

Bioavailable energy distributions in the hydrothermal systems on Enceladus and early Earth

SHIBUYA, Takazo^{1*}; SEKINE, Yasuhito²; RUSSELL, Michael³; TAKAI, Ken¹

¹JAMSTEC, ²University of Tokyo, ³Jet Propulsion Laboratory

A recent research by Cassini spacecraft suggests that there are silica nanoparticles in Saturn's E-ring derived from the Enceladus plume (Hsu et al., submitted). The findings of silica nanoparticles imply active water-rock reactions. Furthermore, an experimental study simulating the reactions between chondritic material and alkaline seawater revealed that the formation of silica nanoparticles requires hydrothermal reactions at temperatures higher than 100 deg. C (Sekine et al., submitted). Considering a short residence time of nanoparticles in the ocean, these studies imply geologically-recent or on-going hydrothermal activity in the Enceladus' subsurface ocean. Therefore, we modeled possible hydrothermal fluid/rock reactions and bioavailable energy in the mixing zone between hydrothermal fluid and seawater on Enceladus. The thermodynamic calculations of reactions between CI chondrite and alkaline NaCl-NaHCO₃ seawater at 100 deg.C indicate that the pH of fluid increases up to about 10 and hydrogen concentration in the fluid is elevated up to 20 mmolal through the water/rock reaction. Based on the estimated fluid compositions, we calculated chemical property of the mixing zone between seawater and hydrogen-rich alkaline hydrothermal fluid, which revealed that a certain level of bioavailable energy is derived from redox reactions based on CO₂ and H₂ in the mixing zone whereas there are unlikely other electron acceptors such as sulfate and nitrate that are abundant in the terrestrial seawater. Thus, the CO₂-H₂ pair can be used for possible metabolic reaction, namely hydrogenotrophic methanogenesis and acetogenesis. In the low-temperature zone, the available energy of the Enceladus methanogenesis is higher than that of methanogenesis in the Rainbow field (Mid-Atlantic Ridge) where methanogens are certainly separated. It is therefore highly possible that H₂-based energy metabolisms have been generated in the Enceladus hydrothermal vent system. Considering that the most ancient metabolisms in the Hadean terrestrial hydrothermal vent system could be also H₂-based redox reactions, there is an energetic similarity between hydrothermal vent systems on Enceladus and Hadean Earth. The future exploration of Enceladus' plume would potentially provide clues to the origin of life on Earth.

Impact-induced D/L chiral changes of valine in early Earth's oceans

SEKINE, Toshimori^{1*} ; TAKASE, Atsushi¹ ; FURUKAWA, Yoshihiro² ; KAKEGAWA, Takeshi² ; KOBAYASHI, Takamichi³

¹Hiroshima University, ²Tohoku University, ³National Institute for Materials Science

It has widely known that proteins are composed of L-amino acid monomers and that nucleic acids contains exclusively D-sugars. Homochirality selection may be contributed to the consequence of life materials and their generation conditions. Regarding the enantiomeric excess in biomolecules, there are several proposals at present. Because the enantiomeric excess occurs in photoreactions by circularly polarized light, it has been believed that interstellar environments play an important role to the formation of chiral amino acids identified in chondrites and interstellar ices. However, it is also important to know whether the enantiomeric excess of amino acids occurs during oceanic impacts or not, because the enantiomeric enrichments are known under critical states of fluids due to density fluctuations.

We have investigated the shock-induced chiral changes of valine in aqueous solution coexisting with given solids. Powders of olivine, hematite, and calcite were selected to represent solids. Hypervelocity plane impact experiments were carried out using a propellant gun. Sample solution of each of L- and D-valine in sealed steel containers was subjected to impact at velocities of about 1 km/s. The calculated shock pressures are 5-6 GPa by the impedance match solution. The recovered solutions were analyzed with LC/MS (2695 separation module; Waters Corp. and Quattro micro API; Waters Corp) after the FDLA derivatization that makes a difference in hydrophobicity between D- and L-valine. The enantiomeric excess ($ee(\%)=100(L-D)/(L+D)$), the yield of the initial valine, and shock pressure are plotted to see their relationship. The results indicate a difference among the solid. Although there was no significant change from the racemic valine solution, the reaction from L-valine to D-valine was significantly faster than that from D-valine to L-valine in calcite. The adsorption of calcite powders was checked to display no difference between D- and L-valine. These results may suggest that oceanic impacts may change the chirality of amino acids in oceans. However the enrichment of L-amino acids on the Earth need another mechanism.

Keywords: Impact-induced D/L chiral changes, D/L valine, Calcite

The oldest remnant of life in 3.8 Ga old early Archaean rocks

OHTOMO, Yoko^{1*} ; KAKEGAWA, Takeshi²

¹Kochi Institute for Core Sample Research, JAMSTEC, ²Graduate School of Science, Tohoku University

The suggestion that graphite in early Archaean rocks represents materials of biogenic origin has met with a degree of scepticism. Isotopic compositions of graphite in >3.7-billion-year-old rocks from the Isua Supracrustal Belt (ISB), western Greenland, which are believed to be of sedimentary origin, suggest that vast microbial ecosystems were present in early Archaean oceans. However, results of more recent studies suggest that most of graphite-bearing rocks were formed through interactions between crustal fluids and surrounding igneous rocks during later metasomatic events, thereby casting doubt on the existence of an extensive sedimentary sequence in the ISB and on the biogenic origin of constituents. In contrast, ¹³C-depleted graphite globules, which are considered to form from biogenic precursors, have been reported from the metamorphosed clastic sedimentary rocks in the ISB. However, these were found at a single locality. It therefore remains unclear whether traces of life at other localities in the ISB were lost during metamorphism or were originally absent. The presence of additional clastic sedimentary rocks containing graphite may provide evidence for the preservation of organic constituents in early Archaean rocks, thus supporting the notion that microbes were active in early Archaean oceans.

We conducted a geological survey along the northwestern area of the ISB. Banded iron formations contain interbedded black to grey schist layers, typically 40-80 cm thick. Rare earth element patterns in samples lie close to that in Post Archaean Australian Shale, suggesting that the protoliths of the schist was clastic marine sediments. The black-grey schist samples contain abundant reduced carbon (0.1-8.8 wt%), identified as graphite by X-ray diffraction analysis. The range of $\delta^{13}\text{C}$ values was -23.8 to -12.5 per mil (average, -17.9 per mil), which is within the range of values reported in previous studies. Scanning transmission electron microscope and high-resolution electron microscope observations present different nanoscale morphologies between the graphite of metasediment and secondary vein samples. Examined metasediment included graphitic polygonal grains and nanotubes. Sheeted flakes were a dominant morphology of secondary graphite, whereas polygonal grains and nanotubes were absent from them, suggesting a different origin from the secondarily derived graphite.

We modelled the theoretical $\delta^{13}\text{C}$ values of fluid-precipitated graphites. The lowest $\delta^{13}\text{C}$ values exceed -16.4 per mil when Rayleigh-type isotope fractionation operates in the fluids. Therefore, ¹³C-depleted biogenic organic matter in Isua clastic sediments is postulated as an initial carbon source to explain the lightest carbon isotope compositions (e.g., -23.8 per mil) in the present study. Distorted structures are common in pyrolysed and pressurized organic compounds. Such precursors commonly contain non-planar carbon ring compounds associated with abundant pores. Biogenic organic matter, which contains various molecules and functional groups, is suggested as the precursors of the graphite observed in metasediment.

In summary, the graphite in metasediment from the northwest ISB is distinct from the graphite in secondary vein samples. The combined information on geological occurrences, graphite morphologies, nanoscale structures, and isotopic compositions of the graphite in the metasediment suggests a biogenic origin of the graphite. High concentrations of ¹³C-depleted graphite in these rocks would require widespread biological activity to support the high rate of production and sedimentary delivery of organic matter to the >3.7-billion-year-old ocean floor.

Keywords: origin of life, Greenland, Isua Supracrustal Belt, graphite, remnants of life

Mineralogical and geochemical study of clastic sedimentary rocks in Barberton greenstone belt, South Africa

KAWAI, Shohji^{1*} ; KAKEGAWA, Takeshi¹

¹Graduate School of Science, Tohoku University

Cyanobacteria became active and oxidize surface ocean water in Archean. However, chronological constraint is still uncertain as to when ocean water became oxic. Some redox sensitive minerals in clastic sediments are often used to indicate the absence or presence of oxidative weathering, oxic sea water and diagenesis. Clastic sedimentary rocks in Barberton Greenstone Belt are studied by many previous investigators. However, detailed examination of redox sensitive minerals and elements are rare. Therefore, we set objectives of the present study (1) to investigate mineralogical and geochemical characteristics of clastic sedimentary rocks deposited in shallow water environments in ca.3.2Ga Moodies Group, (2) to discuss the origin of redox sensitive minerals in clastic sediments and (3) to decipher the redox conditions of the surface environments at the time of Moodies sedimentation.

We examined clastic sedimentary rocks (mainly sandstone) of the Joes Luck Formation in the Moodies Group. Samples were collected from drilled core collections of Sheba mine. All samples are belonging to Eureka Syncline blocks. Those samples are not affected by modern weathering.

The examined sandstones contained rounded quartz, K-feldspar, albite, minor zircon, and rutile. These minerals were detrital origins mainly from felsic crustal materials. Rounded chromite also occurs and we interpret that such chromite is a weathering product from mafic to ultramafic rocks. Rounded chromite is always surrounded by forming aggregates Cr-rich micas, and chromite never occurs without micas. We interpret that chromite was protected by micas, and survived from dissolution during weathering, transportation and diagenesis. Detrital pyrite and uraninite were not seen in these samples. Those mineral features indirectly indicate that presence of oxidative weathering, transportation and/or diagenesis at the sedimentation of Moodies Group. Geochemical analyses of the bulk samples indicate that most elements (e.g., Ti, Zr and V) are correlated to Al. Therefore, chemistry of examined samples are controlled by detrital components. On the other hand, Cu, Pb, Mn, and Mo are not correlated to Al, and apparently enriched in clastic sediments. Cu and Pb were mobilized in sediments during early to late diagenesis associated with late sulfide formations. Enrichment of Mn and Mo in the examined samples more reflected precipitation process from ocean water and diagenesis. In particular, enrichment of Mo is found in some samples with moderate amount of organic carbon. This suggests that Mo was dissolved in Moodies ocean water as oxidized species, and then reduced by microbial activities followed by sedimentation with organic matter. Overall results of this study suggested that oxygenic phototrophs already flourished in the photic zone of the 3.2 Ga ocean, making surface ocean water oxic.

Keywords: Cyanobacteria, Chromite, Barberton, RSE

Cerium stable isotopic fractionation as a potential paleo-redox proxy

NAKADA, Ryoichi^{1*} ; TANAKA, Masato¹ ; TANIMIZU, Masaharu² ; TAKAHASHI, Yoshio¹

¹Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, ²Kochi Institute for Core Sample Research, JAMSTEC

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 one based on the REE pattern. This study, therefore, aims to provide more quantitative 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 responds differently to various geochemical processes such as (i) oxidative scavenging on Mn oxide, (ii) precipitation as Ce(OH)₄, and (iii) adsorption of Ce³⁺ without oxidation, it is possible that Ce stable isotope ratio can give more information on redox condition in paleoenvironment.

Cerium(III) chloride solution was added to manganese oxide and iron hydroxide, respectively, with the concentration of Ce systematically changed. In both systems, pH was adjusted to 5.00, 6.80, 8.20, and 11.0 (±0.05) and shaken for 6 hours before the filtration using 0.2 μm 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 MC-ICP-MS at Kochi Institute for Core Sample Research. The CeCl₃ solution used in the adsorption experiment was employed as standard solutions and the isotope ratio of each element was expressed in delta notation relative to the average standards, which is shown in the equation as follows: $\delta^{142}\text{Ce} = [(142\text{Ce}/140\text{Ce})_{\text{sample}} / (142\text{Ce}/140\text{Ce})_{\text{CeCl}_3} - 1] \times 10^3$.

Assuming equilibrium isotopic fractionation, the mean isotopic fractionation factor between the liquid and solid phases $\alpha_{Lq?So}$ of Ce adsorbed on ferrihydrite was within the analytical uncertainty for all the pH conditions. Meanwhile, the $\alpha_{Lq?So}$ of Ce adsorbed on δ-MnO₂ was gradually decreased with increasing pH. Most surprisingly, the $\alpha_{Lq?So}$ of spontaneous precipitation of Ce showed that, with increasing pH, the direction of the isotopic fractionation was in contrast to those in the adsorbed systems. These results suggest that the degree of mass-dependent fractionation of Ce can be used to clearly distinguish spontaneous precipitation from oxidative adsorption on δ-MnO₂, that occurs under more oxic conditions than the Ce(III)/Ce(IV) boundary. Our results suggest that the combination of the degrees of mass-dependent fractionation and chemical state of Ce can be used to classify the redox condition into the three stages based on Ce geochemistry, thereby offering a powerful tool for exploring redox conditions in paleo-ocean environments.

Keywords: cerium, stable isotope, redox

Decoding the Evolution of Early Atmosphere: Experimental Reconstruction of the D36S/D33S Chemostratigraphy

UENO, Yuichiro^{1*} ; ENDO, Yoshiaki¹ ; MISHIMA, Kaoru¹ ; DANIELACHE, Sebastian⁴

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, ²Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, ³Precambrian Ecosystems Laboratory, JAMSTEC, ⁴Faculty of Science & Technology, Sophia University

Sulfur Mass-Independent Fractionation (S-MIF) has potential to monitor chemistry of the Earth's early atmosphere (Farquhar et al., 2000). Nonetheless, detailed mechanism of the S-MIF occurred in the Archean atmosphere is still poorly understood. Previous laboratory experiments indicate the anomalous isotopic fractionation depends largely on (1) wavelength or spectrum of the incident light source and (2) partial pressure of SO₂, though none of these experiments have not yet succeeded to fully reproduce the S-MIF recorded in the Archean sedimentary rocks (e.g., Danielache et al., 2008; Masterson et al., 2011; Whitehill & Ono, 2012). We have developed a new photochemical chamber for determining isotopic effect of the SO₂ photolysis under optically thin condition. Also, a new direct fluorination technique of carbonyl sulfide allowed us precise isotopic analysis down to 50 nmolS of photolysis product. The results indicate that the basic character of the S-MIF observed in the Archean record can be reproduced when SO₂ column density is reasonably low (i.e. 10 to 50 times higher than preindustrial atmosphere). The results with a numerical modeling of the atmospheric reaction network suggest that the observed change in D36S/D33S ratio can be adequately explained by the two factors: (1) SO₂ partial pressure and (2) amount of reducing gas (H₂, CH₄ and CO). In light of the new perspective, we have re-evaluated the geological record of the D36S/D33S ratio with additional analyses of Archean sedimentary sulfides from South Africa and India. Based on the magnitude of the S-MIF and the D36S/D33S ratio, the Archean period can be subdivided into four stages (i.e. > 3.0 Ga, 3.0-2.7 Ga, 2.7-2.5 Ga and 2.5-2.4 Ga). These changes probably reflect both intensity of volcanic SO₂ emission and concentration of reducing gasses under the O₂-free atmosphere. Particularly, the maximum scatter of D33S values observed in the stage 3 (2.7-2.5 Ga) requires high volcanic emission as well as very reducing atmospheric condition in the atmosphere at that time.

Keywords: Archean, atmospheric chemistry, mass independent fractionation

Archean Atmospheres Modeled with the KROME Chemistry Package

DANIELACHE, Sebastian^{1*} ; UENO, Yuichiro³ ; SIMONCINI, Eugenio²

¹Sophia University, Faculty of Science & Technology, Department of Materials and Life Sciences, ²INAF, Astrophysical Observatory of Arcetri, Italy., ³Earth & Planetary Sciences, Tokyo Institute of Technology, ⁴Earth-Life Science Institute (ELSI), Tokyo Institute of Technology

Sulfur isotopic fractionation has been used as a tool to understand the composition of reducing atmospheres. Our previous work (Danielache et al., 2008 and 2012) have shown that UV-light triggers a large Sulfur Mass-Independent Fractionation (S-MIF) on the SO₂ photodissociation products. However photodissociation of unshielded UV-light alone cannot reproduce the S-MIF signals reported for the Archean and Early Proterozoic (>2300 Ma) nor its large variability mainly at 2600 Ma (D33S = +11 ‰) (Johnston, 2011). In order to study a planetary-like chemical network capable of accounting for a sulfur cycle in reducing conditions we have introduced a high-order solver (DLSODES) administrated by the KROME (Grassi et al.,) chemistry package. The package automatically generates a set of FORTRAN subroutines with build-in rate equations and solves them with accuracy and efficiency for sparse networks. This technique allows us to couple a detailed 4 sulfur isotopes chemistry to a 1D transport model capable of calculating the opacities influencing photochemistry and the temperature structure of an Archean atmosphere. We present preliminary results showing the ability of the code to deal with small isotopic fractionations and compare with already existing model studies of the Archean atmosphere.

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Keywords: Archean Atmosphere, Sulphur, Stable Isotopes

Effects of atmospheric composition on apparent activation energy of silicate weathering

KANZAKI, Yoshiki^{1*} ; MURAKAMI, Takashi¹

¹Department of Earth and Planetary Science, Graduate School of Science, University of Tokyo

Silicate weathering is a major sink of atmospheric CO₂. Because CO₂ is an important greenhouse gas, silicate weathering regulates not only the partial pressure of atmospheric CO₂ (P_{CO_2}) but also the surface temperature (T). The apparent activation energy of silicate weathering represents the temperature dependence of silicate weathering and thus interrelates the intensity of silicate weathering, P_{CO_2} and surface temperature. It has been reported that solution composition can affect the apparent activation energy of dissolution/precipitation of silicates (e.g., Casey and Sposito, 1992; Lasaga, 1995; Cama et al., 1999). However, the relationship between the solution composition and the apparent activation energy of silicate reaction is not yet fully understood.

To investigate the apparent activation energy of silicate weathering in a natural weathering system, we formulated the apparent activation energy of silicate weathering in three different scales, namely, (i) dissolution/precipitation of each mineral, (ii) elemental loss as the net reactions of the minerals and (iii) weathering flux from a weathering profile, based on the rate expressions in the three scales. It was found that, due to the effects of solution composition on the apparent activation energy, the temperature dependence of atmospheric CO₂ ($\Delta H^*_{CO_2}$) affects the apparent activation energy of silicate weathering. Based on the formulated apparent activation energy, we estimated the apparent activation energy of silicate-weathering flux as a function of $\Delta H^*_{CO_2}$. Then, the compensation law between the pre-exponential factor and the apparent activation energy of silicate-weathering flux was introduced from the literature, leading to the establishment of the relationship between silicate-weathering flux (F_{CO_2}), T and $\Delta H^*_{CO_2}$.

Based on the F_{CO_2} - T - $\Delta H^*_{CO_2}$ relationship and the greenhouse effects of atmospheric CO₂ in the literature, we calculated the ratio of change in F_{CO_2} to that in P_{CO_2} as an indicator of silicate-weathering feedback in the Precambrian. The calculation revealed that when $P_{CO_2} > \sim 10^{-0.5}$ atm, the feedback is negative and independent of P_{CO_2} and surface temperature. On the other hand, when $P_{CO_2} < \sim 10^{-0.5}$ atm, the feedback is independent of P_{CO_2} but dependent on surface temperature; at low ($< \sim 30$ °C) and high ($> \sim 30$ °C) temperatures, the feedback is negative and positive, respectively. Due to the positive feedback, the conditions of $P_{CO_2} < \sim 10^{-0.5}$ atm and $T > \sim 30$ °C are unstable, and immediately change, with a slight change in P_{CO_2} , to either the conditions of $P_{CO_2} > \sim 10^{-0.5}$ atm or those of $P_{CO_2} < \sim 10^{-0.5}$ atm and $T < \sim 30$ °C. When $P_{CO_2} < \sim 10^{-0.5}$ atm and $< \sim 30$ °C, the feedback is not only negative, but also becomes more negative as temperature decreases, suggesting that global glaciations are harder to bring about than previously thought.

Keywords: silicate weathering, carbon dioxide, feedback, Precambrian

Kinetics and Mechanisms of Zeolite Crystallization at Hyperalkaline Conditions

FRANCISCO, Paul clarence^{1*} ; SATO, Tsutomu¹ ; OTAKE, Tsubasa¹

¹Graduate School of Engineering, Hokkaido University

The predicted precipitation of zeolites in geologic barrier systems for radioactive wastes due to the alkaline alteration of bentonite may result in the modification or loss of favorable physicochemical properties of the bentonite as a suitable barrier material. Zeolites formation is typically preceded by an amorphous precursor, the transformation of which is seen as the rate-controlling step. However, the structure of the precursor phase and the rates and mechanisms by which it transforms into crystalline zeolites are poorly understood. In this study, we investigated the rates and mechanisms of zeolite crystallization from solutions.

Batch synthesis experiments were carried out over a range of solution compositions ($\text{Si}/\text{Al} = 0.1$ to 8.0), pH (9.5 to 13.5) and temperature (25C to 90C) conditions in order to clarify the effects of these parameters on zeolite crystallization. Solid products were characterized using XRD, SEM-EDX, FTIR spectroscopy, Raman spectroscopy and MAS NMR spectroscopy.

Zeolite crystallization proceeds by the rapid formation of an amorphous precursor phase, followed by the slower transformation of this precursor into crystalline zeolite. Depending on the Si/Al ratio of the parent solution, the species of zeolite may vary. At $\text{Si}/\text{Al} > 1$, Faujasite forms slowly, whereas for $\text{Si}/\text{Al} < 1$, Zeolite A forms more rapidly. Higher pH and temperatures favor transformation.

Morphological information from SEM shows intimate physical relationship between crystalline zeolites and the amorphous precursor phase. Spectroscopic results from FTIR, Raman and MAS NMR indicate that ring structures are present in both amorphous and crystalline phases, indicating structural similarity between the two phases. These data may suggest that amorphous phases transform directly into crystalline zeolites. The activation energy of crystallization suggests that solid-state processes occur alongside dissolution of the amorphous phase in order for the transformation of the amorphous phase into crystalline zeolite to proceed.

Keywords: zeolite, mechanisms, transformation, spectroscopy

Effects on Phosphate Ion for the Phase Changes of Amorphous Calcium Carbonate

SUGIURA, Yuki^{1*} ; ONUMA, Kazuo² ; YAMAZAKI, Astushi¹

¹Department of Creative Science and Technology, Waseda University, ²National Institute of Advanced Industrial Science and Technology, Central 6

Under the biometric simulated environment, amorphous calcium carbonate (ACC) appears as initiation phase by reaction of calcium and carbonate ions. There is a strong relationship between the ACC phase and the forming crystalline polymorphs. We have shown a significant inhibit effect on the vaterite formation and calcite crystallized instead, and also stabilize ACC under higher PO₄ concentration conditions. We hypothesized that PO₄ ions incorporated in the ACC in that suspect that the adjusting the transfer mechanism of the amorphous phase. The structure and stability of ACC under various PO₄ concentrations were examined using in situ ultra violet/visible spectroscopy (UV/Vis). Further, in order to observe in detail the coupling state, the ex situ measurement of ACC by Raman spectroscopy and by using a Ca ion electrode were performed to evaluation of the presence time of the ACC phase. The bicarbonate buffer was mixed with supersaturated solution of calcium chloride and sodium bicarbonate solution to precipitate the ACC, under conditions of pH ~8.6. By mixing the potassium hydrogen phosphate at a concentration of any carbonate solution side during mixing, PO₄ ions was adjusted between 0-50 μ M concentrations. The ACC contains no PO₄ ions shows a spectrum similar to calcite. However the concentration of PO₄ ions increase, UV / Vis absorption spectrum was carried out changed to spectrum like vaterite gradually. The similar behavior showed in the spectrum observed by Raman spectroscopy. By results of measurements of the molecular weight and particle size of the ACC by scattered light spectroscopy, the increasing both density and particle size of ACC was observed. Ion electrode measurements showed that the residence time of the ACC increased exponentially as increasing PO₄ concentration.

In the presence of PO₄ ion, ACC showed a structure similar to vaterite and its stability was increased. Moreover, the type of forming polymorphs greatly changes in variation of PO₄ ions in μ M scale, and stability amorphous structure is also highly variable. The results suggest a need to consider the effects of coexisting PO₄ ions on ACC, when calcium carbonate tissue is formed in the organism.

Keywords: Amorphous, Calcium carbonate, Phosphate, Phase transformation, Biomineralization

Re-evaluation of mineral particles in geothermal fluid: Focus on polysilicic acid and adsorbed particles

YONEZU, Kotaro^{1*} ; MASUDA, Chisato¹ ; MASUNAGA, Sachi² ; ETOU, Mayumi² ; WATANABE, Koichiro¹ ; YOKOYAMA, Takushi²

¹Dept. of Earth Resources Engineering, Kyushu Univ., ²Dept. of Chemistry, Faculty of Sciences, Kyushu Univ.

In geothermal system, the solubility of monosilicic acid concentration in geothermal fluid is controlled by physicochemical conditions. Once the supersaturated condition with respect to amorphous silica attained, the polymerization of silicic acid begins followed by the formation of the particles of polysilicic acid. In addition, the particles adsorbed on the solid surface can be a trigger for the further siliceous deposit. Therefore, in order to investigate the formation mechanism of siliceous deposit, the polysilicic acid particles formed by polymerization of silicic acid and the particles adsorbed on the solid surface in geothermal fluid are focused in terms of those size and chemical composition.

In this study, the polymerization mechanism of silicic acid is discussed based on the size variation of polysilicic acid in geothermal fluid as a function of time measured by dynamic light scattering (DLS) in addition to TEM observation of fractionated polysilicic acid. The filtered particles with different pore size and the adsorbed particles on the copper pipe are analyzed by SEM-EDX to characterize the particle size and chemical composition of the particles.

We expect that these results can be basic information for the prevention technology of siliceous deposit formation on the surface of heat exchanger during geothermal binary power generation.

Keywords: polysilicic acid, geothermal fluid, binary power generation, polymerization of silicic acid, mineral particles

Geomicrobiology of Uranium - Challenges for the Deep Geological Environment

SUZUKI, Yohey^{1*}

¹Department of Earth & Planetary Science, The University of Tokyo

Our understanding of uranium mobility in the environment has been rapidly expanding in the past decades, especially due to problems associated with environmental remediation of uranium-contaminated sites and geological disposal of spent fuels composed mostly of UO_2 . Although neither of these environmental problems was relevant in Japan, Fukushima Daiichi nuclear disaster has dramatically changed our situation. Despite the significant advancement, it is still difficult to predict the form, distribution and fate of uranium in the deep subsurface, as exemplified by studies of a Swedish geological disposal site where high concentrations of uranium was unexpectedly found in the granitic aquifer. In this presentation, the state of the art investigations of microbially mediated redox reactions and uranium mobility in the deep granitic aquifer at Mizunami Underground Research Laboratory (URL) will be presented to discuss factors controlling long-term uranium migration, as well as the relevance to the formation processes of Tono uranium deposit nearby the URL.

Keywords: uranium, microorganisms, redox transformation, underground research laboratory

Haloarcula strains regulate transcription of two types of 16S rRNA genes by growth temperatures

SATO, Yu^{1*} ; KIMURA, Hiroyuki¹

¹Graduate school of Science, Shizuoka university

Translation is the process in which ribosome creates protein. The ribosome consists of two major components, the small and large subunits. In prokaryotes, small subunit of ribosome is composed of 16S rRNA and some ribosomal proteins. Many microbiologist use the 16S rRNA gene sequence for phylogenetic analysis and identification of prokaryotes. Previous studies have reported that the 16S rRNA gene sequence is naturally inscribed with the temperature adaptations of the prokaryotic host. This observation was based on the high correlation between the growth temperatures of prokaryotes and the guanine-plus-cytosine (G+C) contents of the 16S rRNA sequences. Thermophilic and hyperthermophilic prokaryotes generally have high G+C contents of 16S rRNA genes (56-69%). In contrast, mesophilic and psychrophilic prokaryotes have relatively low G+C contents of 16S rRNA genes (51-59%).

Haloarcula strains, belonging to a diverse group of salt-loving organisms in the archaeal phylum Euryarchaeota, have two types of 16S rRNA genes on the genome. These 16S rRNA genes indicate different sequences and G+C contents. Here, we proposed a hypothesis that *Haloarcula* strains preferentially expresses the high G+C contents of 16S rRNA gene (58%), having the stability to heat, during growth in high temperature, whereas they express low G+C contents of 16S rRNA gene (56%) during growth in low temperature. In order to verify this hypothesis, we surveyed transcriptional responses of *Haloarcula* strains in a wide range of temperature conditions by using RT-qPCR method. As the result, high G+C contents of 16S rRNA gene showed significant upregulation in high temperature conditions (40 to 55°C). In contrast, low G+C contents of the 16S rRNA gene expressed at significantly higher levels in low temperature conditions (25 to 35°C). The results suggest that *Haloarcula* strains regulate the transcription of two types of 16S rRNA genes by growth temperatures.

Keywords: halophilic archaea, 16S rRNA, G+C contents, translation, environmental temperature

The effect of methane concentration on methanotrophic bathymodiolid mussels in the Okinawa Trough hydrothermal fields

MIYAZAKI, Yukari^{1*} ; SUNAMURA, Michinari¹ ; ISHIBASHI, Junichiro² ; WATANABE, Hiromi³ ; KONNO, Uta³ ; SUZUKI, Yohey¹

¹Graduate School of Science, the University of Tokyo, ²Graduate School of Science, the University of Kyusyu, ³JAMSTEC

As methane (CH₄) is a greenhouse effect gas, the emergence and activity of CH₄-oxidizing organisms is suggested to have triggered global glaciation. Although the threshold concentrations of CH₄ for the growth of CH₄-oxidizing microorganisms under laboratory conditions are well known, CH₄-oxidizing organisms in the field is poorly constrained for the threshold concentration of CH₄ for growth. This information is critical to reconstruct atmospheric and oceanic CH₄ levels when the activities of methanotrophic organisms are indicated from geologic records with ¹²C-enriched organic matter. We investigated sediment-hosted deep-sea hydrothermal fields in the Okinawa Trough where abundantly emitted CH₄ is known to support methanotrophic ecosystem represented by Bathymodiolid mussels. The distribution of Bathymodiolid mussels and the CH₄ concentrations of their habitats were determined in five hydrothermal fields throughout the Okinawa Trough, and it is suggested that approximately 10 μM is a threshold CH₄ concentration for the methanotrophic organism in the deep-sea ecosystem.

Keywords: hydrothermal vent, Bathymodiolus sp., Neoverruca sp., methanotroph, Okinawa Trough

Biogeochemical cycles of iron and carbon in biogenic iron-rich sediment

KIKUCHI, Sakiko^{1*} ; MAKITA, Hiroko² ; KONNO, Uta² ; SHIRAIISHI, Fumito¹ ; TAKAI, Ken² ; TAKAHASHI, Yoshio¹

¹Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, ²Japan Agency for Marine-Earth Science and Technology

Biogenic iron oxides are the mixture of iron oxyhydroxides and organic materials which are produced by the metabolic activities of bacteria. These biogenic iron oxides work not only as adsorbent for various trace elements, but also as a source of iron and carbon for microorganisms. However, there is only little information about the degradation process of biogenic iron oxides and the effect to microbial activities after their sedimentation. Thus, the purpose of our study is to identify the spatial changes of iron species and microbial communities in biogenic iron-rich sediment (10 cm long).

We observed the existence sharp shifts for iron mineral species and microbial communities in the sediment. The dominance of ferrihydrite at the surface sediment (0-2 cm) subsequently turned into goethite and siderite at sediment depth 2-5 cm, corresponding to the iron reduction. However, iron reduction was depleted at depth deeper than 5 cm, as opposed to the remarkable increase of methane concentration. The microbial clone libraries were dominated by iron-oxidizing chemolithoautotrophic bacteria in the sediment 0-2 cm. In contrast, phylotypes represented by iron reducing and fermenting bacteria at 4 cm, and uncultured delta-proteobacteria and methanogenic archaea were recovered at 10 cm depth. These changes of iron mineral species, carbon metabolisms, and microbial communities only within a few centimeter intervals will also couple to the drastic change in cycles of trace element around the biogenic iron-rich sediment.

Keywords: iron oxides, iron-oxidizing bacteria, Ferrihydrite, Siderite, iron-reducing bacteria, methane

Interaction of nanoparticles with microorganisms

UTSUNOMIYA, Satoshi^{1*} ; SHIOTSU, Hiroyuki¹ ; MASAKI, Shota¹ ; JIANG, Mingyu¹ ; OHNUKI, Toshihiko²

¹Kyushu University, ²JAEA

Nano-mineralization by microorganisms is a key process that can constrain the migration of actinides and REEs. This study demonstrates the REEs accumulation experiments to understand the effect of pH, coexistent REEs and the functional group of cells surfaces on the crystal chemistry of biogenic nanoparticle formation. During the experiment at 25 oC, all REEs were removed from the solution by 24 h at pH 4 and 5, while 50 % of the initial amount remained in the solution at pH 3 after 24 h. The nano-particles at pH 3 had monazite structure, while the particles forming at pH 4 and 5 were amorphous. The REE pattern at 24 h indicated the preferential uptake of LREEs. In case transuranic elements coexist, those elements should be preferentially incorporated into the particles compared to REEs. No cytotoxicity of CeNPs was detected; however, CeNPs induced an excess expression of two proteins: Eno2p and Rps24bp. The released organic substances enhanced anion adsorption and changed surface property of CeNPs. This leads to high colloid stability in solutions. This process is of great importance in the migration of radionuclides in the subsurface environment.

Keywords: Nanoparticles, Microorganisms, Rare earth elements

Microbial methanogenesis in coal seams and diatomaceous formations: Topics and application prospects

SHIMIZU, Satoru^{1*}

¹Horonobe Research Institute for the Subsurface Environment

1. Introduction

Microbial methanogenesis occurs in diverse subsurface environments. For example, biogenic methane has been detected from all representative ecosystems of the world and has been reviewed¹⁾. However, the process of methanogenesis in those subsurface environments has yet to be revealed. Understanding the methanogenesis process is necessary for discerning the global-scale carbon-cycle and for a more effective utilization of biological methane as an energy resource from subsurface environments.

2. Methanogenic archaea from coal-beds and diatomaceous rock

Research topics on biogenic methanogenesis in the Ishikari (bituminous coal)²⁾ and Tenpoku (brown coal) basin and the diatomaceous formations^{3,4,5)} of northernmost Japan will be introduced in this presentation. We were successful in isolating and culturing methanogens from these habitats. In particular, the dominant methanogens isolated from diatomaceous shale formation^{4,5)} will help in understanding some of the processes of methanogenesis in subsurface environments.

3. Biological methanogenic potential of coal-beds and diatomaceous rock formations as geobioreactors

The bottleneck of methanogenesis in subsurface environments is the production of suitable substrates for methanogens from persistent geomacromolecules. One of our approaches for eliminating the bottleneck is a geobioreactor for methanogenesis using hydrogen peroxide. Oxidation of low-rank coal using hydrogen peroxide produces a high yield of small-molecule substrates for methanogenic microorganisms (e.g., methanol, acetate, formate)⁶⁾. Substrate production from diatomaceous rock is considerably less than that from low-rank coal. However, the stratum thickness of diatomaceous rock (1 km or more) is much more than that of coal seams (several meters). Therefore, although the methanogenic potential of diatomaceous rock is low, by quantity, it constitutes an abundant resource. Furthermore, we have had success in microbial methanogenesis from small molecules produced from brown coal using hydrogen peroxide.

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Keywords: Methane, Coal, diatomaceous rock, subsurface microorganisms, methanogenesis, Geo-bioreactor

Transportation process of As in surface and shallow ground waters

MASUDA, Harue^{1*}

¹Osaka City University

Natural As contaminated groundwater has been a serious problem in the world. Instead of numerous studies, sources and pollution mechanism are still in debate. Most accepted source of As is Fe-oxyhydroxides that adsorb the As, and reduction-dissolution of the Fe-oxyhydroxides is believed to release the As into groundwater. Biotite and pyrite would be candidate sources of As, however, few studies assured the presence of As in those minerals. Here, transportation process of the As in surface water and As release mechanism in shallow sediments.

Arsenic is transported as dissolved components and suspended matters. Total As concentration of Red River water is ~10 ppb, and dissolved As and As with suspended particles are 6:4. Although the Red River water contained gibbsite and goethite as suspended matters, those do not but clay minerals host the As as adsorbent. Concentrations of As of the riverbed sediments of Ganges-Bramaptra and Red Rivers are a few to 15 ppm, most of which are in insoluble detrital phases such as silicates and sulfides. Chlorite was the host phase of As in As contaminated groundwater aquifer in our study areas of Bangladesh and Pakistan, although different detrital minerals can host As in each rivers, of which tributaries As contaminated groundwater occurs. These results suggest that the transportation of As with detrital minerals is more important than that as dissolved components and adsorbed phases onto clay minerals and goethite.

In the shallow sediments, As concentration changes with redox potential and pH. Geochemical condition would be controlled by microbial activity in the aquifer. Dissolution of As occurs at the depths where detrital As host minerals are decomposed via oxidation. Newly formed Fe-oxyhydroxides would adsorb parts of the As but not all. Thus, the dissolution of As host minerals are the main reaction to cause As contaminated groundwater.

Keywords: arsenic contaminated groundwater, microbial geochemical reactio, chlorite, goethite, gibbsite

Adsorption behavior of organoarsenic compounds in soils

TANAKA, Masato^{1*} ; TAKAHASHI, Yoshio¹

¹Graduate School of Science, Hiroshima University

The arsenic pollution is a world problem. Natural originated inorganic arsenic compounds are predominant cause of the water-related disease. In addition, anthropogenic originated organoarsenic compounds such as phenylarsonic acid (PAA) and diphenylarsinic acid (DPAA) are also pollution source. For example, DPAA polluted well water caused serious health problems in Kamisu, Japan [1]. These phenyl arsenic compounds are considered as a decomposition product of chemical warfare agents produced during World Wars I and II, and even now such compounds still remain in the ground [2]. Recently, adsorption and mobility of these aromatic arsenic compounds in agricultural soils have been investigated [3]. However, their adsorption mechanisms on soil are still unknown. In general, the adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. Thus, it is important to understand the adsorption mechanism of the arsenic compounds to predict future fate of them in environment. Recently, we reported adsorption structures of PAA and DPAA on ferrihydrite obtained by X-ray absorption fine structure (XAFS) analysis and quantum chemical calculations [4]. In this study, we conducted As K-edge XAFS measurements for organoarsenic compounds adsorbed on soil, as well as a sequential extraction, to understand their adsorption behavior in the soil. EXAFS analysis suggests that all arsenic compounds in this study adsorbed on Fe or Al (oxyhydr)oxide in the soil mainly regardless of the organic functional groups. This fact indicates that the Fe/Al (oxyhydr)oxide can control the mobility of organoarsenic compounds in the ground.

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Keywords: soil, adsorption, XAFS, organoarsenic