

## Development of a new method to observe the biomineralization using FISH combined with micro-XAFS

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Ubiquitous presence of microbes in aquatic systems and their inherent ability of biomineralization make them extremely important agents in the geochemical cycling of inorganic elements. However, the detailed mechanisms in environments are largely unknown, because there are few adequate analytical techniques to observe in situ the biogenic reactions. Here, we report a novel technical approach to characterize specific biomineral associated with a target microbe on high spatial resolution. The technique was developed by combining directly in situ phylogenetic analysis, fluorescence in situ hybridization (FISH), with a synchrotron microprobe method, micro X-ray absorption fine structure spectroscopy (micro-XAFS), and was applied to iron deposition by iron-oxidizing bacteria (IOB). In situ visualization of microbes revealed that in natural iron mats, Betaproteobacteria dominated by IOB were dominantly localized within 10 micrometer of the surface. Furthermore, in situ chemical speciation by the synchrotron microprobe suggested that the Fe local structure at the IOB accumulating parts was dominantly composed of short-ordered Fe-O6 linkage, which is not observed in bulk iron mat samples. The present study demonstrated that coupled XAFS-FISH technique could provide direct information on specific biogenic reaction mediated by target microorganism.

Keywords: XAFS, biomineral, FISH, micro-XAFS

## An experimental study on stable isotopic fractionation of rare earth elements (REE) during the adsorption on iron and ma

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Regarding the isotopic fractionation during the adsorption, it has been clarified that heavier isotopes adsorb onto a solid phase for elements existing as cations in a solution, while elements existing as oxyanions in a solution adsorb lighter isotope fractionation onto a solid phase. However, our study on the stable isotope fractionation of Ce during adsorption on ferrihydrite and d-MnO<sub>2</sub> showed that the heavier isotopes remained in the liquid phase, though Ce should be dissolved as free cation under the experimental condition. This study, therefore, exhibits the results of stable isotopic fractionation of rare earth element (REE) during the adsorption experiment to discuss the cause of the isotopic fractionation among REE.

Lanthanum, Ce, Nd, and Sm chloride solutions were respectively added to both synthesized ferrihydrite and d-MnO<sub>2</sub>, with the concentration of REE systematically changed. In all the systems, pH was adjusted to 5.00 ( $\pm 0.05$ ) and shaken for 6 hours before the filtration. Stable isotope ratios in both liquid and solid phases were determined using MC-ICP-MS. REE-Cl<sub>3</sub> solutions used in the adsorption experiment were employed as standard solutions and the isotope ratio of each element was expressed in epsilon notation relative to the average standards, which is shown in the equation as follows:  $\epsilon = (R_{sample}/R_{STD} - 1) \times 10^4$ , where  $R = {}^{139}\text{La}/{}^{138}\text{La}$ ,  ${}^{142}\text{Ce}/{}^{140}\text{Ce}$ ,  ${}^{145}\text{Nd}/{}^{143}\text{Nd}$ , and  ${}^{149}\text{Sm}/{}^{147}\text{Sm}$ , respectively. For solid phase, K-edge EXAFS was measured at BL01B1 in SPring-8 to obtain the information of the coordination environment.

Though accurate determination of La isotope ratio was difficult due to the large difference in the isotopic abundance between  ${}^{138}\text{La}$  and  ${}^{139}\text{La}$ , a broad trend obtained here suggested that the lighter isotope was partitioned into the solid phase. On the other hand, in Nd and Sm systems, results clearly show that lighter isotopes remain in the liquid phase, suggesting that physicochemical factors have been changed between Ce and Nd. According to the EXAFS analysis, split first shell (La-O bond) was observed for La-adsorption system, which suggests that the first coordination sphere is distorted in the system. Such distortion is also expected for Ce-adsorption system. On the other hand, split first shell was not observed for Nd and Sm systems. Thus, it is expected that the coordination environment, which can also cause the difference in their hydration numbers, affect the different isotope fractionations among REE.

Keywords: rare earth element, stable isotopic fractionation, XAFS

## Organic chemistry within submicron regions of Earth and planetary materials using Scanning Transmission X-ray Microscopy

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Scanning Transmission X-ray Microscopy (STXM) is a powerful analytical tool for detecting and quantifying organic functional groups within submicron regions of polymer samples at high spatial resolution less than 30 nm. In a STXM, micron-sized samples are raster-scanned relative to a focused X-ray obtained by a zone plate, and the transmitted photon flux through the sample is detected to acquire an X-ray transmission image. STXM is located at beam line 5.3.2.2 (Polymer STXM), Advanced Light Source, Lawrence Berkeley National Laboratory (Kilcoyne et al. 2003). The beam line employs a bending magnet providing a photon range spanning ~250 to 700 eV ( $10^7$  photons/s) that includes carbon-, nitrogen-, and oxygen- X-ray Absorption Near Edge Structure (XANES) regions. Samples are thin-sectioned (~100 nm of thickness) so that a soft x-ray is well transmitted to the sample. The acquired C-, N-, and O-XANES spectra and STXM images provide a quantitative assessment of the types of the organic functionality present (Cody et al. 2008).

The advanced performance of STXM is that positioning of zone plate with continuously changing energy and scanning of sample are controlled by laser interferometer (Kilcoyne et al. 2003). This eliminates energy-to-energy image position errors from vibrational or other environmental noise and stabilizes microscope. The diffraction limited, high spatial resolution less is achieved by a Fresnel zone plate. Ordering selection aperture (OSA), which is placed between zone plate and sample, allows only the first diffraction order to pass, in order to increase the signal-to-noise ratio. The transmitted photons are detected by photomultiplier systems. A X-ray absorption spectrum is obtained through converting the transmitted X-ray to optical density (OD) as expressed by Lambert Beers' Law;  $OD = -\ln(I/I_0)$ , where  $I$  is the X-ray intensity transmitted from the sample and  $I_0$  is that recorded without the sample.

These days, micro-XANES using STXM has been increasingly applied to geo- and cosmochemistry, as well as polymer material science, environmental chemistry and biology. As one of the well-known achievements, a STXM has been applied in order to obtain the organic functional group distributions on organic solids from comet 81P/Wild 2 dust particles collected by NASA's Stardust comet sample return mission (Sandford et al. 2006; Cody et al. 2008). In biogeochemistry researches using STXM, C and Fe STXM mappings of particulate organic carbon in hydrothermal plume at the mid-ocean ridge (Toner et al. 2009) and structure analyses of young poorly-crystalline graphite in the older than 3.8-Gyr-old banded iron formation (Papineau et al. 2011) have been reported. Furthermore, combination use of focused ion beam (FIB) extraction, STXM, and isotope microscope has enabled the comprehensive investigation of molecular, isotopic, and structural compositions within a very small region of particular interest from sample (Yabuta et al. 2012, JPGU abstract). Also, 3-D chemical imaging using angle-scan nanotomography in a STXM has been developed (Hitchcock et al. 2008). Thus, the requirement for STXM, the highly sensitive technique without preprocessing of samples, e.g., extraction, is becoming greater in geo- and cosmochemistry, regarding the advantages for understanding the chemical heterogeneity and diversity of organic/carbonaceous compounds in nature.

### References:

- Kilcoyne, A. L. D. et al. (2003) *J. Synchrotron. Rad.* 10, 125-136.
- Cody, G. D. (2008) *Meteor. Planet. Sci.* 43, 353-365.
- Sandford, S. A. (2006) *Science* 314, 1720-1724.
- Toner et al. (2009) *Nature Geoscience* 2, 197-201.
- Papineau et al. (2011) *Nature Geoscience* 4, 376-379.
- Yabuta et al. (2012) *JPGU2012*, Abstract 03056.
- Hitchcock et al. (2008) *Appl. Phys. A.* 92, 447-452.

Keywords: Scanning Transmission X-ray Microscopy, X-ray Absorption Near Edge Structure, soft X-ray, organic matter, Advanced Light Source, high spatial resolution

## Depth profile analysis of light elements using J-PARC MUSE

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Recently, the intense pulsed muon source, J-PARC/MUSE has been constructed (Miyake et al. 2009), providing the potential of the 3-D elemental map from the near surface to the interior of the planetary materials.

Here, we report on the depth profile analysis of the four layered sample that consists of SiO<sub>2</sub>, C (graphite), BN (boron nitride) and SiO<sub>2</sub> changing the Muon's momentum from 37.5MeV to 57.5MeV/c. Muonic X-ray from B, C, N and O are successfully detected through SiO<sub>2</sub> plate of which thickness is about 1 mm.

Keywords: Muon, J-PARC, Characteristic X-ray, Non-destructive measurement, depth profile analysis

## Earth surface process study using in situ produced cosmogenic nuclides

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The in-situ terrestrial cosmogenic nuclides (TCN) are produced from the interactions with cosmic ray bombardments with terrestrial rocks. The TCN exposure history measurement method is undergoing major developments in the Earth Science field. This method can be applied to various geological problems including tectonics, coastal environments changes and climate changes. The method is employed in the geological studies of which time scale ranges from  $10^2$  to  $10^7$  years using currently established method ( $^3\text{He}$ ,  $^{10}\text{Be}$ ,  $^{21}\text{Ne}$ ,  $^{26}\text{Al}$ , and  $^{36}\text{Cl}$ ). Combining measurements of nuclides which have different half-lives is particularly useful to determine the history of the surface process and hence quartz grains have been widely used for this types of research since they contain both in-situ  $^{10}\text{Be}$  and  $^{26}\text{Al}$ . In this paper we present some examples using TCN to reveal past histories of earth surface processes.

Keywords: cosmogenic nuclides, geomorphology, glacier, erosion, accelerator mass spectrometry, dating

## Chemopaleontology: 3D images and trace element and isotope analyses of fossils

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Earth is a unique planet, which is filled with a large variety and number of life. Recent active planetary expeditions and telescopic observations of extrasolar planets allow us to expect possibility of life in other planets. But, presence of metazoan distinguishes biosphere of the earth from others. Conventional paleontology is based on morphological comparison of fossils with modern biota. The methods are very useful to investigate ancient animals and plants with the same body forms and tissues of modern biota, and allow to successfully decoding biological evolution based on some fossils with well-preserved tissues since the Cambrian (e.g. Shu, 2008 Gondwana Research). However, it is well known that body forms of *trial* animals at the dawn of the Metazoa are very strange and are often out of our insight even for the Cambrian fauna (e.g. Gould, 1989) as well as for many biota in the Ediacaran (e.g. Huldtgren et al., 2011, Science; Schiffbauer et al., 2011, GSA meeting). We need another tool to investigate fossils: 3D observations and chemical compositions of microfossils.

Recent X-ray micro-CT analyses of the microfossils provide new methods to observe the internal structures (e.g. Donoghue et al., 2006). Compared with microscopic and SEM observations of cutting planes of the microfossils, this technique has two advantages of *nondestructive* analyses on *any* cross-sections of internal structures. We started to observe three-dimensional structures of the Early Cambrian microfossils including embryo and larvae stage fossils and SSF, and Chengjiang fossils including an echinoderm, a fish, arthropods with/without eggs, a mollusk, and a brachiopod, South China with a Synchrotron X-ray micro-CT at SPring-8. The observations of microfossils reveal the internal structures of animal embryo fossils, which are partly covered with envelopes and contain, often shriveled, globules, larvae of cnidarians, which comprise an umbrella-like top and relatively small column at bottom, often with pentaradial symmetry, and a polyp or a sea anemone. Although preliminary, the three dimensional observation of an echinoderm, which possesses gill-like structures, shows a relict of an internal cavity. The synchrotron micro-CT technique provides convenient and effective observations of internal structures for microfossils with complicated, small internal structures and even for completely compressed fossils. In addition, the reconstructed 3D images are very helpful to determine the most effective crosscutting planes for geochemical analyses.

Recent drastic progress of paleontology of the earliest metazoan fossils provides many candidates for arthropods with their eggs, chordates with notochords, the oldest fishes with spines and gills, and putative animal embryos, calcite, aragonite and Ca-phosphate biomineralizing fauna, earliest animals with sexuality, quite high trophic levels and others. However, only morphological comparison with the modern equivalents is still insufficient to provide the evidence for the above. Another tools to obtain the evidence for evolution of biological functions are required. We would like to propose some geochemical possibilities such as Ca, Fe, Mo, N, C and Cu isotopes, and trace element accumulation in specific tissues.

Keywords: chemopaleontology, micro-CT, 3D images, trace element distribution, isotope composition

## High Resolution Imaging Mass Spectrometry using Laser Ablation-ICPMS Technique : multifaced tool in Earth and Bioscienc

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As a result of its continuous development, LA-ICP-MS provides ever more precise elemental and isotopic data. Enhancements in elemental sensitivity achieved for ICP-MS, together with newly developed dual or triplicated-ion detection system (combination of multiplier ion counting and a charge integration-Faraday collectors), provides flexible multi-element determinations for both the trace- and major-elements in the samples. Moreover, fast-mass scanning protocol achieved by the ion deflector devices, equipped on a magnetic sector, have led to successive improvements in the precision of isotope ratio measurements. The ICP-MS technique is likely to become a method of choice for many geochemists because it is much more versatile and user friendly and efficient method for elemental and isotopic analyses of trace elements.

Many geologists and geochemists are increasingly interested in processes in rocks that operate at the microscopic scale such as zoning or metamorphic recrystallizations. These processes have implications for the larger scale behavior of the Earth and new technique for chemical and isotopic measurements at the  $\mu\text{m}$ -scale need to be developed. The combination of laser ablation sample introduction technique and ICP-mass spectrometry (LA-ICPMS) has now become a fast and accurate method of in-situ trace-elements and isotopic analysis for solid geochemical and biochemical samples [1]. Laser ablation utilizing UV-light ? with a frequency-quintupled (213 nm) Nd:YAG laser, Ti:S femtosecond lasers equipped with THG devices (260 nm) or an ArF Excimer laser (193 nm) ? offers reduced elemental fractionation during ablation and better spatial resolution with a small ablation pit size, and is now the most widely used system for LA-ICP-MS. The progresses in the LA-ICPMS technique are well demonstrated in the precision and accuracy of the U-Pb age data for zircons. We are now trying to measure the U-Pb age data for zircons from smaller ablation pit sizes (2-5  $\mu\text{m}$ ). For zircons with U contents of higher than 100  $\mu\text{g/g}$ , we can measure U-Pb ages from zircons with the ablation pit size of smaller than 5  $\mu\text{m}$ . Moreover, 2-dimensional mapping (imaging mass spectrometry) for trace-elements can be made with a ablation pit size of 2  $\mu\text{m}$ . The resulting analytical-spatial resolution achieved in this study was better than 5 $\mu\text{m}$ , and this is almost comparable to the conventional ion microprobe technique. It should be noted that the spatial resolution achieved by the LA-ICPMS technique can be improved by the new generation laser optics. In fact, ablation pit size of smaller than 1 $\mu\text{m}$  could be achieved by the near field optics. Moreover, it should be noted that the laser ablation was made under the atmospheric pressure. This suggests that in-situ elemental and isotopic analyses can be made on a wet samples including cell or fluid samples (biochemical samples). With high-sensitivity ICP-MS instrument with new generation laser ablation technique, the LA-ICPMS technique has immediate potential as a reconnaissance method and given increasing improvement in instrumentation will in the future produce data comparable or even better quality to ion probes of nano-SIMS type.

### References

[1] D. Gunther and B. Hattendorf, Trends in Anal. Chem., 24, 255-265 (2005).

Keywords: Geochemistry, Cosmochemistry, Imaging mass spectrometry, Isotope chronology, Laser ablation technique, Plasma mass spectrometry

## U-Pb age determination for Quaternary zircons using a laser ablation-ICP-mass spectrometry

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Age data for the Quaternary zircons are very important to understand the time sequence of many interesting and scientifically valuable events in the past, such as origin and evolution of the life, climate changes as well as geological events including volcanic eruption and earthquakes. Among the various chronometers, fission-track (FT) and K-Ar (Ar/Ar) method of dating have been widely used to define the age of young rocks or minerals. Despite the obvious success in obtaining reliable age data, because of very long half-life of the spontaneous fission, the number of tracks found in minerals is not large enough to define the precise age data for the young samples. For the age data obtained by the K-Ar (Ar/Ar) systems, better time resolution (i.e., precision and reliability) could be achieved from single grain of K-bearing minerals such as biotite or sanidine. However, system closure for the K-Ar isotope systems could be lost through weathering of the biotite grains. Moreover, the sanidine grains are not ubiquitously presented in the rocks, and the practical utility of the sanidine K-Ar (Ar/Ar) dating method is severely restricted. Zircon geochronology is one of the principal dating tools available to geologists and its use has revolutionized our understanding of the evolution of continental crust or unveiled Archean history. Especially, the U-Pb chronology on zircons has been widely used to understand the timing of the geological events with high time resolution. This is because, (a) age data were intrinsically very accurate because the decay constants for both the <sup>235</sup>U and <sup>238</sup>U are well calibrated and established, (b) system closure can be evaluated by comparing the <sup>238</sup>U-<sup>206</sup>Pb and <sup>235</sup>U-<sup>207</sup>Pb ages (i.e., level of concordance) and (c) zircon contains high concentration U with almost very low Pb. In order to take full advantage of the zircon U-Pb chronology, we have developed a new analytical protocol to measure U-Pb age data for Quaternary zircons using a laser ablation-ICP-mass spectrometry.

In order to derive the precise and reliable U-Pb age data from young zircons, both the high elemental sensitivity of the ICPMS instrument and high transportation efficiency of the laser-induced sample aerosols from sample to the ICP ion source are essential. Moreover, evaluation and correction of the background signal especially on <sup>207</sup>Pb is still key issue. We have applied the ABLATION BLANK protocol to obtain the true background signal of <sup>207</sup>Pb using laser ablation of Pb-free samples. The resulting signal intensities of <sup>206</sup>Pb and <sup>207</sup>Pb obtained with the laser ablation (ablation blank) were systematically higher than the signal intensities obtained without laser ablation (gas blank). Moreover, signal intensities of <sup>206</sup>Pb and <sup>207</sup>Pb obtained by laser ablation of synthesized zircons were higher than those obtained with the ablation blank for high-purity Si wafer. This suggests that the release of the residual sample aerosols can be enhanced through the laser-induced shockwave on the zircon materials, and therefore, ablation blank must be measured on identical sample matrix or minerals. For the U-Pb age determinations for young zircons, isotope ratio measurements with high dynamic range over 5 orders of magnitude is highly desired. To overcome this, we have employed the suppressor technique on our ion counting devices, which enables us to measure isotope ratio with over 9 orders of magnitude. Using this technique, we can measure signal intensity of very small <sup>207</sup>Pb signals together with very high intensity <sup>238</sup>U signal from the optimum laser ablation conditions. We will demonstrate the resulting U-Pb age for young zircons of various ages ranging from 0.6 to over 2000 Ma. The U-Pb age data obtained in this study demonstrate clearly that the LA-ICPMS technique has a potential to become a significant tool for geological study using Quaternary zircons.

Keywords: ICP-MS, laser ablation, U-Pb, dating, zircon, Quaternary



## Quantifying nitrate dynamics in hydrosphere using the natural stable isotopes as tracers

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In most studies that have been conducted to date, the gross uptake rate of nitrate has been estimated by incubation experiments using <sup>15</sup>N tracer techniques. In this conventional approach, <sup>15</sup>N labeled NO<sub>3</sub><sup>-</sup> is added into bottles or mesocosms that simulate in situ conditions, which leads to the production of particulate organic-<sup>15</sup>N (PO<sup>15</sup>N) through assimilation over a known incubation period of several hours to several days. This PO<sup>15</sup>N is then gathered and quantified by mass spectrometry. However, these experimental procedures are generally costly, complicated, and time consuming, especially those that employ mesocosms. Furthermore, the <sup>15</sup>N tracer method has several problems with determining accurate nitrate uptake rates. For example, the usual <sup>15</sup>N tracer method does not include assimilated nitrogen released to dissolved organic-<sup>15</sup>N (DO<sup>15</sup>N) during incubation within the estimated uptake rates, which results in the rates being underestimated. Additionally, incubation itself could also result in the production of artifacts by changing the physical/chemical environments. Finally, it is difficult to simulate nitrate uptake by periphyton or microbes on the lake floor through typical incubation in bottles.

In this study, we estimated the gross nitrate uptake rate in several lakes in Japan using average *Delta*<sup>17</sup>O values of NO<sub>3</sub><sup>-</sup> (*Delta*<sup>17</sup>O method) dissolved in each studied lake. Besides, we compared the results with those estimated using the traditional <sup>15</sup>N tracer method.

Based on the observation, we concluded that the *Delta*<sup>17</sup>O method overcomes the aforementioned problems inherent in the conventional <sup>15</sup>N-labelled tracer methods. Accordingly, the *Delta*<sup>17</sup>O method can be an alternative to standard techniques for the determination of accurate gross nitrate uptake rates in hydrosphere that contain detectable quantities of atmospheric nitrate within the total nitrate.

Keywords: nitrate, atmospheric deposition, assimilation, nitrification, nitrogen cycle, triple oxygen isotopes

## Ultrahigh-sensitive simultaneous determination of halogens and noble gases reveals the origin of water in the mantle

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Noble gas isotope ratios in various geochemical components in the Earth are significantly different, making them useful tracers to constrain origin of volatiles in the mantle. The development of noble gas mass spectrometry during the last decade has enabled us to detect less than 10000 noble gas atoms (e.g., [1]). Noble gases are generally concentrated in fluid/melt inclusions in mantle-derived minerals resulting from their high incompatibility and volatility. Noble gases in the inclusions can be extracted distinctively from mineral-hosted component by use of in vacuo crushing or laser microprobe. The great advantages of the latter are that it makes it possible to analyze an individual inclusion or small clusters of inclusions having the same origin and that it can be applied for the inclusion samples on which preceding non-destructive analyses, such as microthermometry and micro spectroscopy have been performed. Although this method remains quite challenging due to extremely low noble gas concentrations in a fluid inclusion, we have successfully applied the laser-microprobe to noble gas analysis of melt/mineral inclusions in olivine phenocrysts in kimberlites.

An extension of Ar-Ar and I-Xe dating methods enables us to simultaneously determine trace amounts of noble gases, halogens, K, Ca, Ba and U by use of ultrahigh-sensitive noble gas mass spectrometry on neutron-irradiated samples. This method has several advantages: (i) detection limits for halogens are two or three orders of magnitude lower than those of other conventional analytical methods, and (ii) several components of different origin can be distinguished based on their relationships with specific noble gas isotopes such as mantle-derived <sup>3</sup>He and by using various noble gas extraction methods.

By using this method, we analyzed halogens and noble gases in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan in which relicts of slab-derived water are contained as hydrous mineral/fluid inclusions trapped at a depth ranging from 40 to 100 km [2, 3]. The striking similarities of the observed noble gas and halogen compositions with marine pore fluids challenge a popular concept, in which the water flux into the mantle wedge is only by hydrous minerals in altered oceanic crust and sediment (e.g., [4]). This is the first evidence of subduction of porefluid-derived water into the mantle wedge.

On the other hand, MORB-like <sup>3</sup>He/<sup>4</sup>He and halogen ratios of olivines in lavas from the northern Izu-Ogasawara arc and a peridotite from the Horoman alpine-type peridotite complex in northern Japan indicate insignificant contribution to the mantle wedge of radiogenic <sup>4</sup>He and porefluid-like halogens both observed in the subduction fluids in the Sanbagawa samples. This implies a relatively small amount of the pore water subduction fluids would be released from the Izu slab at a sub-arc depth resulting in further subduction to great depths in the mantle, resulting in the seawater-like heavy noble gas composition of the convecting mantle [5].

These results demonstrate that simultaneous determination of noble gases and halogens in mantle-derived rocks yields important information about the origin of slab-derived water-rich fluids and recycling of halogens and noble gases in the mantle.

[1] Sumino et al. (2001) *J. Mass Spectrom. Soc. Jpn.* 49, 61-68. [2] Sumino et al. (2010) *Earth Planet. Sci. Lett.* 294, 163-172. [3] Sumino et al. (2011) *Mineral. Mag.* 75, 1963. [4] Schmidt & Poli (1998) *Earth Planet. Sci. Lett.* 163, 361-379. [5] Holland & Ballentine (2006) *Nature* 441, 186-191.

Keywords: noble gas, halogen, mass spectrometry, mantle, water, subduction

## Development of pulse counting system for TOF-MS with high-speed digitizer

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Secondary ion mass spectrometry (SIMS) is useful to determine elemental and isotopically abundances of various materials in a microscopic region. Multi-isotopes can be simultaneously detected by using time-of-flight mass spectrometry (TOF-MS), which is one of the features for TOF-MS. A mass resolving power is proportional to its flight distance. We are developing a spattered neutral mass spectrometer (Laser Ionization MAss nanoscope: LIMAS) [1]. LIMAS is consisted of focused Ga ion beam in order to examine a nano-scale region, femto-second laser which ionized spattered neutral particles, and multi-turn TOF-MS (MULTUM-II, [2]). The detection system of TOF-MS is as follows. Ions of each isotope (or compound) pass through the MULTUM-II. The ions are separated from each other during the flight, which depend on their  $m/z$  then they are detected by ion detection system with multi-channel plate (MCP). The ions are introduced as a packet of which time scale is several nano-seconds (ns) during the ion detection. High-speed digitizer with an analog bandwidths of  $>GHz$  distinguish a pulse from another. Extracted ions by single spatter are about ten thousand less than those by continues beam because pulse width of the primary beam is 300 ns. The low extraction rate leads directly to a low signal output. A pulse counting method in common use can dramatically increase a signal-to-noise ratio and deal with signal intensity quantitatively.

The detection system of LIMAS is composed of two steps MCP and preamp to amplifier the introduced electrical signal. A pulse width from the preamp is 6 ns and the pulse energy is distributed to  $58 \pm 48$  mV (3sigma). Because the noise level is  $-6 \pm 7$  mV (3sigma), the pulse can be distinguished from noise. The output signal is recorded by using NI PXIe-5185 (hereafter 5185) digitizer of  $1.25 \times 10^{10}$  samples per second (S/s) and 8-bit vertical resolution. Two 5185s record the same signal which is split by distributor. One is for recording the analog output with wide input range (0.8 V full scale), another is for pulse counting with higher resolution (0.2 V full scale). A timing synchronization of each component is adjusted by using delay generator (BNC model-575).

The wave forms are recorded for several micro second by 1 kHz post-trigger, which are described as arrays in 8-bit. In pulse counting, the recorded array is simultaneously transformed to 1/0 one. An algorithm of the deconvolution is as follows. When a center value of three arbitrary consecutive points is lower than the other two ones and lower than a threshold which is previously determined from pulse height distribution, the value of the center index is 1. The other cases are 0. A time resolution of this method depends on the sampling rate of 5185 (currently 3 GS/s) and responsively of the MCP (0.5 ns). Consequently, it is about 2 ns. In case of constant recurrence timing the system acquires ions from one to  $5 \times 10^8$  cps. Since there is statistical fluctuation for incident ions, the ions are detected up to  $5 \times 10^7$  cps for practical purpose. The system for a single triggered event cannot determine 1.7 ions or more due to counting loss. Another 5185 is used for digitizing the large analog signal.

[1] Yurimoto et al. (2011) *Oyo Butsuri* (Japanese), 80, 979. [2] Okumura et al. (2005) *Eur. J. Mass Spectrom.*, 11, 261.

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