

New multiple ion counting-ICPMS system for Age Cytometry

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The MC-ICPMS instruments, equipped with a multiple ion counting system setup, can improve the precision of the age determination, and the data quality achieved by the LA-ICPMS technique is comparable or enhanced compared to those obtained by secondary ion mass spectrometry (SIMS). With the conventional ion counting system, the gains of the ion detectors (electron multipliers) must be calibrated regularly through the elemental analysis for standard materials. This results in elongation of the analysis time for the age determinations. To improve the long-term stability, and also to improve the accuracy of the age data, we have developed new ion counting system using Daly collector. In this study, two Daly collectors were adopted to the MC-ICPMS instrument (Nu Plasma II, Wrexham UK), and were used to measure ²⁰⁶Pb and ²⁰⁷Pb signals. With the Daly ion collectors, both the medium to long-term stability could be remarkably improved from 0.1%/hrs to 0.04%/hrs. Moreover, the counting loss due to dead time of the ion counting system can be corrected based on the conventional non-extendable law, and the beam sizes of greater than 10 MHz (cps) can be successfully measured by the Daly collector. With the multi-ion counting technique, the analysis time for U-Th-Pb age determinations can be significantly reduced down to 1 - 10 sec/spot, and the shorter analysis time enabling to obtain an age distribution of the zircons collected from a sample (age cytometry). This analytical approach allows to decipher the contribution of multiple geological events or multiple sources of the zircons. The "age distribution" is a useful approach to understand the geological sequence underlying the sample formation.

With shorter duration time for the laser ablation, the resulting depth of the ablation pit can be smaller than 1 µm, and therefore, age determinations from thin-layer rim of zircon crystal can be made. Schmitt (2011) reported that the U-Th-Pb age derived from the outer rim (<5 µm) of the zircon crystals can reflect the timing of overgrowth through eruption processes [Schmitt, 2011]. This means that multiple chronological information can be derived from a single zircon grain. With the shorter ablation time achieved by the MC-ICPMS system setup, precise U-Th-Pb ages can be derived from the depth of shallower than 1 µm. This technique can be applied for geochemical evolution processes within magma chambers by determining the difference between crystallization of the zircons and timing of eruption, and thus the U-Th-Pb ages obtained from the rim of zircon crystals can reflect low-temperature geological events. In this presentation, analytical capability of the multi-ion counting technique using Daly collector for the age determination will be demonstrated.

Reference

Schmitt A. K. (2011) Uranium Series Accessory Crystal Dating of Magmatic Processes, *Annu. Rev. Earth Planet. Sci.*, 39, 321-349.

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

Evaluation of coupling LA-ICP-MS/MS and collision/reaction cell technique for in-situ zircon analysis

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is not only a relatively cheap, fast, low-costing method, but also has high sensitivity to obtain geochronological/geochemical information from micro region of solid samples. However, the highly-ionization capability of this method easily occurs multiple mass interference from isobaric, polyatomic and multi-charged ion. Hence, in the case of LA-ICP-MS, great care for these potential mass interference must be taken, compared to the traditional solution nebulization sampling in which chemical separation of target element is possible. To overcome these problems in LA-ICP-MS, the instrumental setting at high mass resolution power or low oxide formation rate is common, although the decrease of the sensitivity is unavoidable in many cases. Moreover, it should be noted that there has been no effective strategy for reducing the isobaric interference in LA-ICP-MS. In this presentation, we would like to demonstrate the effectiveness of coupling ICP-MS/MS and collision/reaction cell (CRC) technique for in-situ U-Th-Pb dating and quantitative analysis of rare earth elements (REEs) of zircons using laser ablation sample introduce technique.

In U-Th-Pb dating of zircon, the measurement of ^{204}Pb is critically important because it is the only non-radiogenic nuclide among stable isotopes of lead. Unfortunately, in LA-ICP-MS, there is the isobaric interference on ^{204}Pb from ^{204}Hg which is derived from the impurity of the argon gas for ICP ion source. In this study, the reduction of this interference is tested by flowing a small amount of ammonia gas in the CRC. In this case, while the polyatomic ions made by collision of REEs in zircon and ammonia gas could be overlapped on mass peak of Pb isotopes, the first mass spectrometer (Q1) can effectively remove the REEs and ammonia gas collides with only isotopes of Hg, Pb, Th and U. In this operational settings, the accurate age from several standard zircons was obtained with reducing the isobaric interference from Hg lower than the level of 1/100.

In the quantitative analysis, the instrumental tuning at the low oxide formation rate is important because most of REEs tend to make oxide easily in ICP-MS and polyatomic interference on heavy REEs from the oxide of light REEs is not negligible. However, at the condition of the lower oxide formation rate (<1%), the instrumental sensitivity is greatly depressed as tread off. Therefore, we used mass shift method by flowing the oxygen gas in the CRC. In mass shift method, it is possible for operational settings to be tuned to maximize the sensitivity while removing the mass interference from polyatomic and multi-charged ions. We carried out the quantification of REEs in standard zircon sample at the condition of the high sensitivity (10 times higher than normal condition) and extremely high oxide formation rate (>100%) using mass shift method, and the resulting concentrations of REEs show good agreement with reported values.

In conclusion, the coupling ICP-MS/MS and CRC technique can be not only a great solution for the interference-related problems, but also brings out the potential capability of high sensitivity of LA-ICP-MS.

Keywords: LA-ICP-MS, Zircon geochronology, Trace element quantification, Collision/reaction cell

Evaluation for multi-turn time of flight mass spectrum of laser ionization mass nanoscope

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Introduction: Laser ionization mass nanoscope (LIMAS) is a sputtered neutral mass spectrometer (SNMS) by tunneling ionization effect. This instrument was developed for measuring solar wind particles from extraterrestrial materials collected by planetary exploration missions, such as JAXA Hayabusa and NASA Genesis (Bajo et al., 2015). LIMAS consists of a Ga liquid metal ion source and an aberration corrector system for sputtering of nanometer scale area on samples, a femtosecond laser system for tunneling-ionization of the sputtered particles, and a multi-turn time-of-flight mass spectrometer (MULTUM II) for mass separation of isotope analysis. We have evaluated the performance of MULTUM II equipped with the ion injection optics of LIMAS.

Experimental procedure: We carried out numerical simulations of ion trajectories in the ion injection optics, and then load voltages for each lens were determined experimentally. As a result, Extraction lens L1 was -700 V, L2 was -3300 V. Einzel lenses 1 and 2 were set to -1260 V and -2700 V, respectively. Under these conditions, we evaluated mass resolving power and transmittance of LIMAS using $^{24}\text{Mg}^{2+}$. Data for each cycle were averaged for 1000 shots. We calculated useful yield of each cycle of LIMAS by depth profile of Si ions. The sputtered crater volume was measured by 3D laser scanning confocal microscope.

Results and Discussion: Mass-resolving power of TOF mass spectrometer is defined by time-of-flight of ion " t " and ion packet width " Δt " ($R = t/2\Delta t$). Mass-resolving power increased up to the TOF of 1000 μs (200 multi-turn cycles). After 1000 μs , mass-resolving power became saturated. Saturation of the mass-resolving power ($R = \sim 10^5$) indicates that the averaged peak width increases linearly with increasing the number of cycles. Increasing FWHM was occurred by different TOF of ion packet become large with increasing cycle. 3 factors affect by different TOF of ion packet: 1) modulation by the acceleration voltage (ΔU), 2) modulation of the injection timing for the ion injection optics (Δt_{i1}), and 3) modulation of the electric field for the electric sectors (ΔE) in MULTUM II. Modulations of ΔU and ΔE become dominant if TOF increase. The ΔE was observed at 5 ppm, corresponding to $R = 10^5$, which is consistent with the saturation value of R described above. In order to correct the modulation of ΔE , TOF correction among peaks must be effective. Applying TOF correction, the mass-resolving power of LIMAS increased linearly with increasing the flight path length, and reached 620,000 (FWHM) at 1,000 multi-turn cycles of MULTUM II (flight path length: 1,312 m).

The transmittance up to 20 multi-turn cycles decreased to 60-70%, compared with the transmittance on linear mode. After 20 multi-turn cycles, the transmittance per multi-turn cycle became constant (99.96%).

A useful yield of LIMAS was estimated. As a result, useful yield was 3×10^{-3} at 30 multi-turn cycles ($R = 17,000$), 2×10^{-3} at 1000 multi-turn cycles ($R = 620,000$) of MULTUM II. The calculated useful yields for LIMAS would be better than to those for Cameca ims 6f at the same R (cf. 7×10^{-3} at $R = 4,000$; Hervig et al., 2006).

Keywords: SNMS, TOF, laser tunneling-ionization,, mass-resolving power, ion transmittance, useful yield

Nucleosynthetic Yb isotope anomalies in chondrites

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Recent studies on high precision isotope analyses for bulk aliquots of meteorites discovered the existence of planetary scale nucleosynthetic isotope variabilities for a variety of elements (e.g., Cr, Sr, Mo, Ru) [1-4]. By contrast, some elements (Hf, W, and Os) do not show such anomalies at the current level of analytical precision [5-7]. The processes responsible for generating the isotopic heterogeneity/homogeneity in the early Solar System are not fully resolved yet, however, two plausible models have been proposed to account for the isotopic characteristics recorded in meteorites. The first model considers nebular thermal processing which caused selective destruction of thermally weak-isotopically anomalous carriers, followed by subsequent physical separation of volatile phase and ultra-refractory components [8]. On the other hand, the injection of isotopically anomalous materials from a nearby core-collapse supernova (ccSN) and subsequent aerodynamic sorting of grains in different sizes can be an alternative possibility to cause planetary scale isotope heterogeneity [9].

Ytterbium is an intriguing element which would provide a strong constraint on the origin of planetary scale isotope anomalies in the Solar System. The $T_{50\%}$ for Yb (1487 K) is lower than those of the other heavy-REEs (1659 K) and is comparable to that of Sr. Therefore, the thermal processing would lead to heterogeneous Yb isotope distribution in the Solar System, whereas the injection of a nearby ccSN would not generate *r*-nuclides of Yb. Here we report preliminary results on Yb isotope compositions in one ordinary chondrite (Olivenza, LL5) and one rumuruti chondrite (NWA 753, R3.9). The Yb isotope ratios for meteorite samples are reported as μ Yb notations which represent the parts per 10^6 deviations from the terrestrial isotope ratios. The ordinary and rumuruti chondrites possess large negative anomalies for $\mu^{168}\text{Yb}$ (-2500 ppm on average) and $\mu^{170}\text{Yb}$ (-130 ppm on average) exceeding analytical uncertainties of the standard material, whereas the $\mu^{171}\text{Yb}$, $\mu^{173}\text{Yb}$, and $\mu^{176}\text{Yb}$ values are indistinguishable from the terrestrial component. The patterns of μ Yb for the chondrites are not consistent with that representing the deficit of *s*-process nuclides relative to the terrestrial component. Therefore, the negative anomalies in $\mu^{68}\text{Yb}$ and $\mu^{170}\text{Yb}$ are attributed either to the deficit of *p*-process nuclides relative to the terrestrial component, or to the analytical artifact due to the overcorrection of interferences from ^{168}Er and ^{170}Er . By contrast, the absence of anomalies for $\mu^{171}\text{Yb}$, $\mu^{173}\text{Yb}$, and $\mu^{176}\text{Yb}$ is consistent with the marginal isotope anomalies in ordinary chondrites for Mo and Ru isotopes synthesized by the *s*- and *r*-processes, which are significantly smaller than those observed in carbonaceous chondrites and iron meteorites [3-4].

References: [1] Trinquier, A. et al. (2009) *Science* 324, 374. [2] Yokoyama, T. et al. (2015) *EPSL* 416, 46. [3] Burkhardt, C. et al. (2011) *EPSL* 312, 390. [4] Fischer-Gödde, M. et al. (2015) *GCA* 168, 151. [5] Akram, W. et al. (2013) *ApJ* 777, 169. [6] Yokoyama, T. et al. (2010) *EPSL* 291, 48. [7] Burkhardt, C. et al. (2012) *EPSL* 357-358, 298. [8] Yokoyama, T. and Walker, R.J. (2016) *RiMG* 81, 107. [9] Dauphas, N. et al. (2010) *ApJ* 720, 1577.

Keywords: isotope anomalies, chondrite, Yb

Development of on-site neon measurement system using a portable ultra-high resolution mass spectrometer (MULTUM)

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Dissolved noble gases (He, Ne, Ar, Kr, and Xe) in seawater are chemically inert and their variations are thus solely responsible for physical processes such as temperature change, diapycnal mixing, and mixing of water masses. Since different noble gases have different temperature dependence on diffusivity and solubility, the noble gases show different responses even to the same physical forcing, which make us possible to quantitatively estimate how much physical processes the water mass experienced in the past through the simultaneous measurements and subsequent comparison of the observed noble gas concentrations.

Present measurement of dissolved noble gases requires a comprehensive purification and separation of each noble gases from sample gases extracted from seawater (e.g., Sano and Takahata, 2005, Stanley, et al., 2009) to avoid that residual atmospheric gases interfere subsequent mass spectrometric quantification of the target trace noble gases using a quadruple mass spectrometer (QMS) with a low mass resolution. The pretreatment system is quite large and complicate for its field operation and it is practically impossible to conduct the purification and quantification on-site along with seawater sampling. Water samples, then need to be brought back to a land-based laboratory. The taking seawater samples back to the land-based laboratory without suffering contamination of highly permeable atmospheric noble gases requires to store the samples in copper tubes with the both ends fully squashed and completely sealed, which is quite cumbersome and requires man power. Such time-consuming and labor-intensive sampling and pretreatment in both field and laboratory have limited available number of samplings and measurements, and subsequently resulted in a quite limited number of observed data of noble gases in water environments.

Here we introduce a new method for the direct measurement of atmospheric neon concentration without cumbersome pretreatment and sampling treatment by combining multi-turn time of flight mass spectrometer (MULTUM) and a simple cryo-gas trap as a preliminary stage of the development for the online analysis of dissolved noble gases. The ultra-high mass resolution of the MULTUM (10000~30000) compared to that of ordinary QMS (100~500) allows our Ne^+ (m/z 19.9919) ion detection to be free from interference ions, such as $\text{H}_2^{18}\text{O}^+$ and HF^+ (m/z 20.0057 and 20.0151, respectively) which have close m/z to that of Ne^+ (Fig. 1) and cannot be detected separately with commonly used QMS. Prior to the ultra-high resolution mass spectrometric analysis, most of the major atmospheric gases (e.g., N_2 , O_2 , Ar and CO_2) were removed by a cryo-gas trapping to avoid a saturation effect during ionization in the mass spectrometer and further optimize the mass spectrometer for the detection of trace Ne^+ ion. Such a simple and compact pretreatment system, compared to the ordinary large and complicated one, enables us to bring the pretreatment system to the field and conduct on-site analysis of Ne.

As a test case, atmospheric Ne was analyzed by directly injecting 0.5~5 cm^3 of atmospheric air into the developed system. Atmospheric Ne (18 ppmv) was successfully measured in every 10 minutes by simply injecting sample atmospheric air into the system (Fig. 1-2). An obtained good linearity between injected air volume and Ne^+ ion peak (Fig. 2) shows that the simple cryo-gas trap also can work as a pre-concentrator, which is another advantage for trace gas analysis. The preliminary

result shows that the developed method can be applied for the continuous and direct measurement of dissolved Ne and other noble gases with further modification.

Keywords: MULTUM, dissolved noble gas, on-site measurement, ultra-high resolution mass spectrometry

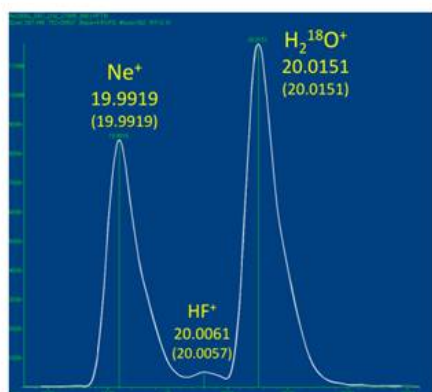


Fig. 1. The high resolution mass spectrum of an atmospheric air sample (m/z 19.19 ~ 21.19) obtained derived from obtained mass chromatogram using MULTUM. The high mass resolution ensured separate detection of Ne^+ (m/z 19.9919) ion from interference ions, such as HF^+ (m/z 20.0057) and $\text{H}_2^{18}\text{O}^+$ (m/z 20.0151).

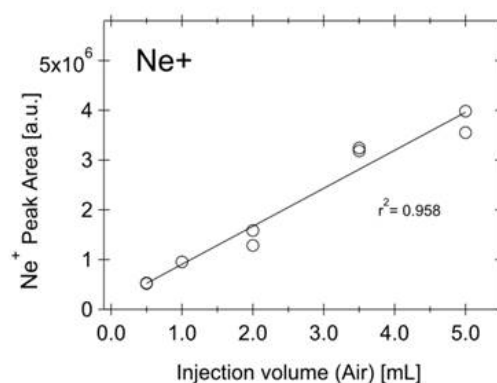


Fig. 2. The relationship between injected volume of atmospheric air samples and the Ne^+ ion peak area obtained using a simple cryo-gas trapping system. A good linear relationship was obtained between the analytical ion peak and injection volume over a range of 0.5~5mL ($r^2 = 0.958$)

Formation Processes and Anthropogenic Influences for Sediments in Majuro Atoll

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Atolls only 1~3 m above sea level are vulnerable to natural disasters and climate change. In spite of such conditions, people have lived in the Majuro Atoll in Marshall Islands for more than 2000 years (Yamaguchi et al., 2009). The life styles in this island have changed dramatically by the modernization. For example, the use of motor vehicles has been increased. Especially in an isolated island, sediments originally composed of coral gravel and foraminifera are easily affected by human activities such as cultivation of crops and well for drink water etc. Therefore, condition of sediments could be proper index of human impact. In particular, when they use modern industrial products, heavy metals contained in the products can be emitted and accumulated in the sediments. However, the influence of these contaminants on the reef island remains unclear. In this study, we focus on the changes of physico-chemical conditions of soil depending on the depth according to time series variation in Majuro and Arno Atolls, since atolls can be an appropriate model site to evaluate anthropogenic impacts.

Dating of each depth was conducted by radiocarbon (¹⁴C) measurement for foraminifera using accelerator mass spectrometry (AMS) and Bayesian age-depth Models. X-ray fluorescence (XRF) and Inductively-coupled plasma mass spectrometry (ICP-MS) analyses were conducted to measure the elements in each layer. X-ray absorption fine structure (XAFS) analysis was also done to examine the detailed chemical form. Also microbeam X-ray Computed Tomography (CT) was used to estimate porosity of foraminifera at different depths.

Dating results showed that rapid sedimentation was likely to occur in each island in atoll in the early stage of the formation. The concentration of toxic elements such as Zn, Cu, and Pb increased sharply around 50 cm depth that are considered to be emitted after the original sedimentation of biological remains such as coral gravel and foraminifera. This result correlated with that of total organic carbon (TOC) from the same depth. The concentration of rare earth elements (REEs) also increased around the same depth and negative cerium anomaly became smaller at shallower depth. However, only Mg increased as the depth increased or as the porosity of foraminifera decreased. XRD analysis showed that magnesian calcite has decreased in the upper layer of the sediments, which suggested the selective dissolution of Mg from magnesian calcite near the surface. Bulk and μ -XAFS analyses showed that (i) Zn exists as Zn-rich particles such as ZnO and ZnS, which are considered to be a tire wear and (ii) chemical species of Fe is ferrihydrite. Taking them into consideration, adsorption of heavy metals on ferrihydrite and/or humic substances inhibit release of heavy metals to aqueous phase even though the atoll was made of porous materials, where water easily flows out from the island by rainfall or tide. XAFS analysis also revealed that aluminum is present either as kaolinite or muscovite. These results show contribution of terrigenous material.

The original sediments of atolls is CaCO₃ contained in biological remains without heavy metals. Therefore, atolls can be appropriate model site to examine the chemical form and amount of elements emitted by anthropogenic effects and to assess the impact of modernization as our studies.

Keywords: Foraminifera, X-ray Absorption Fine Structure, anthropogenic effects, atoll, Marshall Island

The regional characterization of volcanic glass shards for the forensic science by trace element analysis

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Because the soil is widely distributed over the ground surface, the soil has been regarded as one of important evidential matters which links a person with a place in the field of the forensic science. We have developed a nationwide forensic soil sediment database for Japan using stream sediments collected at 3024 points across Japan. While we have previously focused on trace heavy element compositions reflecting the geological background of the soil, we newly focused on the volcanic glass contained within the soil as a new indicator to achieve further regional characterization of soils. The volcanic glass is an amorphous pyroclastic material produced by a rapid cooling of a magma. It is expected that the volcanic glass will be good indicator for soils from all over Japan, because Japan is one of the most famous volcanic countries in the world. In addition, because a chemical composition of the volcanic glass could vary in each volcanic mountain, it is believed that the regional characterization of the volcanic glass is achieved by chemical compositional analysis as shown in previous studies using EPMA. In the present study, we introduced a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), a powerful analytical technique for trace element analysis of a minute specimen (< 100 μ m), to analyze the individual volcanic glass shard.

4 samples (Samples A, B, C and D) collected in the *Kanto Region* were used in the present study. Sampling points are shown in Fig. 1. Samples A and B are stream sediments collected from the *Arakawa River* and they were chosen from 3024 stream sediments for the forensic soil sediment database. They are indistinguishable using the heavy element and heavy mineral compositions. Samples C and D are soils. Sample C contains a volcanic ash from *Mt. Asama* while Sample D contains ashes from *Mt. Fuji* and *Mt. Hakone*. After mesh controls, heavy minerals in these samples were removed by heavy liquid separation (SG ~2.4). Residues were embedded into resin and the surface was polished. 50 particles of volcanic glass were identified for each samples using a polarizing microscope and a micro Raman spectrometer for trace element analysis by LA-ICP-MS. Twelve elements were selected to analyze based on the previous study.

Here we examined the characterization using two elements, ⁸⁹Y and ⁹⁰Zr. It has been pointed out that the tephra deposits of the Kanto Region can be separated into two groups bordering the northern latitude of 36 degrees (see Fig.1): the ash from *Mt. Asama* for north side, the ashes from *Mt. Fuji* and *Mt. Hakone* for south side. Figure 2 shows a plot of intensities of ⁸⁹Y and ⁹⁰Zr (normalized to the intensity of ²⁹Si) of volcanic glasses in Samples C and D. As shown in Fig. 2, there are different compositional tendency between the volcanic glasses in Samples C (Group N) and D (Group S). We confirmed the significant difference between these two groups using an analysis of variance. Because the crystallization differentiation of the magma in *Mt. Asama* was promoted compared to those in *Mt. Fuji* and *Mt. Hakone*, it is considered that the volcanic glasses in Sample C were rich in Y and Zr as incompatible elements. We built a linear discriminant to discriminate two groups of volcanic glasses using the normalized intensities of ⁸⁹Y and ⁹⁰Zr of volcanic glasses in Samples C and D and applied it for volcanic glasses in Samples A and B. As the result, 85.4% of the volcanic glasses in Sample A were classified into Group N while 75.9% of those in Sample B were Group S. Therefore, we could successfully distinguish 2 stream sediments having same heavy element and heavy mineral composition using the trace elemental difference of volcanic glass shards measured by LA-ICP-MS.

Keywords: volcanic glass

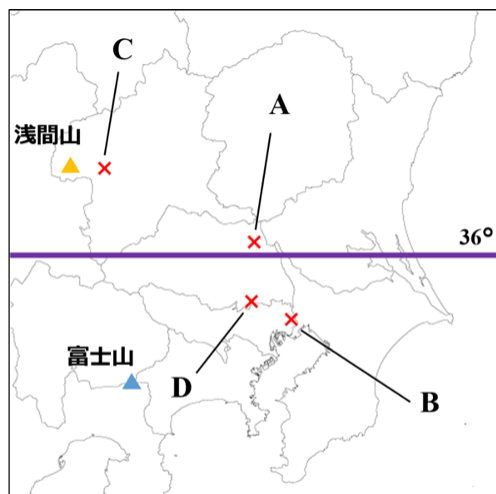


Fig. 1 土砂採取地

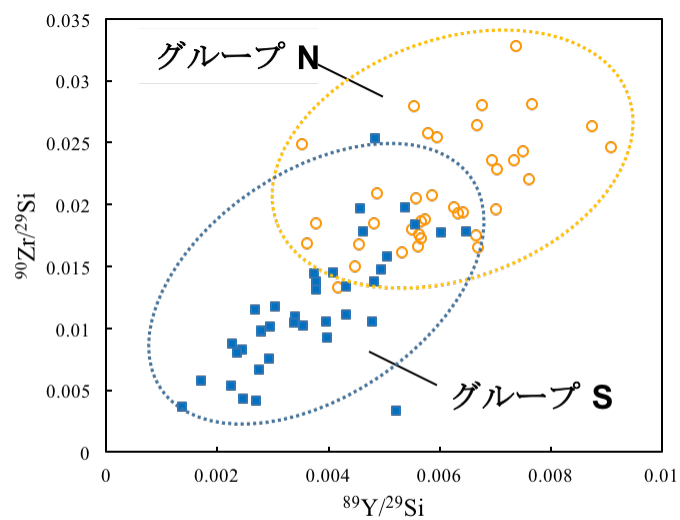


Fig. 2 試料C, Dの比較

Speciation of Cu in seawater by using CLE-CSV with multi-detection windows

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I. Introduction

Copper is an essential micronutrient for all living organisms as it plays an important role in electron transfer in many life-supporting systems, and is present in many enzymes and proteins. On the other hand, at high concentrations in seawater, Cu^{2+} is known to be toxic for marine phytoplankton. Therefore, many phytoplankton and bacterial species have the ability to release Cu-complexing ligands to decrease the concentration of free Cu^{2+} and reduce its toxicity. As a result, at the eutrophic surface waters, most of Cu form complexes with organic ligands. For the Cu speciation study in the ocean, competitive ligand equilibrium/cathodic stripping voltammetry (CLE/CSV) is frequently applied. However, some problems have been proposed on the CLE/CSV methods recently. One problem is concerning on "detection window", which is defined by the conditional stability constant and concentration of the competitive ligands. To measure the conditional stability constants and concentrations of main ligands (usually two ligands) accurately, we have to apply the CLE/CSV method with multi detection windows for the speciation. In this study, we determined the total dissolved Cu concentrations and estimated Cu speciation in seawater by using the CLE/CSV method with multi detection windows in the East China Sea and its surrounding areas.

II. Sampling and methods

Seawater samples were collected using acid-cleaned, Teflon-coated X-type Niskin samplers mounted on conductivity-temperature-depth carousel multi-sampling system (CTD-CMS) onboard R/V Shinsei Maru during KS-15-6 cruise (2015/06/25 - 2015/07/06). The samples were collected in low-density polyethylene bottles through a 0.2 μm -pore size filter. Samples for total Cu analysis were acidified to a pH of less than 1.8 using ultrapure HCl, and stored. Another set of samples, for CLE/CSV analysis, was frozen at -18°C immediately after sampling. The samples were brought back to the laboratory and analyzed using CLE-CSV with salicylaldehyde (SA) as the competing ligand (Campos and van den Berg, 1994).

Samples used for total dissolved Cu were placed under UV radiation for 60 minutes to destroy all organic ligands prior to analysis. Frozen samples for Cu speciation analysis were allowed to thaw for 24 hours at 4°C , and then placed at room temperature for 4-8 hours. 10mL of sample, borate buffer, and a known concentration of Cu were added into two sets of 10 Teflon vials, left for at least 2 hours to allow the natural ligands to equilibrate with the added Cu, and the competing ligand, SA, was then added into the solution. The vials were then left to equilibrate overnight before analysis. 5 μM SA and 1 μM SA were used as the competing ligand for each of the two titrations, respectively.

III. Results and Discussion

Total dissolved Cu concentrations ranged from 0.47 to 4.65 nM. In surface waters with low salinities, higher concentrations of Cu were observed, which can be attributed to the freshwater discharge with high Cu concentrations from Yangtze River. Two classes of ligands were found in the surface waters in this study. The concentration of the stronger ligand, L_1 , ranged from 3.6 nM to 11.2 nM, with log K values of 13 -14.1, whereas for the weaker ligand, L_2 , the concentrations were in the range of 25.6 nM to 47.6 nM, with log K values of 11.7 -12.2. The variation of the strong ligands suggests that these ligands were biologically produced *in situ* by marine microorganisms.

Keywords: ocean, Cu, organic ligand