

U020-01

Room:304

Time:May 23 09:00-09:15

Influence of redox condition on the solubilities of Mo and W

Yoshio Takahashi^{1*}, Teruhiko Kashiwabara¹, Eriko Ohmori¹, Yuka Yokoyama¹, Youko Miyoshi², Shinsuke Kawagucci³, Junichiro Ishibashi²

¹Hiroshima University, ²Kyushu University, ³JAMSTEC

It is well known that concentrations of trace elements in sea water are primarily correlated with their concentrations in serum levels in animals. This fact suggests that the availability of each trace element from the environment is an important factor whether the element is essential or not for biota. Thus, the chemistry deciding the concentrations of trace elements in sea water can be basic information on the understanding of the history of essential elements in biota. From this point of view, a twin element, Mo and W, is of great interest, since (i) Mo is an essential element but W is toxic to almost all biota at present, but (ii) some hyperthermophilic archaea appear to be W dependent. These facts suggest that W could be more abundant in primordial ocean or in hydrothermal water. To approach this matter, we think that it is primarily important to compare the chemistries controlling the solubilities of Mo and W in the preset seawater and primordial marine environment where primitive life evolved.

Solubilities of trace elements in sea water are often controlled by adsorption reactions on solid phases in contact to the aqueous phase. Based on our laboratory experiments and analyses of natural samples in terms of their concentrations and speciation by X-ray absorption spectroscopy (XAS), we found that the solubilities of W and Mo in oxic seawater at present are controlled by their surface complexes on Fe hydroxides, outer sphere complex or inner sphere complex. The former is more soluble than the latter, since the latter has direct chemical bonding to the oxide surface. The formation of inner-sphere complex, in turn, is related to the acidity of the oxyanions such as molybdate and tungstate ions. Thus, it was revealed that the concentrations of oxyanions including Mo, W, As, and Se in sea water are primarily controlled by the acidity of the oxyanions.

On the other hand, solubilities of Mo and W in possible primordial marine environment that can be rich in sulfide were discussed based on the adsorption reactions of Mo and W on sulfide minerals (pyrite and pyrrhotite) and analyses of sediment core samples collected near the hydrothermal vent systems in the Izena Cauldron, Okinawa Trough. The core sample was particularly selected since the sulfide minerals were formed at 20 cm depth, but not at the surface within the core. The analyses of the samples at various depths from the core enable us to compare the Mo and W solubilities and reactions controlling the concentrations. As a result, formation of sulfidic species of Mo was confirmed at the 20 cm depth, but not at the surface for Mo. Although W species cannot be determined by XAS, formation of sulfidic species of W was not found in the sediment samples which were incubated under reducing condition in laboratory, where a small amount of Mo was in the sulfide form. This result suggests that the solubilities of Mo and W in "sulfide world", or the environment where primitive life evolved, can be controlled by their affinities to sulfur.

U020-02

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Time:May 23 09:15-09:30

Relationship between water saturation and reactive surface area of sandstone

Naoki Nishiyama^{1*}, Tadashi Yokoyama¹

¹Dept. Earth & Space Sci., Osaka Univ.

Dissolution and precipitation of minerals and adsorption of dissolved matters onto minerals occur at the contact surface between minerals and water. Estimation of the contact surface area (reactive surface area) is important for quantitative treatment of the reaction and material transport in rocks. Many studies on water-rock interaction have measured the dissolution rate and reactive surface area by inpouring a liquid into a saturated rock. However, in the earth surface the rock pores are not filled only with water but also with air, and the water saturation often changes owing to intermittent supply of water. In such unsaturated condition, only subsets of minerals contact with water. This indicates that the reactive surface area measured by the laboratory experiments using a saturated rock may differ from the values of natural conditions. To our knowledge, few studies have evaluated how the water saturation of a rock affects the reactive surface area.

In the present study, we conducted dissolution experiment under various water saturations and evaluated the effect of water saturation on reactive surface area. Fontainebleau sandstone (porosity: 7.4%, pore radii: 1-10 micro meter, mineral composition: 100% quartz) was used as a sample. Water saturation of the rock sample was first adjusted to 0%, 50%, 100%. Then, for each water saturation, water was in poured into the sample under a constant water head and dissolved Si in the water passed through the rock was measured by Molybdate blue method. By dividing these values by a value for completely saturated condition, relative reactive surface areas, the ratio of reactive surface area for each water saturations to that in completely saturated condition, were calculated for each water saturations. The relative reactive surface area decreased with decreasing water saturation. At a water saturation of 39%, a minimum relative reactive surface area of 50% was obtained.

Although the extent at which water saturation affects reactive surface area may depend of mineral composition and pore structure, the result in the present study indicates that estimation of the effect of water saturation is important in quantitative treatment of water-rock interaction in the earth surface.

Keywords: reactive surface area, water-rock interaction, water flow, water saturation, sandstone

U020-03

Room:304

Time:May 23 09:30-09:45

Effect of water saturation on weathering of a rock: an example of rhyolite

Tadashi Yokoyama^{1*}

¹Dept. Earth & Space Science, Osaka Univ.

Weathering of a rock proceeds by the interplay between reaction and transport. In unsaturated zone above a water table, air and water are present in rock pores and water saturation of a rock has a large variation. In the present study, the effects of the water saturation on chemical reaction rate and transport through rock pores were evaluated, taking the weathering of porous rhyolite from Kozushima, Japan, as an example.

Permeability test and through diffusion experiment were conducted using a rhyolite core which was completely saturated with water under vacuum, and a saturated hydraulic conductivity and a saturated effective diffusion coefficient of dissolved Si were determined. Similar experiments were conducted using a dried sample, and an unsaturated hydraulic conductivity and an unsaturated effective diffusion coefficient were determined. The unsaturated hydraulic conductivity was smaller than the saturated one by a factor of 0.08 and the unsaturated diffusion coefficient was smaller than the saturated one by a factor of 0.4. The changes of hydraulic conductivity and diffusion coefficient are inferred to be due to the changes in tortuosity, connectivity, size, and number of flow paths.

To compare the weathering rate of the rhyolite (dissolution rate of Si) under a saturated condition and that under an unsaturated condition, the weathering rates were computed by a reaction-transport equation using the values determined by the permeability test and diffusion test and a dissolution rate per unit reactive surface area determined separately. The weathering rate calculated for the saturated condition was $7\text{E-}18 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$ and that for the unsaturated condition was $9\text{E-}19 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$ (in the case of a rock size of 50 cm). As to the rhyolite in Kozushima, weathering rate in the field has been estimated to be about $6\text{E-}19 \text{ mol Si cm}^{-2} \text{ sec}^{-1}$, which was determined by comparing the chemical compositions of rhyolites having different duration of weathering. Comparison of the field rate and numerical results reveals that the calculated result under the unsaturated condition agrees well with the field rate. This indicates that evaluation of the effect of water saturation is important for precise prediction of weathering rate.

U020-04

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Time:May 23 09:45-10:00

Mechanisms of adsorptive isotopic fractionation of Mo on ferromanganese oxides based on the systematics of its surface c

Teruhiko Kashiwabara^{1*}, Yoshio Takahashi¹

¹Earth and Planetary Systems Science, Hir

Molybdenum (Mo) shows large mass-dependent isotopic fractionation during adsorption on ferromanganese oxides, which affects isotopic composition of Mo in modern oxic seawater. Due to this fractionation process, isotopic ratio of Mo in marine environment is expected to be used as a paleocean redox proxy. The aim of this study is to reveal the fractionation mechanisms of Mo isotopes during adsorption on natural ferromanganese oxides. We investigated surface complex structures of Mo on various Fe/Mn (oxyhydr)oxides, key factors for isotopic fractionation, and compared them with previously-reported isotopic fractionations.

Adsorption experiments were conducted using synthetic amorphous ferrihydrite and *delta*-MnO₂, and crystalline goethite and hematite as adsorbents. Solutions were adjusted to pH 8 and I = 0.70 M (NaNO₃). The structures of adsorbed species were investigated by conventional fluorescence XAFS method. Measurements for Mo K-edge EXAFS were performed at BL01B1 in SPring-8, and those for Mo L₃-edge were at BL-9A in Photon Factory.

Our XAFS analyses revealed that Mo forms a *Td* outer-sphere complex on ferrihydrite and distorted *Oh* inner-sphere complexes on *delta*-MnO₂ (Kashiwabara et al., 2009). In addition, Mo forms inner-sphere complexes on crystalline goethite and hematite: *Td* edge-sharing (46%) and *Oh* double corner-sharing (54%) for goethite; *Td* double corner-sharing (14%) and *Oh* edge-sharing (86%) for hematite. These structural information showed the excellent correlation with the degree of isotopic fractionation during adsorption reaction of Mo reported in previous studies: the proportion of *Oh* species or their magnitude of distortion in Mo surface complexes become larger in the order of ferrihydrite < goethite < hematite < *delta*-MnO₂, a trend identical to the degree of isotopic fractionation (Goldberg et al., 2009). Based on the comparison with previous reports for Mo surface species on various oxides such as MgO, Al₂O₃, and TiO₂, chemical factors that affect Mo surface complex structures were also discussed. The hydrolysis constant of cation in oxides, log K_{OH}, (or the acidity of the oxide surfaces, PZC) is well correlated with the mode of attachment (inner- or outer-sphere) of Mo surface complexes. Furthermore, the symmetric change in Mo species from *Td* to *Oh* is suggested to be driven by the formation of inner-sphere complexes on specific sites of the oxide surfaces.

References

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Keywords: molybdenum, isotopic fractionation, surface complex structure, ferromanganese oxides

U020-05

Room:304

Time:May 23 10:00-10:15

Experimental study on cerium isotopic fractionation

Ryoichi Nakada^{1*}, Yoshio Takahashi¹, Masaharu Tanimizu²

¹Hiroshima Univ., ²JAMSTEC

Cerium (Ce) anomaly that appears in rare earth element (REE) pattern is a tool to estimate paleoredox condition and has been used for many studies. Discussion in previous studies, however, has been limited to qualitative based on a REE pattern. In addition, the formation process of Ce anomaly is not fully understood. This study, therefore, aims to provide fundamental information on the redox condition in paleoenvironment by Ce stable isotope ratio related to the redox-sensitive property of Ce. If fractionations of Ce stable isotope respond differently to various geochemical processes such as (i) oxidative scavenging on Mn oxide, (ii) precipitation as CeO₂ or Ce(OH)₄, and (iii) adsorption of Ce³⁺ without oxidation, it is possible that Ce stable isotope ratio can give much information on redox condition in paleoenvironment. It is expected that the coupling of the Ce stable isotope ratio and Ce anomaly can be a unique paleoredox tracer.

In this study, a laboratory experiment under equilibrium condition was conducted. Cerium(III) chloride solution was added to manganese oxide and iron hydroxide, respectively, with various Ce concentration. In both systems, pH was adjusted to 5.00 (± 0.05) and shaken for 6 hours before the filtration using 0.2 micrometer membrane filter. In addition, precipitation of Ce was obtained by bubbling of O₂ gas in the same CeCl₃ solution. Stable isotope ratios of Ce in both liquid and solid phases were determined using a MC-ICP-MS at Kochi Institute for Core Sample Research. The isotope ratios are expressed in standard epsilon notation relative to the average standards, which is shown in an equation as follows; $\epsilon^{142}\text{Ce} = [({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{sample}}/({}^{142}\text{Ce}/{}^{140}\text{Ce})_{\text{CeCl}_3} - 1] \times 10000$. For solid phase sample, Ce L_{III}-edge XANES was measured at BL-12C in Photon Factory, and Ce K-edge EXAFS was measured at BL01B1 in SPring-8.

Mean isotopic fractionation factors between liquid and solid phases (α_{Lq-So}) of the systems of (i) adsorption on manganese oxide (ii) adsorption on iron hydroxide, and (iii) spontaneous precipitation of Ce were 1.000411 (± 0.000079), 1.000145 (± 0.000022), and 1.000196 (± 0.000031), respectively. In this case, Ce adsorbed onto Mn oxides was oxidized to tetravalent, while that on Fe hydroxide remains trivalent. In addition, XANES spectrum of the spontaneous precipitation of Ce clearly showed that Ce was tetravalent. These facts indicate that isotopic fractionation of Ce between liquid and solid phases becomes larger as the redox condition becomes oxic in the order of adsorption without oxidation, Ce(IV) precipitation, and oxidative adsorption. Thus, it is suggested that the combination of Ce stable isotope ratio and Ce anomaly which respond differently to various redox conditions can be a useful tracer to discuss the change of redox condition of paleocean.

Keywords: Cerium, Stable isotope, XAFS

U020-06

Room:304

Time:May 23 10:15-10:30

Ferrous iron oxidation under very low O₂ conditions: Rates, mechanisms and application

Yoshiki Kanzaki^{1*}, Takashi Murakami¹

¹Grad. School of Science, Univ. of Tokyo

Although there have been numerous studies on Fe(II) oxidation kinetics, few have paid attention to the kinetics under very low O₂ conditions. The importance of Fe(II) oxidation under very low O₂ conditions has been recognized recently; Fe(II) oxidation kinetics has been shown to be applied to the Fe(II)/Fe(III) compositions of paleosols, ancient soils formed by weathering, which can give a quantitative pattern of atmospheric oxygen increase during the Paleoproterozoic (from < 10⁻⁶ atm to > 10⁻³ atm of partial pressure of atmospheric oxygen, pO₂). The effects of pO₂ on Fe(II) oxidation rate was investigated to establish Fe(II) oxidation rate-pO₂ relationship under very low O₂ conditions. All oxidation experiments were carried out in a glove box by introducing Ar gas under conditions of 10⁻³ - 10⁻⁵ atm of pO₂ and 7.57 - 8.12 of pH at room temperature. Because of very low concentrations of Fe(II) (down to ~ 0.1 ppb), new methods were developed to measure Fe(II) concentrations. The dominant species related to oxidation in the pH range examined is suggested to be Fe(OH)₂. The rate law changes from $d[\text{Fe}^{2+}]/dt = k'_{0-high} [\text{Fe(II)}][\text{OH}^-]^{2.0} [\text{O}_2]^{1.0}$ to $-k'_{0-low} [\text{Fe(II)}][\text{OH}^-]^{2.0} [\text{O}_2]^{0.5}$ (k'_0 , the rate constant; [O₂], the concentration of dissolved oxygen) at 0.2 - 0.005 and < 0.005 atm of pO₂, respectively. The former rate law is explained by well-known mechanisms of the four-step reactions. The latter law is established for the first time, where the Fe(II) oxidation rate is faster than that predicted by the classical rate law. To explain the mechanisms, it is suggested that reactions where oxygen produces radicals and hydrogen peroxide play a critical role in addition to the four-step reactions. Such a reaction occurs due to dilute nature of the solutions of ~ 5 - 0.5 ppb of [O₂] and ~ 10 - 0.1 ppb of [Fe(II)], and therefore, will have impact on red-ox chemistry in very dilute solutions. Application of this new oxidation rate law to Fe(II)/Fe(III) ratios of paleosols gives a new quantitative pattern of atmospheric oxygen evolution between 2.5 and 2.0 Ga; atmospheric oxygen evolved rapidly from very low O₂ levels (pO₂ < 10⁻⁶ atm) to ~ 10⁻⁶ atm of pO₂ at ~ 2.45 Ga and then gradually increased to 10⁻³ atm of pO₂ at 2.0 Ga. Although the constraints set by geological records such as mass independent fractionation of sulfur (i.e., < 10⁻⁶ atm prior to ~ 2.45 Ga, > 10⁻⁶ atm at 2.32 Ga and > 10⁻³ atm at < 2.0 Ga) were not used for the calculations, the atmospheric oxygen evolution model proposed here is consistent with these constraints.

Keywords: Fe(II) oxidation rate, low oxygen, weathering, atmospheric oxygen evolution

Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

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U020-07

Room:304

Time:May 23 10:45-11:10

Perspectives on resource geology

Yasuhiro Kato^{1*}

¹University of Tokyo

Here I present several examples of my current researches on resource geology. One is a research on a new type of submarine mineral deposit that may potentially produce huge amounts of rare-earth resource. Last September, a "rare-earth shock" accompanied the announcement that China would reduce its exports of rare-earth elements to the West. The newly-discovered mineral deposit may break such a concern about a deficient supply of rare-earth resource to the world in the future. Secondly, I discuss about a genesis of Besshi-type Cu deposits in the Sambagawa metamorphic belt in Japan. The Besshi-type Cu deposits are strata-bound volcanogenic massive sulfide deposits that were the ancient counterparts of modern Cu-rich seafloor massive sulfide deposits and were formed/preserved as products of environmental changes of the Earth's surface. Finally, I present a new concept on origins of hydrothermal deposits in the Japanese island arc. These hydrothermal deposits in the island arc crust may have been directly formed from slab-derived fluids in the deep crust.

U020-08

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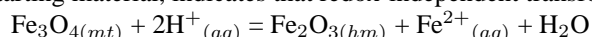
Mechanisms of Iron Oxide Transformations in Hydrothermal Systems

Tsubasa Otake^{1*}, David J. Wesolowski², Lawrence F. Allard², Lawrence M. Anovitz², Hiroshi Ohmoto³

¹Dept. of Earth Science, Tohoku Univ., ²Oak Ridge National Laboratory, ³Penn State University

Coexistence of magnetite and hematite is observed in various hydrothermal systems (e.g., banded iron formations (BIF), seafloor hydrothermal systems, volcanogenic massive sulfide (VMS) deposits, iron oxide copper gold ore (IOCG) deposits). They have often been used to constrain the redox potential of fluids, assuming that the redox equilibrium is attained among all minerals and aqueous species. However, as temperature decreases, disequilibrium mineral assemblages may occur due to the slow kinetics of reaction involving the minerals and fluids. In this study, we conducted a series of experiments in which hematite or magnetite was reacted with an acidic solution under H₂-rich hydrothermal conditions (T = 100-250 degree C, P of hydrogen = 0.05-5 MPa) to investigate the kinetics of redox and redox-independent transformations between hematite and magnetite, and the mechanisms of iron oxide transformation under hydrothermal conditions.

The formation of euhedral crystals of hematite in 150 and 200 degree C experiments, in which magnetite was used as the starting material, indicates that redox-independent transformation of magnetite to hematite occurred within 24 hours:



The chemical composition of the experimental solutions was controlled by the redox-independent transformation between magnetite and hematite throughout the experiments. While solution compositions were controlled by the redox-independent transformation in the first 3 days in a 250 degree C experiment, reductive dissolution of magnetite became important after 5 days and affected the solution chemistry. At 100 degree C, the presence of maghemite was indicated in the first 7 days. Based on these results, equilibrium constants of redox-independent transformation between magnetite and hematite and those of redox-independent transformation between magnetite and maghemite were calculated. Our results suggest that the redox transformation of hematite to magnetite occurs in the following steps: (1) reductive dissolution of hematite to Fe²⁺(aq) and (2) non-redox transformation of hematite and Fe²⁺(aq) to magnetite.

We propose that transformation mechanisms observed in the experimental study are applicable to various natural systems involving low-temperature hydrothermal solutions. For example, coexistence of magnetite and hematite is commonly observed in typical oxide-type BIFs. Many geochemical and mineralogical studies (e.g., Hoashi et al., 2009) suggested that hematite is a primary mineral in the BIFs, and that magnetite is a transformation product of primary hematite. Our study showed that redox-independent transformation of hematite to magnetite is a plausible process in the BIFs, by a reaction between primary hematite and Fe²⁺-rich hydrothermal fluids during early diagenesis. An important implication in considering the origin of magnetite in BIFs is that magnetite was likely formed under the conditions where the system was far from redox equilibrium. Therefore, the presence of magnetite in BIFs cannot be used to constrain the atmospheric or oceanic oxygen levels during the deposition of BIFs.

Reference

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Keywords: hydrothermal system, iron oxide, redox reaction, banded iron formation, hematite, magnetite

U020-09

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Time:May 23 11:25-11:40

Influence of size, morphology and aggregation state on reductive dissolution of hematite nanoparticles

Takuya Echigo^{1*}, Deborah M. Aruguete², Mitsuhiro Murayama², Michael F. Hochella Jr.²

¹JIRCAS, ²Virginia Tech

Nanoscale iron (oxyhydr)oxide minerals are omnipresent in natural environments and initial studies have found their size can influence chemical reactivity, e.g., dissolution kinetics. Their dissolution behavior is important because it influences the bioavailability of nutrients for plant growth and the migration of pollutant metals and organic compounds. In natural environments, reductive dissolution is the most important dissolution mechanism (Sulzberger et. al. 1989). Madden and Hochella (2005) reported the oxidation of Mn²⁺ catalyzed by hematite nanoparticles depended upon nanoparticle size. These results suggest that other redox reactions occurring on hematite surfaces may be size-dependent as well. In this study, we have investigated the size dependence of the reductive dissolution of hematite with ascorbic acid using two types of nanoparticles with average diameters of 7 nm and 30 nm.

Hematite nanoparticles were synthesized by forced hydrolysis of ferric nitrate and characterized with powder XRD, TEM, and BET surface area measurements. Reductive dissolution experiments were carried out in continuously stirred Teflon beakers at 302 K in the absence of light under approximately 1 atm nitrogen gas. Aqueous [Fe(II)] was measured by the ferrozine assay. The evolution of crystal morphology by reductive dissolution was examined by high resolution TEM (HRTEM). In addition, electron tomography technique was employed to understand the real three-dimensional structure of individual particles and aggregates. This technique allows us to reconstruct 3D images from a series of TEM images taken from an area of interest. HRTEM revealed that the 7 nm hematite crystals are pseudo-hexagonal plates and the 30 nm hematite crystals are rhombohedral. Hematite nanoparticles of both sizes have defective surfaces. The two types of dissolution rates, initial rate and steady state rate, were determined and compared after surface areanormalization. The surface area-normalized initial rates of reductive dissolution are more than 2 times greater in 7 nm hematite. However, no significant size dependence is observed for steady state rates. TEM observation of individual crystals and aggregates of partially-dissolved hematite reveal that dissolution initiates from surface defects or sharp edges on crystals. Also, aggregation state changes as the dissolution progresses. This study directly shows the importance of surface roughness, defects, crystal morphology and aggregation states on dissolution rates.

Keywords: Hematite, dissolution kinetics, particle size, crystal morphology, aggregation state, transmission electron microscopy

U020-10

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Time:May 23 11:40-11:55

Iodine speciation and $^{129}\text{I}/^{127}\text{I}$ ratios in sedimentary rocks in Horonobe, Hokkaido

Yoko Shimamoto^{1*}, Yoshio Takahashi¹, Yuki Amano², Hiroyuki Matsuzaki³, Yasuyuki Muramatsu⁴, Teruki Iwatsuki²

¹Hiroshima Univ., ²JAEA, ³Univ. of Tokyo, ⁴Gakushuin Univ.

Introduction

Iodine-129 is one of the most problematic radionuclides, which is produced by nuclear related activities such as nuclear power generation and nuclear fuel reprocessing, because of its long half-life (15.7 million years) and high mobility. To investigate behavior of iodine in sedimentary rocks is important to evaluate the effectiveness of the natural barrier for nuclear waste repositories. In Horonobe area, iodine rich brine exists in deep underground. The region is underlain mainly by Neogene to Quaternary marine sedimentary rocks, the Wakkanai Formation (Wk Fm), and the overlying Koetoi Formation (Kt Fm): siliceous and diatomaceous shale. We determined iodine distribution, speciation, and isotope ratio ($^{129}\text{I}/^{127}\text{I}$), to investigate long-term migration of iodine in diatomaceous and siliceous shale.

Experiment

All core and groundwater samples were collected by at JAEA Horonobe underground research center. Iodine concentrations in groundwater samples were determined by ICP-MS. For core samples iodine was separated by pyrohydrolysis or alkaline extraction (using Tetramethyl ammonium hydroxide) and determined by ICP-MS. Iodine species in groundwater were separately detected by high performance liquid chromatography (HPLC)-ICP-MS, using anion exchange column and size exclusion column for separation of IO_3^- and I^- , and organic and inorganic iodine, respectively. Iodine species in core samples were determined by iodine K-edge XANES (SPring-8 BL01B1). Thin sections of core samples were prepared, and iodine mapping were obtained by micro-XRF analysis (SPring-8 BL37XU). $^{129}\text{I}/^{127}\text{I}$ ratios in groundwater and core samples were measured by accelerator mass spectrometry (MALT, Univ. of Tokyo).

Results and discussion

Concentration of iodine in groundwater varied widely and was much higher than that of seawater with high correlation with that of chlorine ($R^2 = 0.90$). Iodine in core samples decreased near the boundary between Wk and Kt Fm. Iodine existed as I^- in groundwater, while that in shale was a mixture of organic and inorganic I. Iodine mapping showed that iodine accumulated to micro region (< 30 micron). Iodine isotope ratios ($^{129}\text{I}/^{127}\text{I}$) were higher in siliceous shale compared with that of groundwater. According to these results, migration of iodine in this area can be expected as follows; 1) iodine accumulated as organic iodine in siliceous sediment, 2) iodine was released from layers deeper than Wk Fm during diagenetic process where I^- was dissolved into iodine-rich groundwater, 3) iodine-rich groundwater was distributed to Wk and Kt Fm due to the compaction of the layers, 4) both iodine and chlorine were diluted by freshwater from the surface.

It was suggested that I^- is released to the ground water during the maturation of organic matter. Dissociated I^- can move toward the surface because of the upward water flow driven by compaction. Thus, iodine rich brine is created by integration of iodine released from underlying formation. Because of high mobility of I^- , released I^- remains in solution phase, and concentration of the iodine in solution has increased during sedimentation history.

Keywords: Iodine, XANES, HPLC-ICP-MS, Iodine isotope ratio

U020-11

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Time:May 23 11:55-12:10

The effect of secondary mineral formation for the migration behavior of iodine at hyperalkaline springs in Oman

Sohtaro ANRAKU^{1*}, Jun Hoshino¹, Kazuya Morimoto², Tsutomu Sato³, Tetsuro Yoneda³

¹Graduate School of Eng., Hokkaido Univ., ²Advanced Industrial Science & Technology, ³Faculty of Engineering, Hokkaido Univ.

In Japanese transuranic (TRU) waste disposal facilities, ¹²⁹I is the most important key nuclide for the long-term safety assessment. Thus, the distribution coefficients (K_d values) of I to natural minerals are important factor in the safety assessment. However, the degradation of cement materials in the repositories can produce high pH pore fluid which can affect the anion transport behaviour. Therefore, it should be necessary to understand the behaviour of anions such as I⁻ under the hyperalkaline conditions.

This study examined the naturally-occurring hyperalkaline conditions near the springs in Oman as natural analogue for the interaction between cement pore fluid and natural Mg-HCO₃⁻ river water. The generated natural hyperalkaline spring water (pH>11) from the partly serpentinized peridotite in the Oman ophiolite is characterized as hyperalkaline, reducing, low-Mg, Si and HCO₃⁻, and high-Ca while the river water where the alkaline spring, is moderately alkaline, oxidizing, high-Mg and HCO₃⁻. The mixing of these spring and river water resulted in the formation of secondary minerals, forming river terrace with height of more than 10 meters. The present aim of this paper is to examine the conditions of secondary mineral formation and the anion uptake capacity of these mineral phases generated. The long-term stability of this sorption behaviour in this system was also investigated.

Water and precipitate samples were collected at various distances from the spring vent to identify the effect of mixing ratios between spring and river water on mineral composition and water-mineral distribution coefficient of various anions. On-site synthesis was also carried out to support these data quantitatively. Furthermore, samples of deposits were collected from the river terrace at different height which corresponds approximately to the depositional age in order to find out the alteration of minerals and possible anion desorption.

The results of the mineralogical and chemical characterization of the collected samples confirmed that the formation of secondary mineral was dominated by aragonite at the mixing points of the spring and surface water, due to high Mg content of the latter. Hydrotalcite like compound (Mg-Al hydroxides) was also detected as accessory minerals since the hyperalkaline springs contain relatively rich in Al.

During the formation of the minerals at the mixing points, HCO₃⁻ in the river water was fixed as carbonate minerals in aragonite and calcite phases while H₃SiO₄⁻ in the river water was dominantly fixed into the interlayers and surfaces of HTlc. Iodine in spring and river water was mainly fixed in aragonite. XRD quantitative analysis by Rietveld method indicated K_d values of iodine increase proportionally to the aragonite content in the precipitate samples. Consequently, in terms of short-term assessment, particularly for I⁻, uptake by secondary minerals can be expected at hyperalkaline conditions as observed at Oman hyperalkaline springs.

Keywords: calcium carbonate, iodine, aragonite, calcite, hydrotalcite, natural analogue study

U020-12

Room:304

Time:May 23 12:10-12:35

Morphology, physiology, and ecology of the fish inhabiting highly alkaline environments in Oman

Masakazu Suzuki^{1*}, Hisashi Sato²

¹Fac. Sci., Shizuoka Univ., ²Grad. Sch. Sci., Shizuoka Univ.

Hyperalkaline hot springs (pH11-12) occur in and beside the rivers in the mountain area of the Sultanate of Oman. The aim of this study is to identify the species of fish inhabit the highly alkaline environments around the springs, and to reveal the histological and physiological mechanisms for the adaptation of these vertebrates, which would be important for the understanding of not only the ability of adaptation in vertebrates, but also the ecosystem in Oman. In December, 2009, and December, 2010, we carried out field research at Bat, Faydh, Fizh, and Hilti, and identified *Garra barreimiae*, *Cyprinion microphthalmum*, and *Aphanius dispar*. *G. barreimiae* and *C. microphthalmum* were very common at Bat, Faydh, Fizh, and Hilti, and *Aphanius dispar* was found in Fizh. To examine the tolerance of *G. barreimiae* to high alkalinity, we transferred the fish to the mixtures of hot spring water and river water. It was revealed that *G. barreimiae* died in the 80% alkaline spring water, but survived in the 70% spring water. Intriguingly, after exposed to the 70% spring water for 24 hours, the fish tended to survive even in the 80% spring water, suggesting that crucial physiological changes occurred in the fish exposed to the 70% spring water.

In the morphological analysis of *G. barreimiae*, whole fish and scales were stained with alizarin red and alcian blue. The material of vertebral column was found to be bone. The head skeleton mainly calcified, whereas the surface area and lower jaw appeared to consist of cartilage. For fins, the proximal part ossified, while the distal part was cartilaginous. Remarkably, the scales were cartilaginous, in contrast to the bony ones of other teleosts such as goldfish and medaka. However, the scales of the fish around alkaline hot springs also were not different from those of the fish upstream of the river. Further study is needed to elucidate whether cartilaginous scales have any physiological roles in the adaptation of *G. barreimiae* to the highly alkaline water. Staining histological sections of the skin with hematoxylin and eosin localized mucus cells in the epidermis. The gills were also analyzed by staining histological sections with hematoxylin and eosin. Mucus cells and/or chloride cells were detected in the gill filaments, and localized beside the base of lamellae. The gill filaments were further examined using a transmission electron-microscope. Chloride cells and mucus cells were observed beside the base of lamellae, confirming the localization of these cells by hematoxylin-eosin staining. It would be important to study the physiological roles of chloride cells and mucus cells in the adaptation of the fish to highly alkaline environments.

Keywords: Oman, highly alkaline environment, fish, animals

Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

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U020-13

Room:304

Time:May 23 14:15-14:40

A new Central dogma for life in the Universe after 1958

Ken Takai^{1*}

¹SUGAR Project & PEL, JAMSTEC

It is more than 10 years since a session dedicated to interaction of "Life-Water-Mineral-Atmosphere" (initially "Life-Water-Mineral") was established in JpGU Meeting. Every year, lots of examples and case studies for understanding the interaction of "Life-Water-Mineral-Atmosphere" were presented and there were increasing enthusiasm and passion in discussion at this session. The session is now a place of very ordinary scientific discussion and communication but not a special opportunity for meeting of different fields of scientists any more. Probably due to its foreseen role in the JpGU, this session evolves to an Union session from a Baiogeosciences session this year.

Depth of interdisciplinary discussion at this session has become greater in recent years. However, it is also frequent that discussion goes like skew lines between the scientists of different background fields. As one of the possible rational horizons, an energy mass balance concept of life, habitability or interaction between Life and Environment has been pointed. This concept is commonly applicable to any living system in everywhere of the Earth, in any the scale and the period, and even in the Universe. In other words, it can be a principal rationale for the interdisciplinary scientists comprehensively to approach "Life", and can be much more crucial than "Central dogma" for life stated by Francis Crick in 1958 and re-stated in a Nature paper published in 1970. It is uncertain why Everett Shock, Tori Hoehler and their groups, primary researchers of biogeochemistry of microbial energy metabolisms, have never declared so, but I would like to propose that an energy mass balance concept of life, habitability or interaction between Life and Environment is a new "Central dogma" for life.

Keywords: habitability, central dogma, energy mass balance

U020-14

Room:304

Time:May 23 14:40-14:55

A new approach for clarifying the population genetic structure of chemoautotrophic bacteria in deep-sea hydrothermal fields

Sayaka Mino^{1*}, Satoshi Nakagawa¹, Hiroko Makita², Fumio Inagaki², Masahiro Yamamoto², Takuro Nunoura², Koichi Nakamura³, Anne Godfroy⁴, Ken Takai², Tomoo Sawabe¹

¹Hokkaido Univ., ²JAMSTEC, ³AIST, ⁴IFREMER

Deep-sea hydrothermal fields are areas on the seafloor of high biological productivity fueled primarily by microbial chemosynthesis. Chemoautotrophic Epsilonproteobacteria utilizing inorganic substrates such as H₂S and H₂ are dominant in deep-sea hydrothermal vents around the world. Beside deep-sea chemoautotrophs, the class Epsilonproteobacteria contains important human pathogens, i.e. *Helicobacter pylori* and *Campylobacter jejuni*. Previous population genetic studies about these pathogenic Epsilonproteobacteria have revealed that they have extremely high rates of genetic mutation and recombination. However, little is known about the population genetic structure of deep-sea Epsilonproteobacteria. In this study, we performed multilocus sequence analysis (MLSA) on deep-sea Epsilonproteobacteria to clarify their population genetic structure.

Epsilonproteobacterial strains used in this study were isolated from geographically separated hydrothermal fields by using dilution-to-extinction method. We focused on strains sharing similar 16S rRNA gene sequences. Based on some housekeeping gene sequences, various population genetic analyses including the construction of phylogenetic trees were performed.

The phylogenetic trees inferred from all concatenated loci led to the identification of geographic barriers isolating Epsilonproteobacterial populations, although 'everything is everywhere; the environment selects' is widely accepted in microbiology.

In our presentation, the biogeography and evolution of deep-sea Epsilonproteobacteria will be discussed.

U020-15

Room:304

Time:May 23 14:55-15:20

Iron supply processes which support biological production in the western subarctic Pacific

Jun Nishioka^{1*}

¹Hokkaido University, ILTS

Iron is an essential nutrient and plays an important role in the control of phytoplankton growth. Atmospheric dust has been thought to be the most important source of iron, supporting annual biological production in the Western Subarctic Pacific (WSP). We argue here for another source of iron to the WSP. Multi-year (2003-2008) time series observations along the A-line provided information on the temporal variability of the dissolved iron (diss-Fe) concentration in the Oyashio region of the western subarctic Pacific and the data indicate that an annual cycle of surface diss-Fe occurs every year. Diss-Fe was supplied into the surface water in this region every winter and supports the spring phytoplankton bloom after development of the thermocline. The diss-Fe concentration was drawn down during the phytoplankton bloom period, and was depleted in summer in some water masses. Then diss-Fe increased from autumn to winter with the increasing depth of the surface mixed layer. The high diss-Fe concentrations in the surface layer in winter were controlled by mesoscale oceanic intrinsic processes, such as vertical winter mixing and horizontal Fe-rich intermediate water transport. Difference in magnitude of the winter mixing processes among different water masses caused the heterogeneous distribution of diss-Fe concentration in the surface layer. Moreover, the vertical section profiles along a cross-Oyashio transect showed the occurrence of Fe-rich intermediate water, and upward transport of materials from the intermediate water to the surface layer via winter mixing processes are important mechanisms to explain the high winter surface diss-Fe concentrations. Additionally, the substantially higher diss-Fe/NO₃ ratio in the winter surface layer in this studied area than the other HNLC region indicating that the winter surface water in the Oyashio and the Oyashio-Kuroshio transition zone has a high potential to stimulate phytoplankton growth.

Keywords: ocean, iron, supply processes, phytoplankton

U020-16

Room:304

Time:May 23 15:20-15:35

Comparison of crystallographic texture coral skeleton with synthesized aragonite

Satoko Motai^{1*}, Takaya Nagai¹

¹School of Science, Hokkaido Uni

Coral skeletons are constituted of aragonite (CaCO_3). Aragonite is a metastable phase compared to calcite under the coral growing environment. The growth process of aragonite has been interested for long years but not been revealed clearly, although it should be greatly important for the reconstructing paleoclimate using variation of the trace elements and isotope in coral skeletons.

Organic matters play important role in biomineralization, and sometimes control the growth texture of minerals. For example, the nacre of the shell is composed of layered aragonite platelets shaped hexagonal and the crystallographic c-axis normal to the plane of platelets. It is well known that organic matrix sheets between the platelets control the formation of mineral texture in nacre. However aragonite crystals in coral skeletons formed by biomineralization show needle-like shape and elongate along the c-axis.

In this study, we compared mineral textures of the synthetic of aragonite with natural coral skeleton in order to consider the biomineralization process of coral skeleton growth.

Synthetic aragonite was prepared by precipitating from quasi-seawater without organic matrix at 25 degrees C. Observation was made by using a scanning microscope and a transmission electron microscope.

Keywords: coral skeleton, aragonite

U020-17

Room:304

Time:May 23 15:35-15:50

Effects of magnesium ion on alteration rate and solubility of hydrated calcium carbonate

Takashi Munemoto^{1*}, Takashi Murakami¹

¹The University of Tokyo

INTRODUCTION

Calcium carbonates are abundant in nature. There are six distinct calcium carbonate species. Anhydrous polymorphs are calcite, aragonite, and vaterite, and hydrated forms are monohydrocalcite (monohydrate), ikate (hexahydrate), and amorphous calcium carbonate. Although calcite is most stable among these six phases, solutions containing Mg^{2+} , SO_4^{2-} , and organic matter, such as sea waters and brines have been known to inhibit the formation of calcite [1]. Monohydrocalcite have been found in saline and alkaline lakes and sea water environment [2]. Monohydrocalcite is metastable unlike anhydrous calcium carbonates and transformed to aragonite in aqueous solutions [3]. However there have been few studies that examine the metastability of monohydrocalcite quantitatively. In the present study, effects of magnesium ion on the alteration rate of monohydrocalcite to aragonite and on the solubility of monohydrocalcite have been examined in the laboratory experiments.

METHODS

Monohydrocalcite was synthesized by mixing solutions containing 60 mM $CaCl_2$ and 6, 30, 45, 60, and 120 mM $MgCl_2$ ([Mg]/[Ca] ratio was 0.1 to 2), where Na_2CO_3 was added to yield a 80 mM CO_3^{2-} solution. The resulting suspension was collected every several hours and filtered through a 0.22 μ m membrane. Total alkalinity of filtered solutions were evaluated by acid titration and the total concentrations of Ca^{2+} and Mg^{2+} were measured with inductive coupled plasma optical emission spectrometry (ICP-OES, SII SPS7700). The filtered solid were air-dried, and analyzed by X-ray diffraction (XRD, Rigaku RINT2000). The amounts of monohydrocalcite and aragonite contained in the resulting solid were evaluated by the external standard method [4]. Solubility products of monohydrocalcite were calculated by Geochemist's Workbench [5] based on total alkalinity, total concentrations of cations, and pH.

RESULT AND DISCUSSION

Monohydrocalcite formed when mother solution contained Mg^{2+} of 30, 45, 60, and 120 mM. XRD analyses revealed that aragonite was formed 78-98, 101-126, 79-106, and 101-126 hours after beginning of the experiments of 30, 45, 60, and 120 mM of Mg^{2+} , respectively. After aragonite was formed, the peak intensity of monohydrocalcite decreased with time, while that of aragonite increased with time. Alkalinity, Mg^{2+} , and pH of the solution gradually decreased with time. Ca^{2+} increased with time until XRD peak intensity of monohydrocalcite completely disappeared. After monohydrocalcite disappeared, Ca^{2+} slightly decreased. The increment of Ca^{2+} resulted in decrement of alkalinity, because the concentrations of dissolved components must be determined by a solubility product of solid phase. The calculated solubility products of monohydrocalcite were constant in the series of Mg^{2+} concentrations, but different among experimental conditions. The solubility products of monohydrocalcite may be affected by the concentration of Mg^{2+} in solution. However, our result suggests the induction time of transformation of monohydrocalcite to aragonite were not affected macroscopically by Mg^{2+} contents in mother solutions.

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Keywords: calcium carbonate, metastable, alteration rate, solubility

U020-18

Room:304

Time:May 23 15:50-16:05

Biogeochemistry of laminated travertines in Central Java, Indonesia

Tomoyo Okumura^{1*}, Chizuru Takashima², Fumito Shiraishi¹, Akmaluddine³, Akihiro Kano¹

¹Kyushu University, ²Saga University, ³Kyushu University

Travertines are calcite or aragonite precipitates from hot-spring water containing a sufficient amount of calcium and carbon dioxide. Most of travertines show sub-mm order laminations that were formed by daily microbial activities. Two previous studies have suggested different processes in terms of responsible microbe for lamina formation; cyanobacteria that can grow and trap detritus on the travertine surface in the daytime and heterotrophic bacteria that can quickly degrade organic matter from cyanobacteria on the travertine surface in the daytime. The former model was consistent to some calcite travertines (e.g. Takashima and Kano, 2008) and an aragonite precipitates on microbial mat (Okumura et al. 2010), while the latter model was confined to one aragonite travertine (Okumura et al. 2011). Here, we study a huge travertine mound in Indonesia to consider the applicability of these processes for the diverse laminated texture of the travertines.

Pancuran Pitu is one of the hot springs that occur around Mt. Slamet, an active stratovolcano in Central Java, Indonesia. Here, a huge travertine mound was formed along the water passage flowing on the mountain surface, which is 180 m long, 60 m wide and 70 m relative elevation. The water temperature was 51°C at the vent, 45 to 35°C at the mid stream, and decreased to 29°C at the downstream. pH increased from 6.2 to 8.3, and Ca²⁺ concentration decreased toward the downstream (273 to 100 ppm) with respect to CO₂-degassing and CaCO₃ precipitation. The other chemical components were constant throughout the water passage. The mineralogy of the travertines was mainly aragonite throughout the mound, which likely reflects high Mg/Ca molar ratio (1.6 to 3.8) in water. Three types of travertine were observed in the mound; (1) brown hard travertine at the upper stream, (2) light yellow friable travertine with green microbial mats at the midstream, and (3) light yellow crystalline hard travertine at the downstream cascade. All types of travertines have sub-mm order lamination, however irregularity in the lamina thickness was recognized only in the brown hard travertine formed near the vent where the water had the highest temperature and iron concentration. The lamination of the brown travertine was unlikely formed by the daily cycle. Light yellow crystalline travertine was formed only under high flow condition as in the cascade, while friable travertine with green microbial mat was formed under low flow condition. The microbial abundance in the friable mat increased with decreased water flow and temperature. Observation using fluorescence microscope revealed that distribution of phototrophs along the lamination was only recognized in the friable travertine with microbial mat, but not in the other types of travertines, in which some other microbes were responsible for the lamination.

The difference in depositional conditions, such as temperature and water flow, resulted in different types of laminations that were likely formed by different microbial processes. Understanding such variations provide some useful information for interpretation of the ancient stromatolites.

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Keywords: travertine, lamination, aragonite, Central Java

U020-19

Room:304

Time:May 23 16:30-16:55

Animal multicellularity induced by the snowball Earth

Akihiro Kano^{1*}

¹Kyushu University

Late Neoproterozoic is a period of climatic changes and animal evolution. It is still unknown whether there is a strong crucial link between the two events. However, one can believe the presence of the linkage if any biological evolution has progressed with biological effort to overcome the environmental tribulation. Recent advance in Neoproterozoic earth sciences permits discussion on this subject.

Currently well-accepted idea is that increased oxygen concentration induced the animal evolution. Here, the accumulated nutrients induced explosive photosynthesis immediately after the Marinoan snowball (635 Ma), and the raised oxygen supported collagen formation and animal respiration. In fact, this hypothesis fits well with the evolution of bilaterians (~550 Ma). However, the distinct ocean oxygenation was far much later (~585 Ma), and more primitive animals have already appeared before.

Primitive animals, sponges and cnidarians, also have evolved during a period of the Neoproterozoic climatic change. In order to understand their evolution, the stratified ocean can be taken into account. Nutrient source for the high productivity of the post-snowball ocean was unlikely from hydrothermal but rather from continental weathering because of the high Sr isotopic ratios. Thus, weak upwelling could not homogenize the water column, and the low-density and ice-molten water sealed the ocean. Huge amount of organic matter was at least partly suspended at the density gradient and provided food for animals. Similar circumstances can be seen in habitat of the modern deep-sea coral reefs. In addition, this hypothesis fits the fact that the primitive multicellular animals are all filter feeders (Kano et al., in press). Keyword for the evolution existed in food rather than oxygen.

The most primitive multicellular animal, a sponge, was likely originated from choanoflagellate. This filter-feeding protozoa is morphologically similar to the choanocytes of sponges, and genetically encoded for cell adhesion as preadaptation for multicellularity. Further interesting characteristics is symbiotic microbes in the sponge body. Microbes extracted from the cell-adhering matrix are sponge specific, and appear similar association independently with species and geographic distribution. Thus, Hentschel et al. (2002) hypothesized that they have own evolution since the appearance of the sponges. The sponge specific microbes include Chloroflexi group and delta-proteobacteria, for which a suitable habitat is redox interface. They were probably captured when choanoflagellates gather the suspended organic matter, stopped swimming in oxygen-poor water, and became multicellular.

Hentschel, U. et al. (2002) Molecular evidence for a uniform microbial community in sponges from different oceans. *Applied and Environmental Microbiology*, 68, 4431-4440.

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Kano, A. et al. (in press) The evolution of animal multicellularity stimulated by dissolved organic carbon in early Ediacaran ocean: DOXAM hypothesis. *Island Arc*.

Keywords: Neoproterozoic, Sponges, Ocean stratification

U020-20

Room:304

Time:May 23 16:55-17:10

Role(s) of oxygenic photosynthesis in Precambrian stromatolite formation

Fumito Shiraishi^{1*}

¹Kyushu University

Stromatolite is a microbial sedimentary structure formed by the life-water-mineral interactions, and widely spread especially in Precambrian sedimentary successions. The key process in stromatolite formation is mineral precipitation by microbial metabolisms for producing and consolidating the deposits, while particle trapping/binding and crystal nucleation by microorganisms play rather passive roles. Among the metabolisms, oxygenic photosynthesis, which appeared in Archean, is expected to be one of most important metabolism for stromatolite formation throughout the Earth history, because it can induce CaCO_3 precipitation and occur in a wide range of shallow marine environments where light and dissolved inorganic carbon (DIC) are available. However, the researches based on modern open marine stromatolite suggested that carbonate mineral precipitated by photosynthesis is dissolved by aerobic respiration, and results in little or no net precipitation (Reid et al. 2000, Nature 406, 989-992). In addition, the researches based on numerical simulations suggested that the influence of photosynthesis on carbonate mineral precipitation is negligible in high DIC condition such as Precambrian ocean (Arp et al. 2001, Science 292, 1701-1704; Aloisi 2008, GCA 72, 6037-6060). Nevertheless, these suggestions based on indirect observations, which are still need to be confirmed by direct measurement.

The present study measured chemical profiles of pH, O_2 , CO_2 , Ca^{2+} and CO_3^{2-} at the stromatolite surface using micro-electrodes, in order to evaluate the actual influences photosynthesis on stromatolite formation. The measurements conducted in natural water condition revealed that photosynthesis significantly induced CaCO_3 precipitation, while the influence of respiration on carbonate chemistry was negligible and no detectable dissolution was observed. The measurements conducted in various DIC condition revealed that photosynthesis significantly induced precipitation even in high DIC condition (up to 300 mM), indicating that tiny influence of photosynthesis on carbonate chemistry is sufficient for inducing precipitation if ambient saturation is high enough.

Therefore, it is considered that oxygenic photosynthesis played important role(s) in stromatolite formation even in Precambrian ocean.

Keywords: stromatolite, photosynthesis, cyanobacteria, microelectrode

Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

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U020-21

Room:304

Time:May 23 17:10-17:25

Impact chemical evolution processes for biomolecules formed by oceanic impacts

Nao Fukunaga¹, Toshimori Sekine^{1*}, Shunsuke Izumi², Yoshihiro Furukawa³, Takeshi Kakegawa³, Takamichi Kobayashi⁴, Hiromoto Nakazawa⁴

¹DEPSS, Hiroshima University, ²Math. & Life Sci., Hiroshima Univ., ³DEPMS, Tohoku University, ⁴NIMS

The biomolecules on Earth are thought either to have come from the extraterrestrial parts carried with flying meteorites or to have been formed on Earth from the inorganic carbon through given energy. From the standpoint to address impact energy, we need to know possible process how the simple biomolecules formed at a violent impact have been evolved subsequently through several impacts at the time of the late heavy bombardment. In this study we investigated the simplest amino acid, glycine marked by ¹³C, in order to understand how it will be evolved chemically when it is subjected to further impacts. The results indicate that some new molecules are formed and others are decomposed, and suggest not only that the impact-induced process is not so simple to proceed just to one way, but also that there are complicated and multi-process ways. It also must be taken into account the heterogeneous distribution of impact energy in an impact that may cause a significant effect on the chemical evolution.

Keywords: Biomolecules, Impact energy, Chemical evolution, Amino acids, Late heavy bombardment

U020-22

Room:304

Time:May 23 17:25-17:40

Geochemical signatures pointing to an oxygenated shallow ocean 3.2 billion years ago

Yuki Sakamoto^{1*}, Tsubasa Otake¹, Takeshi Kakegawa¹

¹Graduate school of Science, Tohoku Univ.

Timing of the emergence of oxygenic photoautotrophs (e.g., cyanobacteria) is critical to understanding the evolution of life and the earth's surface environments. Yet, no palaeontological or biochemical signature in rocks has provided unequivocal evidence for the emergence of cyanobacteria in the Archean era. Recently, Javaux et al. (2010) discovered large, well-preserved microfossils, which are possibly the remnants of eukaryotes, from sedimentary rocks of the Moodies Group, South Africa (-3.2 Gyr). Since the emergence of eukaryotes likely requires molecular oxygen, cyanobacteria is expected to have been evolved before 3.2 Gyr if the microfossils are indeed the remnants of eukaryotes. Therefore, the objective of this study was to find geochemical signatures for the emergence of cyanobacteria in a shallow ocean environment from the same stratigraphic unit as that Javaux et al. found the microfossils.

We collected 26 sample of the Moodies Group both from outcrops and underground mining sites (e.g., Sheba gold mine) in the Barberton Greenstone Belt, South Africa. Sedimentary rock samples from the Sheba mine were divided into Magnetite-Rich Shale (MRS) group and Banded Chert (BC) group. Samples in the MRS group contain quartz, magnetite, hematite, chlorite, biotite, and chromite. While fine-grained hematite (less than 5 micro meter in diameter) is interpreted as a primary mineral in the rock, large-grained (more than 100 micro meter in diameter) magnetite is interpreted as a secondary mineral transformed from hematite during diagenesis. All chromites observed in the MRS group is euhedral and overgrown by magnetite. The boundary between chromite and magnetite is sharp. These characteristics of the chromites in the MRS group indicate that they were syn-genetically formed during diagenesis. On the other hand, samples in the BC group contain quartz, siderite, chlorite, biotite, and chromite. Chromites in the BC group are included in silicate minerals (e.g., chlorite and biotite), and often unehedral crystals.

Chemical compositions of the bulk samples in the MRS group showed that U/Th ratios have a negative correlation with both Cr/Ti and Fe_{tot}/Ti ratios. This correlation is very difficult to explain if minerals containing these elements were detrital in origin, because while U is enriched in a felsic rock, Cr is enriched in a mafic rock. Furthermore, the changes in the U/Th and Cr/Ti require the oxidation of U and Cr to decouple geochemical behaviors of U relative to Th and Cr relative to Ti. Correlations of Fe_{tot}/Ti ratios with U/Th and Cr/Ti ratios indicate that dissolved Cr and U species (e.g., CrO_4^{2-} and UO_2^{2+}) in ocean were adsorbed onto the surface of ferric (hydr)oxides during the formation of iron-rich sediments. These results suggest that a part of shallow ocean was oxygenated -3.2 Gyr, containing oxidized Cr and U species, and that ferric (hydr)oxides were precipitated due to the oxidation of dissolved ferrous iron by molecular oxygen. Therefore, our findings imply that oxygenic photoautotrophs flourished in the photic zone of the 3.2 Gyr ocean.

Keywords: South Africa, hematite, magnetite, chromite

U020-23

Room:304

Time:May 23 17:40-17:55

Geological and geochemical study of Archean sedimentary rocks of the 3.0 Ga Lumby Lake Group, Canada

Kazuya Yokota^{1*}, Takeshi Kakegawa¹

¹Graduate School of Science, Tohoku Univ.

Ecosystems at ca. 3.0 Ga on the Earth's surface environments are not well understood. In particular, it is uncertain (1) whether phototrophic microorganisms were active and (2) where methanogens and methanotrophs were active. In order to answer those questions, we have conducted geological survey of sedimentary rocks of the Lumby Lake Group, located in the Atikokan area, Ontario, Canada.

Ultramafic-mafic volcanic rocks, including pillow and massive lavas and hyaloclastite were dominant in the area. In the studied area, marine sedimentary rocks, including banded iron formations (BIFs), were also observed. Black shales were spatially associated with the BIFs making alternate layer.

Petrographical and geochemical analyses were performed on the BIFs and black shales. The BIFs were composed of alternating magnetite-rich and silica-rich layers. Apatite was found in magnetite-rich zone. This support that a primary phase before magnetite was hematite (or goethite) because phosphates are easily adsorbed on Fe-(hydro) oxides. The black shales contain 0.1 to 4.3 wt% of total organic carbon and 0.0 to 24.9 wt% of Ssulfide. The carbon isotope compositions of organic carbon in the black shales showed a bimodal distribution: -47 to -38 per mil (studied area A) and -27 to -20 per mil (studied area C). The carbon isotope compositions of the black shales is negatively correlated with Ssulfide contents. The lighter values suggest the activity of methanogens and methanotrophs while the heavier values suggest the activity of photoautotrophic primary producer. Methanogens could have been active in this anoxic part of ocean water.

These shales also contain two types of pyrite: fine-grained layered type and nodular type. Layered deposition of pyrites indicates that these pyrites were formed syngenetically with other matrix materials. On the other hand, the nodular pyrites were composed of aggregates of pyrite and other sulfides (e.g., chalcopyrite, sphalerite and pyrrhotite), indicating that they were precipitated from later hydrothermal fluids. Therefore, alterations of the sedimentary rocks by submarine hydrothermal activities was widely recognized in the area.

REEs concentrations in the BIFs were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS). BIFs in the all studied area contain insignificant or positive Ce anomalies. This trend in Ce anomalies indicates that the BIFs would have formed in low oxygen condition. On the other hand, studied area A contains significant positive Eu anomalies which contrast with studied area C having insignificant Eu anomalies. This suggests that submarine hydrothermal activities in the studied area A was more larger than studied area C. In particular, methanogens activities were constrained in very reducing bottom water environments where hydrogen from hydrothermal fluids was available.

Keywords: submarine hydrothermal activity, methanogens, phototrophic microorganisms, REEs

U020-24

Room:304

Time:May 23 17:55-18:10

Filamentous microbial fossils from Paleozoic metabasalts of Northern Chichibu Belt in western and central Shikoku Japan

Masayuki Sakakibara^{1*}, Hisanari Sugawara¹, Tomohiro Tsuji³, Minoru Ikehara²

¹Ehime University, ²Kochi University, ³Shikoku Research Institute Inc.

Metabasaltic rocks from Northern Chichibu Belt in western and central Shikoku, Japan, were found to contain filamentous microbial fossils that indicate that seafloor microbial life once proliferated within these rocks.

These fossils occur as mineralized filaments in carbonate, quartz or pumpellyite domains. Microbial clay authigenesis analogous to the encrustation of prokaryotes in modern iron-rich environments led to the preservation of filaments. The filaments predominantly consist of iron oxide, phengite and pumpellyite. They were found from the northern Chichibu metabasalt.

Delta 13C values in calcite from fossil-bearing metabasalts range from -2.49 to +0.67 per mil in the northern Chichibu belt.

The biogenicity of the filaments is indicated by (1) their size, shape, and branching patterns, which resemble those of modern microorganisms, especially in terms of a constant diameter along the length of curved filaments; (2) the lack of a relationship between filament location and crystal faces or cleavage planes; and (3) their spatial clustering in interstitial domains within basalt.

The putative filamentous microorganisms thrived after the formation of basalt, during the late Paleozoic but before the Early Jurassic timing of accretion. The present results indicate that cryptoendolithic life was once present within water-filled vesicles of pre-Jurassic intraplate basalts. The filament mineralogy can be explained by the low-grade metamorphic recrystallization of authigenetic microbial clay formed by the encrustation of prokaryotes in modern iron-rich environments. This finding suggests that a previously unrecognized niche for life exists within intraplate volcanic rocks in low-grade metamorphosed accretionary complexes.

Keywords: western and central Shikoku, accretionary complex, Northern Chichibu Belt, Paleozoic, basalt, filamentous microbial fossil