Computational Science for Environmental Geochemistry

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Computational science has provided powerful methods for chemistry, physics, biology, and geoscience with the development of computational facilities and methods. Here we discuss atomic-scale simulations in computational science including *ab initio* calculations and molecular simulations using force fields. These atomic-scale simulations have developed in different way depending on research fields such as band calculations for understanding conductivity and magnetism of solids in physics, molecular orbital methods for reproducing weak molecular interactions and chemical reactions in chemistry, and molecular simulations for revealing the stable structure of large protein molecules in biology. A direction of computational science in geochemistry is the development of methods applicable to elevated temperature, pressure, and multi-component systems. In this presentation, we discuss perspectives of computational science for developing environmental geochemistry.

Keywords: ab initio calculation, Molecular simulation, Free energy, pH, Fluid, Solid-liquid interface

Determination of absolute $^3He/^4He$ ratio of He Standard of Japan

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$^3He/^4He$ ratios in terrestrial samples vary more than three orders of magnitude, because primordial helium with $^3He/^4He$ of (1.4-4.6) x 10^{-4} has been diluted by addition of radiogenic ^4He produced by decay of U- and Th-series elements in different degrees depending on $^3He/(U+Th)$ ratio of each reservoir. This feature makes $^3He/^4He$ ratio a powerful tracer in geochemistry and cosmochemistry. Though atmospheric helium with $^3He/^4He$ ratio of 1.4 x 10^{-6} is used to calibrate $^3He/^4He$ measurement with a noble gas mass spectrometer, relatively low concentration and $^3He/^4He$ ratio of the atmospheric helium cause many difficulties to use it as a working standard for daily measurements. Thus noble gas laboratories often use their own working standards prepared from a natural gas sample with high $^3He/^4He$ ratio or by mixing of isotopically pure ^3He and ^4He. "He Standard of Japan" (HESJ) is one of the latter originally prepared by four noble gas laboratories in Japan [1] and now distributed worldwide as an interlaboratory standard [1,2]. However, $^3He/^4He$ ratio of HESJ was determined by comparison with that of atmospheric helium, i.e., absolute $^3He/^4He$ ratio has not been determined yet and the accuracy of the value still rely on the early determinations of absolute $^3He/^4He$ ratio of atmospheric helium [3].

As long as $^3He/^4He$ ratio is used to compare relative contributions of primordial and radiogenic in each geochemical reservoir, absolute $^3He/^4He$ value of atmospheric helium or HESJ is less important. However, it is a critical issue in some applications of helium isotopes, such as tritium-^3He dating and an experimental project to measure the neutron lifetime with total uncertainty of 1 sec (0.1%) using pulsed neutron source at J-PARC [4].

A neutron decays into a proton, an electron, and an anti-neutrino with a lifetime of 880.3 ±1.1 sec [5]. The lifetime is an important constant in the Big Bang nucleosynthesis (BBN) that controls amounts of primordial elements in our universe. In this experiment, the incident neutron flux is measured by counting $^3He(n,p)^3H$ reaction in a time projection chamber detector filled with ^3He, ^4He and CO_2. To determine neutron lifetime with uncertainty less than 0.1%, ^3He number density in the detector must be accurately known with even smaller uncertainty. As a part of this experiment, we are developing a gas handling system to control ^3He number density with uncertainty of 0.1%. The ^3He gas is mixed with research grade He in a vessel with measuring pressures of these gases precisely using a calibrated piezoresistive transducer.

We fabricated control samples of known $^3He/^4He$ ratio using the gas handling system and measured the ratio using a sector type single focusing noble gas mass spectrometer with double collector system [6] at Dept. of Basic Sci., the Univ. of Tokyo by referring to HESJ. The results will contribute to determine the absolute $^3He/^4He$ value of HESJ, and that of atmospheric helium also [6].

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Keywords: Isotope ratio analysis, 3He/4He ratio, Mass spectrometry, Big bang nucleosynthesis, Neutron beta decay

A new high-precision method for determining stable chlorine isotopes using UV-LA-MC-ICP-MS

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Chorine is the dominant anion in many geological fluids and one of the main volatile components on Earth. It has high partition coefficients in aqueous fluid (Bureau et al. 2000) and is enriched in seawater, pore fluid and sediment, but depleted in the mantle. Chlorine has two stable isotopes: ^{35}Cl and ^{37}Cl. The isotope ratios of ^{37}Cl/^{35}Cl are usually expressed by δ-notation relative to Standard Mean Ocean Chloride (SMOC) as

δ^{37}Cl = [(^{37}Cl/ ^{35}Cl)sample / (^{37}Cl/ ^{35}Cl)SMOC −1] x1000. (Eggenkamp 2014)

Their large relative mass difference suggests that these isotopes should fractionate during reactions between aqueous chloride solutions and solid phases in which Cl is at least partly covalently bound. Taken together, the δ^{37}Cl also may provide a good tracer of subducted materials into the mantle. Measurement of chlorine isotope ratios has been performed by the gas source isotope ratio mass spectrometry (IRMS) (Kaufmann et al., 1984), the positive and negative thermal ionization mass spectrometry (P-TIMS / N-TIMS) (Xiao and Zhang 1992; Desaulniers et al., 1986) and the inductively coupled plasma mass spectrometry (ICPMS) (Fietzke et al., 2008).

We report a new rapid high-precision determination method of chlorine isotope ratios in halite and AgCl pellet formed from seawater and igneous rock samples. Use of a 266 nm ultra violet-femtosecond laser ablation (UV-FsLA) provided quantitative sampling of halite and AgCl, and enabled precise determination of ^{37}Cl/^{35}Cl isotope ratios (δ^{37}Cl) coupled with a multiple Faraday collector-inductively coupled plasma mass spectrometer (MFC-ICPMS). We used ^{36}Ar^{+}/^{38}Ar^{+} as an external standard for the mass bias corrections between ^{39}K^{+}–^{41}K^{+}, ^{36}Ar^{1}H^{+}–^{38}Ar^{1}H^{+}–^{40}Ar^{1}H^{+}, and ^{35}Cl^{+}–^{37}Cl^{+} with isobaric overlap corrections between K^{+}, ArH^{+}, and Cl^{+} ions. Sulfur (^{36}S^{+}) isobar on ^{36}Ar^{+} was indirectly monitored and corrected by a baseline modelling using ^{36}Ar^{+}/^{38}Ar^{+} measurement. Those combined to accomplish an accurate and high-precision measurement of ^{37}Cl^{+}/^{35}Cl^{+} ratios. Using the new analytical protocol, δ^{37}Cl in the natural halite samples were analyzed by direct laser ablation. The δ^{37}Cl in igneous rocks were analyzed by AgCl powder pellets produced after pyrohydrolysis separation and co-precipitation of the separated Cl with silver. The external reproducibility of δ^{37}Cl measurement was ±0.2 ‰2SD (2-standard deviation) for halite and ±0.3 ‰2SD for AgCl rivaling to the gas source isotope ratio mass spectrometry. The new analytical protocol enabled a precise and rapid δ^{37}Cl analysis of igneous rock samples from AgCl with as small as 4 μg chlorine. This is also the first report analyzing a high-precision δ^{37}Cl *in situ* from halite of the same amount of chlorine.

Keywords: stable chlorine isotopes, UV-LA-MC-ICP-MS

Development of rapid and precise dating method: Applying on chronology in Jack Hills

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Most of the global events, such as formation of magma ocean, core-mantle segregation, crust formation, and/or chemical evolution of atmosphere, could be completed within the first 0.5 Byr of the Earth History, so called Hadean Eon. Despite the great importance of the Hadean Eon, no petrographic record can be found for this stage, and only geochemical information can be derived from small minerals such as zircons or other accessory minerals within zircons (e.g., apatite, muscovite, or biotite). For geochemical studies for Hadean Eon, many pioneering studies have been made based on the isotope geochemistry on zircons collected from Jack Hills and Mt. Narryer, Western Australia. It is widely recognized that zircons collected from these area have been thought one of the most principal clues for Hadean studies. Moreover, further detailed studies have been carried out from small inclusions in zircon crystals. Zircons from Jack Hills contain various mineral inclusions such as muscovite, quartz, biotite, apatite and so on, and about two-thirds of them are muscovite and quartz, probably due to secondary replacement of primary apatite (Hopkins *et al.*, 2008, Rasmussen *et al.*, 2011). Recently, biogenic carbon, as graphite inclusion, was recovered from 4.1 Ga zircon, but an abundance of carbon-bearing Jack Hills zircons of only about 1-in-10,000 (Bell *et al.*, 2015). In addition, the percentage of Hadean zircons to detrital zircons in Jack Hills was as small as 7% (Holden *et al.*, 2009). For these reasons, large number of age data for zircon grains must be defined to derive reliable and objective information concerning the Hadean history of the Earth. To overcome this, we have developed new analytical technique to define precise age data from combination of U-Pb (Pb-Pb) dating method with high sample throughput.

We have developed rapid and precise dating technique for zircons using laser ablation ICP-mass spectrometer (LA-ICP-MS), equipped with two Daly ion collectors (Nu Plasma IID, Wrexham, UK). Laser ablation instrument used in this study was ESI NWR193 laser ablation system (New Wave Research, Oregon, USA). Combination of multiple collector-ICPMS system and ArF Excimer laser ablation system enables us to measure Pb-Pb age for the sample within 10 second/spot, and uncertainties in the resulting Pb-Pb age data can be minimized by the multiple-collector system setup. Based on the age determination system using LA-MC-ICPMS technique, we just started to measure Pb-Pb age data from 180 grains of zircons within an hour . In this presentation, difference in the resulting age histogram for the zircons collected from Jack Hills will be discussed, and detailed observation for various inclusions in the Hadean zircons will be demonstrated in this talk.

Keywords: Hadean, Jack Hills, LA-ICP-MS, MC-ICP-MS, zircon, mineral inclusion

^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd chronology of basaltic eucrites

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Eucrites are interpreted to have originated from the asteroid 4-Vesta’s crust. They are petrographically classified into basaltic and cumulate eucrites. Determination of precise ages for eucrites will constrain the period of igneous activity and the following thermal metamorphism of Vesta and may further provide insights into its differentiation and thermal history. Sm-Nd dating is one of the most suitable approaches for investigating the crust crystallization age. The Sm-Nd systematics has two chronometers: the long-lived ^{147}Sm-^{143}Nd ($T_{1/2}$ = 1.06×10^{11} y) and the short-lived ^{146}Sm-^{142}Nd ($T_{1/2}$ = 1.03×10^{8} y [1]) systematics. Bouvier et al. [2] revealed that the variation of Sm/Nd ratios for basaltic eucrites were several times smaller than the entire range of Sm/Nd ratios for all eucrites, making it difficult for obtaining the precise Sm-Nd whole-rock isochron age for basaltic eucrites alone.

In this study, we determine the ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd ages for bulk rocks of basaltic eucrites, (NWA 7188, Juvinas, NWA 5229, Nuevo Laredo and Agoult). The samples were decomposed with HF, $HClO_4$ and HNO_3. After the sample digestion, ~10% of the solution was removed and mixed with the ^{149}Sm- and ^{145}Nd-enriched spikes. The spiked solution was passed through TRU Resin (Eichrom) for separating REEs from the matrix elements. We measured the ^{145}Nd/^{146}Nd and ^{147}Sm/^{149}Sm ratios in the sample separated for determining the Sm/Nd ratios by ID-ICP-MS (X-series Ⅱ, Thermo) [3]. The remainder of the sample solution was used for highly precise Nd isotope analysis. The Nd was separated by a three-step column chemistry procedure; 1) major elements were removed by passing through a cation exchange resin, 2) Ce was removed using Ln Resin (Eichrom) by oxidizing Ce^{3+} into Ce^{4+} using $KBrO_3$ [4,5], and 3) Nd was separated from Sm using Ln Resin [3]. We achieved Ce/Nd = ~1.2×10^{-5} and Sm/Nd = ~5.2×10^{-6} with >92% Nd recovery. The ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd ratios were analyzed by TIMS at Tokyo Tech (TRITON plus) with the dynamic multicollection method [6].

The whole-rock isochron ages of five basaltic eucrites yielded the ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd ages of $4565\,^{+41}_{-58}$ Ma and 4529 ±260 Ma, respectively. Although the error of the isochron is relatively large, the whole-rock ^{146}Sm-^{142}Nd age of basaltic eucrites is indistinguishable from that of cumulate eucrites obtained previously ($4556\,^{+30}_{-37}$ Ma). This implies that the whole-rock Sm-Nd isochron ages for basaltic and cumulate eucrites most likely represent the timing of global differentiation of the silicate part of Vesta. It is important to note that the timing of global silicate differentiation is nearly contemporaneous to the timing of metal-silicate segregation in the eucrite parent body deduced from the age obtained by the ^{182}Hf-^{182}W systematics [7]. The result supports an idea that eucrites formed by equilibrium and fractional crystallization of silicate part of the parent body immediately after a magma ocean.

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Keywords: basaltic eucrites, Sm-Nd chronology, whole-rock isochron, Vesta

Nucleosynthetic Strontium isotope variability in Allende CAIs

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Calcium and aluminum rich inclusions (CAIs) are composed of refractory mineral such as melilite, spinel or pyroxene and thought to be the first condensates in the early solar system. Most CAIs possess a variety of nucleosynthetic isotope anomalies for heavy elements. Brennecka et al. [1] reported that Sr, Mo, Ba, Nd and Sm isotope composition in CAIs were uniform, yet distinct from the solar system average compositions. However, most of previous studies analyzed "bulk" CAIs without detailed mineral description. CAIs are composed of various mineral assemblages depending on the environment and/or the timing of individual CAI formation. The difference of mineral assemblages can be observed even within a single CAI. Therefore, it is important to determine the isotope compositions of heavy elements not only for different types of CAIs, but also of multiple spots within a single CAI with detailed mineral description.

In this study, we performed *in-situ* measurements of $^{84}Sr/^{86}Sr$ ratios in two Allende CAIs using TIMS (Triton-plus, Tokyo Tech) coupled with a micro milling system (Geomill 326, Izumo) together with detailed mineral descriptions using SEM-EDS (JSM-5310, Univ. of Tokyo and Hitachi 3400, Tokyo Tech). Three specimens of the Allende meteorite were sliced into two respective slabs of which one sides were used for mineralogical analysis and the other sides were used for Sr isotope analysis. We selected three relatively large CAI grains; a cm-size fluffy type A (FTA) CAI, a type B CAI and a fine-grained spinel-rich (FS) inclusion. Using the micro-milling system, we sampled 8 spots from the FTA CAI, 3 spots from type B and 3 spots from the FS inclusion for the analysis of $^{84}Sr/^{86}Sr$ ratios. Samples were decomposed in a pressure digestion system (Digestec DAB-2, Berghof) with HF and HNO_3. Sr separation for high precision isotope measurement was achieved by column chemistry with extraction chromatographic resin (Sr spec, Eichrom).

The mean $m^{84}Sr$ values (10^6 relative deviations from NIST 987) were 175 ppm for FTA, 129 ppm for type B and 56 ppm for the FS inclusion, respectively. Notably, one spot from the FTA CAI showed the greatest $m^{84}Sr$ value (273 ±21 ppm) compared to those of CAIs ever reported. Assuming that FTA CAI predates type B CAI and the FS inclusion, our results would imply that the extent of Sr isotope anomaly in the CAI-forming region was large and heterogeneous at the earlier stage, which subsequently shifted towards low and relatively homogeneous $m^{84}Sr$ values when type B CAI and FS inclusion formed. The isotopic shift was most likely caused by the effective mixing of nebular dusts including p- and/or r-process-enriched carries (i.e., high $m^{84}Sr$) and isotopically normal grains.

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Keywords: CAI, Isotope

Development of highly precise molybdenum isotop analysis by negative thermal ionization mass spectrometry (N-TIMS) for the study of isotope anomalies in bulk meteorites

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Molybdenum is one of promising elements to investigate physical or chemical processes in various fields, including cosmochemistry. Improvements of techniques utilizing state-of-the-art mass spectrometry instruments over the last 15 years made it possible for detecting marginal mass-independent Mo isotopic fractionations (isotope anomalies) observed in extraterrestrial samples. The Mo isotope anomalies for various meteorites provide strong constrains on studies concerning environmental sciences, stellar nucleosynthesis, and the origin and evolution of the Solar System. For example, Mo isotope anomalies in bulk aliquot of meteorites indicated that the anomalies were originated from the heterogeneous distribution of presolar materials in the early Solar System [1]. However, previous studies predominantly focused on carbonaceous chondrites and iron meteorites; otherwise data for the other non-carbonaceous meteorites are limited because the degree of Mo isotope anomalies for these meteorites are only marginal and nearly equal to the analytical uncertainties of standard materials. Here we developed a new, highly precise, and accurate Mo isotope analysis by thermal ionization mass spectrometry in negative ionization mode (N-TIMS) for the study of Mo isotope anomalies in non-carbonaceous meteorites.

A Mo standard solution for atomic absorption spectrometry (Kanto Chem.) was used as an in-house standard. Iron meteorites (Tambo Quemado (IIIAB), Henbury (IIIAB), and Alibion (IVA)) were leached in 6 M HCl and digested with 16 M HNO_3–12 M HCl. After recovering solutions including Mo, the samples were dissolved in 0.4M HCl–0.5M HF to separate Mo by employing the anion exchange resin (Eichrom AG1-X8) through HCl–HF and HF–HNO_3 media [2]. Molybdenum isotopes (MoO^-) were measured by negative-TIMS using TRITON *plus* (Thermo-Fisher Scientific) installed at Tokyo Tech. The instrument was equipped with 9 Faraday cups with 10^{11} Ωamplifiers. Approximately 3 μg of Mo was loaded on a zone-refined Re filament together with $La(NO_3)_3$ as an activator (La/Mo ~5). The results were obtained by averaging 360 ratios collected in the static multicollection mode.

For achieving highly precise Mo isotope analysis, it is important to determe the oxygen isotopic composition of MoO_3 ions in each measurement by monitoring masses 149 ($^{100}Mo^{16}O_2{}^{17}O$) and 150 ($^{100}Mo^{16}O_2{}^{18}O$) ions and to use the data for correcting for the O isotope interferences. After correcting the O isotopic interference and performing mass-dependent fractionation during the TIMS measurement, the acquired Mo isotopic ratios yielded the following reproducibilities (2SD; n = 21): 47, 16, 10, 13, and 33 ppm for $^{92}Mo/^{96}Mo$, $^{94}Mo/^{96}Mo$, $^{95}Mo/^{96}Mo$, $^{97}Mo/^{96}Mo$,and $^{100}Mo/^{96}Mo$, respectively. The reproducibilities have been improved by 1.3–2.7 times compared tothose obtained in previous studies using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).The accuracy of our technique was confirmed by measuring Mo isotopic compositions for two iron meteorites, i.e., Henbury (IIIAB) and Albion (IVA). Molybdenum isotope anoamlies for these meteorites are consistent with those obtained in the previous study [1]. Moreover, we determined positive Mo isotope anomalies for a new iron meteorite, Tambo Quemado (IIIAB). Our N-TIMS technique can be applied to the studies of nucleosynthetic isotope anomalies in extraterrestrial materials as well as mass-dependent Mo isotopic shift in environmental samples.

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Keywords: meteorite, TIMS, molybdenum

Investigetion of atmospheric mercury isotopic compositions: technical development and applications

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Mercury (Hg) is a toxic heavy metal, which exists in various chemical forms in the environmental system. In the atmosphere, Hg exists in three forms ($Hg^0_{(g)}$, gaseous elemental Hg (GEM); $Hg^{2+}_{(g)}$, gaseous oxidized Hg compounds; and $Hg_{(p)}$, particulate/aerosol bound Hg). $Hg^0_{(g)}$ is the dominant species of atmospheric Hg, accounting for >95% of the total Hg in the atmosphere. Because $Hg^0_{(g)}$ is highly volatile and has limited solubility in water, it cannot be easily removed by wet or dry deposition processes. Therefore, the residence time of $Hg^0_{(g)}$ in the atmosphere is relatively long (0.5 to 1 years), which allows long-range transport from mercury emission source(s). Conversely, $Hg^{+2}_{(g)}$ and $Hg_{(p)}$ are effectively removed from the atmosphere through wet and dry depositions. Because $Hg^0_{(g)}$ deposit upon oxidation to $Hg^{2+}_{(g)}$ far from its emission source(s), deposition on local/regional scales represents a combination of multiple sources of Hg (global, regional, or local; natural or anthropogenic).

Over the last decade, the development of analytical methods of highly precise Hg isotopic measurements demonstrated mass dependent fractionation (MDF) and mass independent fractionation (MIF) of Hg isotopes in environmental samples. MDF of Hg isotopes occur during various natural and industrial Hg transformations. MIF of Hg isotopes is observed during abiotic reduction, photochemical and non-photochemical, and physical and chemical processes. Such processes lead to differences in the Hg isotopic composition of different emission sources, both natural and anthropogenic, and atmospheric processes (i.e., transportation, oxidation/reduction, deposition, and reemission). Therefore, Hg isotopic compositions could be used as a tracer of the sources and processes of atmospheric Hg. In this study, we aimed to develop the methods of collection and pretreatment for isotopic measurement of $Hg^0_{(g)}$, and then isotopic composition of $Hg^0_{(g)}$ was investigated for various regions in Japan.

To identify potential mercury sources, air mass back trajectories were calculated for each sample using the NOAA HYSPLIT model. We divided the back trajectory patterns observed in the results into three groups of air masses predominantly derived from (1) a marine source derived from the Pacific Ocean, (2) coastal and land sources that probably contain anthropogenic mercury emitted from urban-industrial regions, and (3) continental sources associated with northwesterly flow at higher altitude (>1500 m) and long-range transportation. Although multiple sources were possibly impacted during the 24 hr ambient sampling, we were able to observe a correlation between the back-trajectory types and Hg isotopic composition.

Keywords: Mercury isotopes, MC-ICP-MS, atmospheric mercury

Δ^{14}C variability obtained from high-resolution radiocarbon measurements in coral skeletons from the western Pacific

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Corals skeletons consistent with calcium carbonate and are widely used as archives of paleoenvironments such as sea surface temperature reconstruction. Radiocarbon (^{14}C) in coral skeletons is used as a tracer of ocean circulation because corals take dissolved inorganic carbon (DIC) of seawater in their skeletons. Sample size requirement for conventional ^{14}C measurement, however, need more than 10 mg of $CaCO_3$ (1 mgC), which prevent us to establish a history of high-resolution seawater properties.

In this study, we established a new ^{14}C analytical method, which requires smaller amount of carbonate samples using the accelerator mass spectrometry (AMS) at the Atmosphere and Ocean Research Institute, The University of Tokyo (YS-AMS). Coral skeletons along the Kuroshio trajectory were used to understand the variations of Kuroshio, which were compared with published radiocarbon ratio (Δ^{14}C) data in the western Pacific.

Our results showed that Δ^{14}C in Luzon, Ishigaki and Kikai Is, along Kuroshio current, were similar after 1950 (Post-bomb period). Before 1950 (Pre-Bomb period), our data showed that Δ^{14}C in 1940s were different from Δ^{14}C in 1900s previously reported by Yoneda et al. (2007). It is suggested that sea surface Δ^{14}C fluctuates during a short period of time in the western Pacific. This variability would influence significantly to the calibration of local marine reservoir effects when calibrating ^{14}C ages to calendar ages.

Keywords: Radiocarbon, Δ14C variability, ΔR, coral, sea surface water

Freshwater eel conservation and Geochemistry

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The Japanese eel, *Anguilla japonica*, have continued to decrease since the 1970’s and appear to have reached a historically critical situation in recent years. Finally, this commercially important species was listed as endangered in the IUCN Red List of Threatened Species. Serious decline of the Japanese eel population requires feasible countermeasures for conservation and sustainable use.

The Japanese eels have been intensively stocked by the national government and fisheries cooperatives for the purpose of stock enhancement in various areas of Japan. The primary method of this is to release small yellow eels from eel farms into rivers and lakes. This stocking practice has been conducted for more than 100 years without being validated its effectiveness to enhance eel stock, while fish stocking includes several kinds of risks such as disturbances of distribution range, disturbances of genetic structures, and spreading diseases and parasites. A method to discriminate naturally recruited wild eels from stocked ones is undoubtedly important, however, no technics had been developed to our knowledge.

Because Japanese eel is a panmictic fish species consisting of a single spawning population, wild and stocked individuals cannot be discriminated genetically. Geochemistry, however, has opened up a possibility to discriminate eels of different origins recently. Oxygen and carbon stable isotope ratios of otolith (calcium carbonate crystal in the fish inner ear) basically depends on the source of environmental water. According to quadratic discriminant analysis based on otolith oxygen and carbon stable isotope ratios, 98.6% of 420 Japanese eels (106 wild and 314 cultured eels) were successfully discriminated into wild and cultured individuals.

Same as the Japanese eels, 8 of 13 freshwater eel species assessed are categorized as threatened or near threatened in the IUCN Red List of Threatened Species. The discrimination method shown above can be applied on these species such as European eel that intensively stocked under Eel Management Plans. Through otolith stable isotope analysis, geochemistry sheds light upon depletion of freshwater eel populations.

Keywords: eel, otolith, stable isotope

Application of FTICR-MS analysis to soil organic matter

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Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) has an ultrahigh resolution which makes it possible that respective organic molecules detected are accurately assigned to a molecular formula. Soil organic matter plays important roles associated with crop productivity and carbon sequestration. However, the chemical structure is still unknown. We applied this technique to some humic and fulvic acids that were chemically extracted and separated from some typical soils in Japan.

Materials and methods

Humic acids (HAs) were prepared from ten Japanese soils to cover varying degrees of humification and fulvic acids (FAs) were prepared from four Japanese and one Chinese soils according to NAGOYA method or IHSS method. The degree of humification of HAs was evaluated with the absorbance at 600 nm per mg C mL^{-1} (A_{600}/C) and the ratio of absorbances at 400 and 600 nm on a logarithmic scale [$\log(A_{400}/A_{600})$]. Based on these two variables, HAs were classified into four types: Rp < P < B < A, with the degree of humificaiton increasing in this order. The FTICR-MS was performed according to Sleighter and Hatcher (2008). The molecular formulas assigned were examined using the van Krevelen diagram, double bond equivalent (DBE), and Kendrick mass defect (KMD) analysis that focusing on condensed aromatic structure.

Results

1) The number of molecular formulas in the condensed aromatic region increased from Type Rp (124-374) HAs to Type A HAs (751-1008). The sum of the peak magnitudes of the condensed aromatic components increased with increasing degree of humification.

2) The largest DBE values tended to be larger in the order: Type A (33) > Type B (30) > Type P (27) > Type Rp (25) HAs.

3) The KMD analysis indicated that potential structures of condensed aromatic components having 2-10 rings could occur in the soil HAs. The largest number of the rings increased in the order: Types Rp and P (7) < Type B (9) < Type A (10) HAs.

4) The KMD analysis indicated that potential structures of condensed aromatic components having up to 7 rings could occur in the five FAs.

Keywords: soil organic matter, mass spectrometry

Stereochemical feedback with “an achiral amino acid precursor” and “a chiral amino acid”: Experimental verifications

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To our best knowledge, the one-handedness of terrestrial amino acids and sugars is essential to the formation, structure, and function of biopolymers and is a defining molecular trait of life on the Earth. Since the time of Pasteur, the development of specific chirality in terrestrial biomolecules has remained one of the most important issues with regard to organic chemical evolution, astrochemistry, and the early Earth chemistry. Numerous hypotheses regarding the origins of homochirality have been presented, from both biogenic and abiogenic processes (e.g., Bonner, 1991; Meierhenrich, 2008). According to the former, life initially was based on achiral molecules and/or racemates and the use of specific enantiomers came about through evolution, whereas the latter theories propose that a tendency toward homochirality was inherent in prebiotic chemical evolution. When we simply imagine a coin toss chemical reaction, prebiotic enantiomers are equally racemic outcomes as 50.0 : 50.0, likewise two sides of a coin. Among these racemic reactions (e.g., the typical nucleophilic substitution reaction), enantiomer-specific isotopic analysis (ESIA) showed infinitely homogeneous components for each enantiomer (Takano et al., 2010). D, L-alpha-alanine (C3 carbon frame; potentially, including D, L-alpha-alanine precursors: Takano et al., 2007) is most abundant chiral amino acid in prebiotic chemistry, except of glycine (C2). For further information of molecular-specific homochiral verification, here we developed a stereochemical feedback reaction with an “achiral amino acid precursor “and “a chiral amino acid trigger”, resulting unique and large enantiomeric excesses in the reaction products. Here, we discuss the reaction mechanism focusing on an amino acid precursor formula and a transition state inducing optically active amino acids. This research was supported in part by a grant for Scientific Research on Innovative Areas (No. 25108001; A. Kouchi & H. Yurimoto) from the Japan Society for the Promotion of Science (JSPS).

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Keywords: “an achiral amino acid precursor” and “a chiral amino acid”, Stereochemical feedbacks

New multiple ion counting-ICPMS system for Age Cytometry

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The MC-ICPMS instruments, equipped with a multiple ion counting system setup, can improve the precision of the age determination, and the data quality achieved by the LA-ICPMS technique is comparable or enhanced compared to those obtained by secondary ion mass spectrometry (SIMS). With the conventional ion counting system, the gains of the ion detectors (electron multipliers) must be calibrated regularly through the elemental analysis for standard materials. This results in elongation of the analysis time for the age determinations. To improve the long-term stability, and also to improve the accuracy of the age data, we have developed new ion counting system using Dalty collector. In this study, two Daly collectors were adopted to the MC-ICPMS instrument (Nu Plasma II, Wrexham UK), and were used to measure 206-Pb and 207-Pb signals. With the Daly ion collectors, both the medium to long-term stability could be remarkably improved from 0.1%/hrs to 0.04%/hrs. Moreover, the counting loss due to dead time of the ion counting system can be corrected based on the conventional non-extendable law, and the beam sizes of greater than 10 MHz (cps) can be successfully measured by the Daly collector. With the multi-ion counting technique, the analysis time for U-Th-Pb age determinations can be significantly reduced down to 1 - 10 sec/spot, and the shorter analysis time enabling to obtain an age distribution of the zircons collected from a sample (age cytometry). This analytical approach allows to decipher the contribution of multiple geological events or multiple sources of the zircons. The “age distribution” is a useful approach to understand the geological sequence underlying the sample formation.

With shorter duration time for the laser ablation, the resulting depth of the ablation pit can be smaller than 1 μm, and therefore, age determinations from thin-layer rim of zircon crystal can be made. Schmitt (2011) reported that the U-Th-Pb age derived from the outer rim (<5 μm) of the zircon crystals can reflect the timing of overgrowth through eruption processes [Schmitt, 2011]. This means that multiple chronological information can be derived from a single zircon grain. With the shorter ablation time achieved by the MC-ICPMS system setup, precise U-Th-Pb ages can be derived from the depth of shallower than 1 μm. This technique can be applied for geochemical evolution processes within magma chambers by determining the difference between crystallization of the zircons and timing of eruption, and thus the U-Th-Pb ages obtained from the rim of zircon crystals can reflect low-temperature geological events. In this presentation, analytical capability of the multi-ion counting technique using Daly collector for the age determination will be demonstrated.

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Keywords: High throughput age determination, Multiple collector-ICPMS, Laser Ablation, Daly ion counter, Thin layer U-Pb chronology

Evaluation of coupling LA-ICP-MS/MS and collision/reaction cell technique for in-situ zircon analysis

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is not only a relatively cheap, fast, low-costing method, but also has high sensitivity to obtain geochronological/geochemical information from micro region of solid samples. However, the highly-ionization capability of this method easily occurs multiple mass interference from isobaric, polyatomic and multi-charged ion. Hence, in the case of LA-ICP-MS, great care for these potential mass interference must be taken, compared to the traditional solution nebulization sampling in which chemical separation of target element is possible. To overcome these problems in LA-ICP-MS, the instrumental setting at high mass resolution power or low oxide formation rate is common, although the decrease of the sensitivity is unavoidable in many cases. Moreover, it should be noted that there has been no effective strategy for reducing the isobaric interference in LA-ICP-MS. In this presentation, we would like to demonstrate the effectiveness of coupling ICP-MS/MS and collision/reaction cell (CRC) technique for in-situ U-Th-Pb dating and quantitative analysis of rare earth elements (REEs) of zircons using laser ablation sample introduce technique.

In U-Th-Pb dating of zircon, the measurement of ^{204}Pb is critically important because it is the only non-radiogenic nuclide among stable isotopes of lead. Unfortunately, in LA-ICP-MS, there is the isobaric interference on ^{204}Pb from ^{204}Hg which is derived from the impurity of the argon gas for ICP ion source. In this study, the reduction of this interference is tested by flowing a small amount of ammonia gas in the CRC. In this case, while the polyatomic ions made by collision of REEs in zircon and ammonia gas could be overlapped on mass peak of Pb isotopes, the first mass spectrometer (Q1) can effectively remove the REEs and ammonia gas collides with only isotopes of Hg, Pb, Th and U. In this operational settings, the accurate age from several standard zircons was obtained with reducing the isobaric interference from Hg lower than the level of 1/100.

In the quantitative analysis, the instrumental tuning at the low oxide formation rate is important because most of REEs tend to make oxide easily in ICP-MS and polyatomic interference on heavy REEs from the oxide of light REEs is not negligible. However, at the condition of the lower oxide formation rate (<1%), the instrumental sensitivity is greatly depressed as tread off. Therefore, we used mass shift method by flowing the oxygen gas in the CRC. In mass shift method, it is possible for operational settings to be tuned to maximize the sensitivity while removing the mass interference from polyatomic and multi-charged ions. We carried out the quantification of REEs in standard zircon sample at the condition of the high sensitivity (10 times higher than normal condition) and extremely high oxide formation rate (>100%) using mass shift method, and the resulting concentrations of REEs show good agreement with reported values.

In conclusion, the coupling ICP-MS/MS and CRC technique can be not only a great solution for the interference-related problems, but also brings out the potential capability of high sensitivity of LA-ICP-MS.

Keywords: LA-ICP-MS, Zircon geochronology, Trace element quantification, Collision/reaction cell

Evaluation for multi-turn time of flight mass spectrum of laser ionization mass nanoscope

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Introduction: Laser ionization mass nanoscope (LIMAS) is a sputtered neutral mass spectrometer (SNMS) by tunneling ionization effect. This instrument was developed for measuring solar wind particles from extraterrestrial materials collected by planetary exploration missions, such as JAXA Hayabusa and NASA Genesis (Bajo et al., 2015). LIMAS consists of a Ga liquid metal ion source and an aberration corrector system for sputtering of nanometer scale area on samples, a femtosecond laser system for tunneling-ionization of the sputtered particles, and a multi-turn time-of-flight mass spectrometer (MULTUM II) for mass separation of isotope analysis. We have evaluated the performance of MULTUM II equipped with the ion injection optics of LIMAS.

Experimental procedure: We carried out numerical simulations of ion trajectories in the ion injection optics, and then load voltages for each lens were determined experimentally. As a result, Extraction lens L1 was -700 V, L2 was -3300 V. Einzel lenses 1 and 2 were set to -1260 V and -2700 V, respectively. Under these conditions, we evaluated mass resolving power and transmittance of LIMAS using $^{24}Mg^{2+}$. Data for each cycle were averaged for 1000 shots. We calculated useful yield of each cycle of LIMAS by depth profile of Si ions. The sputtered crater volume was measured by 3D laser scanning confocal microscope.

Results and Discussion: Mass-resolving power of TOF mass spectrometer is defined by time-of-flight of ion “t” and ion packet width “Δt” (R = t/2Δt). Mass-resolving power increased up to the TOF of 1000 μs (200 multi-turn cycles). After 1000 μs, mass-resolving power became saturated. Saturation of the mass-resolving power ($R = \sim10^5$) indicates that the averaged peak width increases linearly with increasing the number of cycles. Increasing FWHM was occurred by different TOF of ion packet become large with increasing cycle. 3 factors affect by different TOF of ion packet: 1) modulation by the acceleration voltage (ΔU), 2) modulation of the injection timing for the ion injection optics (Δt_{L1}), and 3) modulation of the electric field for the electric sectors (ΔE) in MULTUM II. Modulations of ΔU and ΔE become dominant if TOF increase. The ΔE was observed at 5 ppm, corresponding to $R = 10^5$, which is consistent with the saturation value of R described above. In order to correct the modulation of ΔE, TOF correction among peaks must be effective. Appling TOF correction, the mass-resolving power of LIMAS increased linearly with increasing the flight path length, and reached 620,000 (FWHM) at 1,000 multi-turn cycles of MULTUM II (flight path length: 1,312 m).

The transmittance up to 20 multi-turn cycles decreased to 60–70%, compared with the transmittance on linear mode. After 20 multi-turn cycles, the transmittance per multi-turn cycle became constant (99.96%).

A useful yield of LIMAS was estimated. As a result, useful yield was 3×10^{-3} at 30 multi-turn cycles (R = 17,000), 2×10^{-3} at 1000 multi-turn cycles (R = 620,000) of MULTUM II. The calculated useful yields for LIMAS would be better than to those for Cameca ims 6f at the same R (cf. 7×10^{-3} at R = 4,000; Hervig et al., 2006).

Keywords: SNMS, TOF, laser tunneling-ionization,, mass-resolving power, ion transmittance, useful yield

Nucleosynthetic Yb isotope anomalies in chondrites

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Recent studies on high precision isotope analyses for bulk aliquots of meteorites discovered the existence of planetary scale nucleosynthetic isotope variabilities for a variety of elements (e.g., Cr, Sr, Mo, Ru) [1-4]. By contrast, some elements (Hf, W, and Os) do not show such anomalies at the current level of analytical precision [5-7]. The processes responsible for generating the isotopic heterogeneity/homogeneity in the early Solar System are not fully resolved yet, however, two plausible models have been proposed to account for the isotopic characteristics recorded in meteorites. The first model considers nebular thermal processing which caused selective destruction of thermally weak-isotopically anomalous carriers, followed by subsequent physical separation of volatile phase and ultra-refractory components [8]. On the other hand, the injection of isotopically anomalous materials from a nearby core-collapse supernova (ccSN) and subsequent aerodynamic sorting of grains in different sizes can be an alternative possibility to cause planetary scale isotope heterogeneity [9].

Ytterbium is an intriguing element which would provide a strong constraint on the origin of planetary scale isotope anomalies in the Solar System. The $T_{50\%}$ for Yb (1487 K) is lower than those of the other heavy-REEs (1659 K) and is comparable to that of Sr. Therefore, the thermal processing would lead to heterogeneous Yb isotope distribution in the Solar System, whereas the injection of a nearby ccSN would not generate *r*-nuclides of Yb. Here we report preliminary results on Yb isotope compositions in one ordinary chondrite (Olivenza, LL5) and one rumuruti chondrite (NWA 753, R3.9). The Yb isotope ratios for meteorite samples are reported as μYb notations which represent the parts par 10^6 deviations from the terrestrial isotope ratios. The ordinary and rumuruti chondrites possess large negative anomalies for μ^{168}Yb (−2500 ppm on average) and μ^{170}Yb (−130 ppm on average) exceeding analytical uncertainties of the standard material, whereas the μ^{171}Yb, μ^{173}Yb, and μ^{176}Yb values are indistinguishable from the terrestrial component. The patterns of μYb for the chondrites are not consistent with that representing the deficit of *s*-process nuclides relative to the terrestrial component. Therefore, the negative anomalies in in μ^{68}Yb and μ^{170}Yb are attributed either to the deficit of *p*-process nuclides relative to the terrestrial component, or to the analytical artifact due to the overcorrection of interferences from ^{168}Er and ^{170}Er. By contrast, the absence of anomalies for μ^{171}Yb, μ^{173}Yb, and μ^{176}Yb is consistent with the marginal isotope anomalies in ordinary chondrites for Mo and Ru isotopes synthesized by the *s*- and *r*-processes, which are significantly smaller than those observed in carbonaceous chondrites and iron meteorites [3-4].

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Keywords: isotope anomalies, chondrite, Yb

Development of on-site neon measurement system using a portable ultra-high resolution mass spectrometer (MULTUM)

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Dissolved noble gases (He, Ne, Ar, Kr, and Xe) in seawater are chemically inert and their variations are thus solely responsible for physical processes such as temperature change, diapycnal mixing, and mixing of water masses. Since different noble gases have different temperature dependence on diffusivity and solubility, the noble gases show different responses even to the same physical forcing, which make us possible to quantitatively estimate how much physical processes the water mass experienced in the past through the simultaneous measurements and subsequent comparison of the observed noble gas concentrations.

Present measurement of dissolved noble gases requires a comprehensive purification and separation of each noble gases from sample gases extracted from seawater (*e.g.*, Sano and Takahata, 2005, Stanley, et al., 2009) to avoid that residual atmospheric gases interfere subsequent mass spectrometric quantification of the target trace noble gases using a quadruple mass spectrometer (QMS) with a low mass resolution. The pretreatment system is quite large and complicate for its field operation and it is practically impossible to conduct the purification and quantification on-site along with seawater sampling. Water samples, then need to be brought back to a land-based laboratory. The taking seawater samples back to the land-based laboratory without suffering contamination of highly permeable atmospheric noble gases requires to store the samples in copper tubes with the both ends fully squashed and completely sealed, which is quite cumbersome and requires man power. Such time-consuming and labor-intensive sampling and pretreatment in both field and laboratory have limited available number of samplings and measurements, and subsequently resulted in a quite limited number of observed data of noble gases in water environments.

Here we introduce a new method for the direct measurement of atmospheric neon concentration without cumbersome pretreatment and sampling treatment by combining multi-turn time of flight mass spectrometer (MULTUM) and a simple cryo-gas trap as a preliminary stage of the development for the online analysis of dissolved noble gases. The ultra-high mass resolution of the MULTUM (10000~30000) compared to that of ordinary QMS (100~500) allows our Ne^+ (*m/z* 19.9919) ion detection to be free from interference ions, such as $H_2{}^{18}O^+$ and HF^+ (*m/z* 20.0057 and 20.0151, respectively) which have close *m/z* to that of Ne^+ (Fig. 1) and cannot be detected separately with commonly used QMS. Prior to the ultra-high resolution mass spectrometric analysis, most of the major atmospheric gases (*e.g.*, N_2, O_2, Ar and CO_2) were removed by a cryo-gas trapping to avoid a saturation effect during ionization in the mass spectrometer and further optimize the mass spectrometer for the detection of trace Ne^+ ion. Such a simple and compact pretreatment system, compared to the ordinary large and complicated one, enables us to bring the pretreatment system to the field and conduct on-site analysis of Ne.

As a test case, atmospheric Ne was analyzed by directly injecting 0.5~5 cm^3 of atmospheric air into the developed system. Atmospheric Ne (18 ppmv) was successfully measured in every 10 minutes by simply injecting sample atmospheric air into the system (Fig. 1-2). An obtained good linearity between injected air volume and Ne^+ ion peak (Fig. 2) shows that the simple cryo-gas trap also can work as a pre-concentrator, which is another advantage for trace gas analysis. The preliminary

result shows that the developed method can be applied for the continuous and direct measurement of dissolved Ne and other noble gases with further modification.

Keywords: MULTUM, dissolved noble gas, on-site measurement, ultra-high resolution mass spectrometry

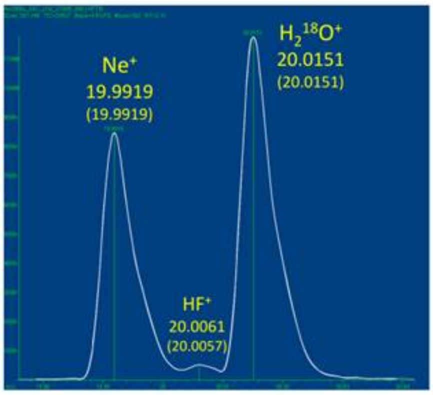

Fig. 1. The high resolution mass spectrum of an atmospheric air sample (*m/z* 19.19 ~ 21.19) obtained derived from obtained mass chromatogram using MULTUM. The high mass resolution ensured separate detection of Ne^+ (*m/z* 19.9919) ion from interference ions, such as HF^+ (*m/z* 20.0057) and $H_2{}^{18}O^+$ (*m/z* 20.0151).

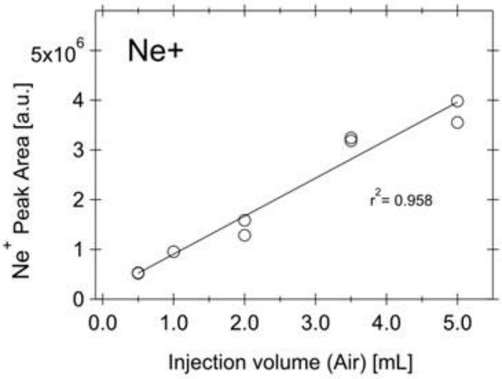

Fig. 2. The relationship between injected volume of atmospheric air samples and the Ne^+ ion peak area obtained using a simple cryo-gas trapping system. A good linear relationship was obtained between the analytical ion peak and injection volume over a range of 0.5~5mlL ($r^2 = 0.958$)

Formation Processes and Anthropogenic Influences for Sediments in Majuro Atoll

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Atolls only 1~3 m above sea level are vulnerable to natural disasters and climate change. In spite of such conditions, people have lived in the Majuro Atoll in Marshall Islands for more than 2000 years (Yamaguchi et al., 2009). The life styles in this island have changed dramatically by the modernization. For example, the use of motor vehicles has been increased. Especially in an isolated island, sediments originally composed of coral gravel and foraminifera are easily affected by human activities such as cultivation of crops and well for drink water etc. Therefore, condition of sediments could be proper index of human impact. In particular, when they use modern industrial products, heavy metals contained in the products can be emitted and accumulated in the sediments. However, the influence of these contaminants on the reef island remains unclear. In this study, we focus on the changes of physico-chemical conditions of soil depending on the depth according to time series variation in Majuro and Arno Atolls, since atolls can be an appropriate model site to evaluate anthropogenic impacts.

Dating of each depth was conducted by radiocarbon (^{14}C) measurement for foraminifera using accelerator mass spectrometry (AMS) and Bayesian age-depth Models. X-ray fluorescence (XRF) and Inductively-coupled plasma mass spectrometry (ICP-MS) analyses were conducted to measure the elements in each layer. X-ray absorption fine structure (XAFS) analysis was also done to examine the detailed chemical form. Also microbeam X-ray Computed Tomography (CT) was used to estimate porosity of foraminifera at different depths.

Dating results showed that rapid sedimentation was likely to occur in each island in atoll in the early stage of the formation. The concentration of toxic elements such as Zn, Cu, and Pb increased sharply around 50 cm depth that are considered to be emitted after the original sedimentation of biological remains such as coral gravel and foraminifera. This result correlated with that of total organic carbon (TOC) from the same depth. The concentration of rare earth elements (REEs) also increased around the same depth and negative cerium anomaly became smaller at shallower depth. However, only Mg increased as the depth increased or as the porosity of foraminifera decreased. XRD analysis showed that magnesian calcite has decreased in the upper layer of the sediments, which suggested the selective dissolution of Mg from magnesian calcite near the surface. Bulk and μ-XAFS analyses showed that (i) Zn exists as Zn-rich particles such as as ZnO and ZnS, which are considered to be a tire wear and (ii) chemical species of Fe is ferrihydrite. Taking them into consideration, adsorption of heavy metals on ferrihydrite and/or humic substances inhibit release of heavy metals to aqueous phase even though the atoll was made of porous materials, where water easily flows out from the island by rainfall or tide. XAFS analysis also revealed that aluminum is present either as kaolinite or muscovite. These results show contribution of terrigenous material.

The original sediments of atolls is $CaCO_3$ contained in biological remains without heavy metals. Therefore, atolls can be appropriate model site to examine the chemical form and amount of elements emitted by anthropogenic effects and to assess the impact of modernization as our studies.

Keywords: Foraminifera, X-ray Absorption Fine Structure, anthropogenic effects, atoll, Marshall Island

The regional characterization of volcanic glass shards for the forensic science by trace element analysis

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Because the soil is widely distributed over the ground surface, the soil has been regarded as one of important evidential matters which links a person with a place in the field of the forensic science. We have developed a nationwide forensic soil sediment database for Japan using stream sediments collected at 3024 points across Japan. While we have previously focused on trace heavy element compositions reflecting the geological background of the soil, we newly focused on the volcanic glass contained within the soil as a new indicator to achieve further regional characterization of soils. The volcanic glass is an amorphous pyroclastic material produced by a rapid cooling of a magma. It is expected that the volcanic glass will be good indicator for soils from all over Japan, because Japan is one of the most famous volcanic countries in the world. In addition, because a chemical composition of the volcanic glass could vary in each volcanic mountain, it is believed that the regional characterization of the volcanic glass is achieved by chemical compositional analysis as shown in previous studies using EPMA. In the present study, we introduced a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), a powerful analytical technique for trace element analysis of a minute specimen (< 100μm), to analyze the individual volcanic glass shard.

4 samples (Samples A, B, C and D) collected in the *Kanto Region* were used in the present study. Sampling points are shown in Fig. 1. Samples A and B are stream sediments collected from the *Arakawa River* and they were chosen from 3024 stream sediments for the forensic soil sediment database. They are indistinguishable using the heavy element and heavy mineral compositions. Samples C and D are soils. Sample C contains a volcanic ash from *Mt. Asama* while Sample D contains ashes from *Mt. Fuji* and *Mt. Hakone*. After mesh controls, heavy minerals in these samples were removed by heavy liquid separation (SG ~2.4). Residues were embedded into resin and the surface was polished. 50 particles of volcanic glass were identified for each samples using a polarizing microscope and a micro Raman spectrometer for trace element analysis by LA-ICP-MS. Twelve elements were selected to analyze based on the previous study.

Here we examined the characterization using two elements, ^{89}Y and ^{90}Zr. It has been pointed out that the tephra deposits of the Kanto Region can be separated into two groups bordering the northern latitude of 36 degrees (see Fig.1): the ash from *Mt. Asama* for north side, the ashes from *Mt. Fuji* and *Mt. Hakone* for south side. Figure 2 shows a plot of intensities of ^{89}Y and ^{90}Zr (normalized to the intensity of ^{29}Si) of volcanic glasses in Samples C and D. As shown in Fig. 2, there are different compositional tendency between the volcanic glasses in Samples C (Group N) and D (Group S). We confirmed the significant difference between these two groups using an analysis of variance. Because the crystallization differentiation of the magma in *Mt. Asama* was promoted compared to those in *Mt. Fuji* and *Mt. Hakone*, it is considered that the volcanic glasses in Sample C were rich in Y and Zr as incompatible elements. We built a linear discriminant to discriminate two groups of volcanic glasses using the normalized intensities of ^{89}Y and ^{90}Zr of volcanic glasses in Samples C and D and applied it for volcanic glasses in Samples A and B. As the result, 85.4% of the volcanic glasses in Sample A were classified into Group N while 75.9% of those in Sample B were Group S. Therefore, we could successfully distinguish 2 stream sediments having same heavy element and heavy mineral composition using the trace elemental difference of volcanic glass shards measured by LA-ICP-MS.

Keywords: volcanic glass

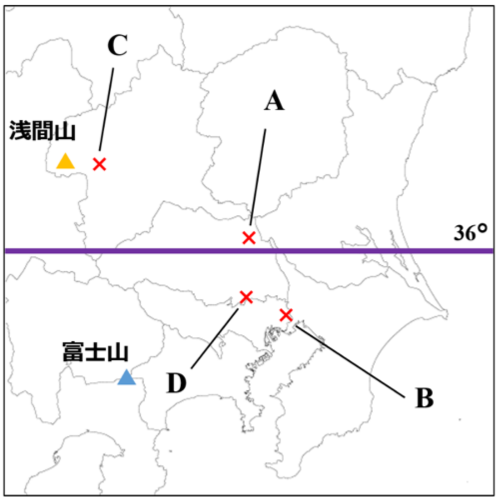

Fig. 1 土砂採取地

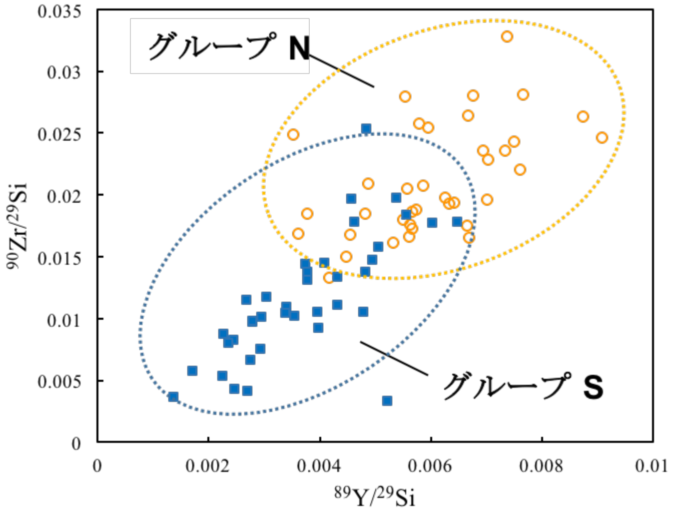

Fig. 2 試料C, Dの比較

Speciation of Cu in seawater by using CLE-CSV with multi-detection windows

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I. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life-supporting systems, and is present in many enzymes and proteins. On the other hand, at high concentrations in seawater, Cu^{2+} is known to be toxic for marine phytoplankton. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of free Cu^{2+} and reduce its toxicity. As a result, at the eutrophic surface waters, most of Cu form complexes with organic ligands.

For the Cu speciation study in the ocean, competitive ligand equilibrium/cathodic stripping voltammetry (CLE/CSV) is frequently applied. However, some problems have been proposed on the CLE/CSV methods recently. One problem is concerning on “detection window”, which is defined by the conditional stability constant and concentration of the competitive ligands. To measure the conditional stability constants and concentrations of main ligands (usually two ligands) accurately, we have to apply the CLE/CSV method with multi detection windows for the speciation. In this study, we determined the total dissolved Cu concentrations and estimated Cu speciation in seawater by using the CLE/CSV method with multi detection windows in the East China Sea and its surrounding areas.

II. Sampling and methods

Seawater samples were collected using acid-cleaned, Teflon-coated X-type Niskin samplers mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) onboard R/V Shinsei Maru during KS-15-6 cruise (2015/06/25 - 2015/07/06). The samples were collected in low-density polyethylene bottles through a 0.2 μm-pore size filter. Samples for total Cu analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for CLE/CSV analysis, was frozen at -18°C immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV with salicylaldoxime (SA) as the competing ligand (Campos and van den Berg, 1994).

Samples used for total dissolved Cu were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. Frozen samples for Cu speciation analysis were allowed to thaw for 24 hours at 4°C, and then placed at room temperature for 4-8 hours. 10mL of sample, borate buffer, and a known concentration of Cu were added into two sets of 10 Teflon vials, left for at least 2 hours to allow the natural ligands to equilibrate with the added Cu, and the competing ligand, SA, was then added into the solution. The vials were then left to equilibrate overnight before analysis. 5 μM SA and 1 μM SA were used as the competing ligand for each of the two titrations, respectively.

III. Results and Discussion

Total dissolved Cu concentrations ranged from 0.47 to 4.65 nM. In surface waters with low salinities, higher concentrations of Cu were observed, which can be attributed to the freshwater discharge with high Cu concentrations from Yangtze River. Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand, L_1, ranged from 3.6 nM to 11.2 nM, with log K values of 13 –14.1, whereas for the weaker ligand, L_2, the concentrations were in the range of 25.6 nM to 47.6 nM, with log K values of 11.7 –12.2. The variation of the strong ligands suggests that these ligands were biologically produced *in situ* by marine microorganisms.

Keywords: ocean, Cu, organic ligand