

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⁺, Pb⁺）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 μ 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、 1.2×10^{14} W/cm² 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。

参考文献

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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 ¹²⁹I as a new tracer for marine ecosystem was examined.

The iodine isotopic ratio (¹²⁹I/¹²⁷I) in seawater is determined by the anthropogenic ¹²⁹I transferred from the atmosphere, i.e., it shows very high ratio as the order of 10⁻¹⁰ for ¹²⁹I/¹²⁷I at the surface or surface mixing layer and suddenly decreases going deeper to some of 10⁻¹² or lower. Iodine isotopic ratio (¹²⁹I/¹²⁷I) 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 ¹²⁹I for marine ecosystem. This is because ¹²⁹I is so trace in the marine lives that ordinary analytical techniques cannot detect.

Recent development of analytical technique for ¹²⁹I using AMS (Accelerator Mass Spectrometry) enables determine trace amount of ¹²⁹I 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 (¹²⁷I) concentration. The remaining was, added with carrier iodine (about 1 mg), purified by solvent extraction and collected as AgI precipitation. ¹²⁹I/¹²⁷I ratio was determined by AMS. From the AMS result and the ¹²⁷I concentration, the ¹²⁹I/¹²⁷I 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 1×10⁻¹⁰ to 7×10⁻¹⁰, 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 (~ 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 ~ 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 ~ 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}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}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}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}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}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}Be -AMS 測定のための前処理法の改良を行い、 ^{10}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