

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.

Development on submicron-scale U-Pb dating by Laser post-ionized SNMS

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In order to decipher the history of the Solar System, in-situ U-Pb dating method using SIMS (Secondary Ion Mass Spectrometry) has been used over 40 years, of which spatial resolution is 2-10 micron. In general, the secondary ion yield of SIMS is so low (less than 1 %) that it has been the weak point of this in-situ analysis. Here, we report the performance of Pb isotope measurement using the Laser SNMS that consist of of Ga-ion source for primary beam, femto-second laser for post-ionization, and the multi-turn TOF-SIMS for mass spectroscopy (Ishihara et al. 2010).

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

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

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.

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

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 (^{23}Na , ^{25}Mg , ^{55}Mn , ^{88}Sr and ^{137}Ba / ^{43}Ca) 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.

Keywords: otolith, trace element, oxygen isotope, LA-HR-ICPMS, Gulf of Kutch

Improved ^{10}Be preparation to reduce analytical background for earth surface process studies

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Due to advancement of Accelerator Mass Spectrometry (AMS), *in situ* produced beryllium-10 (^{10}Be) in quartz has been used for earth surface process studies, such as surface exposure dating (*e.g.* Yamane *et al.*, 2011), erosion rate estimations (*e.g.* Shiroya *et al.*, 2012), tectonic processes (Yokoyama *et al.*, 2005) and so forth (*e.g.* Gosse and Phillips, 2001). In order to expand the applicability of this technique, the sample with low ^{10}Be concentration need to be measured with high precision. This requires reduction of background that is often affected isobars (boron-10). We have conducted several attempts and found that the length of time exposed to the ambient atmosphere during the oxidization process is the most important step to increase ^{10}Be background (Yokoyama *et al.*, submitted). In this presentation, we discussed our experimental results and potential improvement of topics for understanding of earth surface process.

Keywords: beryllium-10, background, earth surface process, Accelerator Mass Spectrometry

Radiocarbon pretreatment system of AORI AMS

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The Accelerator Mass Spectrometry(AMS)is effective in radiocarbon dating. By the conventional method, a large tandem accelerator(e.g.Accelerating voltage = 5MV) was used. However, the small accelerator(e.g.Accelerating voltage = 500kV) is used in the new AMS analysis.

The small AMS machine is handy.We installed small AMS machine in our laboratory. We will present the outline of new AMS pretreatment system and the geochemical application research using that.

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