Japan Geoscience Union Meeting 2012
(May 20-25 2012 at Makuhari, Chiba, Japan)

MTT37-01 Room:101B Time:May 21 09:00-09:15

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

MITSUNOBU, Satoshi[1*], SHIRAISHI, Fumito[2]

[1]Institute for Environmental Science, University of Shizuoka, [2]Graduate School of Science, Hiroshima University

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

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MTT37-02 Room:101B Time:May 21 09:15-09:30

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

NAKADA, Ryoichi[1*], Yoshio Takahashi[1], Masaharu Tanimizu[2]

[1]Graduate School of Science, Hiroshima University, [2]Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Regarding the isotopic fractionation during the adsorption, it has been clarified that heavier isotopes adsorbs 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_2 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_2, with the concentration of REE systematically changed. In all the systems, pH was adjusted to 5.00 (±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_3 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: e = (R_{sample}/R_{STD} - 1) x 10^4, where R = $^{139}La/^{138}La$, $^{142}Ce/^{140}Ce$, $^{145}Nd/^{143}Nd$, and $^{149}Sm/^{147}Sm$, 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}La and ^{139}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

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MTT37-03 Room:101B Time:May 21 09:30-09:45

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

YABUTA, Hikaru[1]*

[1]Department of Earth and Space Science, Osaka University

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 Fresznel 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.

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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

MTT37-04 Room:101B Time:May 21 09:45-10:00

Depth profile analysis of light elements using J-PARC MUSE

TERADA, Kentaro[1*], Takahito Osawa[2], TACHIBANA, Shogo[3], UESUGI, Masayuki[4], Kazuhiko Ninomiya[2], Yasuhiro Miyake[5], Kenya Kubo[6], Naritoshi Kawamura[5], Wataru Higemoto[2], TSUCHIYAMA, Akira[7], EBIHARA, Mitsuru[8]

[1]Osaka University, [2]Japan Atomic Energy Agency, [3]University of Tokyo, [4]Japan Aerospace Exploration Agency, [5]High Energy Accelerator Research Organization, [6]International Christian University, [7]Kyoto University, [8]Tokyo Metropolitan University

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_2, C (graphite), BN (boron nitride) and SiO_2 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_2 plate of which thickness is about 1 mm.

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

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MTT37-05 Room:101B Time:May 21 10:00-10:15

Earth surface process study using in situ produced cosmogenic nuclides

YOKOYAMA, Yusuke[1]*, NAKAMURA, Atsunori[1], SHIROYA, Kazuyo[1], YAMANE, Masako[1], MIYAIRI, Yosuke[1]

[1] Yusuke Yokoyama

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 10ˆ2 to 10ˆ7 years using currently established method (3He, 10Be, 21Ne, 26Al, and 36Cl). 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 10Be and 26Al. 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

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MTT37-06 Room:101B Time:May 21 10:15-10:30

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

KOMIYA, Tsuyoshi[1*]

[1]Dept. Earth Science & Astronomy, Komaba, The University of Tokyo

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

MTT37-07 Room:101B Time:May 21 10:45-11:00

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

HIRATA, Takafumi[1]*, Hideki Iwano[2], Kenshi Maki[1], Takaomi D. Yokoyama[1], Toshihiro Suzuki[3], Yoshiaki Kon[4]

[1]Kyoto University, [2]Kyoto Fission Track Co Ltd., [3]JAMSTEC, [4]Geological Survey of Japan

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 um-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 um). For zircons with U contents of higher than 100 ug/g, we can measure U-Pb ages from zircons with the ablation pit size of smaller than 5 um. Moreover, 2-dimensional mapping (imaging mass spectrometry) for trace-elements can be made with a ablation pit size of 2 um. The resulting analytical-spatial resolution achieved in this study was better than 5um, 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 1um 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.

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

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MTT37-08 Room:101B Time:May 21 11:00-11:18

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

IWANO, Hideki[1]*, HIRATA, Takafumi[2]

[1]Kyoto Fission-Track Co., [2]Graduate School of Science, Kyoto University

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 revolutionalized 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 235U and 238U are well calibrated and established, (b) system closure can be evaluated by comparing the 238U-206Pb and 235U-207Pb 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 207Pb is still key issue. We have applied the ABLATION BLANK protocol to obtain the true background signal of 207Pb using laser ablation of Pb-free samples. The resulting signal intensities of 206Pb and 207Pb obtained with the laser ablation (ablation blank) were systematically higher than the signal intensities obtained without laser ablation (gas blank). Moreover, signal intensities of 206Pb and 207Pb 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 207Pb signals together with very high intensity 238U 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

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MTT37-09 Room:101B Time:May 21 11:24-11:39

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

TSUNOGAI, Urumu[1*], Yukie Tadenuma[1], OHYAMA, Takuya[1], KOMATSU, Daisuke[1], NAKAGAWA, Fumiko[1], UMEDA, Makoto[2], Atsushi Tanaka[3]

[1]Earth and Planetary System Science, Faculty of Science, Hokkaido University, [2]Graduate School of Engineering, Tohoku University, [3]National Institute for Environmental Studies

In most studies that have been conducted to date, the gross uptake rate of nitrate has been estimated by incubation experiments using ^{15}N tracer techniques. In this conventional approach, ^{15}N labeled NO_3^- is added into bottles or mesocosms that simulate in situ conditions, which leads to the production of particulate organic-^{15}N (PO^{15}N) through assimilation over a known incubation period of several hours to several days. This PO^{15}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 ^{15}N tracer method has several problems with determining accurate nitrate uptake rates. For example, the usual ^{15}N tracer method does not include assimilated nitrogen released to dissolved organic-^{15}N (DO^{15}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*^{17}O values of NO_3^- (*Delta*^{17}O method) dissolved in each studied lake. Besides, we compared the results with those estimated using the traditional ^{15}N tracer method.

Based on the observation, we concluded that the *Delta*^{17}O method overcomes the aforementioned problems inherent in the conventional ^{15}N-labelled tracer methods. Accordingly, the *Delta*^{17}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

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MTT37-10 Room:101B Time:May 21 11:39-11:54

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

SUMINO, Hirochika[1]*, KOBAYASHI, Masahiro[1], SHIMIZU, Aya[2], NAGAO, Keisuke[1], BURGESS, RAY[3], BALLENTINE, Chris J.[3]

[1]GCRC, University of Tokyo, [2]Tokyo Metropolitan Industrial Technology Research Institute, [3]SEAES, University of Manchester, UK

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 ^{3}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 ^{3}He/^{4} 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 ^{4} 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.

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

MTT37-11 Room:101B Time:May 21 11:54-12:09

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

BAJO, Ken-ichi[1*], Fujioka Osamu[2], Ebata Shingo[1], Ishihara Morio[3], Uchino Kiichiro[4], Yurimoto Hisayoshi[1]

[1]Hokkaido University, [2]National Instruments Japan Corporation, [3]Osaka University, [4]Kyushu University

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 +/- 48 mV (3sigma). Because the noise level is -6 +/- 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 x 10^{10} samples per second (S/s) and 8-bit vertical resolution. Two 5185s record the same signal which is split by distributer. 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 algorism 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 x 10^8 cps. Since there is statistical fluctuation for incident ions, the ions are detected up to 5 x 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.

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Keywords: NI PXIe-5185, High-speed digitizer, Pulse counting, TOF-MS

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MTT37-P01 Room:Convention Hall Time:May 21 17:15-18:30

Applying dual isotopic fractionation of methane as sensitive tracers for microbial oxidation

KOMATSU, Daisuke[1*], Shintaro Sato[1], NAKAGAWA, Fumiko[1], TSUNOGAI, Urumu[1], Atsushi Tanaka[2]

[1]Faculty of Science, Hokkaido University, [2]National Institute for Environmental Studies

The dual (carbon and hydrogen) isotopic compositions in methane have provided important information regarding their sources, transportations, and reactions in the environments. Recently, a highly sensitive continuous-flow IRMS (CF-IRMS) method was developed to analyze the carbon and hydrogen isotope compositions of methane in atmosphere and environment with enriched methane. They have reduced the required sample size drastically. However, they have room for improvement. Applying methods to various environmental samples has been difficult, especially for those with depleted levels of methane.

We developed a rapid, sensitive, and automated analytical system to determine carbon and hydrogen isotope compositions of methane in nmol quantities in natural waters by using continuous-flow isotope ratio mass spectrometry (CF-IRMS).

The analytical system consisted of a purging line to extract dissolved methane in waters, a gas chromatograph for further purification of methane, a thermal furnace to decompose methane to molecular hydrogen, and a CF-IRMS system. In addition, we used pneumatic valves and pneumatic actuators in the system so that we could operate the system automatically based on timing software on a personal computer. The analytical precision was better than 4 per mil for hydrogen isotopic analysis with more than 2 nmol methane injections for a single measurement.

We determined the dual isotopic compositions of methane in Lake Towada in September in 2011. We found distinct carbon and hydrogen isotopic fractionation of methane during microbial oxidation in hydrothermal plume.

Keywords: methane, hydrothermal plume, hydrogen isotope fractionation, carbon isotope fractionation, dual isotopic compositions

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Laser Ablation ICP-MS for analyzing trace elements in biological carbonates at AORI, The University of Tokyo

KAWAKUBO, Yuta[1*], YOKOYAMA, Yusuke[1], NOT, Christelle[1], MIYAIRI, Yosuke[1], INOUE, Mayuri[1], KAWAHATA, hodaka[1]

[1]Atmosphere and Oceanic Research Institute, University of Tokyo

Geochemical features in biological carbonates such as foraminifera, coral, shell and otolith have been widely used as a useful recorder of the past oceanic conditions. During their growth, biological calcium carbonates composed of their skeleton may incorporate trace elements from their ambient seawater. The amount of the trace elements contained in the skeleton is depending on the seawater environments when they grown, hence trace elements in their skeleton preserve historical records of the physical and/or chemical oceanographic information. For example, corals, which live in the low latitude, has the potential for recording the seasonal variations of the oceanic conditions since they have annual bandings and the rapid rates of growth. Strontium in coral skeleton is currently used widely as a proxy of sea surface temperature and uranium is used for ocean redox condition.

In these days, Laser Ablation Inductively Coupled Mas Spectrometry (LA-ICP-MS) has been introduced in the marine environmental studies, which is the powerful technique for analyzing small samples almost undisruptive way. Compared with the conventional solution-based method, it enables us to measure multi-elements in high spatial resolution with little sample preparation. These advantages make LA-ICP-MS a cost effective and attractive analytical tool for analyzing trace elements in biological carbonates.

At present we are trying to set up and develop the method to measure the trace elements in biological carbonates using LA-HR-SF-ICP-MS system at the Atmosphere and Ocean Research Institute, The University of Tokyo. We will present the preliminary results we have obtained so far and the future prospects of our studies.

Keywords: Biological carbonate, Laser ablation Inductively Coupled Plasma Mass Spectrometry, Paleoclimate

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Development of NanoAMS

SANO, Yuji[1]*, HIRATA, Takafumi[2], KOMIYA, Tsuyoshi[3]

[1]Atmosphere and Ocean Research Institute, University of Tokyo, [2]Graduate School of Science, Kyoto University, [3]Graduate School of Arts and Sciences, University of Tokyo

Recent years, we are expanding our knowledge to deep sea, deep earth, and space. Based on the samples collected from the earth and space, it is possible to study early geological history and very deep earth. However important geochemical information is located very small region in rock and mineral samples. In addition it is necessary to develop the nano-scale analytical instrument to study element distribution in a single biological cell. Thus the development of Nano-scale Accelerator Mass Spectrometry (NanoAMS) is highly desirable.

(1) Feature of NanoAMS
We aim at the development of the machine to detect trace elements and isotopic ratios of samples at 50 nano-meter scale. It may be possible to extract an important information from 1 micron scale melt inclusion in minerals, interfacial mass between minerals, inside of biological cell, aerosol, tiny suspending particle in sea water, fossil of cellular membrane, and cosmic dust.

(2) Component of NanoAMS
We develop two types of ion source. First one is the secondary ion source of NanoSIMS (Cameca) with 30-50 nano-meter resolution. Second one is ICP ion source with a laser ablation system with 60 nano-meter resolution. Both ion sources are connected with AMS (NEC, 6MeV). It is necessary to develop the interface between the nano-ion source and AMS. Post ionization system is also invented.

Keywords: AMS, NanoSIMS, Isotopes, Trace elements

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Determination of picomolar Fe(II) in seawater using an automated in-situ flow analyzer

OBATA, Hajime[1*], WAKIYAMA, Shin[1], MASE, Akira[1], GAMO, Toshitaka[1], MARUO, Masahiro[2], OKAMURA, Kei[3], KIMOTO, Hideshi[4]

[1]AORI Univ. Tokyo, [2]Univ. Shiga Prefecture, [3]Kochi Univ., [4]Kimoto Electronics

In the open ocean, iron is widely recognized as an essential element for the phytoplankton growth. Since the bioavailability of iron depends on its chemical form in seawater, many of iron studies in the ocean now focus on the chemical speciation of iron. Regardless of increasing interests in iron speciation in the ocean, marine biogeochemical process of Fe(II) is not fully investigated. In oxic conditions, Fe(II) is rapidly oxidized to Fe(III), which makes it difficult for us to determine Fe(II) in seawaters. To prevent the Fe(II) oxidation after sampling, we developed an in-situ flow analytical method of Fe(II) in seawater.

The in-situ analyzer was composed of an acrylic, oil- and water-filled, pressure-compensated vessel containing a flow through analyzing system, an aluminum pressure housing for electronic modules, a battery for the power supply. The Al pressure housing can hold a CPU for system control, a photomultiplier detector with amplifiers, an AD converter, and a flash memory for data logging. Highly sensitive luminol chemiluminescence detection, previously used for the onboard Fe(II) determination in oceanic waters, was applied for the flow through analytical system. In this study, we examined the optimal conditions for the chemiluminescence detection and adopted the conditions to this system. We also developed a system for the in-situ calibration of Fe(II) concentration during the hydrographic cast for vertical measurement. The detection limit was low enough to apply for Fe(II) determination in the open ocean.

By using the in-situ analyzer, we obtained 1000m vertical profiles of Fe(II) in the western North Pacific and eastern South Pacific during the research cruise KH-10-2 and KH-11-10 with R.V. Hakuho-maru.

Keywords: In-situ autoanalyzer, seawater, Fe(II), Pacific Ocean

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In-situ infrared spectroscopic observations of sulfate surface

YANG, Chen[1*], KITADAI, Norio[2], FUKUSHI, Keisuke[3]

[1]Graduate School of Natural Science and Technology,Kanazawa University, [2]Graduate School of Science, Osaka University, [3]Graduate School of Science, Osaka UniversityInstitute of Nature & Environmental Technology, Kanazawa

<<In-situ infrared spectroscopic observations of sulfate surface complexation on ferrihydrite>>

Adsorption of solute to the surface of metal oxide is an important process that can control the mobility and solute concentration in natural water. Adsorption behavior of solute is related to the structure of solute on the surface (surface complex). The type of surface complex on a solute of a mineral surface depends not only is not the type of minerals and solutes but also the solution conditions such as pH, ionic strength and solute concentration. Therefore, the understanding of the adsorption behavior is necessary to understand the surface complex as function of the mineral types and solution compositions.

Sulfate is a major anion in nature and affects the mobility of coexisting trace dissolved species on mineral surfaces. Ferrihydrite is a low-crystalline iron oxide widely distributed in nature. Because of the huge specific surface area and the positively charged behavior, it is considered as an excellent scavenger for oxyanions. Although the adsorption of sulfate on ferrihydrite must be important process governing the motilities of trace dissolved species, there are very limitied knowledge about the adsorption behavior of sulfate on ferrihydrite including the structure of surface complex.

Attenuated total reflectance-infrared spectroscopy (ATR-IR) method enbles the direct observation of surface complex structure in aqueous system. The purpose of this experiment is to determine the structure of surface complex of sulfate on ferrihydrite from the in-situ observation by using ATR-FTIR under a wide range of environment conditions.

Keywords: surface complexation, In-situ infrared spectroscopic observations, ferrihydrite, sulfate, Adsorption, Attenuated total reflectance-infrared spectroscopy (ATR-IR)

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A XAFS study of isotopic fractionation mechanisms of molybdenum and tungsten at solid/water interface

KASHIWABARA, Teruhiko[1]*, TAKAHASHI, Yoshio[2]

[1]Japan Agency for Marine-Earth Science and Technology, [2]Earth and Planetary System Science, Hiroshima University

Recent development of mass spectrometry has revealed isotopic variations for a number of heavy elements in natural environment. However, a large part of the molecular mechanisms of their isotopic fractionation in natural environment have not been understood, yet. We suggest that X-ray absorption fine structure (XAFS) spectroscopy is a promising approach to understand the *non-traditional* stable isotope systems, especially, at the solid/water interface.

Molybdenum (Mo) shows large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which is responsible for isotopic composition of Mo in modern oxic seawater. This fractionation process, although its mechanism is still unclear, is the basis of the utility of Mo isotope system as a paleocean redox proxy. We investigated the structure of Mo species on ferromanganese oxides by XAFS to understand the mechanism of its isotopic fractionation during adsorption on natural ferromanganese oxides.

Ferromanganese oxides are aggregates of amorphous Fe (oxyhydr)oxide (ferrihydrite) and Mn oxide (delta-MnO_2). Our XAFS analyses revealed that (i) Mo forms a T_d outer-sphere complex on ferrihydrite, (ii) distorted O_h inner-sphere complexes on delta-MnO_2, and (iii) delta-MnO_2 is the dominant host phase of Mo in the natural ferromanganese oxides [1]. This structural information provides a molecular explanation for preferential adsorption of lighter Mo isotopes on natural ferromanganese oxides that the structural change from T_d $MoO_4{}^{2-}$ ion, major species in seawater, into distorted O_h species sorbed on delta-MnO_2 phase in natural ferromanganese oxides is the cause of observed isotopic fractionation of Mo, which is supported by quantum mechanical insights [2]. The structure of Mo on a series of other crystalline Fe oxides were also revealed by our studies and showed the excellent correlation with the isotopic fractionation of Mo reported in previous studies: the proportion of *Oh* species in Mo surface species become larger along with the degree of isotopic fractionation [3,4]. These relationships between molecular structure and isotopic fractionation imply that isotopic fractionation as the case of Mo could occur for other elements when the symmetry change occurred between dissolved and adsorbed species. We expect that tungsten (W), which is a congener of Mo, could also show isotopic fractionation during adsorption on ferromanganese oxides because it shows symmetry change between dissolved T_d $WO_4{}^{2-}$ ion in seawater and distorted O_h species on ferromanganese oxides as is the case of Mo [5].

Reference

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Keywords: XAFS, isotopic fractionation, solid/water interface, molybdenum, tungsten, structure of adsorbed species

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In-situ spectroscopic observation of transformation of monohydrocalcite in aqueous solutions

SHIRAI, Ryota[1*], KITADAI, Norio[1], FUKUSHI, Keisuke[1]

[1]Graduate School of Natural Science and Technology,Kanazawa University

In-situ spectroscopic observation of transformation of monohydrocalcite in aqueous solutions

Monohydrocalcite (CaCO3?H2O: MHC) is metastable phase of calcium carbonates. Synthesized MHC in laboratory transforms to calcite or aragonite within several hours or days. On the other hand, MHC was found in the deep sediments formed several hundreds of thousand years ago in the Lake Hovsgol. In order to elucidate the reason of different transformation rate, it is necessary to understand the transformation behavior of MHC quantitatively.

Munemoto and Fukushi (2008) examined the mechanism and rate of the transformation of MHC. They conducted batch aging experiments of the suspension of MHC at several temperature. After the some reaction intervals, the solid phases were separated from the solution. The solid phases were dried and served from mineralogical examination by using X-ray diffraction. However, there are two limitations for their experiments. Firstly, the time interval of the solid phase collections was 120 minutes at 25 oC. Therefore, the time resolution is not enough. Secondly, the possible artifacts arising from the drying processes was inevitable.

Attenuated total reflectance infrared spectroscopy (ATR-IR) enables to the in-situ time resolved observation of the transformation of MHC in aqueous solution. The present study aims to develop the observation system and to clarify the transformation behavior of MHC by using the observation system.

Keywords: monohydrocalcite, in-situ spectroscopic observation

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Experimental and computational studies on immobilization of oxyanions at the calcite-water interface

YOKOYAMA, Yuka[1*], TAKAHASHI, Yoshio[1], TANAKA, Masato[1]

[1]Graduate School of Science, Hiroshima University

Geochemical processes at mineral-water interfaces (e.g., mineral growth/dissolution, mobilization/immobilization of trace elements) play a critical role in determining contaminant transport and nutrient availability in natural water environments. Understanding such processes is central to many environmental challenges we are facing today such as the prediction of the long term fate of contaminants for nuclear waste disposal, the design and implementation of carbon sequestration strategies, and trapping of metal contaminants as impurities. Recent advances in computing power and development of computational methods have made possible their physicochemical investigation at the molecular level. This presentation introduces one of the geochemical studies at mineral-water interfaces based both on laboratory experiments and quantum chemical calculations (QCC).

Calcite ($CaCO_3$) is known as a mineral which can play a role as an effective scavenger of toxic elements in the surface environment. This study focused on the interactions of arsenic (As) and selenium (Se) oxyanions with calcite. The contamination of natural water with them is occurring in various areas in the world. Especially, migration of ^{79}Se from nuclear wastes to biosphere will pose a serious problem for the safe geological disposal of nuclear wastes.

Our coprecipitation experiments and XANES measurements revealed that calcite selectively incorporated arsenate rather than arsenite, and selenite was selectively incorporated rather than selenate. Although molecular geometries of dissolved selenite and selenate are similar to those of arsenite and arsenate, respectively, there is no relationship between their molecular geometries and incorporation behavior into calcite. EXAFS analyses using FEFF shows that these oxyanions are incorporated into calcite through substitution with carbonate ion, which indicated that these impurities are combined with Ca^{2+} ion when they deposit on the calcite surface. In order to determine the factor controlling the preferences of arsenate and selenite for the incorporation of As and Se, respectively, into calcite, their affinities to Ca^{2+} ion, which reflect their reactivities with calcite at the calcite-water interface, were evaluated based on the QCC.

Estimation of intermolecular binding energies between each oxyanion and Ca^{2+} ion by QCC shows that the affinity orders for Ca^{2+} ion are arsenite $>$ arsenate and selenite $>$ selenate. The preference of selenite for incorporation into calcite is related to its higher affinity to Ca^{2+} ion than selenate. On the other hand, though QCC shows that arsenite has higher affinity for Ca^{2+} ion than arsenate, arsenite is hardly incorporated into calcite as shown experimentally. This preference can be attributed to the much lower abundance of deprotonated arsenite as shown in its large dissociation constant ($pKa = 9.3$). Other oxyanions (arsenate, selenite, and selenate) dissociate into their anionic forms and can interact with Ca^{2+} ion under pH conditions where calcite can precipitate, whereas neutrally charged arsenite cannot display its high affinity for Ca^{2+} ion except for under high alkaline condition. Hence, the factors controlling their preferences for the incorporation into calcite are different between As and Se; for As, the charge of the aqueous species is important, whereas affinity to Ca^{2+} ion is important for Se. Additional QCC on the interactions between the oxyanions and calcite surface with the cluster models mimicking calcite-water mineral interface is expected to contribute to further investigation at the molecular level. The present findings should provide some insights into natural behavior of As and Se because their oxidation states are variable in subsurface environment, and into physicochemical systematics of oxyanions interaction with calcite.

Keywords: XAFS, Quantum chemical calculation, Mineral-water interface, Calcite

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X-ray absorption spectroscopy in geochemistry and environmental chemistry: present status and future prospect

TAKAHASHI, Yoshio[1]*

[1] Hiroshima University

In this session, we include a series of presentations related to X-ray absorption spectroscopy (XAS), or X-ray absorption fine structure (XAFS). The presentations in this session focus on the applications of XAS technique to relatively new fields in geochemistry and environmental chemistry including (i) application of scanning transmission X-ray microscopy (STXM) to carbons in geochemical samples, (ii) understanding of mechanism of isotopic fractionation based on the speciation analysis by XAS, (iii) interpretation of XAS results by molecular simulation, and (iv) coupling of micro-XAFS with fluorescence in-situ hybridization (FISH) method.