

## Mass-independent fractionation of mercury stable isotopes in deep-sea hydrothermal systems

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It has been recognized that mercury (Hg) isotope analysis is an important new tool for identifying Hg source and tracking Hg transformations in the environment. Mass-dependent (MDF) and -independent (MIF) fractionations of Hg isotopes are caused by a wide variety of biogeochemical processes including redox reactions and volatilization. Volcanic activities and its associated hydrothermal activities are the main sources of naturally-emitted Hg in the environment. Several previous studies suggested that the naturally-emitted Hg indicated both MDF and MIF. It was thought that the MDF was caused by a process of liquid-vapor partitioning during ascending and the MIF was caused by photoreduction. It was, however, suggested that both photoreduction and volatilization could cause the MIF, and it has never been distinguish from each other in the hydrothermal systems. In this study, geological samples in active deep-sea hydrothermal systems at Izu-Bonin arc were collected and measured their Hg isotopic compositions. They indicate both MDF and MIF. The  $\delta^{202}\text{Hg}$  values range from -1.0 to 0.5 ‰, indicating the liquid-vapor partitioning, whereas the calculated  $\Delta^{199}\text{Hg}$  values are mostly between 0.1 and 0.2 ‰, indicating the MIF in the deep-sea hydrothermal systems without photoreduction. The linear relationship between  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ , ranging from 1.6 and 2.0, also indicates the nuclear volume effect. This result suggest that MDF and MIF of Hg isotopic compositions can be utilized to distinguish naturally-emitted Hg from anthropogenic Hg.

Keywords: Mercury Isotope, MIF, Deep-sea Hydrothermal Systems, CV-MC-ICP/MS

## Speciation of metal ions in water: comparison of their reactivities with oxygen-donor hard ligands

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Complexation of metal cations with ligands such as hydroxide ion, carbonate ion, carboxylate ion, and phosphate ion is one of the most important factors controlling behaviors of metal ions in natural environment. Previous studies showed that these ligands were classified as "intermediate hard ligands" having oxygen donor, which favors to form ionic bonding. However, it was found that the reactivity of these ligands depends on ionic radius and that there is a difference of the reactivity between hydroxide ion and other intermediate hard ligands such as carbonate and carboxylate. For example, among divalent alkaline earth metal ions, Mg<sup>2+</sup> mainly precipitates as hydroxide (brucite), while Ca<sup>2+</sup> prefers to form carbonate (calcite) or phosphate (apatite) minerals rather than hydroxide. However, quantitative discussion on the selectivity of metal cations has not been performed.

In this study, we evaluated the standard Gibbs free energy, entropy, and enthalpy for the complex formation of hydrated metal cations with these ligands based on a critical thermodynamic database. As a result, we found that the entropic contribution to the free energy was large in the case of hydroxide complex of smaller cation. In contrast, the entropic contribution to the free energy was small in the case of hydroxide complex of larger cation and other complexes. In addition, the enthalpy contribution was not significant in this reaction. In the aqueous complexation reaction, entropy was controlled by the number of water molecules replaced by the ligand, suggesting that hydroxide complex for large cation was not stable due to the small effect of dehydration.

This suggestion was confirmed by quantum mechanical calculations, which was performed with B3LYP/6-311+G\* level using Gaussian 09. We calculated distance between metal (M) in the center and oxygen (O) in the ligand with the increase of number of water molecules placed in the vicinity of the metal ion. As a result, it was found that the M-O distance for hydroxide complex is larger than that of carbonate in the case of larger cation and vice versa. This means that hydroxide prefers to form outer-sphere complex for larger metal ion, which is not the case of other intermediate hard ligands. This result is consistent with what we suggested based on the thermodynamic data.

Keywords: Speciation, Entropy, Complexation, Hydrolysis, Quantum chemical calculation

## Consistency between fission-track and U-Pb ages of zircon and its implications

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Following the recommendation by the Fission Track Working Group of the IUGS Subcommittee on Geochronology (Hurford, 1990), the fission-track method was transformed into a simplified and user-friendly dating tool. Standardization based on the common use of international age standards is what is called the zeta calibration. However, the adoption of the standardization scheme in which fission-track ages are determined against reference ages (K-Ar, Ar/Ar, Rb-Sr), and not based on physical parameters directly associated with the fission process, meant that the fission-track method lost its status as an independent geochronometer. Over the last two decades, we have investigated the problems of the absolute calibration approach, and we have finally demonstrated that it works well for zircon when using the external detector method (Danhara and Iwano, 2013). One of our conclusions is that the fission-track age for the Fish Canyon Tuff is 28.4+/-0.2 Ma. This is concordant with the recent zircon U-Pb ages (Schmitz and Bowring, 2001; Bachmann et al., 2007) and slightly older than the sanidine Ar/Ar age of 27.8+/-0.2 Ma, which is the reference age for the zeta calibration. We will discuss the consistency between fission-track and U-Pb ages of zircon from volcanic samples and give some comments on fission-track age standardization.

Bachmann et al. (2007) *Chemical Geology* 236, 134-166.

Danhara and Iwano (2013) *Island Arc*, 22, 264-279.

Hurford (1990) *Chemical Geology*, 80, 171-178.

Schmitz and Bowring (2001) *Geochimica et Cosmochimica Acta* 65, 2571-2587.

Keywords: zircon, fission-track age, U-Pb age, calibration

## Fe isotope measurement of taenite using LA-MC-ICPMS technique with Galvano scanner system

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The laser ablation-multicollector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) is widely accepted as the powerful technique to reveal the isotope ratios of solid sample. This technique can achieve the in-situ analysis of micro region with swiftness. On the other hand, it is difficult to avoid the mass spectrometric and non-mass spectrometric interferences from coexistent elements in this technique because the produced sample particles by laser ablation are directly introduced into the ICP with carrier gas. Such interferences have a potential to intercept to reveal the precise and accurate isotope data. The effect on the isotope ratios of analyte from coexistent elements can be corrected by using the standard material which include same amount of coexistent elements as the sample. However, synthesis of isotopic homogeneous solid material is extremely difficult.

In this study, we have developed a technique to measure the Fe isotope ratios of taenite in iron meteorites. The Fe isotope signature of iron meteorites is one of the key information to understand the core formation of planetesimals and terrestrial planets. However, the in-situ Fe isotope measurement of taenite is difficult because of the abundant Ni (>25 wt%) in it. In order to overcome this problem, we have applied Galvano mirrors and a telecentric optical system (Yokoyama et al., 2011) for LA-MC-ICPMS technique. In this technique, pure iron (IRMM-014) and pure Ni were ablated at a time using femtosecond laser with Galvano system as the Fe isotope standard. The ablated Ni amount was adjusted to the Ni amount in the taenite sample. The Fe isotope ratios ( $^{56}\text{Fe}/^{54}\text{Fe}$  and  $^{57}\text{Fe}/^{54}\text{Fe}$ ) of taenite phases were measured using MC-ICPMS and the mass fractionation in the mass spectrometry was corrected by sample-standard bracketing technique. The precision and accuracy of Fe isotope data obtained by the presented technique will be discussed in this presentation. The isotope analytical technique developed in this study can be applied not only for taenite phase in iron meteorite but also for other sample which include coexistent elements.

Keywords: ICP-MS, laser ablation, taenite, Fe isotope, Galvano

## High-Pressure Neutron Beamline PLANET for investigating "Water" in the Earth

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The PLANET is the world's first neutron beamline specialized for high-pressure and high-temperature experiments. The most characteristic feature is the capability to investigate the state of water and hydrogen in minerals at high-pressure and high-temperatures up to 20GPa and 2000K with the multi-anvil high-pressure apparatus. The construction was started in 2008 and the experiments have been conducted since Nov. 2012. In this talk, the design and performance of the PLANET are introduced.

PLANET is designed so as to investigate structures not only of crystalline but also of amorphous (liquid) materials. The resolution of the diffraction pattern ( $\Delta d/d=0.6\%$ ) was found to be almost equal to the designed value(0.5%). The elimination of the background from the sample surrounding materials, which is the most important issue in the high-pressure experiments, was found to be accomplished by using the severe incident and receiving collimators. With this development, PLANET offers very clear patterns even at high pressures. This character made the PLANET one of the most innovative beamlines among several high-pressure neutron beamlines in the world.

Keywords: neutron, high pressure, beamline, hydrous



## High-pressure neutron beamline at J-PARC and applications to earth and planetary sciences

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Construction of the high-pressure dedicated beamline, PLANET, in Japan Proton Accelerator Research Complex (J-PARC) has been completed in 2012 and scientific programs for general users have just started in 2014. The PLANET beamline has a focusing mirror for incident neutron and two 90-degree detector banks. Each bank has 160 pieces of Position Sensitive Detectors (PSDs) filled with <sup>3</sup>He gas. Each bank has a detector coverage of  $90 \pm 11$  degree against the incident beam in the horizontal direction and  $0 \pm 35$  degree in the vertical direction. Radial collimators are attached in front of the detector banks to reduce the background. The instrumental resolution is 0.6% in  $\Delta d/d$ . The accessible d-spacing is normally 0.2-4.2 Å and is doubled in a double-frame setup. The power of the proton beam is around 300 kW and will be increased to 600 kW in 2014. The most characteristic feature of the PLANET beamline is the multi-anvil apparatus with six independently acting 500-tonne rams (6-axis press called ATSUHIME). Using ATSUHIME, we successfully observed neutron diffraction patterns of hydrous minerals at high pressure and high temperature without any contamination from sample-surrounding materials such as pressure transmitting media, anvils, and so on. This clearly shows that the incident slit and radial collimator installed in the beamline are very effective to obtain the diffractions under high pressure.

We focus on pressure-responses on the structure of materials with hydrogen-bonding networks through neutron diffraction measurements at high pressure. These results will contribute to fundamental understanding of hydrous materials in the deep earth and icy material in the planets.

Keywords: neutron, neutron diffraction, hydrogen, water, high pressure, ices

## Geo-neutrinos for advanced earth studies

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Neutrinos generated in Earth (geo-neutrinos) gives us information about the distribution of Uranium (U), thorium (Th), and potassium (K) inside Earth. Beta-decays of radionuclides U/Th/K inside Earth produce low energy anti-electron neutrinos (U and Th produces  $7.41 \times 10^7$  neutrinos  $\text{kg}^{-1}\text{s}^{-1}$  and  $1.62 \times 10^7$  neutrinos  $\text{kg}^{-1}\text{s}^{-1}$  respectively (without considering neutrino oscillation)) that traverse through Earth without being disturbed due to their extremely small interaction cross section with matter. Recent geo-neutrino observations have produced results that have a potential to support and clarify the current concerns of earth science: estimating the amount of contribution to the surface heat flux; constraining existing Earth's compositional estimates; and clarifying the origin of low shear velocity regions found at the core mantle boundary (CMB). Today, there are two detectors capable of measuring geoneutrinos: KamLAND, in Japan, and Borexino, in Italy. The KamLAND research team has found  $116 \pm 28$ , 27 geoneutrino candidate events (generated through the decay processes of  $^{238}\text{U}$  and  $^{232}\text{Th}$ ) during 2,991 days of geoneutrino observation (Gando et al. 2013). The contribution from geonuclear reactions to the heat flow, estimated from examination of the geoneutrino flux, reached  $11.2 \pm 7.9$ , 5.1 TW. Although the volume of the Borexino detector (280 t) is much smaller than that of KamLAND (1,000 t), the background from reactor neutrinos is much lower than that for KamLAND because there are no nuclear power plants in Italy. Borexino detected  $14.3 \pm 4.4$  geoneutrino candidates over 1353 days of observation. Both measurement results are consistent each other, and also reject the fully radiogenic model, which assumes that the total Earth's surface heat flux is completely originated from radiogenic heat from U, Th and K. The upper limit on the fully radiogenic heat flux hypothesis (Herndon 1996) was set to be 4.5 TW at 95% confidence level (Bellini et al. 2013).

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Bellini, G., Ianni, A., Ludhova, L., Mantovani, F., McDonough, W.F. 2013. Geo-neutrinos, *Prog.Part.Nucl.Phys.* 73:1-34

Keywords: Neutrino, Uranium, Thorium, Mantle

## Multi-range imaging mass spectrometry using laser ablation-ICP-mass spectrometry

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Time-resolved elemental and isotopic data can provide key information about the time changes of the geochemical conditions of the surface environment of the Earth, and therefore, critical restriction for the origin or evolutionary sequence of the surface environment of the Earth and the life could be derived. To obtain reliable and exclusive information from the samples, tremendous efforts have been given to develop various analytical techniques, which could provide both the higher elemental sensitivity and higher analytical throughput. Among the analytical techniques, plasma ion source mass spectrometer coupled with the laser ablation sample introduction technique (LA-ICPMS) has now become the most sensitive and user-friendly analytical tool to derive elemental and isotopic distribution among the different phases or minerals. Moreover, in the LA-ICPMS technique, atomization and ionization of the analytes were independently carried out from the sampling (i.e., post ionization technique), and therefore, the sampling and ionization conditions could be separately optimized. The post ionization technique results in the smaller contribution of the matrix effect, which could be the major source of analytical error. Furthermore, for the LA-ICPMS technique, sample was located under the atmospheric pressure sample cell, and laser induced sample aerosols were carried into the ICP ion source using a He carrier gas. This suggests that no evacuation of the sample housing is required, and therefore, biological cell or tissue samples (i.e., wet samples) can be directly subsidized to elemental imaging analysis, obviating the drying or freezing procedure for the analysis. The LA-ICPMS technique has further advantages of imaging analysis for samples with various sizes, ranging from 10 microns to >10 mm. Because of high capability for quantitative imaging of ultratrace-elements, together with high analytical capability to measure large-sized samples, the LA-ICPMS technique has blossomed to become the key analytical technique for the imaging analysis of trace-elementals and isotopes. This is very important to obtain elemental and isotopic images for not only biological samples, but also various rock or minerals. In fact, imaging data for whole rock pierces or minerals can tell us the substantial process for the elemental distribution or diffusion among the samples. We should recall that we could not see the forest for the trees. Despite the obvious success in obtaining the elemental and isotopic imaging data, neither quantitative evaluation of the detection limits for the elements nor the dependence of the analytical conditions (e.g., laser pit size, raster rate, system setup or condition for data acquisition) onto the resulting spatial resolution were made. To investigate these, we have measured imaging analyses of several trace- and ultratrace-elements from meteorite samples and biochemical samples under the various analytical conditions. In this presentation, we will described the effect of the system setup and operational settings onto the resulting spatial resolution and onto the limit of detection for the elements.

Keywords: laser ablation, ICP-mass spectrometry, imaging mass spectrometry, multi-scale imaging, trace-elements, quantitative imaging

## Cavity ring-down spectroscopy for the isotope ratio measurements of water from fluid inclusions in stalagmites

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Oxygen isotope record in stalagmites is useful to reconstruct past environmental changes. However, the interpretation of calcite isotope record is not straightforward because it is affected by various factors affect such as amount of precipitation and temperature. Water isotope composition of fluid inclusions, and oxygen isotope difference between water and host calcite, from stalagmite are potentially important proxies to estimate the paleo-temperature. Recently, infrared spectroscopy (IRIS) has been widely used for stable isotope ratio measurement of water. Unlike traditional isotope mass spectrometer (IRMS), the IRIS does not require pre-treatment processes (e.g., high-temperature furnace or equilibration device). A limitation of IRIS is that commercially available IRIS systems need large sample volume (1 - 2 micro litres) for liquid water measurement. In this study, we developed a custom-designed device suitable for precise measurement of smaller volume (0.05 to 0.20 microlitres) of water, and tested two extraction methods (thermal extraction and mechanical crushing). Oxygen and hydrogen isotope ratios of water were measured using cavity ring down spectroscopy (WS-CRDS Picarro L2130-i). Stalagmites samples were collected in several caves in Okinawa, Japan. Pieces of stalagmites (80-300mg) subsampled from homogeneous layers, and reproducibilities of the inclusion measurement were 0.2 permil for  $\delta^{18}\text{O}$  and 1 permil for  $\delta\text{D}$ . The measured  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of inclusion water from recently grown stalagmites agrees with modern dripwaters, indicating that our extraction technique is useful to measure isotope ratios of past inclusion water.

Keywords: Stable isotope, Fluid inclusion, Speleothem, Stalagmite, Paleoclimate, CRDS

## Coral growth-rate insensitive Sr/Ca as a robust temperature recorder at the extreme latitudinal limits of Porites

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Corals are rich archives of climatic changes with high-resolution record of seasonal change such as sea-surface temperature (SST), in tropical and sub-tropical seas during recent and distant past. Past SST are commonly reconstructed from the trace elements present in annually-banded coral skeletons. Recently, reef building corals were found in temperate regions due to coral habitat range shifts and/or expansions. Therefore, it could be a powerful tool for reconstructing climatic changes such as global warming and ocean acidification over long period. However, because of the more stressful environment for corals in temperate region than tropic or subtropics, we have to know how to reconstruct palaeo-SST using temperate corals.

This paper was reported Sr/Ca-based SST reconstructions for temperate Porites corals collected from Kyushu, Japan, near the northern latitudinal extent of hermatypic corals. New, high-resolution Sr/Ca data, measured along the growth axes of Porites from Ushibuka, were compared to previously published  $\delta^{18}\text{O}$  data from the same specimens (Omata et al., 2006). Results indicate that Sr/Ca variations in a low-growth coral remain independent from growth rate, in contrast to the oxygen isotope ratios of the same coral. Results clearly indicate that Sr/Ca robustly reproduces SST variations from regions along the extreme latitudinal limits of hermatypic coral habitat, independent of growth rate variations.

Additionally, Sr/Ca of the other two Porites corals collected in Ushibuka were measured and the inter-colony variation of reconstructed SST was shown. At this stage, it is difficult to reconstruct accurate SST using only one specimen of Porites in temperate region. However, we can reconstruct SST within only 1 °C difference from observed SST if we calibrate Sr/Ca-SST using more than two corals. It is expected that in the future the fossil temperate corals will be commonly used for palaeo-SST reconstruction.

## Maximizing organic records: Recent achievements and future directions

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Molecular isotopic record in either organisms or sediments has been proven useful for better understanding the bio(geo)chemical processes, reconstructing paleo-environment, etc. During the last decades, target molecules have been expanding from simple lipids to complex physiologically active compounds. There are two key issues to push this molecular tool more useful and more efficient: 1) Purity of the target compounds that are extracted from environmental samples (generally a complex mixture of organic compounds), and 2) sensitivity of isotope-ratio mass spectrometry (IRMS) system for precisely measuring isotopic compositions. In this presentation we will overview the recent advances in these two issues, and how these achievements contributed to the progresses in our knowledge. We also try to mention in the future challenges of molecular isotopic signatures.

Keywords: Organic molecule, isotopic composition, nitrogen, carbon

## Precise and sensitive determination of stable isotopic compositions of amino acids

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Amino acids are biologically central and functional organic compounds. Their molecular and stable isotope profiles have been employed as a tool in various fields of studies, particularly for understanding of the trophic energy flow of food web ecology as well as for estimating the origin of amino acid procurers in extraterrestrial samples (e.g., meteorites). One of the most powerful techniques in the stable isotope studies of amino acids is compound-specific isotope analysis (CSIA) by gas chromatography/isotope ratio mass spectrometry (GC/IRMS), which potentially allows a rapid and precise determination of H, C, N, O, and S isotopic compositions of individual amino acids in complex mixture of samples. However, (1) isotopic fractionation and exchange during pretreatment (e.g., hydrolysis, extraction, purification, and derivatization) of samples, (2) chromatographic separation among individual amino acids, and (3) less sensitivity on GC/C/IRMS (i.e., 10-50 nmol of elements is required) are always problematic in CSIA of amino acids.

In the presentation, we will briefly review these issues on CSIA of amino acids, and show current advances in the precise and sensitive determination of C and N isotopic compositions of amino acids (i.e., within 0.4-0.8 permil for a minimum sample amount of 0.5 nmol element), based on the minimizing isotopic fractionation during HPLC purification and derivatization as well as reducing leak and background variation in GC/IRMS instrument. With this method, we can access C and N isotopic signature of wide range of samples including amino acids in bacteria and archea isolated from natural environments as well as amino acid procurers in meteorites.

Keywords: stable isotope, amino acids, food web, meteorite

## On the role of amino acid metabolism and a biogeochemical linkage

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Deep-sea sediments harbor a novel and vast biosphere with yet unconstrained importance in the global biogeochemical cycle. To explore these habitats is interdisciplinary challenges for the biogeochemical and geomicrobiological scientific community. The limits of deep biosphere are on-going subject, which were not yet known in terms of environmental properties, including depth, temperature, energy availability, and geologic age; however, it is known that seafloor microbes play a significant role in chemical reactions that were previously thought to have been abiotic.

Since the novel classification by Woese and Fox (1977), Archaea, one of three domains of life, had been originally believed to exist in extreme environments including high temperature, high salinity, low oxygen concentration. However, recent advances in molecular and phylogenetic approaches revealed their widespread distribution in marine and terrestrial environment including deep subsurface biosphere. The planktonic and benthic archaeal assemblages include two major phyla Euryarchaeota and Crenarchaeota. The novel phylum have been also proposed recently as Thaumarchaeota, Korarchaeota, and Nanoarchaeota.

In the present study, we reviewed the recent knowledge of prokaryotic ecology and biogeochemistry from molecular-specific isotopic signatures. Among these, we focused on the role of amino acid metabolism and a biogeochemical linkage mediated by deep-sea benthic archaea.

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Keywords: amino acid metabolism, deep-sea benthic archaea, a biogeochemical linkage

## Simple method for separation of boron from volcanic rocks for isotopic analysis by MC-ICP-MS

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We developed a simple and thus effective method of separation of boron from volcanic rocks.

It has been suggested that easy volatilization of boron and isotopic fractionation during evaporation step after HF decomposition of silicate rock samples; therefore procedure of evaporation at low-temperature (<80C) with mannitol (which suppress volatilization) under boron-free specific experiment environment has been utilized.

Our new method dose not require evaporation step, thus effectively preventing boron volatilization and related fractionation. Contamination opportunity can also be reduced. In our method, supernatant HF solution at sample digestion step is loaded onto mini-column cartridge of Amberlite IRA 743 (0.25mL) with no evaporation step. Recovery yield for silicate rocks was generally >80%. To evaluate our method, the GSJ rock standards (JB-2, JB-3 and JR-2) were analyzed by following the proposed method. Measured boron isotopic compositions for these rocks were in good agreement with preferred values.

## Development on submicron-scale U-Pb dating by Laser post-ionized SNMS

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In order to decipher the history of the Solar System, in-situ U-Pb dating method using SIMS (Secondary Ion Mass Spectrometry) has been used over 40 years, of which spatial resolution is 2-10 micron. In general, the secondary ion yield of SIMS is so low (less than 1 %) that it has been the weak point of this in-situ analysis. Here, we report the performance of Pb isotope measurement using the Laser SNMS that consist of of Ga-ion source for primary beam, femto-second laser for post-ionization, and the multi-turn TOF-SIMS for mass spectroscopy (Ishihara et al. 2010).

Keywords: U-Pb dating, mass spectrometry, in-situ analysis, isotope analysis

## Inhibition effect of natural organic matter on adsorption of radiocesium onto particulate matters in Pripyat River

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Radiocesium have been emitted to environment originated from nuclear weapon tests and nuclear accidents such as in Chernobyl and Fukushima. Among various sources, the nuclear accidents in Chernobyl and Fukushima have caused serious contaminations in land-surface around these areas due to the deposition of the radionuclides dispersed via atmosphere as aerosols. Subsequently, radiocesium can be transported via rivers into oceans. In the soil- river-sediment system, radiocesium has high affinity for particulate matters, in particular for clay minerals. The high affinity has been shown to be the results of specific adsorption to frayed edge site (FES) and interlayer site in 2:1 phyllosilicate as inner-sphere (IS) complexes. However, it has been indicated that cesium adsorption to clay minerals can be blocked by natural organic matters (NOM) that adsorb on the mineral surface. NOM are ubiquitous and play various important roles on the adsorption of metal ions on particulate matters such as (i) promotion of adsorption of metal ions by the complexation with NOM and (ii) inhibition of adsorption by covering the particulate matters. High availability of Cs in soils with relatively high organic matter content was explained in terms of the blocking of access of cesium to specific adsorption sites (such as FES and interlayer site) of the clay mineral.

In river waters in Fukushima, it has been indicated that more than 70% of radiocesium is adsorbed on particulate matters. In contrast, Sansone et al. (1996) showed that more than 70% of radiocesium was in the dissolved fraction in Chernobyl. One critically important difference between the two sites is that peat, which contains large amount of NOM, is the main surface layer in the Chernobyl area. These NOM can be introduced into the Pripyat River that can coat on the particulate matters in river waters. Thus, it is possible that high content of NOM in rivers (e.g., Pripyat River) in Chernobyl can be responsible for the larger fraction of dissolved radiocesium compared with that in Fukushima due to the blocking effect by the NOM. In this study, therefore, adsorption of cesium on particulate matters collected in the Pripyat River with the characterization of the particulate matters have been conducted to study whether the blocking effect is affecting the adsorption behavior of cesium.

Here, we examined Cs LIII-edge extended x-ray absorption fine structure (EXAFS) to study the cesium species adsorbed on the particulate matters collected from Pripyat River and also on the particulate matters after the removal of NOM by the treatment with hydrogen peroxide. To characterize the particulate matter, distribution image of organic substances on the particulate matter was analyzed by compact Scanning Transmission X-ray Microscope (cSTXM) newly developed in Photon Factory, KEK in Tsukuba, Japan. After the cSTXM imaging, characterization of NOM was conducted by near edge X-ray absorption fine structure (NEXAFS) at the C K-edge measured for the NOM by cSTXM.

From this study, blocking effect of cesium adsorption to clay minerals by humic acid was confirmed in natural particulate matter in Pripyat River, which might be related to the larger dissolved fraction of radiocesium around Chernobyl area, compared with that in rivers in Fukushima area.

Keywords: chernobyl, natural organic carbon, STXM

## Development of the technique for determination of I-129 in fish samples as new tracer of marine ecosystem

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The availability of <sup>129</sup>I as a new tracer for marine ecosystem was examined.

The iodine isotopic ratio (<sup>129</sup>I/<sup>127</sup>I) in seawater is determined by the anthropogenic <sup>129</sup>I transferred from the atmosphere, i.e., it shows very high ratio as the order of 10<sup>-10</sup> for <sup>129</sup>I/<sup>127</sup>I at the surface or surface mixing layer and suddenly decreases going deeper to some of 10<sup>-12</sup> or lower. Iodine isotopic ratio (<sup>129</sup>I/<sup>127</sup>I) of marine lives like fish should be determined by their habitats and the ways exchanging iodine with seawater. This means that the iodine isotopic ratio is potential indicator of marine ecosystem. However there have been only few studies using <sup>129</sup>I for marine ecosystem. This is because <sup>129</sup>I is so trace in the marine lives that ordinary analytical techniques cannot detect.

Recent development of analytical technique for <sup>129</sup>I using AMS (Accelerator Mass Spectrometry) enables determine trace amount of <sup>129</sup>I concentration in environmental samples.

In this study the pyrohydrolysis method was applied to extract iodine from fish samples. A freeze-dried and homogenized fish sample, 0.1g to 0.5g, was combusted in the quartz tube under oxygen and water vapor flow. Iodine was extracted into an alkaline solution. An aliquot of this solution was taken for ICP-MS analysis to determine the stable iodine (<sup>127</sup>I) concentration. The remaining was, added with carrier iodine (about 1 mg), purified by solvent extraction and collected as AgI precipitation. <sup>129</sup>I/<sup>127</sup>I ratio was determined by AMS. From the AMS result and the <sup>127</sup>I concentration, the <sup>129</sup>I/<sup>127</sup>I ratio of the fish samples themselves can be calculated.

The extraction yield was evaluated using IAEA-414 fish standard sample. Background in the pyrohydrolysis was also examined.

The preliminary results of fish samples, collected from Suruga-bay (located on Pacific coast in the middle of Honshu, Japan) showed 1×10<sup>-10</sup> to 7×10<sup>-10</sup>, which was consistent with that of surface seawater.

Keywords: Iodine-129, tracer, marine ecosystem, fish, AMS

## Exploring the ecology of catfish through trace elements analyses of otolith by LA-HR-ICPMS to reconstruct palaeo-SST

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Otoliths are incrementally precipitated aragonite biominerals found within the inner ear of all teleost fish. Previous studies show that oxygen isotopes ( $\delta^{18}\text{O}$ ) of otolith aragonite precipitate in equilibrium with those of seawater regarding ambient water temperature (Campana, 1999). Therefore, ( $\delta^{18}\text{O}$ ) of otolith can be used as a strong thermometer for reconstructing the past environment. In the meantime, fish habitats are necessary to be revealed before understanding the palaeoenvironments using otolith due to its nature as biomineral associated with fish. Thus we applied trace element measurements in the specimens to identify the habitable zones namely marine, brackish and freshwater. Strontium abundance in carbonate samples (Sr/Ca) is the best indicator to be employed because of distinct differences in concentration in marine and riverine waters (Walther and Thorrold, 2006). The present study is therefore aiming for identifying the past fish ecology using Sr/Ca in otoliths measured by newly developed laser ablation (ArF excimer) high resolution inductively coupled plasma mass spectrometry (LA-HR-ICPMS). The study area is the Gulf of Kutch in Gujarat district, northwestern part of India. This area is strongly influenced by Indian monsoon, which is characterized as distinct seasonal rainfall (humid summer and dry winter). Salinity distribution within the Gulf of Kutch is unusual compared with general river-estuary system. Lower salinity ( $\sim 37$ ) is observed in the inner part, whereas higher values ( $>40$ ) are observed near the mouth (Vethamony et al., 2007). In this study, we analyze both modern and fossil otoliths. Fossil otoliths were excavated from archaeological sites of Harappan Civilization located in Bagasra and Datrana. According to otolith morphology, they probably the otoliths of Siluriformes Ariidae catfish, known as marine catfish. Trace element concentrations relative to Ca ( $^{23}\text{Na}$ ,  $^{25}\text{Mg}$ ,  $^{55}\text{Mn}$ ,  $^{88}\text{Sr}$  and  $^{137}\text{Ba}$  /  $^{43}\text{Ca}$ ) were measured along with growth bands of otoliths. They are measured using LA-HR-ICPMS. The system is consisted with Thermo Finnigan Element XR high resolution inductively coupled plasma mass spectrometer coupled to Resonetics 193 nm excimer laser ablation system installed at Atmosphere and Ocean Research Institute. Nine modern and 16 fossil otoliths thin sections were prepared and 6 modern and 4 fossil sections were analyzed using LA-HR-ICPMS. Abrupt changes in Sr/Ca with an amplitude of as much as 3 mmol/mol within  $\sim 2$  weeks suggest fish migration between freshwater and the seawater. From a conservative mixing model for Sr/Ca of estuarine water, the fish has migrated to riverine environment sometimes in their life since the model predicts small changes in Sr/Ca of water if salinity is higher than  $\sim 5$  unit. It is rather changes in Sr concentrations in ambient water than that for water temperature or salinity in the gulf.

Keywords: otolith, trace element, oxygen isotope, LA-HR-ICPMS, Gulf of Kutch

## Improved $^{10}\text{Be}$ preparation to reduce analytical background for earth surface process studies

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Due to advancement of Accelerator Mass Spectrometry (AMS), *in situ* produced beryllium-10 ( $^{10}\text{Be}$ ) in quartz has been used for earth surface process studies, such as surface exposure dating (*e.g.* Yamane *et al.*, 2011), erosion rate estimations (*e.g.* Shiroya *et al.*, 2012), tectonic processes (Yokoyama *et al.*, 2005) and so forth (*e.g.* Gosse and Phillips, 2001). In order to expand the applicability of this technique, the sample with low  $^{10}\text{Be}$  concentration need to be measured with high precision. This requires reduction of background that is often affected isobars (boron-10). We have conducted several attempts and found that the length of time exposed to the ambient atmosphere during the oxidization process is the most important step to increase  $^{10}\text{Be}$  background (Yokoyama *et al.*, submitted). In this presentation, we discussed our experimental results and potential improvement of topics for understanding of earth surface process.

Keywords: beryllium-10, background, earth surface process, Accelerator Mass Spectrometry

## Radiocarbon pretreatment system of AORI AMS

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The Accelerator Mass Spectrometry(AMS)is effective in radiocarbon dating. By the conventional method, a large tandem accelerator(e.g.Accelerating voltage = 5MV) was used. However, the small accelerator(e.g.Accelerating voltage = 500kV) is used in the new AMS analysis.

The small AMS machine is handy.We installed small AMS machine in our laboratory. We will present the outline of new AMS pretreatment system and the geochemical application research using that.

Keywords: Radiocarbon, AMS, Accelerator Mass Spectrometry, 14C