake Biwa

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Climate changes during last Pleistocene to Holocene are characterized by Glacial-Interglacial Cycle, or more shortly, Dansgaard-Oeschger Cycle, and so on(Dansgaard et al., 1993). To reconstruct these millennial scale climate change, it is necessary to analyze high resolution geological records.

Lake sediment is one of geological records that can be analyzed high resolution because of their high accumulation rates. Thus, we can reconstruct paleoenvironments in high precision by analyzing lake sediments(Yancheva et al., 2007; Nakagawa et al., 2006).

In Asian region, climate is largely controlled by East Asian Monsoon(EAM). In summer, EASM (East Asian Summer Monsoon) brings moist and warm climate in the region, whereas EAWM (East Asian Winter Monsoon) is characterized as cold and relatively dry air originated from Siberian High, which intensified in boreal winter. According to paeloclimate archives, it has been said that EAM intensity are related to global climate change(Wang et al., 2001; Katsuta et al., 2007), thus it is important to reconstruct behavior of EAM.

As, Fe/Mn ratio, and Mass Accumulation Rate(MAR) in the sediment of lake Biwa show clear decrease of lake level in 30ka, which has lowest level in past 50kyrs. In same age, there is positive and negative peak in Sr and Nd isotope data respectively. These isotopic data indicates source materials and their contribution rates to sediment. The peak of isotopic data shows greater contribution of dusts from Taklimakan desert, which indicates either stronger Winter Monsoon, or southern shift of Westerly Jet. However, our data set requires higher resolution, so that we can separate source areas of sediment in detail. Furthermore we can reconstruct climate changes that occur in short time scale.

Keywords: Sr isotope, Nd isotope, Paleoenvironment

## Recent anthropogenic environmental change in domestic lakes revealed by multi-elements and isotope analyses

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Multi-elements and Sr isotope analyses of lake sediments were done for Lake

Rausu, Lake Niseko-Ohnume, Lake Mikuriga-Ike, Lake Kizaki, Lake Biwa, Lake Akan, and Lake Oshima-Ohnuma in order to detect recent anthropogenic environmental change.

Increase in Mn and As at the top of the sediment was found in Lake Biwa as reported previously. It is probably due to oxidation and fixation of reduced form of these elements transported from the deeper part of the sediments. Increases in Mn, As, Cu and Zn were also found in Lake Akan and were likely due to the input of material containing these elements to the lake. Pb concentration variation was found in Lake Ohima-Ohnuma and Lake Mikuriga-Ike, suggesting the atmospheric input and influence of regulation for the use of leaded gasoline. In Niseko-Ohnuma, Pb and Zn concentration increased since the beginning of 20th century, which coincided with increased sedimentation rate, suggesting the increased input of detrital material containing these elements. Sr isotopic ratios indicate two components mixing at Niseko-Ohnuma. No large variation in elemental composition was found for the sediment in Lake Rause during the last 100 years. Principle component analysis for the Lake Kizaki analytical data indicates the possibility to distinguish the behavior of elements from anthropogenic origin and that supplied by detrital sediments.

Keywords: lake sediment, multi-element analysis, Sr isotope, anthropogenic environmental change

## Feeding ecology of brown bears of the Southern Kurils revealed by multi-stable isotope analysis

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Various methods have been conducted for food habit analysis in wildlife. Direct observation, contents analysis in scats or in stomach, and bio-element stable analysis are the conventional methods. However, Direct observation is time and labor consuming, and scats and stomach contents analyses only provide information just before the sampling; these methods also cannot evaluate assimilated food variation because of different digestibilities among food items. Furthermore, stomach contents analysis can only apply to dead animals. In contrast, stable isotope analysis has been used more frequently for revealing food habits in recent years, because stable isotopic compositions of animal tissues reflect those of their foods. Any tissues could be used for the analysis, and depending on the tissue turn over time, we can obtain short- and long- term diet information of a specific animal.

Brown bears (*Ursus arctos*) are found on the Kunashiri and Etorofu islands located among the Southern Kuril Islands and their ecology is not well clarified. In September 2010, we conducted an ecological survey of brown bears on the Kunashiri Island and collected the hair samples of brown bears. In this study, we determined stable carbon, nitrogen and sulfur isotopic compositions of these hair samples to estimate the feeding habit of brown bears on the Kunashiri island.

A strong positive correlation between carbon, nitrogen and sulfur isotopic compositions was observed, indicating a small variation in food sources. Moreover, every bear showed a similar isotopic pattern from hair root to tip, which suggests that bears have a similar feeding history; consume plants in spring and salmons from summer to autumn. Compared to brown bears on the nearby Shiretoko Peninsula, which consumed not only plants and salmons but also sika deers (*Cervus nippon*) and anthropogenic crops, Kunashiri bears highly depended on abundant salmon resources under an environment without influences of human activities. We are planning to analyze the hair samples of brown bears on the Etorofu Islands for further information.

Keywords: brown bears, Kunashiri, Etorofu, stable isotope analysis



## Identifying human migration and hunting area revealed through Strontium isotope analysis of mammal remains

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Human migration, exchange and distribution spread the culture and technology and produces regionality and change of the Japanese archipelago.

Cultural transmission of Jomon period revealed by finding evidence that the human movement. In order to clarify aspects of use of animal resources, we are working to clarify the distribution area and hunting and fishing area using stable isotope analysis. In this paper, we report on the study area in the region of the Boso Peninsula Jomon hunting using strontium isotope ratios.

For this study, we used samples from the 55 tooth enamel of deer (*Cervus nippon*) and wild boar (*Sus scrofa*) excavated from 12 sites which located on the Boso Peninsula during the late and final Jomon period. We collected plant samples from 32 locations in the Boso Peninsula and evaluated regional differences in environmental Strontium isotope ratios by these plant samples.

The strontium isotope analyses, including the pretreatment steps, were performed at the Research Institute for Humanity and Nature. Strontium isotope ratios were measured with a TRITON thermal ionization mass spectrometer (Thermo Fisher Scientific). Sample  $87\text{Sr}/86\text{Sr}$  data was normalized to the standard reference material of the NIST SRM 987 (0.710250). Internal precision based on ion counting 100 times was  $\pm 0.000004\text{--}0.000006$  (=1 standard error).

We created the map of a geographic  $87\text{Sr}/86\text{Sr}$  distribution of plants. The graphic representation was performed with ArcGIS (ESRI, Inc.) software by using the kriging calculation method.  $87\text{Sr}/86\text{Sr}$  ratio showed different range, with high ratios (up to 0.7090) dominating the tip area of the peninsula and low ratios (low as 0.7056) occurring in the base and central area. In addition, Strontium isotope ratios in plants from the river basin had intermediate values. We can distinguish  $87\text{Sr}/86\text{Sr}$  ratio of plants in the tip of Boso Peninsula from the value of base and central areas.

The strontium isotope ratio in the mammal tooth enamel was varied in the range of 0.7056-0.7075. The isotope ratio of A site mammal showed the value from 0.7056 to 0.7059, and B site showed 0.7069 to 0.7075. The strontium isotope ratio of A site and B site showed clearly different value.

The strontium isotope ratio of C site showed from 0.7062 to 0.7068 and was intermediate value of A and B site. Thus, we can determine that the mammal carried to these sites inhabited the different area respectively.

In this announcement, we point out that the evidence that strontium isotope ratio to identify the hunting area.

Keywords: animal remains, hunting area, strontium isotope ratio, Jomon period, Boso peninsula

## Reconstruction of horse movement and management in the Kofun period

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### Introduction

The horse management was fundamental steps, contributing to great civilizations. In Japanese archipelago, the founder population of horse was introduced from Continental region during the Kofun period (3th-7th). A number of the Kofun, the large tomb in Japanese archipelago, was constructed by numerous people, and it is possible that the early great civilization started from the Kofun period. On the archaeological contexts in this period, it is thought that the horse management was similar to Continental region, and horses were generally supplied to the urban area from the outer suburb. This relocation system is crucial to establish the large government and nation in Japan.

Recently, the isotope analysis was applied to number of archaeological researches. Especially, the isotope analysis of heavy elements could provide zooarchaeological remains with the information about habitation area and movement history. As effective technique to the reconstruction of mammal habitation area, strontium isotope analysis of hard tissue (tooth enamel) was applied to a number of archaeological researches. In archaeological researches, the strontium isotope ratio has been used for information to distinguish local individual and non-local individual based on the archaeological hypothesis such as introduction and movement of mammals. In this study, we tried to reconstruct the horse movement using stable isotope analysis, and demonstrated the horse management in the Kofun period.

### Materials and Methods

To reconstruct the movement pattern of horses in the Kofun period, the mammal remains excavated from Saragunjori site in Osaka Prefecture was analyzed using strontium isotope analysis. The sample powder was sampled from nine horse enamels, two dog enamels and two wild boar enamels using tungsten bur drill. The local range of bio-available strontium isotope ratio was defined on dog and wild boar remains, to detect the introduction of the horse from outside regions to this site. Mammal enamels were purified by the pretreatment with 0.1N acetic acid buffer and the column extraction which filled a cation exchange resin. The strontium isotope ratio of sample was measured using thermal ionization mass spectrometer (TRITON, Thermo Fisher Scientific). The strontium isotope ratio ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) was normalized by  $^{88}\text{Sr}/^{86}\text{Sr}$  to natural abundance, and  $^{87}\text{Sr}/^{86}\text{Sr}$  was corrected by NBS987 (certified value;  $^{87}\text{Sr}/^{86}\text{Sr}=0.710250$ ). The internal measurement error (standard error) was 3.66 ppm (0.000005).

### Results and Discussion

The mean of the strontium isotope ratio in the horse enamel from the Saragunjori site showed 0.708911, the standard deviation 0.000897, maximum 0.710968 and minimum 0.707903 (Figure). The mean of the strontium isotope ratio in the dog and wild boar enamel from the same site showed 0.708929, standard deviation 0.000787, maximum 0.709644, and minimum 0.708245.

To identify the outlier of horse from the Saragunjori site, the strontium isotope ratio of the horse enamel was compared with the local mammals from the same site. If the strontium of the enamel was more various than the local, it indicate that the individual was introduced from the other regions. To test statistically the difference between the variation of horse enamel and dog and boar from the site, F-test was carried out by dividing two groups (the horse group and the dog group). As a result, the variation of the horse enamel was insignificantly higher than the local mammal ( $P>0.05$ ). Therefore, it was indicated that the Saragunjori horse was not supplied from the larger habitat than the dog and wild boar. Since the range of strontium isotope ratio is 0.708-0.713 based on geochemical background around this site, the population was managed in a local area. This result indicates that there was not yet relocation system in this region for Kofun period.

Keywords: Strontium isotope analysis, Horse, Mobility

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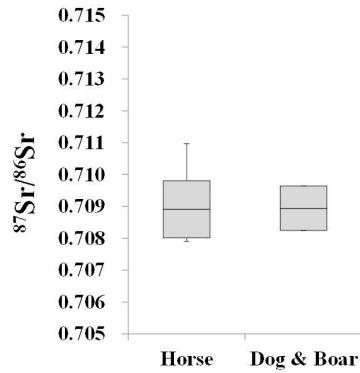


Figure 1. the strontium isotope ratio of mammal remains in Saragunjori site

## Strontium isotope analysis on human skeletal remains of the Jomon period from Tokai and Sanyo regions in Japan.

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Ritual tooth ablation was widely practiced in Jomon societies in the Late-Final phases. Two major patterns in ritual tooth ablation, termed type 4I and type 2C, have been recognized. The meaning of this practice as well as the difference of ablation pattern is unclear although it may reflect a formation of heterogeneous social sub-structure. This study performed strontium isotope analysis on Jomon populations in Japan from the Middle to Final Jomon period (ca. 5000-2300 years BP) to identify immigrants. Then, the results were analyzed in relation to sex and type of ritual tooth ablation. The materials were human skeletal remains from four coastal sites along the Inland Sea in the Sanyo region (Ota and Tsukumo shell mounds) and along Mikawa Bay and the Pacific Ocean in the Tokai region (Yoshigo and Inariyama shell mounds). Plants in the surrounding area were also examined to illustrate the geographic  $^{87}\text{Sr}/^{86}\text{Sr}$  distribution in each region. Only one immigrant was identified in each of Tsukumo and Ota sample. The large variation in the  $^{87}\text{Sr}/^{86}\text{Sr}$  values of local plants in the Sanyo region probably masked potential immigrants in each group. In the Yoshigo samples, individuals with higher Sr isotope ratios in their tooth enamel than seawater Sr values (0.7092) were identified as immigrants (36% of population). The presence of these isotopically identified immigrants among type 4I and type 2C individuals contradicts with the prevailing archaeological hypothesis that type 4I and type 2C individuals are locals and immigrants, respectively. Comparing Sr isotope ratios in plants and seawater with those of tooth enamel, we identified four immigrants among Inariyama samples. Type 4I locals had significantly higher Sr isotope ratios than type 2C locals. This study demonstrated that sex and tooth ablation types had significant relationship with diet and migration of the Jomon people.

Keywords: strontium isotope ratio, human bone, tooth, enamel, isoscape

## Stable isotope ratios of rock and environmental standards

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A wide variety of natural materials (air, water, biota, soil, and rock) and artificial ones (food, agricultural and industrial products) are used in earth environmental studies. Stable isotopes (SI) can be utilized as a fingerprint of element to trace its behavior in the environment. To enhance the ability of this SI fingerprint, it is desired to determine the concentrations and isotope ratios of many elements in an environmental sample with high precision and accuracy, rapidness, and convenience. Further, as biota, soil, and rock are composed of different components (bone, meat, mineral, etc.), whose concentrations and isotope ratios differ one another, analytical precision according to sample processing should be evaluated.

In order to promote the environmental isotope study, organizations hosting analytical instruments are desired to build the network, which can contribute to the improvement of the analytical reliability for elemental and SI data of various environmental samples. As a first step toward the realization of this network, we started to determine the stable isotope ratios of Sr, Nd, and Pb of rock standards from the National Institute of Advanced Industrial Science and Technology (AIST) using and thermal ionization mass spectrometer of TRITON and high resolution multi-collector ICP-MS of NEPTUNE (Thermo Fisher Scientific K. K.). We also determined the  $d^{13}C$  and  $d^{15}N$  values of organic material standards (rice, seaweed, fish tissue etc.) used for heavy metals at AIST by isotope-ratio mass spectrometer of Delta plus XP with Elemental analyzer Flash EA (Thermo Fisher Scientific K. K.).

For Sr-Nd-Pb analysis, all samples digested with concentric acid of high grade in Teflon vessel using Microwave sample digestion system ETHOS One (Milestone General K.K.). Sr and Pb separated with Sr spec resin and Nd processed with cation exchange resin and Ln resin (Eichrom co.). Preliminary results using TRITON showed that the external variation of  $^{87}Sr/^{86}Sr$  ratios for individual rock standard falls in a narrow range of 10 ppm, this variation being two times as the internal one. This difference between the external and internal variation is also observed when NEPTUNE was used. We suggest that this difference is ascribed to the measurement stage by mass-spectrometry rather than sample heterogeneity and sampling procedure.

The  $d^{13}C$  values of four rice standards were uniform  $-25.7 \pm 0.3$  permil, whereas their  $d^{15}N$  values were more variable from 1.2 to 5.6, indicating that this variation of nitrogen isotope is ascribed to the contribution of nitrogen from human activities in different degree. Marine fish standards showed variable  $d^{13}C$  and  $d^{15}N$  values. The  $d^{15}N$  value of Japanese seabass in Tokyo bay is about 5 permil higher than those of cod fish and swordfish tissues in the oceans near Japan, suggesting the input of human-derived nitrogen.

Keywords: stable isotope, environmental standard, analytical precision, sample heterogeneity