

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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

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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

Impact-induced products from glycine polymers in early Earth's oceans

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Early oceans may have contained appreciable amounts of prebiotic organic molecules, since previous studies have indicated that simple organic molecules are capable to be formed through oceanic impact processes by meteorites. Geologic evidence suggests that the root for the origin of life materials occurred just after or during the heavy bombardment period. At that time the impact energy is considered to have been important for molecules present in oceans to react. Shock reactions of organic molecules in aqueous solutions have been subject to few studies.

Here we investigate the reactions for glycine polymers (dimer G2, trimer G3, and tetramer G4) and alanilglycine (AG) in aqueous solutions in order to know their stability and reaction products during impacts. The starting G2 (>99.0% Tokyo Chemical Industry Co. Ltd), G3 (>98.0%, Tokyo Chemical Industry Co. Ltd), G4 (>95%, Tokyo Chemical Industry Co. Ltd), and AG (>98.0%, Tokyo Chemical Industry Co. Ltd) were used in the present study. Hypervelocity plane impact experiments were carried out using a propellant gun. Sample solutions of glycine polymers in sealed steel containers were 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 a hybrid Fourier transform mass spectrometer (Thermo Fisher Scientific LTQ Orbitrap XL) at Hiroshima University.

The analytical results for the recovered samples were compared with those for the initial sample. Limited numbers of amino acids of Glycine, alanine, and their polymers, amines from propylamine to octylamine, and carboxylic acids from acetic acid to decanoic acid were selected due to a measured range of their m/z values. The identification of a molecule was done by the presence of a peak with the calculated m/z value (± 0.002). The results are discussed.

Keywords: Glycine polymers in early Earth's oceans, Impact-induced products

Effect of mineral species on the glycine polymerization

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Protein is a major constituent of life on the earth, and is produced by polymerization due to dehydration condensation of amino acids. Polymerization of amino acids is an important process for the origin of life. The understanding of amino acid polymerization process in the earth surface environment is important for the origin of life. It is well known that polymerization of amino acids under the ambient condition is thermodynamically difficult. Therefore, how the amino acids polymerization in the early earth environment proceeded is still under debates.

Many model experiments for amino acid polymerization had been designed so far. Among them, one of the promising method is mixing the mineral powder with glycine solution with heating (e.g., Bujdak and Rode, 1997a). Bujdak and Rode, (1997b) was confirmed that alumina could promote alanine polymerization than Quartz. They suggested that the effect of mineral type is important on the polymerization of amino acids. However, it is not known which functions of the mineral affect the amino acid polymerization. After Bujdak and Rode, (1997b), amino acid polymerization experiments by using various type of mineral species has been widely examined. However, the experiment condition has not been unified among the studies. We cannot compare the effect of amino acid polymerization on each mineral. In present study, we conducted the experiments of amino acid polymerization using t various types of minerals (Rutile, Anatase, Amorphous silica, Quartz, gamma-Al₂O₃, Corundum, Hematite, Magnetite, Forsterite) under the unified experimental conditions. The purpose of the study is to clarify the factors for promoting the amino acid polymerization in mineral species.

Keywords: amino acid, polymerization, mineral

Role of minerals for hydrogen generation in the interaction between ultramafic rocks and water

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Hydrogen generation by high temperature serpentinization is understood as hydration of mafic and ultramafic rocks, owing to the oxidation of reduced iron present in the olivine or pyroxene. On the other hand, in the Oman Ophiolite and Lost City Hydrothermal Field (LCHF) in the Mid-Atlantic Ridge, hydrogen is generated via low temperature serpentinization. Moreover, previous experimental study shown generating hydrogen at low temperatures (<100 degrees C). However, since even the rate of hydrogen generation by high temperature serpentinization is slow, the mechanism of hydrogen generation by low temperature in short period is yet to be explained. Therefore, the objective of this study is to clarify the mechanism of hydrogen generation via low temperature serpentinization for a short period. Batch experiments were conducted at 30 degrees C, 60 degrees C and 90 degrees C using minerals which constitute ultramafic rocks (olivine, Magnetite, Fe-Ni alloy), and serpentinite. Samples were taken after various reaction times (3h, 6h, 12h, 24h, and 1week). Liquid samples were analyzed by ICP-AES, ion chromatography, UV-Vis, pH, and ORP. Mineral phase changes in the solid samples were characterized by TG-DTA, SEM-EDX and XRD. The concentration of hydrogen gas was determined by GC-RGD.

Hydrogen generation was observed in all samples. Highest concentration of hydrogen gas was observed in the experiment using Fe-Ni alloy. In the experiment using Fe-Ni alloy, apparent surface change was not observed at the surface of Fe-Ni alloy. Therefore, hydrogen gas was generated by catalysis of Fe-Ni. The generation of hydrogen gas by this catalysis would be higher than that of generated hydrogen accomplished by the dissolution of olivine, which is the dominant mineral in the ultramafic rocks.

In this study, the hydrogen generation was confirmed at a temperature of less than 90 degrees C. The hydrogen generation process is catalyzed by Fe-Ni alloys or magnetite present in secondary minerals by serpentinization.

Spatial distribution of chromium enrichment in 3.2 Ga Moodies BIF, Barberton Greenstone Belt, South Africa

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Geochemical data for ferruginous chemical sedimentary rocks (e.g., Banded Iron Formation: BIF) have been used to understand surface environments on early Earth. For example, enrichment of Cr relative to Ti in BIFs that occurred ~2.48 billion years ago has been considered as a result of the chemical mobilization of Cr in acidic aqueous environments due to sulfide oxidation after the oxygenation of atmosphere. While the Archean sedimentary environments studied in most previous works are limited to deeper settings, the 3.2 Ga Moodies BIF in the Barberton Greenstone Belt, South Africa also indicated that Cr was enriched in the BIF and was therefore chemically mobile in a shallow marine environments. This finding could be significant because it may indicate the oxidation of, at least, some parts of the ocean and therefore, imply the emergence of oxygenic photosynthesis. However, spatial distribution of Cr enrichment in the BIF has not been well understood because the data were obtained from an outcrop and an underground mine. Therefore, the objective of this study is to investigate sedimentary environments and Cr enrichment of the Moodies BIF at another locality.

We conducted a geological survey of another outcrop of the Moodies BIF in the Eureka syncline located ~10 km northeast of Barberton. The section of the BIF exposed in the outcrop was underlain by a conglomeratic quartzite, which is stratigraphically correlated with the BIF at Moodies Hills block in the previous study. Whereas the BIF at Moodies Hills block are 22m in the thickness and overlain by 122m thick silty sandstone and sandstone, the BIF in this study has a thickness of 36m and is overlain by a 103m thick layer of greywacke and silty sandstone. Petrographic observation of the BIF samples shows that the reddish layers are composed of microcrystalline quartz and fine grains of hematite (~15 μ m), and that the black layers are composed of large grains of magnetite (~50 μ m). These observations indicate that they are typical oxide-type BIF and therefore were originally formed as precipitates from seawater. Although chromite, which is a host mineral for Cr, was found in both BIF and clastic sedimentary rock (e.g., silty sandstone) samples, chromite in the BIF was always overgrown by magnetite. This observation is also consistent with results from previous studies. The chemical compositions of the chromite determined by FE-EPMA were low Mg# (0.001~0.01) and high Cr# (0.76~0.89). No significant difference in chemistry was observed in chromite between BIF and clastic sedimentary rock samples. Bulk chemical compositions of the samples were also analyzed by XRF. The results show that the Cr/Ti ratio was not significantly different between BIF and clastic sedimentary rock samples. Therefore, Cr enrichment was not observed in the BIF in this study. The apparent contradiction to the previous study at Moodies Hills block can be explained by the difference in (1) analytical method used or (2) the sedimentary environment. The Ti contents of BIF at Moodies Hills block were determined by ICP-MS after acid decomposition, by which the detection limit is one order of magnitude lower than XRF used in this study. Therefore, the high detection limit in this study may lose the sensitivity for Cr enrichment in samples in which Ti content was low. Alternatively, the BIF in this study could have been deposited in a deeper setting than that at the Moodies Hills block. Therefore, the results may suggest that oxygenated seawater was only localized in very shallow parts.

Keywords: Banded Iron Formation, chromium, chromite, Barberton Greenstone Belt, surface environments on early Earth

Change by a diagenesis of first minerals in 1.9 Ga sedimentary rocks of the Gunflint Formation

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Some microfossils in the 1.9 Ga Gunflint Formation show clear morphology of aerobic microorganisms. However, carbon isotope compositions of microfossils and other geochemical characteristics suggest the activity of anaerobic microorganisms in the same rock sample. This leads to the skepticism if the 1.9 Ga surface ocean environments were essentially anoxic and oxic environments were very limited.

In order to examine if oxic world were more common or anoxic world were more common, shallow water sedimentary rocks were collected from Kakabeka (the bottom of the Gunflint) and Telly Fox (the top of the Gunflint) areas. The following features were found in the present study. (1) Chemistry of carbonate change into either Fe-rich or Mg-rich from calcite during diagenesis. Fe-rich feature is only found at the bottom of the Gunflint Formation, suggesting wide injection of reduced fluids in sediments. (2) Carbon isotope compositions were similar to cyanobacteria value, and feature of anaerobic bacteria were not detected. This suggests that previous report of carbon isotope compositions of anaerobic bacteria was limited in a few places and not widespread in the Gunflint Formation. Therefore, aerobic microorganism was the major life forms. (3) Sulfur isotope compositions of pyrite range from -2 to +15 per mil, suggesting closed system sulfate reduction. The closed system was most likely isolated oxic seawater from anoxic sediments, probably high sedimentation of SiO₂ and CaCO₃. In addition, isolated sediments were anaerobic bacterial world, where organic matter from the oxic world was largely consumed.

Keywords: diagenesis, oxic, anoxic, closed system

Origin of phosphate stromatolite formed after the snowball Earth

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The sedimentary rocks formed after Neoproterozoic snowball Earth distribute near Irece, Bahia, Brazil. Salitre Formation is one of them, and contains unique phosphate (apatite) stromatolites. They show dense columnar shape, and are surrounded by laminated dolomite. The relationship between stromatolite and dolomite is mostly sharply bounded, although some parts appear transitional. Stromatolite contains various shape of microfossils. Filamentous microfossil (5-10 μm diameter, about 300 μm long) is most abundant and resembles to filamentous cyanobacteria, and thus, photosynthetic microorganisms such as cyanobacteria are considered to be involved in the formation of stromatolite.

In order to understand the influence of microbial photosynthesis on apatite precipitation, saturation state of apatite after removing 200 μM of CO_2 from seawater was calculated by Phreeqc. The result indicated that photosynthesis can significantly increase saturation state of apatite, when the concentration of dissolved phosphate is at least 1 μM . Although the saturation state of CaCO_3 is also increased by photosynthesis, its degree is much smaller than that of apatite. As a result, apatite is more likely to precipitate than carbonate, and phosphate stromatolite is formed.

The concentration of dissolved phosphate is extremely low at the surface ocean due to the uptake by phytoplankton, and its concentration is as high as several μM even at the deep ocean. At the time of post-snowball Earth, similar situation is expected for the surface ocean, while the concentration of phosphate in the deep ocean is considered to be much higher than today. If occasional upwelling transported such water mass to the shallow sedimentary basin where cyanobacterial mat is developed, phosphate stromatolite will be formed even if dissolved phosphate concentration is several μM .

Large Fe isotope fractionations in ferruginous sedimentary rocks above Kuroko deposits in the Hokuroku district

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The Hokuroku district in Akita Prefecture, Japan, hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits formed around 15.3 million years ago by ancient submarine hydrothermal activity. VMS deposits were formed by the precipitation of metals from hydrothermal fluids and could have contacted with seawater in geological timescales. Because they are composed of sulfide minerals that are stable in a reducing environment, such as pyrite and chalcopyrite, an anoxic environment in the Hokuroku basin may play an important role in the preservation of the sulfide ores containing valuable metals in Kuroko deposits. However, geochemical evidence of such an environment occurring in Hokuroku district is currently lacking. Therefore, objective of this study is to investigate the distribution of REEs and the variation of Fe isotope compositions in the Fe-Mn-rich sedimentary rocks associated with VMS deposits in the Hokuroku district to understand the depositional environments and ancient sea-floor hydrothermal systems in the Hokuroku basin. Sedimentary rock samples obtained from both outcrops and mines in the Hokuroku district include ferruginous cherts occurring directly on or above a Kuroko deposit, manganese-rich siliceous mudstone, and amber in mudstone or tuff. Samples were analyzed by XRD, petrography, and SEM-EDS for mineralogy, by XRF and LA-ICPMS for chemical composition and MC-ICPMS for iron isotope composition ($\delta^{56}\text{Fe}$ (‰) = $1000 * [(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}} - 1]$).

The results of these analyses show the $\delta^{56}\text{Fe}$ values of mine samples occurring directly on and above Kuroko deposits were -1.5 to 0.5 ‰. These values are largely fractionated from $\delta^{56}\text{Fe}$ value that is similar with igneous rock's $\delta^{56}\text{Fe}$. Iron isotopic fractionation occurs when ferrioxide precipitate part of the bivalent iron present in the reservoir. These values are largely fractionated from the $\delta^{56}\text{Fe}$ value of the standard (i.e., 0 ‰), which is a similar to that of igneous rocks. The samples that have a large negative value also bears negative Ce anomaly. These signatures indicate that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the sea-floor of the Hokuroku Basin was anoxic. On the other hand, $\delta^{56}\text{Fe}$ values of chemical sedimentary rocks formed during 2 -3 Ma after Kuroko deposits formed ranges from -0.8 to -0.3 ‰. These values are similar to that of dissolved ferrous ion in a modern sea-floor hydrothermal fluid. Therefore, the $\delta^{56}\text{Fe}$ values of the samples indicate near complete oxidation of dissolved ferrous iron in an oxic environment. Therefore, the results of this Fe isotope study suggest that the depositional environment in the Hokuroku basin shifted from anoxic to oxic after the formation of Kuroko deposit.

Keywords: iron isotope, rare earth pattern, anoxic environment, Volcanogenic massive sulfide, hydrothermal system

SEM and TEM observations of carbonate, Fe-oxide and silica minerals in Okuoku-hachikuro hot spring, Akita Prefecture

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Recent studies of biomineralization mainly treated biominerals produced by evolved life. It is uncertain if primordial microbes are capable to precipitate biominerals. If biomineralization by early life is well documented, it will help to understand the Precambrian environments more in details.

Abundant carbonates are precipitating at Okuoku-hachikuro hot spring, located in Kosaka, Akita Prefecture, Japan. We collected sinters, soft to solidified sediments and microbial mats. Then, those constituents were observed using field emission-scanning electron microscopy (FE-SEM). Minerals around microbial sheath were also observed by transmitted electron microscopy (TEM). Analyses of X-ray diffraction, pH, DO, dissolved amino acids, carbon isotope compositions and chlorophyll compositions were also performed.

Hot spring water does not contain appreciable amounts of dissolved oxygen, but Fe-oxides immediately precipitated after discharge. Chlorophyll analyses indicate no presence of anoxygenic photosynthesizing bacteria. These results suggest that Fe were precipitated by Fe-oxidizing bacteria dominantly, supported by SEM observation of characteristic morphology of the sheath. Cyanobacteria become more dominant in the distance.

Most samples contain radial aggregates of needle-shape aragonite. Such morphology was found in bubble in the "first" discharging fluid. Each needle in radial aggregates seems to be bigger depending on a distance from the discharging point. Aggregates of coarser and random orientated needles of aragonite are found in lower stream zone, where evaporation and cooling of hot spring water are more visible. Because of no systematic correlation to biological activities (microbial mat, amino acid, organic carbon, etc.) to those morphological changes, all aragonites are formed inorganically. On the other hand, Fe-oxide covering sheath are found locally. Using dilute hydrochloric acid etching, Fe-oxide is observed clearly, especially in zone 1. It has 3 morphological types: sheath-like, agglomerated and needle in radial aggregates. It is noteworthy that Fe-oxides never grow in large crystals. This can possibly because microbial activities or organic molecules may prohibit the growth of Fe-oxides. Furthermore Si was detected in Fe-oxide. This result suggests that Fe-oxide probably adsorbs amorphous silica selectively. Such unique morphology may help to interpret the origin of hematite in Precambrian banded iron formations.

Keywords: aragonite, Fe-oxide, Fe-oxidizing bacteria, SEM, TEM

Microbial processes forming lamination in hot spring stromatolites by sulfur oxidizing bacteria and cyanobacteria.

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Travertines are carbonate precipitates from hot-spring water containing a sufficient amount of calcium and carbon dioxide. Most of travertines show sub-mm order laminations that were resemble to ancient stromatolites. Recently, daily microbial processes were identified in some travertines precipitated from some sulfide-poor and moderate temperature (<55 degree C) springs. In the process, daily growth of biofilms consisting cyanobacteria or heterotrophic bacteria, which inhibited inorganic mineral precipitation (1,2). While, lamination is less common in the travertines at higher temperature (>60 degree C) and sulfide-rich springs (3) likely because such daily microbe-mineral interaction might not be occurred. In order to understand the geomicrobiological system in high temperature and sulfide-rich spring, this study investigates a travertine in Sipoholon, Northern Sumatra, Indonesia.

Sipoholon hot spring forms the hugest travertine mound among the hot springs in Tarutung area located about 30 km south from the Lake Toba. The travertine mound spread in total area of 50,000 km². The actively precipitated region was separated 3 areas; A is natural mound without artificial effect, B is the mounds in a quarry, C is exposes the rim pools behind spa facilities. In all area, sulfur-rich yellow sediments were formed near the vents, while white laminated sediment was formed from midstream to downstream. The surface color of the laminated travertine was changed with water temperature; pale pink around 55 degree C and green below 50 degree C. Lamination in the green travertine consisted of light colored crystalline layer and dark colored biofilm-rich porous layer in the interval of 0.5-1.0 mm. While, some lamination in the pink travertine was not clear.

12 sequences of water and travertine samples were collected at a green travertine and a pink travertine in Area C every 4 hours during 48 hours. Samples of both types of the travertine showed that the dark layer was formed during daytime and light colored layer was formed during nighttime without variation in pH, water temperature, Ca ion concentration, alkalinity, and flow. Only dissolved oxygen concentration showed the daily variation in the water chemistry, which was higher during the daytime and lower during the nighttime. Phylogenetic analysis on 16S rRNA gene showed that the pink and green travertines have a microbial composition dominated by obligatory chemolithoautotrophic sulfur-oxidizing bacteria. Phototrophs, cyanobacteria and chloroflexus were more diverse in the green travertine than in the pink one. Epifluorescence microscopy showed that phototrophs were concentrated in the diurnal dark layer in the green travertine, while sparsely distributed near the surface in the pink travertine.

These results suggest that formation of phototroph biofilm in daily cycle was responsible for lamina formation in the green travertine same as previous study. On the other hand, formation of sulfur-oxidizer biofilm stimulated daytime increment of oxygen concentration was likely responsible for lamina formation in the pink travertine. The obscure lamination in the pink travertine possibly due to growth of chemolithoautotrophs stimulated by extrinsic factor that is daily supplement of oxygen, in contrast to intrinsic daily growth of phototrophs. This novel microbial process could be occurred in ancient stromatolites formed under the anoxic sulfide-rich ancient ocean.

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Keywords: travertine, lamination, stromatolite, cyanobacteria, sulfur-oxidizing bacteria

Influences of silica and embedding on thermal alteration of aliphatic hydrocarbons in cyanobacteria as evaluated by FTIR

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To study influences of the presence of silica and embedding on thermal changes of aliphatic hydrocarbons in prokaryotic cells, cyanobacteria *Synechocystis* sp. PCC6803 were isothermally heated at 250-400 °C and the changes in IR signals were monitored by micro-Fourier transform infrared (FTIR) spectroscopy. The absorbance of aliphatic C-H decreased with heating time, indicating the degradation of aliphatic hydrocarbons. Both the presence of silica and embedding delayed the degradation of the aliphatic C-H. The absorbance ratios of 2960 cm⁻¹ band (aliphatic CH₃) to 2925 cm⁻¹ band (aliphatic CH₂) (R_{3/2} values) increased or changed little by the heating. Raman spectral features showed that some experimental products had a structural ordering similar to the Proterozoic microfossils, indicating that they were carbonized to a degree similar to the microfossils. These results reveal that the presence of silica and embedding affect the thermal degradation rate of aliphatic C-H in cyanobacteria but do not lead to the decrease in R_{3/2} values. The low R_{3/2} values of Proterozoic prokaryotic fossils from Bitter Springs and Gunflint Formations are not considered to be due to thermal degradation upon fossilization during diagenesis. Although other possibility cannot be ruled out, the results suggest that precursor lipids, having low R_{3/2} values, were selectively preserved in microfossils.

Keywords: micro-FTIR, cyanobacteria, silica, thermal alteration, aliphatic hydrocarbon

Role(s) of extracellular polymeric substance in microbial mineralization

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Microbialites are defined as organosedimentary deposits that have accreted as a result of benthic microbial community binding detrital sediment or forming the locus of mineral precipitation. Most of microbialites are consisted of carbonate minerals, and considered to be formed by microorganism, such as cyanobacteria and sulfate reducing bacteria. Microbialite records the history of interaction between life and Earth environment, and therefore, it is important to understand their formation. Microbialites are formed mainly by three processes, including grain-trapping, mineral precipitation by metabolism and mineral nucleation by extracellular polymeric substances (EPS). Grain-trapping is locally important, but key processes are precipitation and nucleation. The knowledge of precipitation process by bacterial metabolism has increased, while that of EPS is still limited. Therefore, this study aims to investigate the influences of EPS on microbialite formation. We examined carbonate deposit developed at Kibedani hot spring, Shimane Prefecture. Calcite was despite of undersaturation in bulk water. Microelectrode measurement revealed that this deposit is formed as a result of photosynthesis-induced CaCO_3 precipitation. The result of EPS staining observation by Confocal Laser Scanning Microscope revealed that this deposit contains abundant acidic EPS, which is generally considered to have important roles in mineral nucleation. This deposit composed of two layers: the upper layer is consisted of empty EPS sheaths and the lower layer is of cyanobacteria with EPS sheaths. Both layers contain acidic EPS, while only lower layer was mineralized. This observation implies that acidic EPS cannot solely cause nucleation, and requires high mineral saturation state induced e.g. by photosynthesis.

Controlling factors of microbialite textures inferred by a tufa deposit

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Microbialite is organosedimentary deposits that are formed by the interaction between life, water and mineral. It has accreted as a result of a benthic microbial community trapping and binding detrital sediment and/or forming the locus of mineral precipitation. Typical examples of microbialite are laminated stromatolite, and clotted thrombolite. In the Earth history, stromatolite appeared from about 3500 Ma, followed by its peak at 1300 Ma. At about 500 Ma, stromatolite rapidly declined, and thrombolite appeared. Although this transition is considered to reflect evolution of life and Earth environment, its detail is still not well understood. To understand the basic mechanisms forming microbialites, the geomicrobiological studies of recent samples are essential. While microbialite in modern marine environment is scarce, it is relatively common at freshwater environment as a tufa. The present study focuses on tufa for investigating the relationship between depositional structure and microbial composition. Tufa deposit usually has laminated structure resembling stromatolite. However, tufa deposit developed in Takahashi city (Okayama prefecture) exhibits both stromatolitic and thrombolitic structures by reflecting the difference of hydrodynamic condition. The chemical compositions of creek water at the sites where stromatolitic and thrombolitic tufa are depositing are almost the same, and similar to that of common tufa-depositing creek. Extracellular polymeric substances (EPS) staining observation applied for deposits surface by Confocal Laser Scanning Microscope (CLSM) showed that the distribution patterns of phototrophs and EPS were different between stromatolitic and thrombolitic tufa. At the surface of thrombolitic tufa, coccoid cyanobacteria densely colonized to form small mounds (500 μm in diameter) and EPS located inner and marginal part of the mounds. On the other hand, at the surface of stromatolitic tufa, filamentous cyanobacteria distributed sparsely with EPS, and calcite was widely exposed. Vertical thin section observation revealed that there were large calcite crystals (500 μm in diameter) at the surface of thrombolitic tufa, and filamentous one colonized around them. Stromatolitic tufa, on the other hand, was consisted of fine grained calcite (10 μm in diameter) with filamentous cyanobacteria colonized perpendicular to the lamination. Microbial composition of both deposits was examined by 16S rRNA gene analysis. The result indicated that cyanobacteria were abundant and some strains were common between thrombolitic and stromatolitic tufa. However, the diversity of microbial population microbial population was higher in thrombolitic tufa than stromatolitic ones.

From the results above, it is inferred that the transition from stromatolite to thrombolite in \sim 500 Ma was caused by microbial diversification and resultant EPS composition change.

Keywords: microbialite, stromatolite, thrombolite, tufa, carbonate rock

Soil micromorphology and the effect of biotic activity

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Soil is formed on a boundary between geosphere and biosphere in relation with hydrosphere and atmosphere. The major component is quite very fine-grained particles which are not still unknown in detail. A great variety of microbes are associated in soil (e.g., Hattori, 1987). Hattori (2006) suggests that there is a possibility some bacteria produce very fine-grained mineral particles, silica-nano particle as a part of soil material. Micromorphology is observed under petrological microscope. The technique for preparation to make thin section from unconsolidated soil is followed by method in FitzPatrick (1993). Soil fragments are examined by scanning electron microscope. Samples are collected from recent cultivated soil (Okayama University Farm), fluvial soil (Sendai City), rice field soil (150 to 2000 years old fluvial soil from Okayama University), paleosol (about 3000 years old organic rich fluvial soil from Dhaka City, Bangladesh).

The formation of microaggregates: The structure of soil macroaggregate (1~2mm) which is composed of microaggregates (0.05~0.3mm) and sand grains of mineral and rock fragments is observed in the recent cultivated soil from Okayama University Farm. Similar microaggregates (0.1~0.5mm), structure with heterogeneous granular domains is observed in rice field soil from Okayama University. A paleosol from Dhaka, which is not considered to have artificial effects, also consists of microaggregate. The aggregates do not have distinctive boundary but are distinguished by different compositions (content of organic materials, deposited ferri-hydrate and manganese dioxide, particles of mineral and rock fragment). Root pipes and cracks are associated in the soil. The compound structure is interpreted to be formed under effects of microorganisms, root and physical process as demonstrated by previous soil research (e.g., FitzPatrick, 1993).

The formation of silica-nano particle: Under scanning electron microscope, surface of mineral grain has structures caused by weathering, for example embayment, fracture and etch pit. Crystallized nano-sized minerals are formed on weathered surface of a mineral. A bacterial cell surrounded by radiate fibrous mineral is found. The feature indicates a possibility that some bacteria promote to form minerals. And also there is a possibility that a part of inorganic soil materials might be formed relation with organism.

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Keywords: soil, microaggregate, silica-nano particle, bacteria

A novel remediation method for nickel-bearing wastewater at neutral conditions

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Advances in technology such as the electronics and metal plating industries have increased the demand of Ni year by year. On the other hand, the resources are unevenly distributed in a few countries and the supply is highly dependent on strategic policies. Moreover, since Ni is not produced in Japan and it is dependent on imports from foreign countries, the supply structures of Ni are vulnerable. Because of this, the necessity of recovering Ni from wastewaters and other waste forms has been increasing. Some industrial wastewaters contain large amounts of Ni. Generally, the removal of Ni from contaminated wastewater by adding antalkaline and flocculants to increase the pH to 10 or above would result in the generation of Ni-hydroxides after treatment. After that, it is necessary to adjust the pH below the effluent standard (pH 5.8~8.6). However, this method suffers from some disadvantages, such as the high cost for chemical reagents, problems in the disposal of alkali sludge and inefficient treatment system. Therefore, a more sustainable remediation method must be developed to achieve sustainable wastewater treatment operations. This study focused on natural attenuation processes which are safer, cost-effective and more environmentally friendly than traditional methods. For example, at Dougamaru abandoned mine in Japan, high concentrations of Cu and Zn in wastewater are naturally incorporated in the structure of layered double hydroxides (LDH), which forms in the presence of Al ions, hence, natural attenuation of Cu and Zn occurs (Okamoto et al., 2010). Because LDH has the hydroxide structure, six-coordinated heavy metals such as Cu, Ni and Co can be incorporated into the structure during the formation process. Therefore the objective of this study is to develop a remediation method for Ni-bearing wastewaters at neutral conditions, and to clarify the behavior of Ni in the neutralization and precipitation process.

In this context, to check the applicability of LDH in the treatment of Ni-bearing wastewaters, synthesis experiments were carried out by co-precipitation of Ni-bearing LDHs containing SO_4^{2-} as the interlayer anion with different concentrations of dissolved Al ions. Analysis of water chemistry before and after the co-precipitation show that the removal efficiencies of Ni from the synthetic wastewaters increased with increasing dissolved Al concentration. The results further show that the presence of Al in the formation of LDH removed Ni at pH values lower than previous methods which precipitated Ni-hydroxides. It is expected that treatment costs will be reduced in actual wastewater treatment systems because Al addition leads to the reduction of antalkaline use and the neutralization process.

Ni adsorption experiments and extraction experiments were conducted to investigate the sorption behavior of Ni. Only a small amount of Ni was adsorbed to LDH and basaluminite (major minerals in coprecipitation experiments) as inner- and outer-sphere complexes. From the result of XAFS analysis, Ni was incorporated into the structure by being able to precipitate LDH selectively. This shows Ni is fixed securely in the structure of LDH and that the mobility of Ni will be governed by the solubility of LDH. Thermodynamic modeling suggests that the precipitation of LDHs with the optimum Al/Ni molar ratio (0.25~0.50) is determined by the initial conditions (e.g. pH, Al, Ni concentrations). Furthermore, modeling results reproduce the experimental results such as removal efficiency and mineral species well, opening the possibility of its application in actual wastewater treatment operations.

Keywords: Remediation, Layered double hydroxide, Nickel

Changes in water properties and microbial facies along a flow path of a travertine developed in northern Sumatra Island,

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Sumatra Island has many hot springs related with volcanoes belonged to the Ring of fire. Geothermal studies for these hot springs have been performed actively, but hot spring sediments including travertines have rarely been reported. Travertine is a useful modern analog for the Precambrian stromatolites (Takashima and Kano, 2008; Okumura et al., 2013).

We studied travertines at Sipoholon hot spring located about 30 km south from the Lake Toba which is the largest caldera lake in the world. The travertines spread in total area of 50,000 km², in which active deposition occurs mainly in three separated sites; Area A, B and C from north to south, respectively. This study focused on Area A that lacks artificial effect.

In this study, we measured chemical components and stable isotopes of water and observed textures and bacteria of the travertine. Based on these results, we cleared that relationship between water properties, travertine textures and distribution of bacteria.

The travertine deposit occurs along ~35-m-long flow path. The water from the vent first flows 15 m on a narrow (50 cm) and gentle passage and then widely on a steep slope on the travertine dome. Below the dome, the water passes on terrace-like rim pools and finally flows into a pool about 5 m in diameter.

The water with sulfurous smell emits from a vent at a rate of 286 L/min. This water is high temperature (61.4 degree Celsius), neutral pH (6.48) and microaerobic (DO of 0.6 mg/L). The water is rich in Ca²⁺ and SO₄²⁻, and poor in Mg²⁺ and Cl⁻. To the downstream, the water temperature decreases, pH increase, and conversely alkalinity and Ca²⁺ concentration decrease. These and increased carbon isotope of dissolved inorganic carbon indicate that CO₂ degassing increased supersaturation and induced deposition of calcium.

The travertine in Sipoholon hot spring is mainly composed of aragonite, but in one place, calcite coexists. It tends to become softer from the upstream to the downstream. This may reflect difference in crystal shape and texture. The harder travertines consist of tightly packed spherical aggregates of aragonite needles, while softer travertines have loose textures containing dumbbell-shape crystals.

Microbial facies on the travertine surface changes obviously from the upstream to the downstream. A white sulfur-turf in upper stream is composed of sulfur oxidizing bacteria with sulfur particles (Maki et al., 2004). It is known that the sulfur-turf prefers in high temperature, neutral pH and rich in hydrogen sulfide, which corresponds the conditions of the upstream. On high flow parts of the travertine dome, the travertine colored in pale pink likely due to the occurrence of purple sulfur bacteria. Green microbial mat covers the travertine deposited in in lower part with low flow rate. The mat is composed of filamentous bacteria with photosynthesis pigment identified in fluorescence observation. These are cyanobacteria. Water temperatures on the mat are all below 45 degree Celsius. Thus, color change of travertine surface reflect that of microbial composition responded to water properties, such as water temperature, flow rate, flow volume, nutrient.

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Keywords: travertine, aragonite, sulfur oxidizing bacteria, cyanobacteria

A study of irregular shaped tests formation of planktonic foraminifera

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Planktonic foraminifera are protist forming carbonate tests. They are used as useful index fossils, and moreover, the oxygen isotopic and trace element compositions in their calcite tests are recognized as a promised archive representing paleo-ocean environments. Foraminifera generally consist of multipul chambers, and each chamber forms spirally for the center of the first chamber. Culturing observations have contributed for understanding relationships between trace elements and isotopic indices, and environmental factors. However, the transfer of elements and trigger of test formation are poorly understood. Cultured specimens sometimes show irregular-shaped tests, which are unlikely formed under natural condition in the ocean.

In this study, we focused the test formation of planktonic foraminifera, and cultured two species (*Globigerina bulloides*, *Globigerinoides ruber*) collected at Sagami bay. Culturing temperature was controlled at 19, 21, 23 and 25 °C. Calcium isotopic reagents were added to the culturing seawater to mark the timing of test formation. Moreover, we also investigated the other specimens cultured with seawater, whose calcium concentration was raised for 10% respective to the original concentration. In those cases, the pH of calcium reagents were adjusted to appropriate pH, and therefore, the seawater pH was kept at constant during the observation.

As a result, three of ten specimens of *G. ruber* have newly formed a regular test at 19, 21 and 23 °C. On the other hand, 5 of 7 specimens of *G. bulloides* have formed new tests, three of which have formed irregular shaped tests. These three specimens are ones survived more than a couple of weeks after sampling. The water temperature of irregular test formation was 21 or 25 °C, suggesting that the temperature was not a direct controlling factor of irregular test formation. Potential factors are concentrations of dissolved oxygen or dissolved organic matters. Foraminifera first forms organic layer called POM at the beginning of test formation. Anomalously high organic concentration in crystallization liquid may impede the regular formation of POM, consequently resulting in the formation of irregular-shaped tests.

For the specimens with increasing calcium concentration of seawater, the spines fell out within 12 hours. Because calcium is an essential element not only for test formation but also various biological reactions, rapid increase of calcium concentration might disturb the biofunction of planktonic foraminifera.

Keywords: planktonic foraminifera, laboratory culture

Anion adsorption and post-adsorption behavior of metastable iron hydroxides

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Pollution by dissolved anions has been a pertinent environmental concern in many areas around the world. For example, acid mine drainage from abandoned mines and contaminated waters resulting from the Fukushima nuclear power plant accident emphasize the importance of predicting the behavior of the dissolved trace elements on Earth's surface environments. Iron minerals may play a potentially important role in the control of dissolved trace elements in the environment. In particular, poorly crystalline iron minerals exhibit excellent adsorption capacities for toxic anions due to their high specific surface areas and reactivity. In order to evaluate the potential of poorly crystalline iron minerals as stable sinks of dissolved hazardous ions, it is necessary to investigate the adsorption mechanism on these minerals and their post-adsorption behaviors.

Adsorption experiments using arsenate, phosphate, chromate, sulfate, selenate, fluoride, and chloride were performed to investigate the selectivity of Schwertmannite and Ferrihydrite for various anions. Adsorption selectivity decreases in the following order: $\text{H}_2\text{AsO}_4^- > \text{H}_2\text{PO}_4^- > \text{HCrO}_4^- > \text{SeO}_4^{2-} \approx \text{SO}_4^{2-} \gg \text{F}^- \approx \text{Cl}^-$. Schwertmannite and Ferrihydrite didn't have an ability to adsorb F^- and Cl^- . The adsorption mechanism of these anions was investigated using zeta potential measurements. The results indicated that H_2AsO_4^- , H_2PO_4^- and HCrO_4^- formed inner-sphere complexes while SeO_4^{2-} and SO_4^{2-} formed outer-sphere complexes. The adsorption mechanism of these anions to both Schwertmannite and Ferrihydrite is generally similar, except in the case of HCrO_4^- .

Accelerated alteration experiments were performed to observe post-adsorption behaviors of Schwertmannite and Ferrihydrite. Oriented specimens loaded with varying amounts of adsorbed anions were aged under saturated water vapor pressure conditions at 50 °C for 30 days and analyzed by XRD. Results show that larger amounts of adsorbed anions delay the transformation of Schwertmannite and Ferrihydrite into more stable phases, indicating that adsorption of anions, particularly as inner-sphere complexes, stabilizes poorly crystalline iron minerals.

These results show that poorly crystalline iron minerals are capable of taking up a range of toxic anions from contaminated waters and that the stability of these minerals will be affected by the amount of anions sorbed on the surface. These suggest that poorly crystalline iron minerals may serve as stable, long-term sinks for toxic anions.

Anion adsorption and post-adsorption behavior of metastable calcium carbonate polymorph

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In Japanese transuranic (TRU) waste disposal facilities, I-129 is the most important radionuclide that must be considered in long-term safety assessments of the repository. However, the degradation of cement materials used in the repositories can produce high pH pore fluids that can affect to anion transport behavior. Therefore, it is necessary to understand the behavior of anions such as I⁻ in hyperalkaline conditions. Examples of I⁻ behavior in natural hyperalkaline environments, such as in Oman, show that I⁻ is taken up by aragonite, opening up the possibility of calcium carbonates as inhibitors of I⁻ migration. This concept is currently being applied in the development of the Advanced Liquid Processing System (ALPS), which employs carbonate coprecipitation to treat contaminated waters resulting from the Fukushima Daiichi nuclear power plant accident. However, the stability of the carbonate phases precipitated in this system as well as the anion uptake capacities of these phases are poorly understood. In a previous study, (Kasahara, 2012), it was found that monohydrocalcite (MHC), a precursor of aragonite, affects the iodine capacity of aragonite, making it a possibly important material that can control the behavior of anions. The objective of this study therefore, is to investigate the sorption capacity of MHC for anions and its stability. MHC ($Mg^{2+}/Ca^{2+}=6$; $Ca^{2+}/CO_3^{2-}=1$) was synthesized and used for sorption experiments involving F⁻, Br⁻, I⁻, IO₃⁻, SO₄²⁻, CrO₄²⁻, HAsO₄²⁻, and phase transformation experiments. Results show that K_d values of HAsO₄²⁻ and F⁻ on MHC are high, while IO₃⁻, SO₄²⁻ are relatively low. On the other hand, Br⁻, I⁻, NO₃⁻, CrO₄²⁻ were not taken up. It is because MHC has high chemical reactivity and high specific surface (4 times large of aragonite, 15 times large of calcite), in addition MHC is most low density of calcium carbonate, so MHC can take up relatively large amount of anions than other calcium carbonate. And other thing, MHC involves Mg²⁺ abundantly. This study indicates that Mg²⁺ form fluoride adsorption site. Results of the transformation experiments show that MHC with no adsorbed anions easily transforms into a stable phase, whereas MHC loaded with increasing amounts of anions transform after longer durations. It is because the driving force for the transformation decreases with the anions content in the solution. In conclusion, MHC can take up fluoride and oxyanions that ionic radii is similar to carbonate but larger than that. In addition, MHC is stabilized as a function of uptake amount of anions.