

## 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 0.703-0710 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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