

## 海底熱水域における水銀の質量非依存同位体分別 Mass-independent fractionation of mercury stable isotopes in deep-sea hydrothermal systems

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近年、CV-MC-ICP/MSを用いた水銀同位体分析システムによって、より詳細な水銀の環境動態や発生源を識別することが可能になってきた。水銀同位体比 ( $\delta^{202}\text{Hg}$ ) は酸化還元作用や気液分離などの現象による質量依存同位体分別 (MDF) を示すのと同時に、奇数の同位体比 ( $\delta^{199}\text{Hg}$  &  $\delta^{201}\text{Hg}$ ) には質量非依存同位体分別 (MIF) を示すことが知られている。火山や熱水活動は、主要な自然由来の水銀放出源であり、これまでの先行研究によって地殻中を上昇する過程で気液分離が起こり、比較的低い  $\delta^{202}\text{Hg}$  をもつ水銀が放出されていることが示されている。またこうした水銀は  $\Delta^{199}\text{Hg}$  ( $= \delta^{199}\text{Hg} - 0.252 \times \delta^{202}\text{Hg}$ ) に概ね約 0.2 ‰ の MIF を示すことが知られているが、その発生メカニズムは不明である。その理由に、これまでの研究は地表で採集した試料を対象としていたために、MIF が光還元反応による磁性同位体効果の影響で引き起こされたのか、それとも気液分離による核の体積効果によって引き起こされたのかを識別することができていないことが挙げられる。そこで本研究では、光還元反応の影響を受けない海底熱水域 (伊豆小笠原海域 明神礁 & 明神海丘) で採集した地質試料の水銀同位体比を分析した。分析した試料は概ね負の  $\delta^{202}\text{Hg}$  (-1.0 - 0.5 ‰) を示したために、気液分離の影響で比較的低い  $\delta^{202}\text{Hg}$  をもつ水銀が放出されているという知見を得た。それと同時に、こうした水銀の  $\Delta^{199}\text{Hg}$  は、概ね約 0.1 - 0.2 ‰ であるという知見を得た。また奇数の同位体比の  $\Delta^{199}\text{Hg} / \Delta^{201}\text{Hg}$  が 1.6 - 2.0 であることから、これらの水銀が核の体積効果の影響を受けていることが示唆される。この結果から火山活動によって放出される水銀に検出される MIF は、気液分離に伴う核の体積効果によって引き起こされていると考えられ、水銀汚染の発生源を識別する上で貴重な情報と成りうると思われる。

キーワード: 水銀同位体, 質量非依存同位体分別, 海底熱水域, 還元気化/マルチコレクター ICP/MS

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

## 水圏での金属イオンのスペシエーション：多種の酸素配位配位子の比較 Speciation of metal ions in water: comparison of their reactivities with oxygen-donor hard ligands

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

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

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

キーワード: スペシエーション, エントロピー, 錯生成, 加水分解, 量子化学計算

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

## ジルコン FT 年代と U-Pb 年代の一致性とその意義 Consistency between fission-track and U-Pb ages of zircon and its implications

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

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

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

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

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

キーワード: ジルコン, FT 年代, U-Pb 年代, キャリブレーション  
Keywords: zircon, fission-track age, U-Pb age, calibration

## ガルバノ光学系を用いたLA-MC-ICPMSによるテーナイト相の鉄同位体比分析 Fe isotope measurement of taenite using LA-MC-ICPMS technique with Galvano scanner system

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

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

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

## 地球内部の「水」を見るツール～超高压中性子ビームライン PLANET～ High-Pressure Neutron Beamline PLANET for investigating "Water" in the Earth

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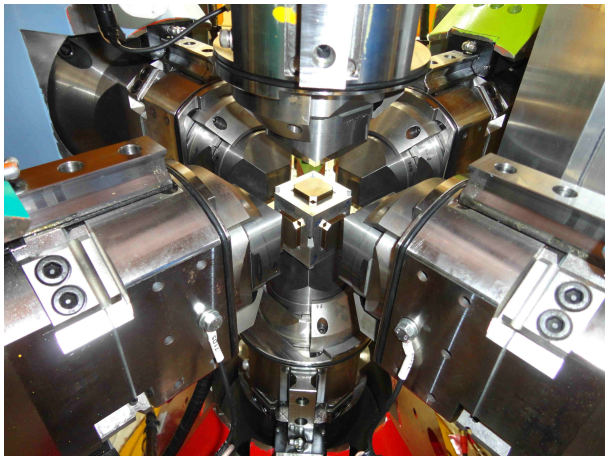
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PLANET は、BL11 に建設された世界初の高温高压専用の中性子分光器である。その最大の特徴は、高温高压発生に優れたマルチアンビル型高压発生装置を用いて、約 20 万気圧 2000 度にある物質中の水、水素の状態を「中性子回折」及び「ラジオグラフィー」を用いて調べられる点にある。2008 年度から建設が始められ、2012 度下半期から実験が行われている。本発表では、装置デザイン及びこれまでに明らかとなった装置性能を紹介する。

PLANET は、さまざまな高压ユーザーの実験を想定し、結晶のみならず液体の構造解析が行える仕様となっている。回折パターンの分解能を実測した結果、デルタ  $d/d \sim 0.6\%$  が実現しており、ほぼ設計値 (0.5%) に近い性能が出ていることが分かった。また、高压実験において問題となる試料周りの物質（ヒータや、試料容器）からの散乱を除去するために、シビアな入射および受光スリットを配置しており、加圧されたアセンブリ内の試料のみの情報を取り出せるようになっている。これらの工夫により、高压下でも、常圧データと比べ遜色ない大変クリアなパターンを取得することができ、これまでの高压中性子回折実験の常識を覆す革新的な中性子分光器となっている。

キーワード: 中性子, 高压, ビームライン, 含水

Keywords: neutron, high pressure, beamline, hydrous



## J-PARC 高圧中性子ビームライン (PLANET) の地球惑星科学への応用 High-pressure neutron beamline at J-PARC and applications to earth and planetary sciences

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

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

キーワード: 中性子, 中性子回折, 水素, 水, 高圧, 氷

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

## 地球内起源ニュートリノによる新しい地球観測 Geo-neutrinos for advanced earth studies

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

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Herndon JM. 1996. Substructure of the inner core of the Earth. Proc. Natl. Acad. Sci. USA 93:646-48.

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

キーワード: ニュートリノ, ウラニウム, トリウム, マントル  
Keywords: Neutrino, Uranium, Thorium, Mantle

## マルチレンジ同位体イメージング技術の開発 Multi-range imaging mass spectrometry using laser ablation-ICP-mass spectrometry

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

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



## 分光式質量分析計による石筍中の流体包有物の水の同位体組成測定法の開発 Cavity ring-down spectroscopy for the isotope ratio measurements of water from fluid inclusions in stalagmites

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氷床コアと同様に過去の環境変動を記録し、かつ正確に年代が決定できる鍾乳石は、近年世界中で盛んに研究されている。なかでも、石筍の酸素同位体比 ( $\delta^{18}\text{O}$ ) はモンスーン強度の復元などに利用されるが、降水や気温など様々な要因がその変動に寄与していると考えられ、その解釈は容易ではない。一般に、石筍の内部には  $\text{CaCO}_3$  を生成した原料の滴下水が保存されていることが多い。高湿度の鍾乳洞内では、蒸発に起因する同位体分別が生じないため、石筍に含まれる流体包有物の水は、滴下水の同位体比を保存していると考えられる。 $\text{CaCO}_3$  を生成した水 ( $\text{H}_2\text{O}$ ) と  $\text{CaCO}_3$  のあいだの酸素同位体比の差は、温度のみに依存すると予想されるため、これに基づいて石筍生成時の気温を定量的に復元できると考えられる。これまでの研究では、水の同位体比は、水を他の気体に変換した後で磁場型の質量分析計を用いて測定されてきた (e.g. Dennis et al., 2001)。本研究では、測定の簡略化を目指して、抽出した水の同位体比を水分子のままキャビティリングダウン式分光計 (CRDS) で測定するラインを作成した。測定ラインは、真空下で水を抽出する前処理部と水同位体比を測定する検出器 (L2130-I Picarro) から構成されている。市販の液体試料を気化し CRDS に導入する装置 (Vaporizer, V1102-I, Picarro Ltd.) を参考にして、少試料量での測定に適した気化装置を制作した。開発した気化装置は内容積の小型化などにより、市販装置の約 10 分の 1 の試料量で測定可能となった。石筍中の流体包有物の測定精度は、同位体比が均一な同一層から石筍試料を複数切り出し、測定することで評価した。測定した石筍試料の重さは平均 151 mg (77 - 286 mg) で、抽出された水の量は平均 0.12 micro-L (0.01-0.26 micro-L)、同位体比測定の繰り返し精度は  $\delta^{18}\text{O}$  で  $\pm 0.2\text{permil}$ 、 $\delta\text{D}$  で  $\pm 1\text{permil}$  であった。この結果は、一般に高精度・高感度であるとされる IRMS を用いた研究と比較しても最高精度の研究と同等であり、必要試料量についてはこれまでの研究よりも少ない。年代が現在に近い沖縄の石筍の流体包有物の同位体組成は、現在の沖縄の降水と誤差範囲内で一致していた。この結果は、石筍中の流体包有物から過去の降水の同位体比組成を保存していることを示している。

キーワード: 安定同位体比, 流体包有物, 鍾乳石, 石筍, 古気候, CRDS

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

高緯度サンゴを用いた酸素同位体比と Sr/Ca 比の骨格成長量依存性の評価および水温復元  
Coral growth-rate insensitive Sr/Ca as a robust temperature recorder at the extreme latitudinal limits of Porites

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サンゴは過去数百年間の気候変動を季節単位で復元することが可能であるため、熱帯から亜熱帯域の詳細な気候復元に用いられている。近年の地球温暖化により、熱帯・亜熱帯に生息する造礁サンゴが北上し、日本列島の温帯域にも造礁サンゴが分布していることが確認された。したがって、これまで熱帯、亜熱帯域に限られていたサンゴ骨格気候学を適用し、より詳細な温帯域の長期気候値の復元可能性が出てきた。温帯域の造礁サンゴは地球温暖化や海洋酸性化の影響を敏感に反映し、骨格に記録していることが期待される。しかし、温帯域は熱帯・亜熱帯域とは SST や気候が異なり、サンゴ礁の形成可能な下限水温といわれる 18 °C を下回るような低水温や大型藻類との競争など、サンゴにとって過酷な生息環境であるため、温帯サンゴの SST 復元に用いられる Sr/Ca 比と酸素同位体比が水温をどのように骨格に記録するのか、検証する必要がある。

本研究では、サンゴの北限に近い熊本県天草市牛深にて採取されたサンゴの Sr/Ca 比を測定し、先行研究で測定された酸素同位体比と比較することで、酸素同位体比よりも Sr/Ca 比は成長量に依存せず、より正確に水温を記録するプロキシであることが確認された。したがって、成長量が小さい温帯サンゴから水温を復元するには、Sr/Ca 比の方が酸素同位体比よりも適していることが明らかになった。また、牛深にて採取した別のサンゴ 2 群体についても Sr/Ca 比測定を行い、異なる群体による水温復元の違いの評価を行った。現段階では、1 群体のみを使用して精度の良い水温換算式を作成するのは難しいが、複数群体用いて復元をすれば、温帯サンゴであっても観測水温と復元水温の差は約 1 °C におさまり、今後、温帯域の化石サンゴを用いて水温復元をするという古環境復元の利用の可能性が期待できる。

有機物から最大限の情報を引き出すために  
Maximizing organic records: Recent achievements and future directions

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

キーワード: 有機分子, 同位体比, 窒素, 炭素

Keywords: Organic molecule, isotopic composition, nitrogen, carbon

## アミノ酸の安定同位体比を正確かつ感度良く測定するための分析法 Precise and sensitive determination of stable isotopic compositions of amino acids

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

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

キーワード: 安定同位体, アミノ酸, 食物連鎖, 隕石

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

## 「軽い」アミノ酸と地球化学の接点 On the role of amino acid metabolism and a biogeochemical linkage

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### 1. はじめに

近年、「地下圏あるいは地球深部」のサイエンスで最も興味深いトピックの一つは、「Deep Biosphere」(地下生物圏あるいは地下生命圏とも呼ばれる)であろう。その共通概念は、異分野間でも広く認識されるようになった。地球科学と生命科学を分野横断的にカバーする新しい分野とも言える。ある環境から「地下生物圏」ではなく、化学(純粋な物質組成のみ)と物理(温度、圧力、pH等)のみが支配する「非生命圏」となる。ミクロな世界で駆動されている有機的な地球化学プロセスは、分子情報として入手することができる。最先端の知見をさらに詳しく明らかにするためには、分子レベルで解読できるような新しい技術開発が、一つの鍵になる。

### 2. 世界的に存在する第3の生物界「アーキア」(Archaea)と物質循環

新しい生物界「アーキア(古細菌)」の提唱以来(Woese and Fox, 1977)、その存在は、高温や高塩等の極限環境だけでなく、海洋(水柱・海底下)や陸上(水圏・土壌)を問わず、広汎的に棲息する原核生物であることが理解されるようになった。近年、これまで認知されてきたアーキアの2大門レベルであるユーリアーキオータ門およびクレンアーキオータ門の他、さらに新しい分類群のタウムアーキオータ門、コルアーキオータ門、ナノアーキオータ門の多様性が見えつつある。

アーキアは、全球的な物質循環の主役の一つともいえる。炭素の形態は、最も酸化的なCO<sub>2</sub>、最も還元的なCH<sub>4</sub>、そしてその中間である有機態炭素C<sub>n</sub>(H<sub>2</sub>O)<sub>m</sub>の3つである。海底下に広く棲息するメタン生成アーキアは、深部の還元環境でもメタンを生成している(cf. Coenzyme F430: Takano et al., 2013)。地下圏には、逆に、メタンを炭素源にする嫌気的メタン酸化アーキア群も存在する。そのANME(Anaerobic Methanotroph)-1, ANME-2, ANME-3と呼ばれる系統分類群は、メタンを生化学的に分解している。さらに、嫌気的メタン酸化アーキア群集の中では、窒素固定が行われていること(Dekas et al., 2009)、そのメタン酸化アーキアは、メタン生成の逆反応から炭素源を同時に得ていること(Shima et al., 2012)等の発見が相次いでいる。

### 3. 中央代謝系としてのアミノ酸の重要性

原核生物1細胞あたりの化学組成を比較すると、主にタンパク質、核酸、炭水化物、脂質の4つに分類される。このうち、タンパク質の割合は優に5割を超え、中央代謝としての役割が大きい。タンパク質は、アミノ酸の基礎単位がペプチド結合で連なる生体高分子である。構造タンパク質と触媒タンパク質(酵素)という2つの主要なタンパク質群があり、いずれも加水分解すると $\alpha$ -アミノ酸が得られる。近年、このアミノ酸分子の同位体組成の規格を用いて生態学的な食性を定量的に解析する研究が進められている(e.g., Chikaraishi et al., 2009)。アミノ酸は、地球生物圏(地下生物圏も含む)での合成と分解の間で準安定的に存在し、生細胞内の中央代謝系としてだけではなく、食性連鎖を通じた生体エネルギーの転換の担い手としても重要である。ここでは、最近になって分かってきたアミノ酸分子の知見から、地球化学的に重要な接点の一つを探ってみたい。

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キーワード: アミノ酸, 地球化学, 第3の生物界「アーキア」

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

**MC-ICP-MS による火山岩のホウ素同位体分析のための簡便なホウ素分離方法の開発**  
**Simple method for separation of boron from volcanic rocks for isotopic analysis by MC-ICP-MS**

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

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

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

## サブミクロン局所 U-Pb 年代分析に向けたレーザーイオン化 SNMS の開発 Development on submicron-scale U-Pb dating by Laser post-ionized SNMS

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ウラン放射壊変系を利用した岩石・化石試料の U-Pb 年代分析法は、太陽系の進化や地球史を明らかにする上で必要不可欠な絶対年代情報を与える。特に、ウランを多く含む閉鎖温度の高い鉱物（ジルコンやアパタイトなど）をターゲットにした、2 次イオン質量分析計（SIMS）による局所 U-Pb 年代分析は、地球惑星科学の発展に多大な貢献をしてきた（例えば、Terada and Sano 2012）。しかしながら、1 次イオンビーム（酸素イオン）を照射し生成される 2 次イオン（U<sup>+</sup>, Pb<sup>+</sup>）を質量分離する SIMS は、イオン化効率が 1 % 以下と低い事が最大の弱点であった。そこで我々のグループでは、スパッタされた中性原子を、高強度レーザー照射によってポストイオン化することでイオン収量を増加させるレーザーイオン化 SNMS (Sputtered Neutral Mass Spectrometry) の開発を行ってきた (Ishihara et al. 2010)。本発表では、サブミクロンスケールの高精度 U-Pb 年代測定を行うことを目指し、0.1  $\mu$  m 径まで絞れる Ga イオン源+フェムト秒レーザー+多重周回型 Time of Flight (MULTUM II) からなる装置の開発現状について報告する。Pb 板の測定においては、 $1.2 \times 10^{14}$  W/cm<sup>2</sup> のレーザー照射時にイオン化効率を最大で 700 倍に増加させることに成功した。また 2 次イオンを多重周回型 time-of-flight (TOF) で長時間飛行させることで質量分解能約 1 万を達成した (従来のセクター型の SIMS では約 5000)。当日は、同システムの特長評価、および天然鉱物試料の測定に向けての課題についても報告する。

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キーワード: U-Pb 年代, 質量分析, 局所分析, 同位体分析

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

放射性セシウムの固相吸着に与える有機物の阻害効果：チェルノブイリ市プリピャチ川の懸濁粒子分析  
Inhibition effect of natural organic matter on adsorption of radiocesium onto particulate matters in Pripyat River

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

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

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

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

Keywords: chernobyl, natural organic carbon, STXM



## 新しい海洋生態系トレーサーとしての魚中ヨウ素 129 の分析法確立 Development of the technique for determination of I-129 in fish samples as new tracer of marine ecosystem

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

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

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

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

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

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

キーワード: ヨウ素 129, トレーサー, 海洋生態系, 魚, AMS

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

耳石のLA-HR-ICPMSによる微量元素分析から推定する北西インド Kutch 湾に生息するナマズの生態—中期完新世の古水温復元に向けて—  
Exploring the ecology of catfish through trace elements analyses of otolith by LA-HR-ICPMS to reconstruct palaeo-SST

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

キーワード: 耳石, 微量元素分析, 酸素同位体比, レーザーアブレーション誘導結合プラズマ質量分析, カッチ湾  
Keywords: otolith, trace element, oxygen isotope, LA-HR-ICPMS, Gulf of Kutch

## 地球表層プロセス研究のための $^{10}\text{Be}$ 測定:バックグラウンド低減のための前処理法の改良 Improved $^{10}\text{Be}$ preparation to reduce analytical background for earth surface process studies

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石英中のベリリウム - 10 ( $^{10}\text{Be}$ ) は宇宙線照射生成核種であり、加速器質量分析 (AMS) 法の発展とともに、年代決定や地球表層プロセスの理解などに用いられてきた (例えば、Gosse and Phillips, 2001)。本手法の適用範囲の拡大のためには、 $^{10}\text{Be}$  濃度が低い (すなわち、露出年代が若い、もしくは、浸食速度が早い) 試料の測定が不可欠であり、そのためにはバックグラウンドを下げる必要がある。特に、同重体であるホウ素 - 10 ( $^{10}\text{B}$ ) の混入を防ぐ前処理法の開発は必須である。本研究は、 $^{10}\text{Be}$ -AMS 測定のための前処理法の改良を行い、 $^{10}\text{Be}$  のバックグラウンドを下げることを目的として行った。その結果、バックグラウンドに最も影響を与えるのは、酸化時の試料の大気暴露時間の長さであることが明らかになり、電子レンジるつぼを使用し酸化時間を短縮することなどが重要であることが明らかになった (Yokoyama *et al.*, submitted)。講演では、分析結果の概要などを報告する。

キーワード: ベリリウム - 10, バックグラウンド, 地球表層プロセス, 加速器質量分析  
Keywords: beryllium-10, background, earth surface process, Accelerator Mass Spectrometry

## 東京大学大気海洋研究所 AMS 用試料処理システムの構築 Radiocarbon pretreatment system of AORI AMS

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加速器質量分析 (AMS) 法を用いた放射性炭素分析法の進歩は目覚ましく、現在は測定誤差 2.5 ‰程度の超高精度測定が主流となってきた。さらに分析装置の小型化も進み、以前は加速電圧 5MV 程度の大型タンデム加速器を用いていたものが、現在では小型の 250KV シングルエンド型加速器を用いたシステムも開発がされている。分析装置が小型化されることにより、操作性の向上やメンテナンスが容易になり、低コスト・高効率で高精度 14C 分析が可能となった。

昨年 2 月に国内で初めてシングルステージ型加速器質量分析計を東京大学大気海洋研究所に導入した。本装置は 5m × 7m の小型の放射性炭素分析に特化した AMS 機器であり、250KV と低い加速電圧で放射性炭素分析を可能とした。従来 AMS 装置に比べ、メンテナンスが容易であり、測定効率も一か月に約 600 検体の分析が可能と非常に高い。これらの特徴を備える本装置は今まで困難であった 14C を用いた高精度多点数分析に利用可能な装置であるといえる。AMS 装置の高精度、高効率化に伴い、それらに対応可能な前処理システムの構築も重要となる。

シングルステージ型加速器質量分析計導入に伴い、大気海洋研究所における放射性炭素年代測定前処理システムの構築を行ってきた。本発表ではシステムの詳細と本システムによって可能となる AMS 分析システムの地球化学分野への応用について述べる。

キーワード: 放射性炭素, 加速器質量分析, 試料処理, 放射性炭素年代測定

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