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

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

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

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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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MTT37-P02 Room:Convention Hall Time:May 21 17:15-18:30

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

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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

Japan Geoscience Union Meeting 2012
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MTT37-P03 Room:Convention Hall Time:May 21 17:15-18:30

Development of NanoAMS

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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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MTT37-P04 Room:Convention Hall Time:May 21 17:15-18:30

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

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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

Japan Geoscience Union Meeting 2012
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MTT37-P05 Room:Convention Hall Time:May 21 17:15-18:30

In-situ infrared spectroscopic observations of sulfate surface

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<<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)

Japan Geoscience Union Meeting 2012
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MTT37-P06 Room:Convention Hall Time:May 21 17:15-18:30

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

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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

[1]Kashiwabara et al., (2009) *Geochem. J.*, 43, e31-e36. [2] Bigeleisen and Mayer (1947) *J. Chem. Phys.* 15, 261-267. [3]Kashiwabara et al., (2011) *Geochim. Cosmochim. Acta*, 75, 5762-5784. [4]Goldberg et al., (2009) *Geochim. Cosmochim. Acta*, 73, 6502?6516. [5]Kashiwabara et al., (2010) *Chem. Lett.*, 39, 870-871.

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

Japan Geoscience Union Meeting 2012
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MTT37-P07 Room:Convention Hall Time:May 21 17:15-18:30

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

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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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MTT37-P08 Room:Convention Hall Time:May 21 17:15-18:30

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

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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 ($\mathrm{p}K\mathrm{a} = 9.3$). 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

MTT37-P09 Room:Convention Hall Time:May 21 17:15-18:30

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

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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.