

Mass-independent fractionation of mercury stable isotopes in deep-sea hydrothermal systems

TAKEUCHI, Akinori^{1*} ; TOMIYASU, Takashi² ; KODAMATANI, Hitoshi² ; YAMAMOTO, Masahiro³ ; MARUMO, Katsumi⁴

¹National Institute for Environmental Studies, ²Kagoshima University, ³JAMSTEC, ⁴University of Toyama

It has been recognized that mercury (Hg) isotope analysis is an important new tool for identifying Hg source and tracking Hg transformations in the environment. Mass-dependent (MDF) and -independent (MIF) fractionations of Hg isotopes are caused by a wide variety of biogeochemical processes including redox reactions and volatilization. Volcanic activities and its associated hydrothermal activities are the main sources of naturally-emitted Hg in the environment. Several previous studies suggested that the naturally-emitted Hg indicated both MDF and MIF. It was thought that the MDF was caused by a process of liquid-vapor partitioning during ascending and the MIF was caused by photoreduction. It was, however, suggested that both photoreduction and volatilization could cause the MIF, and it has never been distinguish from each other in the hydrothermal systems. In this study, geological samples in active deep-sea hydrothermal systems at Izu-Bonin arc were collected and measured their Hg isotopic compositions. They indicate both MDF and MIF. The $\delta^{202}\text{Hg}$ values range from -1.0 to 0.5 ‰, indicating the liquid-vapor partitioning, whereas the calculated $\Delta^{199}\text{Hg}$ values are mostly between 0.1 and 0.2 ‰, indicating the MIF in the deep-sea hydrothermal systems without photoreduction. The linear relationship between $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$, ranging from 1.6 and 2.0, also indicates the nuclear volume effect. This result suggest that MDF and MIF of Hg isotopic compositions can be utilized to distinguish naturally-emitted Hg from anthropogenic Hg.

Keywords: Mercury Isotope, MIF, Deep-sea Hydrothermal Systems, CV-MC-ICP/MS

Speciation of metal ions in water: comparison of their reactivities with oxygen-donor hard ligands

TAKAHASHI, Yoshio^{1*} ; MIYAJI, Asami¹ ; TANAKA, Masato¹

¹Graduate School of Science, Hiroshima University

Complexation of metal cations with ligands such as hydroxide ion, carbonate ion, carboxylate ion, and phosphate ion is one of the most important factors controlling behaviors of metal ions in natural environment. Previous studies showed that these ligands were classified as "intermediate hard ligands" having oxygen donor, which favors to form ionic bonding. However, it was found that the reactivity of these ligands depends on ionic radius and that there is a difference of the reactivity between hydroxide ion and other intermediate hard ligands such as carbonate and carboxylate. For example, among divalent alkaline earth metal ions, Mg²⁺ mainly precipitates as hydroxide (brucite), while Ca²⁺ prefers to form carbonate (calcite) or phosphate (apatite) minerals rather than hydroxide. However, quantitative discussion on the selectivity of metal cations has not been performed.

In this study, we evaluated the standard Gibbs free energy, entropy, and enthalpy for the complex formation of hydrated metal cations with these ligands based on a critical thermodynamic database. As a result, we found that the entropic contribution to the free energy was large in the case of hydroxide complex of smaller cation. In contrast, the entropic contribution to the free energy was small in the case of hydroxide complex of larger cation and other complexes. In addition, the enthalpy contribution was not significant in this reaction. In the aqueous complexation reaction, entropy was controlled by the number of water molecules replaced by the ligand, suggesting that hydroxide complex for large cation was not stable due to the small effect of dehydration.

This suggestion was confirmed by quantum mechanical calculations, which was performed with B3LYP/6-311+G* level using Gaussian 09. We calculated distance between metal (M) in the center and oxygen (O) in the ligand with the increase of number of water molecules placed in the vicinity of the metal ion. As a result, it was found that the M-O distance for hydroxide complex is larger than that of carbonate in the case of larger cation and vice versa. This means that hydroxide prefers to form outer-sphere complex for larger metal ion, which is not the case of other intermediate hard ligands. This result is consistent with what we suggested based on the thermodynamic data.

Keywords: Speciation, Entropy, Complexation, Hydrolysis, Quantum chemical calculation

Consistency between fission-track and U-Pb ages of zircon and its implications

IWANO, Hideki^{1*} ; DANHARA, Tohru¹

¹Kyoto Fission-Track Co.

Following the recommendation by the Fission Track Working Group of the IUGS Subcommittee on Geochronology (Hurford, 1990), the fission-track method was transformed into a simplified and user-friendly dating tool. Standardization based on the common use of international age standards is what is called the zeta calibration. However, the adoption of the standardization scheme in which fission-track ages are determined against reference ages (K-Ar, Ar/Ar, Rb-Sr), and not based on physical parameters directly associated with the fission process, meant that the fission-track method lost its status as an independent geochronometer. Over the last two decades, we have investigated the problems of the absolute calibration approach, and we have finally demonstrated that it works well for zircon when using the external detector method (Danhara and Iwano, 2013). One of our conclusions is that the fission-track age for the Fish Canyon Tuff is 28.4+/-0.2 Ma. This is concordant with the recent zircon U-Pb ages (Schmitz and Bowring, 2001; Bachmann et al., 2007) and slightly older than the sanidine Ar/Ar age of 27.8+/-0.2 Ma, which is the reference age for the zeta calibration. We will discuss the consistency between fission-track and U-Pb ages of zircon from volcanic samples and give some comments on fission-track age standardization.

Bachmann et al. (2007) *Chemical Geology* 236, 134-166.

Danhara and Iwano (2013) *Island Arc*, 22, 264-279.

Hurford (1990) *Chemical Geology*, 80, 171-178.

Schmitz and Bowring (2001) *Geochimica et Cosmochimica Acta* 65, 2571-2587.

Keywords: zircon, fission-track age, U-Pb age, calibration

Fe isotope measurement of taenite using LA-MC-ICPMS technique with Galvano scanner system

OKABAYASHI, Satoki^{1*} ; HIRATA, Takafumi¹

¹Division of Earth and Planetary Sciences, Kyoto University

The laser ablation-multicollector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS) is widely accepted as the powerful technique to reveal the isotope ratios of solid sample. This technique can achieve the in-situ analysis of micro region with swiftness. On the other hand, it is difficult to avoid the mass spectrometric and non-mass spectrometric interferences from coexistent elements in this technique because the produced sample particles by laser ablation are directly introduced into the ICP with carrier gas. Such interferences have a potential to intercept to reveal the precise and accurate isotope data. The effect on the isotope ratios of analyte from coexistent elements can be corrected by using the standard material which include same amount of coexistent elements as the sample. However, synthesis of isotopic homogeneous solid material is extremely difficult.

In this study, we have developed a technique to measure the Fe isotope ratios of taenite in iron meteorites. The Fe isotope signature of iron meteorites is one of the key information to understand the core formation of planetesimals and terrestrial planets. However, the in-situ Fe isotope measurement of taenite is difficult because of the abundant Ni (>25 wt%) in it. In order to overcome this problem, we have applied Galvano mirrors and a telecentric optical system (Yokoyama et al., 2011) for LA-MC-ICPMS technique. In this technique, pure iron (IRMM-014) and pure Ni were ablated at a time using femtosecond laser with Galvano system as the Fe isotope standard. The ablated Ni amount was adjusted to the Ni amount in the taenite sample. The Fe isotope ratios ($^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$) of taenite phases were measured using MC-ICPMS and the mass fractionation in the mass spectrometry was corrected by sample-standard bracketing technique. The precision and accuracy of Fe isotope data obtained by the presented technique will be discussed in this presentation. The isotope analytical technique developed in this study can be applied not only for taenite phase in iron meteorite but also for other sample which include coexistent elements.

Keywords: ICP-MS, laser ablation, taenite, Fe isotope, Galvano

High-Pressure Neutron Beamline PLANET for investigating "Water" in the Earth

HATTORI, Takanori^{1*} ; SANO, Asami¹ ; ARIMA, Hiroshi² ; INOUE, Toru³ ; KAGI, Hiroyuki⁴ ; YAGI, Takehiko³

¹Japan Atomic Energy Agency, ²Institute for materials research, Tohoku university, ³Geodynamics Research Center, Ehime University, ⁴Geochemical Laboratory, Graduate School of Science, University of Tokyo

The PLANET is the world's first neutron beamline specialized for high-pressure and high-temperature experiments. The most characteristic feature is the capability to investigate the state of water and hydrogen in minerals at high-pressure and high-temperatures up to 20GPa and 2000K with the multi-anvil high-pressure apparatus. The construction was started in 2008 and the experiments have been conducted since Nov. 2012. In this talk, the design and performance of the PLANET are introduced.

PLANET is designed so as to investigate structures not only of crystalline but also of amorphous (liquid) materials. The resolution of the diffraction pattern ($\Delta d/d=0.6\%$) was found to be almost equal to the designed value(0.5%). The elimination of the background from the sample surrounding materials, which is the most important issue in the high-pressure experiments, was found to be accomplished by using the severe incident and receiving collimators. With this development, PLANET offers very clear patterns even at high pressures. This character made the PLANET one of the most innovative beamlines among several high-pressure neutron beamlines in the world.

Keywords: neutron, high pressure, beamline, hydrous



High-pressure neutron beamline at J-PARC and applications to earth and planetary sciences

KAGI, Hiroyuki^{1*}; IIZUKA, Riko²; KOMATSU, Kazuki¹; YAGI, Takehiko²; NAGAI, Takaya³; INOUE, Toru²; SANNO, Asami⁴; HATTORI, Takanori⁴

¹Graduate School of Science, University of Tokyo, ²Geodynamic Research Center, Ehime University, ³Graduate School of Science, Hokkaido University, ⁴Japan Atomic Energy Agency

Construction of the high-pressure dedicated beamline, PLANET, in Japan Proton Accelerator Research Complex (J-PARC) has been completed in 2012 and scientific programs for general users have just started in 2014. The PLANET beamline has a focusing mirror for incident neutron and two 90-degree detector banks. Each bank has 160 pieces of Position Sensitive Detectors (PSDs) filled with ³He gas. Each bank has a detector coverage of 90 ± 11 degree against the incident beam in the horizontal direction and 0 ± 35 degree in the vertical direction. Radial collimators are attached in front of the detector banks to reduce the background. The instrumental resolution is 0.6% in $\Delta d/d$. The accessible d-spacing is normally 0.2-4.2 Å and is doubled in a double-frame setup. The power of the proton beam is around 300 kW and will be increased to 600 kW in 2014. The most characteristic feature of the PLANET beamline is the multi-anvil apparatus with six independently acting 500-tonne rams (6-axis press called ATSUHIME). Using ATSUHIME, we successfully observed neutron diffraction patterns of hydrous minerals at high pressure and high temperature without any contamination from sample-surrounding materials such as pressure transmitting media, anvils, and so on. This clearly shows that the incident slit and radial collimator installed in the beamline are very effective to obtain the diffractions under high pressure.

We focus on pressure-responses on the structure of materials with hydrogen-bonding networks through neutron diffraction measurements at high pressure. These results will contribute to fundamental understanding of hydrous materials in the deep earth and icy material in the planets.

Keywords: neutron, neutron diffraction, hydrogen, water, high pressure, ices

Geo-neutrinos for advanced earth studies

TANAKA, Hiroyuki^{1*}

¹Earthquake Research Institute, The University of Tokyo

Neutrinos generated in Earth (geo-neutrinos) gives us information about the distribution of Uranium (U), thorium (Th), and potassium (K) inside Earth. Beta-decays of radionuclides U/Th/K inside Earth produce low energy anti-electron neutrinos (U and Th produces 7.41×10^7 neutrinos $\text{kg}^{-1}\text{s}^{-1}$ and 1.62×10^7 neutrinos $\text{kg}^{-1}\text{s}^{-1}$ respectively (without considering neutrino oscillation)) that traverse through Earth without being disturbed due to their extremely small interaction cross section with matter. Recent geo-neutrino observations have produced results that have a potential to support and clarify the current concerns of earth science: estimating the amount of contribution to the surface heat flux; constraining existing Earth's compositional estimates; and clarifying the origin of low shear velocity regions found at the core mantle boundary (CMB). Today, there are two detectors capable of measuring geoneutrinos: KamLAND, in Japan, and Borexino, in Italy. The KamLAND research team has found 116 ± 28 , 27 geoneutrino candidate events (generated through the decay processes of ^{238}U and ^{232}Th) during 2,991 days of geoneutrino observation (Gando et al. 2013). The contribution from geonuclear reactions to the heat flow, estimated from examination of the geoneutrino flux, reached 11.2 ± 7.9 , 5.1 TW. Although the volume of the Borexino detector (280 t) is much smaller than that of KamLAND (1,000 t), the background from reactor neutrinos is much lower than that for KamLAND because there are no nuclear power plants in Italy. Borexino detected 14.3 ± 4.4 geoneutrino candidates over 1353 days of observation. Both measurement results are consistent each other, and also reject the fully radiogenic model, which assumes that the total Earth's surface heat flux is completely originated from radiogenic heat from U, Th and K. The upper limit on the fully radiogenic heat flux hypothesis (Herndon 1996) was set to be 4.5 TW at 95% confidence level (Bellini et al. 2013).

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Bellini, G., Ianni, A., Ludhova, L., Mantovani, F., McDonough, W.F. 2013. Geo-neutrinos, *Prog.Part.Nucl.Phys.* 73:1-34

Keywords: Neutrino, Uranium, Thorium, Mantle

Multi-range imaging mass spectrometry using laser ablation-ICP-mass spectrometry

HIRATA, Takafumi^{1*} ; HATTORI, Kentaro¹ ; OHARA, Seiya¹

¹School of Science, Kyoto University

Time-resolved elemental and isotopic data can provide key information about the time changes of the geochemical conditions of the surface environment of the Earth, and therefore, critical restriction for the origin or evolutionary sequence of the surface environment of the Earth and the life could be derived. To obtain reliable and exclusive information from the samples, tremendous efforts have been given to develop various analytical techniques, which could provide both the higher elemental sensitivity and higher analytical throughput. Among the analytical techniques, plasma ion source mass spectrometer coupled with the laser ablation sample introduction technique (LA-ICPMS) has now become the most sensitive and user-friendly analytical tool to derive elemental and isotopic distribution among the different phases or minerals. Moreover, in the LA-ICPMS technique, atomization and ionization of the analytes were independently carried out from the sampling (i.e., post ionization technique), and therefore, the sampling and ionization conditions could be separately optimized. The post ionization technique results in the smaller contribution of the matrix effect, which could be the major source of analytical error. Furthermore, for the LA-ICPMS technique, sample was located under the atmospheric pressure sample cell, and laser induced sample aerosols were carried into the ICP ion source using a He carrier gas. This suggests that no evacuation of the sample housing is required, and therefore, biological cell or tissue samples (i.e., wet samples) can be directly subsidized to elemental imaging analysis, obviating the drying or freezing procedure for the analysis. The LA-ICPMS technique has further advantages of imaging analysis for samples with various sizes, ranging from 10 microns to >10 mm. Because of high capability for quantitative imaging of ultratrace-elements, together with high analytical capability to measure large-sized samples, the LA-ICPMS technique has blossomed to become the key analytical technique for the imaging analysis of trace-elementals and isotopes. This is very important to obtain elemental and isotopic images for not only biological samples, but also various rock or minerals. In fact, imaging data for whole rock pierces or minerals can tell us the substantial process for the elemental distribution or diffusion among the samples. We should recall that we could not see the forest for the trees. Despite the obvious success in obtaining the elemental and isotopic imaging data, neither quantitative evaluation of the detection limits for the elements nor the dependence of the analytical conditions (e.g., laser pit size, raster rate, system setup or condition for data acquisition) onto the resulting spatial resolution were made. To investigate these, we have measured imaging analyses of several trace- and ultratrace-elements from meteorite samples and biochemical samples under the various analytical conditions. In this presentation, we will described the effect of the system setup and operational settings onto the resulting spatial resolution and onto the limit of detection for the elements.

Keywords: laser ablation, ICP-mass spectrometry, imaging mass spectrometry, multi-scale imaging, trace-elements, quantitative imaging

Cavity ring-down spectroscopy for the isotope ratio measurements of water from fluid inclusions in stalagmites

UEMURA, Ryu^{1*} ; NAKAMOTO, Masashi¹ ; GIBO, Masakazu¹ ; MISHIMA, Satoru¹ ; ASAMI, Ryuji²

¹University of the Ryukyus, ²University of the Ryukyus

Oxygen isotope record in stalagmites is useful to reconstruct past environmental changes. However, the interpretation of calcite isotope record is not straightforward because it is affected by various factors affect such as amount of precipitation and temperature. Water isotope composition of fluid inclusions, and oxygen isotope difference between water and host calcite, from stalagmite are potentially important proxies to estimate the paleo-temperature. Recently, infrared spectroscopy (IRIS) has been widely used for stable isotope ratio measurement of water. Unlike traditional isotope mass spectrometer (IRMS), the IRIS does not require pre-treatment processes (e.g., high-temperature furnace or equilibration device). A limitation of IRIS is that commercially available IRIS systems need large sample volume (1 - 2 micro litres) for liquid water measurement. In this study, we developed a custom-designed device suitable for precise measurement of smaller volume (0.05 to 0.20 microlitres) of water, and tested two extraction methods (thermal extraction and mechanical crushing). Oxygen and hydrogen isotope ratios of water were measured using cavity ring down spectroscopy (WS-CRDS Picarro L2130-i). Stalagmites samples were collected in several caves in Okinawa, Japan. Pieces of stalagmites (80-300mg) subsampled from homogeneous layers, and reproducibilities of the inclusion measurement were 0.2 permil for $\delta^{18}\text{O}$ and 1 permil for δD . The measured $\delta^{18}\text{O}$ and δD of inclusion water from recently grown stalagmites agrees with modern dripwaters, indicating that our extraction technique is useful to measure isotope ratios of past inclusion water.

Keywords: Stable isotope, Fluid inclusion, Speleothem, Stalagmite, Paleoclimate, CRDS

Coral growth-rate insensitive Sr/Ca as a robust temperature recorder at the extreme latitudinal limits of Porites

HIRABAYASHI, Shoko^{1*} ; YOKOYAMA, Yusuke¹ ; SUZUKI, Atsushi² ; KAWAKUBO, Yuta¹ ; MIYAIRI, Yosuke¹ ; OKAI, Takashi² ; NOJIMA, Satoshi³

¹Atmosphere and Ocean Research Institute, The University of Tokyo, ²National Institute of Advanced Industrial Science and Technology, ³Amakusa Marine Biological Laboratory, Kyushu University

Corals are rich archives of climatic changes with high-resolution record of seasonal change such as sea-surface temperature (SST), in tropical and sub-tropical seas during recent and distant past. Past SST are commonly reconstructed from the trace elements present in annually-banded coral skeletons. Recently, reef building corals were found in temperate regions due to coral habitat range shifts and/or expansions. Therefore, it could be a powerful tool for reconstructing climatic changes such as global warming and ocean acidification over long period. However, because of the more stressful environment for corals in temperate region than tropic or subtropics, we have to know how to reconstruct palaeo-SST using temperate corals.

This paper was reported Sr/Ca-based SST reconstructions for temperate Porites corals collected from Kyushu, Japan, near the northern latitudinal extent of hermatypic corals. New, high-resolution Sr/Ca data, measured along the growth axes of Porites from Ushibuka, were compared to previously published $\delta^{18}\text{O}$ data from the same specimens (Omata et al., 2006). Results indicate that Sr/Ca variations in a low-growth coral remain independent from growth rate, in contrast to the oxygen isotope ratios of the same coral. Results clearly indicate that Sr/Ca robustly reproduces SST variations from regions along the extreme latitudinal limits of hermatypic coral habitat, independent of growth rate variations.

Additionally, Sr/Ca of the other two Porites corals collected in Ushibuka were measured and the inter-colony variation of reconstructed SST was shown. At this stage, it is difficult to reconstruct accurate SST using only one specimen of Porites in temperate region. However, we can reconstruct SST within only 1 °C difference from observed SST if we calibrate Sr/Ca-SST using more than two corals. It is expected that in the future the fossil temperate corals will be commonly used for palaeo-SST reconstruction.

Maximizing organic records: Recent achievements and future directions

OHKOUCHI, Naohiko^{1*} ; CHIKARAISHI, Yoshito¹ ; TAKANO, Yoshinori¹ ; OGAWA, Nanako¹

¹JAMSTEC

Molecular isotopic record in either organisms or sediments has been proven useful for better understanding the bio(geo)chemical processes, reconstructing paleo-environment, etc. During the last decades, target molecules have been expanding from simple lipids to complex physiologically active compounds. There are two key issues to push this molecular tool more useful and more efficient: 1) Purity of the target compounds that are extracted from environmental samples (generally a complex mixture of organic compounds), and 2) sensitivity of isotope-ratio mass spectrometry (IRMS) system for precisely measuring isotopic compositions. In this presentation we will overview the recent advances in these two issues, and how these achievements contributed to the progresses in our knowledge. We also try to mention in the future challenges of molecular isotopic signatures.

Keywords: Organic molecule, isotopic composition, nitrogen, carbon

Precise and sensitive determination of stable isotopic compositions of amino acids

CHIKARAISHI, Yoshito^{1*} ; TAKANO, Yoshinori¹ ; OHKOUCHI, Naohiko¹

¹Japan Agency for Marine-Earth Science and Technology

Amino acids are biologically central and functional organic compounds. Their molecular and stable isotope profiles have been employed as a tool in various fields of studies, particularly for understanding of the trophic energy flow of food web ecology as well as for estimating the origin of amino acid procurers in extraterrestrial samples (e.g., meteorites). One of the most powerful techniques in the stable isotope studies of amino acids is compound-specific isotope analysis (CSIA) by gas chromatography/isotope ratio mass spectrometry (GC/IRMS), which potentially allows a rapid and precise determination of H, C, N, O, and S isotopic compositions of individual amino acids in complex mixture of samples. However, (1) isotopic fractionation and exchange during pretreatment (e.g., hydrolysis, extraction, purification, and derivatization) of samples, (2) chromatographic separation among individual amino acids, and (3) less sensitivity on GC/C/IRMS (i.e., 10-50 nmol of elements is required) are always problematic in CSIA of amino acids.

In the presentation, we will briefly review these issues on CSIA of amino acids, and show current advances in the precise and sensitive determination of C and N isotopic compositions of amino acids (i.e., within 0.4-0.8 permil for a minimum sample amount of 0.5 nmol element), based on the minimizing isotopic fractionation during HPLC purification and derivatization as well as reducing leak and background variation in GC/IRMS instrument. With this method, we can access C and N isotopic signature of wide range of samples including amino acids in bacteria and archea isolated from natural environments as well as amino acid procurers in meteorites.

Keywords: stable isotope, amino acids, food web, meteorite

On the role of amino acid metabolism and a biogeochemical linkage

TAKANO, Yoshinori^{1*} ; CHIKARAISHI, Yoshito¹ ; OHKOUCHI, Naohiko¹

¹JAMSTEC

Deep-sea sediments harbor a novel and vast biosphere with yet unconstrained importance in the global biogeochemical cycle. To explore these habitats is interdisciplinary challenges for the biogeochemical and geomicrobiological scientific community. The limits of deep biosphere are on-going subject, which were not yet known in terms of environmental properties, including depth, temperature, energy availability, and geologic age; however, it is known that seafloor microbes play a significant role in chemical reactions that were previously thought to have been abiotic.

Since the novel classification by Woese and Fox (1977), Archaea, one of three domains of life, had been originally believed to exist in extreme environments including high temperature, high salinity, low oxygen concentration. However, recent advances in molecular and phylogenetic approaches revealed their widespread distribution in marine and terrestrial environment including deep subsurface biosphere. The planktonic and benthic archaeal assemblages include two major phyla Euryarchaeota and Crenarchaeota. The novel phylum have been also proposed recently as Thaumarchaeota, Korarchaeota, and Nanoarchaeota.

In the present study, we reviewed the recent knowledge of prokaryotic ecology and biogeochemistry from molecular-specific isotopic signatures. Among these, we focused on the role of amino acid metabolism and a biogeochemical linkage mediated by deep-sea benthic archaea.

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Keywords: amino acid metabolism, deep-sea benthic archaea, a biogeochemical linkage