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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キーワード：同位体比分析、3He/4He比、質量分析、ビッグバン元素合成、中性子ベータ崩壊
Keywords: Isotope ratio analysis, 3He/4He ratio, Mass spectrometry, Big bang nucleosynthesis, Neutron beta decay

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: $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$. The isotope ratios of $^{37}\mathrm{Cl}/^{35}\mathrm{Cl}$ are usually expressed by δ-notation relative to Standard Mean Ocean Chloride (SMOC) as

$\delta^{37}\mathrm{Cl} = [(^{37}\mathrm{Cl}/\ ^{35}\mathrm{Cl})\mathrm{sample} / (^{37}\mathrm{Cl}/\ ^{35}\mathrm{Cl})\mathrm{SMOC} - 1] \times 1000$. (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 $\delta^{37}\mathrm{Cl}$ 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 $^{37}\mathrm{Cl}/^{35}\mathrm{Cl}$ isotope ratios ($\delta^{37}\mathrm{Cl}$) coupled with a multiple Faraday collector-inductively coupled plasma mass spectrometer (MFC-ICPMS). We used $^{36}\mathrm{Ar}^+/^{38}\mathrm{Ar}^+$ as an external standard for the mass bias corrections between $^{39}\mathrm{K}^+$–$^{41}\mathrm{K}^+$, $^{36}\mathrm{Ar}^1\mathrm{H}^+$–$^{38}\mathrm{Ar}^1\mathrm{H}^+$–$^{40}\mathrm{Ar}^1\mathrm{H}^+$, and $^{35}\mathrm{Cl}^+$–$^{37}\mathrm{Cl}^+$ with isobaric overlap corrections between K^+, ArH^+, and Cl^+ ions. Sulfur ($^{36}\mathrm{S}^+$) isobar on $^{36}\mathrm{Ar}^+$ was indirectly monitored and corrected by a baseline modelling using $^{36}\mathrm{Ar}^+/^{38}\mathrm{Ar}^+$ measurement. Those combined to accomplish an accurate and high-precision measurement of $^{37}\mathrm{Cl}^+/^{35}\mathrm{Cl}^+$ ratios. Using the new analytical protocol, $\delta^{37}\mathrm{Cl}$ in the natural halite samples were analyzed by direct laser ablation. The $\delta^{37}\mathrm{Cl}$ 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 $\delta^{37}\mathrm{Cl}$ 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 $\delta^{37}\mathrm{Cl}$ analysis of igneous rock samples from AgCl with as small as 4 μg chlorine. This is also the first report analyzing a high-precision $\delta^{37}\mathrm{Cl}$ *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 ($T_{1/2}$ = 1.06×10^{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

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$\Delta^{14}C$変動復元

$\Delta^{14}C$ 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($\Delta^{14}C$)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、$\Delta^{14}C$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$\Delta^{14}C$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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