表層環境の地球化学における計算科学
Computational Science for Environmental Geochemistry

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計算科学は計算機の性能向上・計算手法の発展とともに、分野を問わず有用な研究手法として成長してきた。本発表で対象とする計算科学は、原子をあらわに扱う計算のことで、第一原理計算や経験的な力場を使用する分子シミュレーションを指す。

物理・化学・生物学をみるとそれぞれに計算科学の主流となる発展方向が異なることがわかる。物理では固体の伝導性・磁性を知るためのバンド計算、化学では分子間相互作用や化学反応を取り扱う分子軌道法、生物ではタンパク質等の大きな分子の構造を知るための粗視化した分子計算が発展しているようにみえる。計算科学は地球化学においても重要な研究手法である。例えば、振動解析計算による固体の同位体分別や振動スペクトル、固体・流体の状態方程式、イオンや有機分子の固体表面への吸着・拡散の予測等が挙げられる。地球化学のこれまでの方向を見ると、今後も物理・化学・生物学の計算領域を含みつつ、高温・高圧・多成分系に計算科学を発展させる必要がある。

本発表では、我々が研究対象としてきた地球表層環境化学に対する計算科学の現状と今後の展開について議論する。特に流体・固液界面・自由エネルギー・pHに注目し、地球化学において革新的な研究成果を生み出す計算科学の将来を探りたい。

キーワード：第一原理計算、分子シミュレーション、自由エネルギー、ｐH、流体、固液界面
Keywords: ab initio calculation, Molecular simulation, Free energy, pH, Fluid, Solid-liquid interface

"He Standard of Japan" (HESJ)の^{3}He/^{4}He比校正

Determination of absolute ^{3}He/^{4}He ratio of He Standard of Japan

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^{3}He/^{4}He ratios in terrestrial samples vary more than three orders of magnitude, because primordial helium with ^{3}He/^{4}He of (1.4–4.6) x 10^{-4} has been diluted by addition of radiogenic ^{4}He produced by decay of U- and Th-series elements in different degrees depending on ^{3}He/(U+Th) ratio of each reservoir. This feature makes ^{3}He/^{4}He ratio a powerful tracer in geochemistry and cosmochemistry. Though atmospheric helium with ^{3}He/^{4}He ratio of 1.4 x 10^{-6} is used to calibrate ^{3}He/^{4}He measurement with a noble gas mass spectrometer, relatively low concentration and ^{3}He/^{4}He 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 ^{3}He/^{4}He ratio or by mixing of isotopically pure ^{3}He and ^{4}He. "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, ^{3}He/^{4}He ratio of HESJ was determined by comparison with that of atmospheric helium, i.e., absolute ^{3}He/^{4}He ratio has not been determined yet and the accuracy of the value still rely on the early determinations of absolute ^{3}He/^{4}He ratio of atmospheric helium [3].

As long as ^{3}He/^{4}He ratio is used to compare relative contributions of primordial and radiogenic in each geochemical reservoir, absolute ^{3}He/^{4}He value of atmospheric helium or HESJ is less important. However, it is a critical issue in some applications of helium isotopes, such as tritium-^{3}He 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 ^{3}He(n,p)^{3}H reaction in a time projection chamber detector filled with ^{3}He, ^{4}He and CO_2. To determine neutron lifetime with uncertainty less than 0.1%, ^{3}He 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 ^{3}He number density with uncertainty of 0.1%. The ^{3}He 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 ^{3}He/^{4}He 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 ^{3}He/^{4}He value of HESJ, and that of atmospheric helium also [6].

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UV-LA-MC-ICP-MSを用いた高精度塩素同位体分析法の開発
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.

キーワード：塩素同位体、UV-LA-MC-ICP-MS
Keywords: stable chlorine isotopes, UV-LA-MC-ICP-MS

高精度・高速U-Th-Pb年代測定法の開発：Jack Hillsジルコン年代学への応用
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.

キーワード：冥王代、ジャックヒルズ、LA-ICP-MS、多重検出器型ICP-MS、ジルコン、鉱物包有物
Keywords: Hadean, Jack Hills, LA-ICP-MS, MC-ICP-MS, zircon, mineral inclusion

玄武岩質ユークライトにおける^{147}Sm-^{143}Nd ・^{146}Sm-^{142}Nd全岩アイソクロン年代
^{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 ($T_{1/2}$ = 1.06x10^{11} y) and the short-lived ^{146}Sm-^{142}Nd ($T_{1/2}$ = 1.03x10^8 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 = ~1.2x10^{-5} and Sm/Nd = ~5.2x10^{-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

Allende CAI中の核合成起源Sr同位体異常

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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キーワード：CAI、同位体
Keywords: CAI, Isotope

隕石全岩の同位体異常の検出に向けた負イオン表面電離質量分析計による精密モリブデン同位体分析法の開発

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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キーワード：隕石、表面電離型質量分析計、モリブデン
Keywords: meteorite, TIMS, molybdenum

大気中水銀同位体分析：手法開発および実大気への適応

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.

キーワード：水銀同位体、マルチコレクター誘導結合プラズマ質量分析計、大気中水銀
Keywords: Mercury isotopes, MC-ICP-MS, atmospheric mercury

高時間分解能高精度加速器分析による西太平洋表層Δ^{14}C変動復元

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

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古気候復元の研究では、炭酸塩骨格を持つサンゴは、水温変動の復元などに有効な試料として広く用いられる。サンゴ骨格は海水の溶存無機炭素（DIC)を取り込むため、骨格中の放射性炭素(^{14}C)を海水の移流・鉛直混合のプロキシとして使用することで、海水動態の復元が可能である。しかし、炭酸塩に含まれる^{14}C測定には、従来の方法では10mgの$CaCO_3$(1mgCに相当)が必要であるとされ、高時間分解能での海水動態復元が難しいという問題があった。

本研究では、東京大学大気海洋研究所にて国内唯一稼働中のシングルステージ加速器質量分析計(YS-AMS）を用いて、マイクログラムオーダーの微量試料での放射性炭素濃度分析法の確立をするとともに、その方法を黒潮海域から採取されたサンゴ骨格に適用し、高時間分解能での放射性炭素同位体比(Δ^{14}C)変動の復元を行うことを目的とした。

その結果、1950年以降の期間については、黒潮起源の海域であるフィリピンから、その下流にあたる喜界島までの海域では、Δ^{14}C値はほぼ一様な値となった。一方で1950年以前の期間については、Yoneda et al. (2007)で報告されていた1900年前後のΔ^{14}Cと本研究で測定した1940年代とで値が大きく異なることが明らかになった。すなわち、西太平洋では海水中の^{14}C濃度が約40年という短期間でも変動していることが示唆された。この現象は、放射性炭素年代に対してローカル海洋リザーバー効果(ΔR)の補正を行う際にも大きな影響を与える可能性があり、地域別のみならず、年代別にΔRの値を決定することが望ましいことが示された。

キーワード：放射性炭素、Δ14C変動、ΔR、サンゴ骨格、表層海水
Keywords: Radiocarbon, Δ14C variability, ΔR, coral, sea surface water

ウナギの保全と地球化学
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.

キーワード：ウナギ、耳石、安定同位体比
Keywords: eel, otolith, stable isotope

FTICR-MS解析の土壌有機物への適用

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.

キーワード：土壌有機物、質量分析
Keywords: soil organic matter, mass spectrometry

アミノ酸前駆体とアミノ酸によるホモキラルフィードバック機構（予察）：どうやって、右と左の対称性を破り、増幅させるか？
Stereochemical feedback with "an achiral amino acid precursor" and "a chiral amino acid": Experimental verifications

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アミノ酸は、アミノ基（$-NH_2$）とカルボキシル基（$-COOH$）を保有する有機分子である。タンパク性アミノ酸の中心炭素のα-位には、水素（$-H$）がある。非タンパク性アミノ酸の中心炭素のα-位には、メチル基（$-CH3$）が付加している分子種も存在する。炭素は、原子価が4であるから、α-位にアミノ基、カルボキシル基ともう一つR-基が付加することにより、分子構造の多様性が生まれる。α-位の炭素は、鏡像異性の中心になり、D-体とL-体の光学異性アミノ酸が存在することになる。また、アミノ酸は、β-アラニンやγ-アミノ酪酸のような非タンパク性の分子構造も存在することから、地球物質中だけでなく、地球外物質中の起源や物質進化のプロセス研究においても常に注目される有機分子である。

さて、コイントスを考えた場合、表と裏の出る確率は、50：50である。これを無限回繰り返したらどうだろうか。やはり、「50.0：50.0」に収束する。ところが、生命が発生する以前の物質だけの世界（＝非生命圏）では、ある時から「51：49」のように分子の対称性が破られた。この左右の対称性の破れは、何に起因するのか。炭素数2のグリシンを除くと、炭素数3のα-アラニンは、非生物的に生成するアミノ酸の中でもっとも存在量の多いキラルアミノ酸（潜在的にはアラニン前駆体を含む：Takano et al., 2007）である。ここでは、右と左の分子対称性（モレキュラーキラリティー）の視点から、アミノ酸前駆体とアミノ酸の水質相互作用によるホモキラルフィードバック機構の実験的検証について、議論してみたい。本研究の一部は、文部科学省（MEXT）の科学研究費補助金・新学術領域研究（No. 25108006）の助成によって行われた。
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キーワード：アミノ酸前駆体とアミノ酸、ホモキラルフィードバック機構
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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キーワード：High throughput age determination、Multiple collector-ICPMS、Laser Ablation、Daly ion counter、Thin layer U-Pb chronology

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

レーザーアブレーションICP-MS/MSとコリジョン/リアクションセル用いたジルコン局所分析法の評価
Evaluation of coupling LA-ICP-MS/MS and collision/reaction cell technique for in-situ
zircon analysis

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レーザーアブレーションICP質量分析法（LA-ICP-MS）は固体試料の直接分析法であり、試料の前処理が簡便なことや高感度かつ迅速な分析が可能なことなどから、地球科学分野で広く利用されている分析手法である。しかし、この手法の持つ高いイオン化能は目的元素と同時にそれ以外の元素のイオン化も引き起こしてしまう。そのため化学的分離手法を用いて目的元素のみを単離することが可能な溶液試料導入法とは異なり、レーザーアブレーション試料導入法では同重体・多原子・二価イオンからの質量スペクトル干渉に対して慎重な対応が求められる。これらの干渉を避けるためにイオン源の状態調節や質量分解能を上げるなどの調整が通常行われるが、同時に感度が低下するという問題が避けられなかった。また、同重体による干渉については低減すら難しいという実態があった。そこで、本発表では二つの四重極型質量分離部（Q1, Q2）とコリジョン/リアクションセル（CRC）と呼ばれる装置を持つICP質量分析計を用いて、代表的なLA-ICP-MSのアプリケーションであるジルコンの年代測定および希土類元素元素濃度測定における質量スペクトル干渉の低減を試みた。

　ジルコンのU-Th-Pb年代測定で測定される同位体のうち質量数204の鉛は非放射壊変起源であるためその精確な測定は年代測定の信頼性を高める上で重要である。しかしLA-ICP-MS法では質量数204の水銀も同時にイオン化されてしまうため同重体干渉が発生し、この干渉の排除は手法が登場して以来、大きな課題となっていた。本発表ではCRCに1 ml/min程度のアンモニアガスを流し水銀イオンと反応させることで、同重体干渉の低減を試みた。この際、アンモニアガスはジルコンに含まれる希土類元素のイオン（Ce+, Eu+, Yb+等）と反応して多原子イオンを作り鉛の同位体に干渉することが考えられる。そこでCRCの前に設置されたQ1で測定に関与する元素の同位体（Hg, Pb, Th, U）のみを通過させるように設定した。このような装置設定で年代値が既に報告されているジルコン標準試料（Plešovice, GJ-1）を年代測定したところ、確度・精度を維持したまま水銀の同重体干渉を100分の1以下に低減することができた。

　希土類元素の多くはICP質量分析計内で周囲の酸素と結合し酸化物を生成する割合が高いことが一般に知られている。そのため、中-重希土類元素のピークに対し軽-中希土類元素の酸化物が質量スペクトル干渉を引き起こすことから、感度とのトレードオフとして酸化物の生成量を抑制したチューニング条件がしばしば使われる。本研究ではCRCに酸素ガスを流し故意に希土類元素酸化物イオンを作り出す通称マスシフトと呼ばれる手法でジルコン中の希土類元素濃度を測定した。マスシフト法では多原子・二価イオンの干渉をほぼ完全に排除可能なため、感度を最大化するチューニング条件での測定が可能であり、本研究では通常の測定条件（酸化物生成率<1%）と比べて約10倍の感度条件（酸化物生成率>100%）で測定を行ったところ、良い確度での定量結果が得られた。

　以上より、CRCとLA-ICP-MS/MSを組み合わせることによってジルコンの年代測定・希土類元素定量分析において顕著な干渉の低減と共に感度の向上が達成可能であると考えられる。

キーワード：レーザーアブレーションICP質量分析法、ジルコン年代学、微量元素定量分析、コリジョン/リアクションセル
Keywords: LA-ICP-MS, Zircon geochronology, Trace element quantification, Collision/reaction cell

レーザーイオン化ナノ質量分析計(LIMAS)の多重周回飛行時間型質量分析計の評価
Evaluation for multi-turn time of flight mass spectrum of laser ionization mass nanoscope

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はじめに：レーザーイオン化ナノ質量分析計（LIMAS）は，原子のトンネルイオン化を利用したスパッタ中性粒子質量分析計（SNMS）である．この装置は，サンプルリターンミッション（はやぶさミッション（JAXA）やGenesisミッション（NASA））により収集された地球外物質中に含まれる太陽風起源粒子を測定するために開発された(Bajo et al., 2015)．LIMASは，液体ガリウムイオン源，ナノメートルスケールの領域をスパッタするための収差補正システム，スパッタ粒子をトンネルイオン化させるためのフェムト秒レーザーシステム，質量分離のための多重周回飛行時間型質量分析計(MULTUM II)からなる(Ebata et al., 2012)．我々は，イオン導入光学系とMULTUM IIで決定されるLIMASの質量分解能とイオン透過性を評価した．

実験手順：最初に，イオン導入光学系のイオン軌道のシミュレーションを行い，その後，各レンズの最良値を決めるための実験を行い，イオン導入光学系の最良パラメータを設定した（L1レンズが-700 V, L2レンズが-3300 V。 1段目と2段目のアインツェルレンズがそれぞれ-1260 Vと-2700 V）．その後，$^{24}Mg^{2+}$イオンをもちい、LIMASの質量分解能とイオン透過性を評価した．各周回の取得データは1000ショット分のデータを積算平均したデータである．最終的に，Siイオンの深さ方向分析から，LIMASの各周回のユースフルイールドを見積もった．スパッタされたクレーター体積は，レーザー顕微鏡により測定した．

結果と考察：飛行時間型質量分析計の質量分解能は，飛行時間"t"とイオンパケットの幅"Δt"によって決定される(R = t/2Δt)．実験の結果，LIMASの質量分解能は飛行時間1000 μs（200周)まで増加した．しかし，1000 μs以降は，周回増加に比例してFWHMが増加するため，質量分解能が飽和状態になった（R = ~10^5）．FWHMの増加は，周回増加にともない，イオンパケットの到達時間のズレが大きくなったことにより生じたものであった．イオンパケットの到達時間のズレの要因として，1）イオン導入光学系内への引き込みのタイミングのズレ（Δt_{L1}），2）加速電圧のゆらぎ（ΔU），3) MULTUM II内のセクター電極電圧のゆらぎ（ΔE）の3つがある．

この中で，飛行時間増加に伴ってFWHMを変化させる因子は，ΔUとΔEである．実際に，電極電圧のゆらぎの実測を行った結果，ΔEに5 ppmのゆらぎがあることが明らかとなった．これは，質量分解能が飽和状態となった値（R = 10^5）に相当する．したがって，MULTUM II内のセクター電極電圧のゆらぎがFWHMの増加の主な要因であると考えられる．これらのゆらぎの影響を補正するために，我々は新しい質量スペクトル取得法を開発した．この新しい補正法により，FWHMは周回数にかかわらず一定となり，質量分解能は理論通りに増加した．その結果，1000周（飛行距離1312 m）時に620,000の質量分解能を達成した．

LIMASのイオン透過性は20周を境に2つに分けられ，20周までのLIMASのイオン透過性は，60-70 ％まで減衰した。20周以降は，1周あたりのイオン透過性が一定となった（99.96 ％）．

LIMASのユースフルイールドを見積もった結果，Siイオン30周（R = 17,000）で3×10^{-3}，1000周（R = 620,000）で2×10^{-3}となった．この値は，Cameca ims 6fのUYである7×10^{-3}（R = 4,000）と同等の結果を示した(Hervig,. et al 2006)．

キーワード：SNMS、TOF、レーザートンネルイオン化、質量分解能、イオン透過性、ユースフルイールド
Keywords: SNMS, TOF, laser tunneling-ionization,, mass-resolving power, ion transmittance, useful yield

コンドライトの核合成起源のイッテルビウム同位体異常
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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キーワード：同位体異常、コンドライト、イッテルビウム

Keywords: isotope anomalies, chondrite, Yb

超高分解能質量分析計「MULTUM」を用いた希ガス(Ne)のオンサイト測定法の開発
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.

キーワード：MULTUM、溶存希ガス、現場測定、超高分解能質量分析
Keywords: MULTUM, dissolved noble gas, on-site measurement, ultra-high resolution mass spectrometry
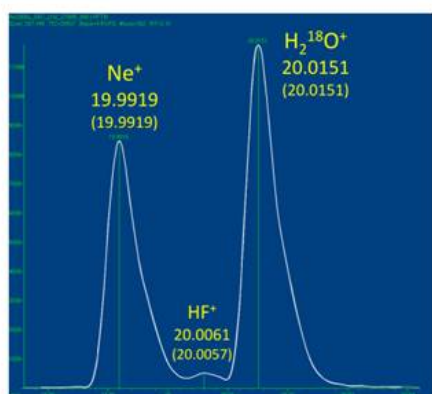
Fig. 1. The high resolution mass spectrum of an atmospheric air sample (m/z 19.19 ~ 21.19) obtained derived from obtained mass chromatogram using MULTUM. The high mass resolution ensured separate detection of Ne$^+$ (m/z 19.9919) ion from interference ions, such as HF$^+$ (m/z 20.0057) and H$_2$^{18}O$^+$ (m/z 20.0151).
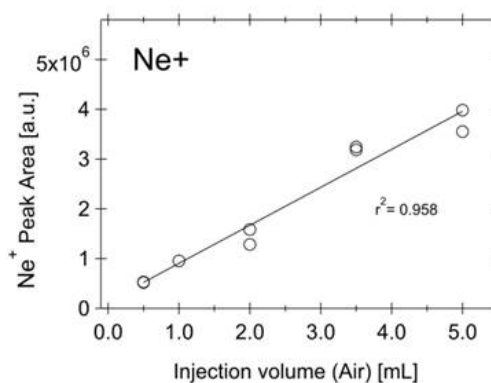
Fig. 2. The relationship between injected volume of atmospheric air samples and the Ne$^+$ ion peak area obtained using a simple cryo-gas trapping system. A good linear relationship was obtained between the analytical ion peak and injection volume over a range of 0.5~5mlL (r^2 = 0.958)

マジュロ環礁の堆積物の起源と人為的影響の評価
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.

キーワード：有孔虫、X線吸収微細構造、人為的影響、環礁、マーシャル諸島
Keywords: Foraminifera, X-ray Absorption Fine Structure, anthropogenic effects, atoll, Marshall
　　　　　Island

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　　　　　Island

法科学応用を目的とした火山ガラスの微量元素分析による地域特性化の試み
The regional characterization of volcanic glass shards for the forensic science by trace element analysis

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本研究では土砂試料の法科学的起源推定を目的として、土砂中に含まれる火山ガラスの微量元素分析を行った。土砂は地表全体に広く分布し、無意識のうちに衣服や靴に付着するため、科学捜査において場所と人とを結びつける微細証拠物件として重要視される。我々は全国3024か所で採取された河川堆積物を用いて、法科学応用を目的とした日本全国土砂データベースの開発を行っている[1]。これまでに、地質的特徴を反映しやすい土砂中の重鉱物・重元素組成に着目してきたが、より詳細な地域特性化を実現するための新しい指標として、土砂に含まれる火山ガラスに着目した。火山ガラスはマグマが急冷されることで生成する非晶質の火山砕屑物であり、世界有数の火山大国である日本において広域に分布することから、日本全国で指標として用いることができると期待される。また、その火山ガラスの化学組成は噴火前のマグマの残余流体の組成を強く反映し給源火山ごとに異なるため、化学組成に着目することで地域特性化が行えると考えられる。先行研究[2]では、火山ガラスの主成分組成をEPMAを用いて分析することでテフラの層序同定が行われており、地質学に大きく貢献している。本研究では、火山ガラス1粒子ごとに微量元素組成を分析するために、数十µmの微小固体の微量元素分析が可能なレーザーアブレーション誘導結合プラズマ質量分析法（LA-ICP-MS）を導入し、その有用性を検証した。

本研究で用いた分析試料は、関東地方のFig. 1に示す採取地で採取された試料A〜Dの4点である。試料AおよびBは荒川の堆積物であり、法科学土砂データベース構築用の河川堆積物3024点から選び出されたものである。重元素および重鉱物組成からでは、これら2地点の土砂を区別することができなかった。試料CおよびDは本研究で採取した土壌試料であり，試料Cは浅間山の火山灰、試料Dは富士山・箱根山の火山灰を含む。これらの試料に対して、篩分けにより粒径を125 µm以下に揃えた後、比重2.4の重液分離で重鉱物を除去し、樹脂包埋後に表面を研磨した。偏光顕微鏡による観察と顕微ラマン分光法を併用して、LA-ICP-MSによる微量元素分析用に、各試料について50粒ずつ火山ガラスを同定した。装置は四重極型ICP-MS Agilent 7500cにLA装置UP213を接続したものを用いた。組成のばらつきを考慮し、1粒子内の3箇所を分析した。測定元素は先行研究において火山ガラスによるテフラの識別に有効であるとされる12元素（Li, B, Y, Zr, La, Ce, Pr, Nd, Tb, Yb, Th, U）を対象とした[3]。

以下では^{89}Yと^{90}Zrの2元素に着目した特性化を行う。関東地方のテフラは北緯36度（Fig. 1参照）を境に北部は浅間山・榛名山、南部は富士山・箱根山を起源とする火山灰が支配しているとされる[4]。Fig. 2に、試料C, D中の火山ガラスの^{89}Yと^{90}ZrのICP-MSの強度（^{29}Si強度によって規格化）をプロットしたものを示す。Fig. 2から分かるように、試料C,D中の火山ガラスには異なる組成的傾向があり、分散分析からも有意水準α=0.01で試料Cのプロット群（グループN）と試料Dのプロット群（グループS）の間に有意差が確認された。浅間山は富士山・箱根山に比べて火山フロントよりも西側に位置しており、マグマ溜まりから火口までの距離が長く、マグマの結晶分化作用が進行していると考えられる。そのため、造岩鉱物の結晶に入り込みにくい不適合元素がより濃集することから、試料C中の火山ガラスには不適合元素であるYおよびZrが多く含まれたものと考えられる。試料C, D中の火山ガラスの^{89}Yと^{90}Zrの規格化強度を用いて両グループを判別する式を構築し、試料A, B中の火山ガラスへと適用した。その結果、試料Aの85.4 %がグループNに、試料Bの75.9 %がグループSに判別された。この結果は、鉱物・重元素組成で特性化できない2地点の河川堆積物について、火山ガラスの微量元素組成を用いることで識別できることを示している。以上より、本研究によって土砂データベースの新しい指標としての火山ガラスの有用性が実証された。

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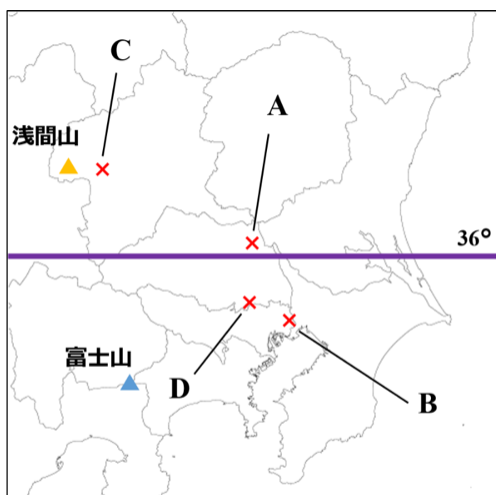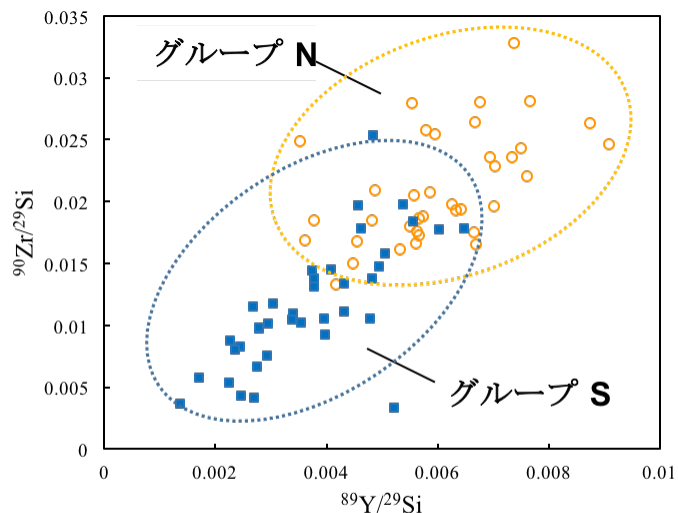4)関東ローム研究グループ，関東ローム-その起源と性状，築地書店，(1965)

Fig. 1 土砂採取地

Fig. 2 試料C, Dの比較

競争配位子平衡CSV法を用いた海水中の銅有機錯体に関する研究–多重検出窓を使って–
Speciation of Cu in seawater by using CLE-CSV with multi-detection windows

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海水中の銅は植物プランクトンにとって必須の元素であるが、水和したフリーの銅イオン濃度が高い場合、毒性を示すことが知られている。しかし、海水中で銅は99.9%以上が有機錯体を形成するため、実際に植物プランクトンに対する毒性は抑えられている。このように生物の成育に密接に関わるため、海水中での銅の存在状態を明らかにすることは重要な課題である。

海水中の銅の存在状態に関する研究では、高感度なカソーディックストリッピングボルタンメトリー(CSV)が最もよく使われている。CSV法では、サリチルアルドキシム(SA)を人工配位子として添加することによって、海水中の銅を測定することが出来る(Campos and van den Berg, 1994)。海水中の天然の有機配位子の濃度と条件安定度定数を求めるためには、海水に既知量の銅を添加して反応する銅をCSV法で測定する「金属滴定法」が一般的に用いられている。この方法では、人工配位子SAと天然の有機配位子が銅との錯生成反応を競うことになるため、「競争配位子平衡(CLE)–CSV法」とも呼ばれている。

このような手法の開発によって海水中の銅の存在状態に関する研究は大きく進展してきたが、問題点も指摘されている。例えば、同じCLE-CSV法を用いて同じ海域で研究を行っても、研究グループによって異なる結果が得られるという点である。このような食い違いの原因の一つとして挙げられるのが、検出窓(Detection Window)の問題である。海水中のどの安定度の有機配位子を検出できるかは、添加する人工配位子の種類と濃度のパラメーター(検出窓)に依存する。これまでの研究では1種類の検出窓がよく用いられてきたが、天然の複数種の有機配位子を研究するには、複数の検出窓で金属滴定を行う必要がある。そこで、本研究では複数の検出窓のCLE-CSV法を用いて、海水中の銅の存在状態を検討した。

＜方法＞
海水試料は新青丸KS-15-6次研究航海(2015年6月25日～7月6日)において、東シナ海、沖縄トラフ、琉球海溝で採取した。X型ニスキン採水器により海水を採取した後、クリーンコンテナラボにおいて試料を濾過した。海水は孔径0.2 mmのカプセルフィルターにより濾過した。全銅濃度測定用の海水試料は高純度塩酸を添加してpH 1.8以下とし、CLE-CSV法用の海水試料は冷凍し、陸上の実験室に持ち帰った。

全銅濃度測定用試料は紫外線照射後、SAを用いたCSV法により測定した(Campos and van den Berg, 1994)。CLE-CSV法用試料は4℃で解凍し、分析を行った。この海水試料は10個のテフロン容器に分注後、ホウ酸緩衝溶液と既知量の銅を加え2時間後にSAを添加した。これらの試料を一晩放置した後、CSV法により測定した。SAを1 mMとなるように調整した場合、5 mMとなるように調整した場合という2種類の試料を用意し、測定を行った。得られた結果はRuzic/van den Berg線形法によって解析し、有機配位子濃度と条件安定度定数を得た。

＜結果と考察＞
東シナ海における溶存態の全銅濃度は0.82 –4.7 nMの範囲であり、揚子江の影響を受けた低塩分海域で濃度の高い傾向が得られた。また、CLE-CSV法による測定の結果、条件安定度定数(K)がlogK = 13 –14.1(強いリガンド), 11.7 –12.2(弱いリガンド)という2種類の配位子を検出できた。それぞれ添加するSAの濃度を1 mM, 5 mMとすることにより、明瞭な結果を得ることが可能となった。これらの有機配位子の条件安定度定数はこれまでの他の海域での報告値と同レベルであり、2種類の検出窓を使うことによって、より詳しい有機配位子の測定が可能となった。弱いリガンド濃度は25.6 –47.6 nMと比較的変動の少ない値となったが、強いリガンドは3.6 –11.2 nMと海域によって大きく変化することも明らかになった。生物生産の高い海域において、強いリガンド濃度が高くなっている可能性が考えられる。

＜引用文献＞
Campos, M.L.A.M., and van den Berg, C.M.G., 1994. Determination of copper complexation in sea water

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