

Indigenous Microbial Populations Dominantly Thriving in Deep Terrestrial Crust

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The terrestrial crust composed of granite is one of the largest, but least-understood, habitats of microbial life on Earth. This is mainly because it is technically challenging to collect microbiological samples without drilling contamination. In comparison to drilling from the land surface, short underground drilling significantly lowers the extent of contamination. However, the construction of underground facilities has tremendous impacts resulted from the intrusion of shallow groundwater into the granitic basement. The Mizunami underground research laboratory (URL) was constructed in the granitic basement, and the hydrologic disturbance caused by the underground construction was not evident in a sparsely fractured aquifer with low hydraulic conductivities. We drilled an underground borehole called 09MI21 and monitored the dynamics of microbial community structures over 4 years. The 09MI21 borehole was sectioned by a multi-packer system, and the interval #2 and #4 (09MI21-2 and -4) were annually monitored over four years immediately after drilling in 2009. The number of microbial cells in groundwater was determined by microscopic observations. For microbial community structure analysis, microbial cells were collected from groundwater by filtration and subjected to DNA extraction. 16S rRNA gene sequences were obtained by Sanger sequencing for Mizunami samples. Phylotypes were determined by grouping of sequences with >97% similarity and phylogenetically characterized by constructing a neighbor joining tree and calculating bootstrap values of branching points using the maximum likelihood algorithm. The total cell numbers were monitored from 2009 to 2012 and ranged from 10^4 to 10^5 cells/ml and decreased with time. 16S rRNA gene sequence analysis of 09MI21-2 and -4 resulted in 128 phylotypes after phylotype assignment with 97% similarity. Immediately after drilling in 2009, both 09MI21-2 and 4 were dominantly colonized by betaproteobacterial phylotypes. The dominant betaproteobacterial phylotypes were closely related to *Hydrogenophaga* spp. known to oxidize H₂ under aerobic conditions. After 2011, a phylotype classified within Nitrospirae phylum was stably dominant over two years. The phylogenetic relationships of Nitrospirae phylotypes were further analyzed by comparing their unambiguously aligned sequences against sequences from environmental clones and cultured species. One of four Nitrospirae clades was dominant in 09MI21-2 and 09MI21-4, and the dominant phylotype has been also detected in deep granitic groundwater from underground boreholes at Grimsel Test Site (GTS) in Switzerland. The most dominant phylotype formed a firm cluster with environmental sequences from hot crustal fluids from South Africa Gold Mine and Yellow Stone National Park rather than from soils and surface sediments. It is most likely that bacteria represented by the Nitrospirae phylotype are widespread and abundant in the terrestrial crust at depth, one of the vastest habitats of life from the early Earth history.

Keywords: subsurface microbiology, granitic basement, 16S rRNA gene sequencing, Mizunami underground research laboratory, Grimsel Test Site, deep biosphere

Novel Lineage of Archaea Dominates Inside an Inactive Deep-Sea Sulfide Chimney

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Origin of life is presumed to emerge from deep-sea hydrothermal vents according to theory of surface metabolism. It is known that microbial habitat is harbored at oxidative condition in inactive metal sulfide deposits formed at deep-sea hydrothermal vents. However the dissolution of metal sulfides is exceedingly slow under anaerobic conditions. It has distrusted the habitat of microbe in such structure, which requires physiological adaptation for microbial life to thrive within metal sulfides. Recent studies have revealed microbial life is also harbored under extremely oligotrophic conditions represented to the crustal biosphere. There might be interaction between anoxic water, metal sulfide, and microbial life. Previous studies of metal sulfide deposits at deep-sea hydrothermal vents have clarified that after the cessation of hydrothermal venting, microbial communities are shifted from thermophilic to psychrophilic microorganisms. However, the dominant microbial populations inside the metal sulfide structures remain to be clarified, because dominant bacterial and archaeal lineages are different between Central Indian Ridge (CIR) and Southern Mariana Trough (SMT). An inactive metal sulfide chimney was collected from SMT and characterized by mineralogical methods such as X-ray diffraction (XRD) pattern analysis and scanning electron microscopy (SEM) coupled to energy-dispersive spectroscopic (EDS) analysis, by which a CIR sample has been characterized. Pyrosequencing of 16S rRNA gene sequences of prokaryotes inside and outside the metal sulfide chimney coupled to quantitative PCR analysis of archaeal populations revealed that the interior and the exterior of the chimney structure were dominantly colonized by bacteria of Nitrospirae phylum and archaea of deep-sea hydrothermal vent euryarchaeal group (DHVE) 6, respectively. As Nitrospirae bacteria are also dominant in CIR, Nitrospirae bacteria are clarified to be cosmopolitan residents in inactive metal sulfide chimneys. This notion is important, because Nitrospirae bacteria are abundantly found in the deep terrestrial crust. DHVE 6 archaea are found in inactive metal sulfide chimneys in SMT, while DHVE 6 archaea are not detected in a mineralogically identical chimney in CIR. As the construction of maximum likelihood trees and the calculations of bootstrap values revealed that most of DHVE 6 sequences from SMT formed a firm monophyletic clade and distinct from other localities and environments, DHVE 6 archaea from SMT are likely adapted to thrive in anaerobic metal sulfide structures. The observations of microbial cells in the interior of the metal sulfide structure without oxidative alteration supports this inference. The existence of anaerobic microbial life in inactive metal sulfide structures has implications for the crustal biosphere and potentially for the emergence of life on the early Earth, because of the analogy to physicochemical conditions around metal sulfide minerals.

Keywords: deep-sea hydrothermal vent, metal sulfide deposit, Archaea, DHVE6

Anoxic Fe-oxidizing bacteria are using deep carbon in hot spring environments

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Oku-oku hachikuro hot spring is discharging anoxic, CO₂- and Fe-rich water. Hot spring water is flowing in distance from vent forming carbonate terrace. Various forms of aragonite (bundle of needle shape, radial aggregates, plate, etc.) comprise terrace. Those aragonites are most likely formed by inorganic processes. Near the vent, significant amounts of iron hydroxides are precipitating. Microscopic and SEM observation identified two forms of iron hydroxides; iron hydroxides covering sheath and stromatolite-like aggregates. Fe-rich precipitates disappear with distance where cyanobacteria start to form mats. Stable carbon isotope compositions of Fe-oxidizing bacteria are similar to that of cyanobacteria. However, radiogenic carbon isotope compositions are significantly different between Fe-oxidizing bacteria and cyanobacteria. Cyanobacteria are using atmospheric CO₂ with abundant ¹⁴C. But Fe-oxidizing bacteria are using dead carbon derived from deep underlying rocks rather than atmospheric CO₂. Those data may constrain carbon ecosystem of Fe-oxidizing bacteria in anoxic hot spring environments.

Keywords: Deep Carbon, Fe-oxidizing, hot spring

New Contamination Test Revealed Microbial Activities Related to Methane Hydrate Formation in the Mogami Trough

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The formation of methane hydrates is generally controlled by methanogenic activity in marine sediments. In case of marine sediments associated with shallow methane hydrates, it is technically challenging to penetrate hard strata with methane hydrates and carbonate crusts by microbiologically suitable piston coring (PC). Alternatively, rotary core barrel (RCB) is used for deep drilling at shallow hydrate sites, whereas microbiological contamination from drilling mud is problematic and requires an accurate contamination test. Although contamination tests using perfluorocarbon and/or fluorescent microspheres are widely used, it is difficult to maintain constant tracer concentrations in drilling mud for accurate evaluation of contamination. In this study, RCB coring was conducted with a new tracer, amino G acid, to deeply penetrate a shallow hydrate site in Mogami Trough. During drilling, the concentration of amino G acid in drilling mud was successfully maintained at $\sim 8 \times 10^5$ ppb within $\pm 10\%$. As the detection limit of amino G acid by high performance liquid chromatography was 0.03 ppb, it is possible to detect the intrusion of 10^2 nl of drilling mud into 1 ml of porewater. Population density in drilling mud was at $\sim 5 \times 10^7$ cells/ml, and it was found that our new method is capable of detect 10 contaminated cells in 1 ml of sediment. Based on the concentration of amino G acid in porewater, the level of contamination was accurately calculated, and it was found by 16S rRNA gene sequence analysis that highly contaminated sediment samples were dominantly colonized by gammaproteobacterial species of the genera *Shewanella*, *Listonella* and *Vibrio*. In sediment samples with low contamination, many sequences were affiliated within bacterial groups commonly found in deep PC sediments such as the phylum Chloroflexi and candidate divisions JS1 and NT-B2. The rates of methanogenesis via acetate fermentation and CO₂ reduction were measured by sediment slurry incubation with ¹⁴C-labeled acetate and bicarbonate, respectively. Although acetate fermentation was greatly influenced by drilling contamination, CO₂ reduction was not apparently influenced. Interestingly, the rate of CO₂ reduction was highest in a deep sediment sample win methane hydrates, which suggests that in-situ microbial activities might contribute to ongoing formation of methane hydrates in Mogami Trough.

Keywords: Methane hydrate, Marine sediment, Contamination test, Microbial community, Methanogenesis

Dense microbial community at the surface of manganese nodule formed in ultra-oligotrophic seafloor

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During IODP Exp. 329, manganese nodule was collected from the seafloor of ultra-oligotrophic South Pacific Gyre, and its microbial and chemical characteristics were investigated. This nodule was formed on red pelagic clay, and its chemical composition and depositional fabrics indicated that this nodule was formed by hydrogenesis. Synchrotron analysis (μ -XAFS) showed that this nodule was mainly composed of δ -MnO₂ and goethite. Microbotryoidal small protrusions at the nodule surface contained relatively high Fe, although there were some high Mn thin layers. Cu content of manganese nodule was about 0.3%, although it was about 10 times higher than that of surrounding sediment.

SYBR Green I staining was applied for cryo-sections prepared from this nodule sample, and revealed that the microbial cell density at the surface part (about 0.5 mm) was almost three orders of magnitude higher than that of surrounding sediment. Sequencing of 16S rDNA (~1400 bp) indicated that the composition of microbial community (both bacteria and archaea) inhabiting in this nodule was different from that of surrounding sediment, showing that manganese nodule provided specific habitat for these microorganisms. Most of recognized bacteria were heterotrophs, and known manganese-oxidizing bacteria were not detected. On the other hand, most of archaea were the member of Marine Group I, and the percentage of *Nitrosopumilus* sp. was especially high at the nodule surface. This organism is ammonia-oxidizing autotrophic archaea, and its metabolism requires multicopper oxidase that utilizes Cu as a cofactor.

Although the availability of electron donor is very limited in the seafloor of ultra-oligotrophic South Pacific Gyre, *Nitrosopumilus* sp. can grow autotrophically even under very low ammonia concentration, and its growth is considered to be stimulated on the Cu-accumulated substances such as manganese nodule. Known manganese-oxidizing microorganisms all possess multicopper oxidase and it has critical roles in manganese oxidation. This fact implies the possibility that *Nitrosopumilus* sp. may contribute to the formation of manganese nodule.

Relationship between arsenic dissolution mechanism to organic matters in the marine sediments from Kumano Basin

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Arsenic is believed to be accumulated in marine sedimentary rocks. In this study, porewater and squeezed cakes were analyzed to trace arsenic concentration with depth and proceeding the diagenetic reaction including maturation of organic matters. Samples for this study were collected at Site C0002 (upper Kumano Basin), C0021 and C0022 (accretionary prism) during IODP Exp.315 and Exp.338.

The analytical result of porewater at the Site C0002 (0-1000 mbsf) (mbsf=meters below seafloor) showed that the arsenic concentration was between 0-15 ppb at 0-100 mbsf, then increased to reach the highest concentration (400 ppb) at 200 mbsf. Below that depth, it was constant about 100 ppb and increased again to 200 ppb from 300-400 mbsf, then decreased to 600 mbsf <30 ppb below that depth. Arsenic concentration of sediments was 5-13 ppm, and the most of samples contained >10 ppm especially at 300-400 mbsf.

At the Site C0021, arsenic concentration of porewater was 10 ppb on the average at 0-160 mbsf and had no relationship to the depth, and the highest concentration was recorded at 200 mbsf (100 ppb). Arsenic concentration of sediments was 5-10 ppm down to 150 mbsf, and peaked at 400 mbsf (23 ppm).

At the Site C0022, arsenic average concentration was 10 ppb between 0-120 mbsf. The highest concentration was observed at 120-150 mbsf (100 ppb), and then drastically decreased to 200 mbsf (20 ppb), then it became constant below that depth. Arsenic concentrations of sediments largely varied between 3-12 ppm.

The arsenic concentration of porewater was higher than that of sea water (1.7 ppb) and varied with depth, suggesting that arsenic fixed in the sediments would be released into the porewater along with changing physico-chemical conditions.

At the Site C0002, the arsenic concentration of porewater is the higher when the pH is 8.3. As/Cl (to take dilution of sea water into account) and pH have positive relationship. It is known that dissolution of iron hydroxide adsorbed arsenic or desorption associated with reduction of arsenate (As^V) to arsenite (As^{III}) occur following the reduction. The similar reaction might occur at this site. In contrast, such a relationship was not observed at the Site C0021 and C0022.

T_{max} value, which is the temperature indicating the complete decomposition of organic matters and can be used for the index of maturation degree, was measured by Rock Eval pyrolysis for the sediments of the Site C0002 (200-500 mbsf). The arsenic concentration of porewater was high with increasing T_{max} (425-430 °C). On proceeding diagenetic reaction, arsenic adsorbed to or fixed in organic matters would be released into the porewater. The similar relationship was observed at Site C0021, but C0022. Maturation stage of sedimentary organic matters would affect to the arsenic dissolution.

Keywords: arsenic, Kumano Basin, IODP

Development of Eh meter based on the enrichment and speciation of arsenic and selenium oxyanion in barite

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It is possible that the distribution behaviors of redox-sensitive elements between water and authigenic minerals can provide information on the oxidation state of the element in the coexistent water during the deposition of the mineral. Our previous study showed that barite-selenium oxyanion system can be used as a reliable redox indicator for oxic-suboxic boundary because the selenate/selenite (Se(VI)/Se(IV)) ratio in barite was primarily correlated with that of the ratio in water. If the method can be applied to other barite-redox-sensitive element systems as well, single barite particles can provide more accurate redox information on the environment where barite precipitated. Thus, in this study, we focus on arsenic oxyanion as a coprecipitated trace elements because arsenic (As) is dissolved in water as arsenite (As(III)) or arsenate (As(V)) ion under suboxic and anoxic conditions, respectively. If barite can incorporate both As(III) and As(V) as well as Se(IV) and Se(VI), the As(V)/As(III) ratio recorded in barite may possibly reflect the ratio in water, which consequently indicates more accurate redox information whether barite precipitated under oxic, suboxic, or anoxic redox environments.

Coprecipitation experiments of As with barite were conducted under various pH conditions (pH=2.0, 5.0, 8.0, or 10.0) to investigate the influence of the oxidation state on its immobilization into barite based on the speciation of As in barite and water phases by As K-edge XANES and HPLC-ICP-MS, respectively. These pH conditions were determined to assume the variation of As species in water: (i) As(III) are mainly dissolved as H_3AsO_3 from pH 2.0 to pH 8.0, and $H_2AsO_3^-$ at pH 11.0, while (ii) As(V) are mainly dissolved as H_3AsO_4 , $H_2AsO_4^-$, $HA_2O_4^{2-}$ at pH 2.0, 5.0, 8.0 and 11.0. The results showed that both As(III) and As(V) can be incorporated into barite depending on their species in water at all pH. These trends are also observed at different chemical composition of water and/or saturation indices of barite. Based on the laboratory experiments, it is suggested that barite-arsenic oxyanion system can be used as a reliable redox indicator to estimate the As(V)/As(III) ratio in water. Moreover, we can estimate absolute Eh value based on the As(V)/As(III) ratio in barite if the oxidation state of As in water was under equilibrium in terms of the redox condition.

Natural barite samples collected in Tamagawa Hot Springs (Akita Prefecture in Japan), where the headwater was very acidic (pH 1.2) with high As concentrations ($1000 \mu g/L$), were also analyzed by micro-XRF and XANES to investigate the applicability of barite-arsenic system as a redox indicator in natural systems. Ogawa et al. (2012) revealed that As predominantly was dissolved as As(III) in this area by anion exchange method. The results showed that As in natural barite can be detected by the micro-XRF-XAFS technique and the presence of As(III) species in barite, suggesting that As(V)/As(III) ratio in barite reflect the ratio in depositional water. Thus, a good correlation between laboratory experiments and natural analysis suggested that barite-arsenic oxyanion system can work as a redox indicator to estimate Eh range where barite precipitated and can be applied to environmental systems where As was incorporated into barite.

Keywords: barite, selenium oxyanion, arsenic oxyanion, redox indicator, XAFS, distribution coefficient

Formation condition of monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$)

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Monohydrocalcite (MHC: $\text{CaCO}_3 \cdot \text{H}_2\text{O}$) is one of calcium carbonates and is metastable phase with respect to calcite and aragonite. MHC was frequently found in the saline environments such as saline lake, cold spring and cold seawater. The solubilities of the minerals formed in saline conditions are usually high. For example, that of gypsum (CaSO_4), which can be frequently found in saline lake, is $10^{-4.6}$. On the other hand, that of MHC is not so high ($10^{-7.7}$) which is 1000 times lower than gypsum. Why MHC, which is not soluble phase, is frequently found in saline conditions?

MHC is rare in nature. On the other hand, MHC can be easily synthesized in laboratory. For example, the simple addition of sodium carbonate (Na_2CO_3) to seawater leads to the immediate formation of MHC. Seawater is mixture of various components. Among them, magnesium is known as the essential component for the formation of MHC. The coordination number of magnesium is six in ambient conditions. On the other hand, that of calcium in monohydrocalcite is eight. Therefore, magnesium cannot be incorporated into the MHC structure. Why the MHC formation requires the coexisting magnesium?

We examined the formation conditions of MHC by the laboratory synthesis experiments by mixing the CaCl_2 , MgCl_2 and Na_2CO_3 solutions in various ratio (Nishiyama et al. 2013). The results showed that the MHC can form from the solutions of which the calcium concentrations were higher than the carbonate concentration in the presence of a certain amount of magnesium. The reacted solutions after MHC formations were equilibria with MHC as well as hydrous magnesium carbonate (nesquehonite: $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). According to the experimental results, the formation conditions of MHC can be considered as the conditions which allow the formation of hydrous magnesium carbonate after the consumption of calcium and carbonate from solutions for the formation of MHC.

Based on the formation conditions, we can answer the mysteries in regard with MHC formation. Although the solubility of MHC is not so high, that of the coexisting hydrous magnesium is relatively high ($10^{-5.3}$ for nesquehonite). Consequently, the formations of MHC have been frequently found in the saline conditions such as saline lakes.

The motivation to study MHC was the finding of MHC in the long sediments core from Lake Hovsgol (largest fresh water lake in Mongolia). Although MHC was not observed in the surface parts of the sediments, it was found in the depths corresponding to the past glacial periods. The presences of MHC in the layer indicates that the water qualities of the lake was salty during the glacial periods. The formation conditions of MHC obtained from the present study enables the quantitative reconstruction of the past water quality in Lake Hovsgol.

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 [1]. 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 [2]. 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.

Stratigraphic correlation within the Moodies group was confirmed by the 3 quartzite marker beds and 1 basaltic flow underlying Mds2. In the previous study, geological survey was conducted Mds2 at Moodies Hills (MH Mds2). We conducted new geological surveys at 4 sections of the Moodies Group: a stratigraphically upper section than the previous study at Moodies Hills (MH Mds3), and 3 sections at a different locality, called Gate of Paradise in the Eureka syncline located ~10 km northeast of Barberton (GP Mds1~3). BIFs were recognized and sampled at all the sections, where the predominant rock types are sandstone and siltstone. Whereas the BIF at MH Mds2 and GP Mds1 are overlain by silty sandstone and sandstone, the BIF at MH Mds3, GP Mds2 and Mds3 are overlain by siltstone. BIFs in Mds2 were the most developed, composed of thick (>5cm) and continuous Fe-rich layers. Petrographic observation of the Fe-rich layers 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. Bulk chemical compositions of the samples were analyzed by WD-XRF or ICP-AES. The Cr/TiO₂ ratios show that BIF at GP Mds1 was enriched in Cr while BIF at GP Mds2~3 and MH Mds3 were not enriched in Cr. MH Mds2 is more enriched in Cr than GP Mds1, which corresponds with the enrichment of Fe in the BIFs. The results suggest that both Cr and Fe were chemically supplied and co-precipitated from the ancient seawater. The results may also imply that oxic ocean were limited at very shallow parts such as sedimentation level of sandstone.

[1] Konhauser et al. (2011) Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event, *Nature*, 478, 369-373.

[2] Otake et al. (2013) Chromium enrichment in sedimentary rocks deposited in shallow water in the 3.2 Ga Moodies Group, South Africa, *Mineralogical Magazine*, 77, 1901.

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

Comparison of Adsorption Behavior of Molybdenum and Tungsten to Pyrite Under Reductive Condition

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Molybdenum (Mo) and tungsten (W) belong to the same group in the periodic table. They exist as molybdate (MoO_4^{2-}) and tungstate (WO_4^{2-}) in modern sea water respectively, and have very similar chemical properties each other. It is considered that the environmental behavior of both elements depend on redox condition. For example, the crustal abundance of W is almost same as that of Mo, while the concentration of W in modern seawater is 1800 times smaller than that of Mo (molar ratio) (Sohrin et al., 1987). It is considered that adsorption to ferromanganese oxides is one of the most important removal processes in sea water (Kashiwabara et al., 2011; 2013). On the other hand, it is possible that sulfide minerals such as pyrite controlled the concentration of trace elements including Mo and W in the palaeocean under reductive condition. Moreover, in some thermophilic bacteria (*hyperthermophilic archaea*) which inhabit in hydrothermal environment, W enzymes are substituting the role of nitrogen fixation performed by Mo enzymes in the present living things. Thus it is possible that solubilities of elements and essentiality for living bodies are related to each other. However, the solubilities of Mo and W in palaeocean are unclear because few studies have been conducted about adsorption behavior of Mo and W to sulfide minerals under reductive condition. In this study, adsorption experiment of Mo and W to pyrite was conducted using anaerobic chamber which can control the concentration of oxygen to clarify the adsorption behavior of these elements under reductive condition. To estimate the distribution coefficient (Kd), adsorbed amount of Mo and W were measured by ICP-MS, and X ray absorption fine structure (XAFS) measurements were conducted to study adsorption mechanisms of these elements to pyrite.

Concentration of sulfide ion (S^{2-}), pH values, and ionic strength were controlled in the adsorption experiment. Under the acidic condition (pH= 4.0), Mo was adsorbed to pyrite better than W, and the adsorbed amount of both elements were decreased with increase in pH. It is suggested that both Mo and W existed as sulfide species both liquid and solid phases from the results of W L3 edge XANES and Mo K edge XANES. On the other hand, in the absence of S^{2-} , both Mo and W existed as oxygen-coordinated species in liquid phase, while only Mo adsorbed on pyrite as sulfur-coordinated species. These results suggest that Mo is adsorbed on pyrite strongly by forming inner sphere complex as sulfide, while W is adsorbed weakly via outer-sphere complexation.

Our experimental study clarified that Mo is adsorbed to pyrite to a larger degree than W, which is the opposite case to distribution behavior to ferromanganese oxide. In palaeocean environment, we suggest the solubility of W was higher than that of Mo, indicating that the solubilities of these elements were varied with changes of the redox condition of earth's environment, and it is possible that the difference of solubilities affected the essentiality of elements for living bodies.

Keywords: Molybdenum, Tungsten, XAFS, Adsorption behavior, Pyrite

Biotite-vermiculite mixed layer minerals from eastern Fukushima, Japan and their Cs-sorption behavior

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It is suggested that clay minerals in the surface soil strongly fix radioactive cesium and limit its migration in Fukushima. Among such minerals, weathered biotite has a high capacity of irreversible sorption and it has been thought that this mineral fixes radioactive cesium at specific sites in the crystals. Because the contaminated areas in Fukushima are mainly covered with weathered granite soil, such minerals are abundant. Therefore, a basic understanding of the structure of weathered biotite and their Cs-sorption behavior should be important to discuss the dynamics of radioactive cesium in the soil.

In this study, we aimed to reveal the two issues: 1) the characteristics of the weathered biotite with biotite-vermiculite (B-V) interstratification that were collected from the eastern area of Fukushima Prefecture, 2) how the weathered biotite incorporate cesium ions inside the crystals.

The weathered biotite sample was collected from weathered granodiorite of Abukuma granitic rocks at Ono City in Tamura District and Kawauchi village in Futaba District, in the eastern part of Fukushima Prefecture, Japan. These samples include fresh biotite and weathered biotite with different weathering state at same/near outcrops.

First, to estimate the proportion of B and V layers in the crystals and the characteristics of their mixing, powder X-ray diffraction (XRD) for oriented specimens and simple simulations (Sybilla, Chevron Energy Technology Company) of one-dimensional XRD for the mixed-layer minerals were conducted. The parameters for mixing were optimized, by comparing the experimental and simulated patterns. The results suggests that different weathering conditions (e.g., in the soil and on the surface of core rocks) resulted in different characteristics of mixings, even though they were formed at the same rock and/or outcrop.

Second, Cs sorption experiments using the CsCl aqueous solution were conducted and the Cs-sorbed specimens were also measured by powder XRD. Then, we also compared the experimental and simulated patterns as the same way as for the original sample. From this procedure, it was suggested that Cs-incorporation at the vermiculate (hydrated) interlayers is a very heterogeneous phenomenon, which was also confirmed by the direct observation of Cs in the crystals, using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM).

Keywords: Fukushima nuclear accident, cesium, biotite, XRD, weathering, mixed layer mineral

An experimental study on the correlation between chemical weathering rate, physical weathering rate, and rock hardness

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Weathering of a rock in stream water often progresses by interplay between the weakening of grain boundary due to dissolution (chemical process) and the detachment of grains due to abrasion by water and collision of other rocks (physical process). Rock hardness is expected to be a controlling factor of these processes. The purpose of the present study is to understand how the chemical process and physical process are correlated each other and how these processes are affected by the rock hardness. Three Berea sandstone samples differing in hardness (Leeb hardness) were prepared. Each sample was soaked in water and a ball was repeatedly collided, and the way at which weathering progresses was monitored. Total weathering rate (physical weathering rate plus chemical weathering rate) was determined from temporal change in total weight of the sample. Chemical weathering rate was determined from temporal change in solute concentration in water. Physical weathering rate was calculated by subtracting the chemical weathering rate from the total weathering rate. The results showed that total weathering rate decreased with increasing rock hardness. The quantitative ratio of "physical weathering / chemical weathering" increased with decreasing Leeb hardness, and the physical weathering rates were 4-371 times greater than the chemical weathering rates. The physical weathering rate was found to be exponentially correlated to Leeb hardness.

Keywords: Chemical weathering rate, Physical weathering rate, Rock hardness

A kinetic study of the formation of iron (hydr)oxides at pH 2-4 and at 5-55 °C

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Iron (hydr)oxides are widely distributed in the earth's surface environment. The formation process and adsorption characteristic of iron (hydr)oxides and the material transport mediated by iron colloids are receiving attention. In the present study, we evaluated (i) the rate at which iron (hydr)oxides are formed from dissolved Fe^{3+} at pH 2-4 and (ii) the effect of the difference of anions on the reaction behavior.

First, a solution of Fe^{3+} 100 ppm was prepared by dissolving FeCl_3 into pure water (chloride system). This solution was reacted at 15, 25, 35, 45, and 55 °C. At 25 °C pH of the solution was ~ 2.7 at the start of the reaction and decreased to ~ 2.2 as reaction time passed. Such change in pH is known to occur as a result of the following reactions: hydration of Fe^{3+} (release of H^+) \rightarrow formation of dissolved $\text{Fe}(\text{OH})_3 \rightarrow$ formation of solid $\text{Fe}(\text{OH})_3$ (Grundl and Delwiche, 1993). Therefore, information of the formation rate of iron (hydr)oxides can be obtained by monitoring the pH of the solution. After the initial stage of the reaction in which the concentration of dissolved $\text{Fe}(\text{OH})_3$ decreased slowly presumably due to nucleation, first-order-like decrease of $\text{Fe}(\text{OH})_3$ concentration proceeded in the intermediate stage, and the reaction behavior deviated from the first-order reaction at the later stage. By focusing on the intermediate stage, rate constants of $3.3\text{E-}5 - 1.1\text{E-}2 \text{ s}^{-1}$ were obtained at 15-55 °C. Good linearity was confirmed in an Arrhenius plot of these rate constants, and an activation energy (E_a) of $118 \pm 5 \text{ kJ/mol}$ was obtained.

Secondly, solutions of Fe^{3+} 100 ppm were prepared by dissolving $\text{Fe}(\text{NO}_3)_3$ nonahydrate and $\text{Fe}_2(\text{SO}_4)_3$ n-hydrate into pure water to compare the reaction behavior between chloride, nitrate, and sulfate systems. Temperatures for the reactions were 15, 25, 35, and 45 °C in the nitrate system, and 25, 35, 45, and 55 °C in the sulfate system. At 25 °C, initial pH were ~ 2.9 for the nitrate solution and ~ 2.7 for the sulfate solution, and pH for both the solutions decreased to ~ 2.5 as time passed. Rate constants obtained in the same way as the chloride system were $2.7\text{E-}5 - 3.6\text{E-}3 \text{ s}^{-1}$ in the nitrate system and $6.7\text{E-}5 - 5.9\text{E-}3 \text{ s}^{-1}$ in the sulfate system, again showed good linearity in Arrhenius plots. $E_a = 122 \pm 4 \text{ kJ/mol}$ for the nitrate system and $E_a = 119 \pm 4 \text{ kJ/mol}$ for the sulfate system were obtained. These results showed that the activation energies agree within the margins of error regardless of the difference of the kind of anions.

Finally, a solution of Fe^{3+} 10 ppm was prepared by dissolving FeCl_3 into pure water to evaluate the reaction rate at pH 3-4. Temperatures for the reactions were 5, 15, 35, and 25 °C. At 25 °C, pH of the solution decreased from ~ 3.8 to ~ 3.3 as reaction time passed. The rate constants obtained was $2.7\text{E-}5 - 2.9\text{E-}3 \text{ s}^{-1}$, which was about 16 times faster than that of Fe^{3+} 100 ppm at pH 2.2-2.7. The activation energy obtained was $E_a = 162 \pm 3 \text{ kJ/mol}$ and higher than that at pH 2.2-2.7.

Keywords: kinetics, iron (hydr)oxide, activation energy

Imbibition rate of water in sandstone and its rate-determining process

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When a rock contacts water, spontaneous imbibition of water proceeds by capillary force. Lucas-Washburn (L-W) equation is often used as the equation which can express the relationship between the distance of water penetration (x), time (t) and pore radius (r): $x^2 = r\gamma t \cos\theta / 2\mu$, where μ is the liquid viscosity, γ is the liquid surface tension, and θ is the contact angle. It is generally known that a pore size significantly smaller than the main pore size is obtained by inserting measured values of x and t in the L-W equation. We evaluated whether the reason is related to a factor not considered in the L-W equation or the imbibition rate is indeed controlled by the imbibition in small pore. Berea sandstone from Ohio, USA, was used in the experiment. The main pore radii of the sandstone are 1-100 μm and more than 95% of the pores have radii greater than 3 μm . First, the bottom of a dried rock core (diameter 2.6 cm; height 5.4 cm) was dipped in water and the imbibition height x and time t were measured (dried condition). In this condition, all the pores can absorb water. Next, the pores smaller than 3 μm radii were filled with water by expelling pore water of the other sizes using a gas injection technique (water-expulsion method) and x and t were measured (wet condition). Under the wet condition, absorption of water proceeds only in the pores greater than 3 μm radii. The imbibition rate in the dry condition was found to be approximately one-half of that under the wet condition. The result suggests that the rate of overall imbibition process is controlled by slow imbibition in small pores.

Keywords: capillary force, imbibition rate, pore

Hydration and hardening process of iron and steel slags used for roadbed material

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Steel slag is a by-product of the steel manufacturing process and produced in large quantities every year. Steel slag is expected to reuse in Japan. However, it was observed that the uniaxial compressive strength (UCS) differs among mixed slag for roadbed materials produced from different factories including even with the same mixing ratio of DCS and GBFS. In particular, the difference between the UCS of slag produced from K ironworks and N ironworks was remarkable. The reason for these differences has not yet been clarified. To extend the market of steel slag, it is essential to clarify the relationship between secondary minerals formed after hydration and the UCS of the slag.

This study firstly investigated the UCS of the MIX slag (DCS / GBFS = 4) from K ironworks and N ironworks. Based on the UCS tests, the slag from N ironworks is stronger than the slag from K ironworks.

Batch experiments were then conducted for samples from K ironworks and N ironworks to investigate and compare the evolution of solution chemistry and precipitation of secondary minerals during slag hydration. Based on the XRD analysis for the samples after the batch experiments, the main product of the MIX sample from K ironworks is α -C₂SH while the MIX sample from N ironworks produced mainly CSH. The difference in mineralogy could be related to the UCS of the slag because of the difference in volume of secondary minerals. Based on the solution analysis of the samples, it is observed that the main source of Ca ion is DCS, while the main source of Si ion is GBFS. In addition, it is possible that the concentration of H₄SiO₄ in the solution, which is present in the form of calcium silicate hydrates, is determined by GBFS. Kinetic model was constructed. The model represent the mineral evolution during slag hydration in the both MIX slags.

Keywords: Slag, Hydration

Shock-induced Strecker Reactions for prebiotic amino acid formation: Experimental simulations

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Amino acid is thought to be one of the most primary biomolecules related to the origin of life. The prebiotic syntheses of amino acids under early Earth condition were simulated in experiments using by several energies such as electric discharge, light, heat and shock wave. According to a previous study by Aubrey et al., 2009, it is considered that amino acid formation from ammonium formate (NH_4HCO_2) depends mainly on concentration of starting materials. It has been known that ammonium formate can produce HCN above 180 °C, and that HCN is a necessary material in order to synthesize amino acid via strecker reaction. Strecker reaction is used for syntheses of amino acids in the presence of NH_3 and HCN. These molecules can be easily formed from ammonium formate at high temperature. They performed hydrothermal experiments at concentrations of 0.1 M and 0.001 M. Then, amino acids such as glycine and alanine were formed from only a high concentration sample (0.1 M). However, this concentration is unrealistically too high for natural marine conditions. We need to know the effect of shock energy on the formation.

In this study, we carried out shock recovery experiments using a propellant gun for aqueous solutions of ammonium formate and formamide. Starting material, encapsulated in steel container as a target, was ammonium formate or formamide aqueous solution immersed in the pressed olivine powder. We used two concentrations (5 mM and 100 mM) to compare with the results of hydrothermal experiments. Olivine was simulated as ordinary chondrite. The peak pressure in this study was about 5 GPa. Recovered solutions were analyzed by using hybrid/MS for biomolecules of the m/z values between 50 and 500 with analytical errors within 3 mmu (0.003). The results indicated that glycine and glycyglycine were detected in all samples and that benzoic acid as carboxylic acid was detected in only formamide samples. Present results suggest that glycine formation by shock reaction might be more effective than that of hydrothermal reaction because glycine was formed from low concentration samples. Detailed discussions will be given as poster.

Keywords: Marine meteorite impact, Amino acids, Strecker reactions

The Study on Removal Efficiency of Ammonium Nitrogen by Four Herbaceous Plants in Artificial Rainwater

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The Study on Removal Efficiency of Ammonium Nitrogen by Four Herbaceous Plants in Artificial Rainwater
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Abstract: To select the best herbaceous plant for ammonium nitrogen removal in a bioretention, the ammonium nitrogen removal efficiency by four herbaceous in bioretention were explicated through a pot experiment. This experiment simultaneously set two scenarios, namely analyzing and measuring the removal efficiency of plants on ammonium nitrogen under the circumstance of different inflow concentration and different soil mediums. The results show that the four herbaceous plants have good removal effects on ammonium nitrogen in the artificial rainwater, and the average removal efficiency of ammonium nitrogen is between 93.90%~99.90%. The ranks of capabilities of different herbaceous plants removing ammonium nitrogen in artificial rainwater from high to low are: *lolium perenne* > *axonopus compressus* > *poa annua* > *festuca elat*. Four herbaceous plants have different removal efficiency on the ammonium nitrogen in the artificial rainwater with different concentrations. In the artificial rainwater, with the increase of inflow concentration of ammonium nitrogen, the removal efficiency of four herbaceous plants on ammonium nitrogen have also enhanced. For the same herbaceous plants with same inflow concentration, soil II is the optimum soil medium, possessing relatively good capacity of removing ammonium nitrogen.

Key words: Bioretention; Herbaceous Plants; Ammonium Nitrogen; Removal Efficiency

Immobilization of hazardous anions in andosol and alluvial soil using magnesium oxide

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Soil contamination by hazardous anions is a significant problem in Japan. Magnesium oxide (MgO) has been used as an immobilization agent for hazardous anions such as fluoride and boron. However, it is difficult to optimize the immobilization process because the immobilization depends on the type of soil and the long-term elution behavior of hazardous substances is uncertain.

In this study, to investigate whether MgO can be applied to immobilize fluoride and boron in andosol and alluvial soil and to clarify the immobilization mechanism, the following experiments were conducted; 1) characterization of different types of soil (andosol, alluvial soil), 2) MgO hydration rate determination, 3) interactions between soils and MgO, 4) fluoride and boron sorption behavior onto MgO, 5) immobilization experiments using the soils under several pH and anion loading.

The possible mechanisms of immobilization of fluoride and boron in andosol and alluvial soil using MgO are as follows. Fluoride is immobilized via incorporation into the magnesium hydroxide (Mg(OH)₂) structure during the MgO hydration reaction. On the other hand, boron is immobilized by coprecipitation with magnesium following the formation of a magnesium borate complex. To summarize, proposals for carrying out immobilization were made. To immobilize the anions, MgO should be added into the soils to establish the above mechanisms. One significant point is that MgO addition should take the pH buffering capacity of soils into account.

Keywords: Fluorine, Boron, Soil, Magnesium oxide, Immobilization

TEM observations of clay minerals in Lake Tega sediment

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1. Introduction

Like minerals and rocks, microbes are ubiquitous in soils and aquatic sediments. It is well known that the interaction between minerals and microbes contribute to mineral dissolution and precipitation (Dong and Lu, 2012). For example, dissimilatory iron reducing bacteria (DIRB), which are widely distributed in natural environment, transform Fe^{3+} to Fe^{2+} at the surface of an iron oxide particle (Lovley et al., 2004). Thus, the minerals-microbes interaction plays an important role in biogeochemistry on the earth's surface. Transmission electron microscopy (TEM) is commonly used as an experimental technique to analyze the interplay between minerals and microbes (Kawano and Tomita, 2001; Tazaki, 2005). Although, detailed mineralogical researches are highly important to elucidate the minerals-microbes interaction, there is little studies of TEM observation on aquatic sediments. This study is focused to describe compositional and crystal chemical features of minerals in lake sediments by using HRTEM observation.

2. Materials and Methods

Sediment samples were collected from a ca. 20 cm core drilled at Lake Tega in Abiko city, Chiba in Japan. The sample core was divided into two types, upper and lower sediments. The samples were examined for mineralogical details with scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and fourier transform infrared spectroscopy (FT-IR).

3. Results and Discussion

The powder XRD patterns of upper and lower layer sediments showed that quartz, orthoclase, plagioclase, and kaolin (kaolinite and halloysite) were included, but clay minerals were mainly composed of the lower layer sediment. The SEM images revealed that organism fragments ranging from 10 to 30 μm in size were widely observable in both upper and lower layer sediments. FT-IR spectroscopy showed that the weak bands derived from organics were observed from the both sediments, indicating that the deposits included the minerals and organic compounds which probably originates from organisms.

The TEM analysis showed that kaolinites in the sediments had plate shape with 1-4 μm in width, which is compatible with previous studies (Sudo et al., 1980; Bergaya et al., 1996). The forms of halloysites with 50-100 nm in length lath-like shape and with ca. 100 nm in width spherical shape are also consistent with those of previous studies (Sudo et al., 1980; Singh and Gilkes, 1992). The EDS analysis of individual particles revealed that kaolinites and halloysites contained not only Si, Al, O but also K, Na, Fe, although the electron diffractions showed clear diffraction spots with their symmetries.

In kaolin minerals, very small amount of Fe^{2+} can be substituted for Al^{3+} , which results in slightly negative charge (Detellier and Schoonheydt, 2014). Therefore, it is likely that substitution of Fe^{2+} for Al^{3+} in the kaolin minerals gives rise to absorption of K^+ and Na^+ to stabilize the charge balance.

Keywords: lake sediment, TEM, clay mineral, kaolinite, halloysite

Study on molecular structure of diatoms frustule by synchrotron X-ray Diffraction and Infrared spectroscopy

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1. INTRODUCTION

The diatoms in ocean, a lake, and a river are responsible for almost a quarter of the photosynthesis of the whole earth (Nelson, et al. 1995). They have a great influence on the element movement of the Earth's surface by absorbing different metal ions selectively (Morel and Price 2003). The diatoms with complicated surface structure have a property to adsorb various substances to their frustules, but the adsorption characteristic depends on the structures of the frustule surface. Furthermore, whether perished diatoms' frustules are stored or not is determined by the structures of the frustules. However, the surface structures of the diatoms' frustules are still unknown very well. Kamatani (1974) researched on the structure of the diatom's frustules by Infrared spectroscopic analysis, but the author didn't separately analyze the collected samples. Recently, Gelibert et al. (2004) classified every species of diatom and studied the structure of the frustules by using the small angle scattering method and Infrared spectroscopic analysis. Because the frustules would be heavily damaged by their samples treatment process, the results of the study have little credibility. This study is aimed to elucidate the molecular structures using Infrared spectroscopic analyses and X-ray diffraction analysis for the diatom's frustules which were collected and cultivated separately in the laboratory.

2. MATERIALS AND METHODS

1) Collection and cultivation processes of diatoms

Diatoms were collected from three sites in Lake Yogo, Siga prefecture, Japan, and in Obitsu River tideland, Chiba prefecture, Japan, and at the northern part of Thailand. They were cultured in nutrient medium f/2 and harvested under red and green LED light at 25 degree C. After multiplying moderately, each species of diatom was carefully transferred into separate Petri dishes and multiplied under a same condition. As a result, 19 species of diatom were isolated and finally three species were successfully obtained in enough quantity for the following experiments.

2) Sample treatments

The each diatom multiplied was filtered through a membrane filter and removed from salts and organic matters by centrifugal separation. After rinsed with acetone, the diatom's frustules were dried at 50 degree C in an oven for three days.

3) The measurement

The synchrotron radiation X-ray diffraction analysis was performed at High Energy Accelerator Research Organization(KEK), Photon Factory(PF), beam line BL8B.

3. RESULT AND DISCUSSION

Gomphonema sp. in the northern part of Thailand, and Nitzschia cf. Frustrum in the Lake Yogo, Siga prefecture form a wedge shape and a spindle shape, respectively. Cyllindrotheca sp. in Obitsu River tideland has a long extended needle shape. The form is characterized by the twisted spindle shape composed of thinly frustules. The SEM observation showed that the Gomphonema sp. and Nitzschia cf. Frustrum maintained their forms during the sample treatment. With centrifugal separation, on the other hand, most of the forms of Cyllindrotheca sp. were destroyed except the spiculums at the both ends, maintained. Synchrotron radiation X-ray diffraction analysis showed that Gomphonema sp. and Nitzschia cf. Frustrum gave basically similar broad diffraction pattern to that of amorphous silica. However, Cyllindrotheca sp. , unlike other two species, showed sharp peaks at the position of $d = 3.920, 2.603, 1.545\text{\AA}$ and a few weak peaks. The results of the Infrared spectroscopic analysis on Gomphonema sp. and Nitzschia cf. Frustrum showed that the absorption spectra were similar to those of amorphous silica, which is consistent with the result of the X-ray diffraction patterns. On the other hand, Cyllindrotheca sp. showed a spectrum similar to that of opal-CT.

Keywords: diatoms, molecular structure, X-ray diffraction, IR spectroscopy

Microbial zonation observed on travertines: a case in northern Sumatra

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Travertines, carbonate developed in calcareous hot springs, often exhibit laminated structures of the ancient stromatolites. Cyanobacteria play a central role to form laminated structures (e.g., Okumura et al. 2013), other microbial groups can be associated with the travertines. An example is the case in Dolok Tinggi Raja in northern Sumatra. Distinct microbial zonation was observed along the flow passage of the two major spring sites. At proximal locations besides the hot spring at 60 degrees, sulfur turf inhabited a high concentration of hydrogen sulfide. Purple sulfur bacteria become dominant from several meters below the spring. The sulfur bacteria that form a biofilm of 1 mm thick have potential to develop laminated structure. Water chemistry indicates that aragonite precipitation was activated from this location. In the lower portion of the flow passage where the temperature is declined below 50 degree, microbial community was replaced by cyanobacteria that formed a biofilm of similar thickness. Decreases in hydrogen sulfide and temperature are responsible factors for this microbial zonation.

Mobilization of manganese and iron in marine sediments and tuffs by dolerite in Hokuroku District.

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Mn rich sediments are often used to evaluate the presence of submarine hydrothermal activities and the redox state of paleoenvironment in the sea. The oldest Mn ore deposit occurs 2.4 billion years ago as the banded manganese formation, corresponded to oxidation of Precambrian ocean water. Those studies suggest that Mn geochemistry is important to consider not only the Earth history but also paleoenvironment evaluation.

Hokuroku district is famous for Kuroko deposits which is rich in metals such as Zn, Cu, and Pb. During the hydrothermal activities, metals of forming Kuroko precipitated in closed area around ores, on the other hand Mn and Fe can be transported in distal by hydrothermal plume, as a result of formation of Mn and Fe rich sediments on the Kuroko horizon without heavy metal deposition. Therefore, the first purpose of this research is to evaluate the exploration potential of Kuroko deposits using Mn, thus the examination of spatial relationship between Mn and Kuroko ores. Presence of Mn rich layers is also known in the Hokuroku district. Their origin was completely unknown. Mn rich layers were potentially formed submarine hydrothermal activities related post Kuroko ore forming activities. Therefore, the second purpose of this research is to discuss whether the submarine hydrothermal activity was present even after Kuroko ore formation and if they are responsible for Mn enrichment in post Kuroko mudstone.

I have investigated the "M2" mudstone which is often overlaid with Kuroko deposits. For the first purposes, 6 Samples of "M2" mudstones were collected from 3 areas. Moreover, I have investigated the Mn rich layer to discuss the second purpose. 31 Samples of "R2", "T2", dolerite, and mudstone were collected from Koyukizawa areas. The mineral and chemical compositions of the samples were examined by standard petrographic microscopy, SEM, and EPMA. Chemical composition of samples were determined by energy dispersive X-ray spectrometry, and EDXRF. Mineral assemblage is determined by X-ray diffraction (XRD).

For the first purpose, Mn concentrations in "M2" mudstones are found to be about 0.04 wt%, which is low concentrations. I can't find the change of Mn concentrations according to the distance from ores. Therefore, it suggested that Mn is not the exploration index of Kuroko deposits at this stage. For the second purpose, the geological survey was performed in the area of Koyukizawa (route A and route B). Tuff breccia and pumice tuff are abundant in this area associated with mudstones. Those were intruded by dolerite. Red to brown alteration are common even in dolerite representing hydrothermal alterations in route A. I could find the Mn rich layers (3.7 wt%, 1.8 wt%) by chemical analyses. Partial Mn enrichments were also found in rocks on the boundary between "T2" and dolerite. On the other hand, I can't find the red alteration in dolerite route B. From those findings, Mn rich layer was formed by the recycle of Mn by heat generated from the intruding dolerite. Mn was enriched in rocks when circulated hydrothermal water was oxidic enough. Moreover, by EDXRF, Mn and Fe have similar behavior, and Mn was oxidized prior to Fe on the oxidative environment.

Keywords: banded manganese deposit, Hokuroku district, Kuroko, hydrothermal activity, redox state

Role(s) of microorganisms on the formation of manganese deposits in hot springs

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The natural manganese distributed widely during environment. The +II, +III, and +IV are the most prevalent oxidation states of Mn in nature, in particular, +III and +IV manganese exist as oxides mainly. It is considered that the manganese oxide (MnO₂) formation is attained by 1) inorganic process including autocatalysis and 2) organic process by microbial oxidation. The latter is further classified into two groups, the direct process and indirect process. In general, it seems the organic process is more important than the inorganic process. The organic direct process with the Mn-oxidizing bacteria attracts attention particularly recently. On the other hand, it has been published the experiment with isolated and cultured photosynthesis microorganisms indicates the Mn-oxidation reaction promoted by photosynthesis. However, those most were speculated by culture experiments and simulations, therefore, the relative importance of above these processes and mechanisms in the natural Mn-oxidation reaction does not yet become clear. In this study, it is intended to clarify an elementary process of the Mn oxides formation based on an in situ evaluation in the environment. The subject of this study is Sanbe hot spring (in Shimane, Japan) and Onneto yuno-taki (in Hokkaido, Japan), the representative example of the terrestrial large-scale Mn oxides deposit.

At the Sanbe hot spring, Mn oxides layer form at thickness up to approximately 1 cm in the lower area by 150 m from the spring site. According to thin section observation, many photosynthetic organisms inhabit in the surface, and it is confirmed most of them are buried in the oxides. In addition, *Hyphomicrobium* sp. was detected by 16S rDNA Analysis. In this study, through four kinds in total of microelectrode-measurement (pH, Eh, dissolved oxygen DO, Mn²⁺), the chemical profiles in the vicinity of the oxide surface were evaluated. Under the light condition, DO, Eh, pH rose in the oxides surface, and Mn²⁺ showed decrease. Under the dark condition, DO decreased, and the tendency to increase or decrease of Eh, pH, Mn²⁺ profiles were remain unchanged in comparison with them under the light condition, but each flux was all smaller than it under the light condition. From the result, it was found the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, and MnO₂ change into the dissolved chemical species (Mn³⁺), by the oxidation-reduction reaction in Mn²⁺ and MnO₂ under the dark condition. This is supported by the observation with the Mn oxides layer being thin for the decrement amount of Mn²⁺ in the surface. Furthermore, regardless of difference of light or dark condition, the contribution to manganese oxidation by Mn-oxidizing bacteria was likely small so that cannot be detected by microelectrode-measurement.

At the Onneto yuno-taki, the manganese deposit layer distribute respectively about 100 m from two spring site and is thick relatively (about 10 cm). Onneto yuno-taki has also many photosynthetic organisms inhabiting in the surface, and it is confirmed by thin section, most of them are buried in the oxides by thin section observation. According to the result of microelectrode-measurement, DO, Eh, pH rose in the oxides surface, and Mn²⁺ showed decrease under the light condition. Under the dark condition, all profile has tendency to decrease. Mn²⁺ flux was especially smaller than its under the light condition. Therefore, it was suggested that the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, on the other hand, it may occur the Mn-oxidation reaction by Mn-oxidizing bacteria (organic direct process) It was also thought that the effect of dissolution of MnO₂ was respectively small. In fact, the manganese deposit of Onneto yuno-taki is very thick.

Establishment of iron microelectrode measurement and its application to iron deposit re-sembling BIF

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Precambrian banded iron formation (BIF) is important for estimating the redox state of the global environment during that period, and many studies have been conducted until now. In the traditional model, BIF had been considered to be formed by oxidation of Fe(II) by cyanobacteria-released oxygen. However, it has been recently suggested that other microbial metabolisms, such as direct iron oxidation associated with carbon fixation of non-oxygenic Fe(II)-oxidizing phototrophic bacteria, were also involved in the formation. Therefore, its formation process is considered to be complicated much more than previously thought, and detailed investigation about the microbial processes that can potentially form BIF is required. This study aimed to reveal the formation processes of iron deposits found in Sambe hot spring in Shimane Prefecture, and applied both geochemical and geomicrobiological techniques. In previous study, it have been described that this deposit is mainly composed of iron hydroxide (ferrihydrite), and microbial composition at the deposit surface is dominated by iron-oxidizing bacteria (*Gallionella* sp.) with minor cyanobacteria. In this study, we applied the Fe(II) microelectrode in addition to the pH, redox, O₂ microelectrodes in order to accurately evaluate the microbial and inorganic precipitation occurring in the surface. By these microelectrodes, we measured the chemical profiles at the vicinity of deposit surface (about 1 mm from the surface) and found that all chemical profiles were almost the same both in light and dark conditions, indicating that contribution of photosynthesis was negligible. Fe(II) and O₂ consumption at the deposit surface implied that iron-oxidizing bacteria (*Gallionella* sp.) oxidized Fe(II) by using oxygen. This kind of iron precipitation process would provide an important knowledge about the formation process of BIF deposited when the ocean gradually became oxidative by cyanobacteria released oxygen. In addition, measurement method of Fe(II) microelectrode established in this study will be applicative to other types of BIF modern analogs, and it is expected that further details of BIF formation processes will be revealed.

Nitrogen and noble gas isotopes of Eoarchean Nuvvuagittuq rocks

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The Nuvvuagittuq greenstone belt is an Eoarchean volcano-sedimentary sequence located in northern Quebec. Rocks are gabbroic intrusions, volcano-sedimentary silicic rocks and banded iron formation (BIFs), enclosed by 3.66 Ga tonalitic gneiss. Rocks are metamorphosed to amphibolite facies and zircon U-Pb ages give a minimum age of 3.75-3.82 Ga to the belt. A deficit in ¹⁴²Nd compared to the terrestrial Nd standard found in some igneous rock which were dated possibly at 4.28 billion years ago, making this rock suite one of the oldest on Earth. Characterization of the fluids in silicic rocks and BIFs, identified by previous works as chemical precipitates in seawater, might give precious constraints on the Earth superficial conditions in Late Hadean, following the Late Heavy Bombardment.

A preliminary survey intended to analyze the fluids trapped into several lithologies of the belt on the noble gas and nitrogen isotopic compositions. Selected samples are an ultramafic intrusion (POR21), a tonalitic gneiss (POR23), three felsic to intermediate silicic volcanoclastic rocks (POR27b, 28c, 28h), a meta-conglomerate (POR29) and a plagioclase-rich amphibolite (POR30). Preliminary noble gas isotopes were carried out at GEOTOP by using a quadrupole mass spectrometer. ⁴He, ²²Ne, ³⁶⁻⁴⁰Ar, ⁸⁴Kr and ^{129,132,136}Xe were analyzed after crushing bulk rock and recovering gases in a purification line. All samples contain radiogenic ⁴He, from 3.7×10^{-8} to 2.5×10^{-7} cm³STP/g_{rock}, although the calculated radiogenic ⁴He/⁴⁰Ar* ratio is only 0.01 to 0.03 against the expected crustal ratio of 4.2. This could indicate large loss of helium during time (which is often observed in Archean rocks) or poor potassium content, the parent element of radiogenic ⁴⁰Ar*. The measured ⁴⁰Ar/³⁶Ar ratios range from 403 to 9635, higher than the atmospheric value of 295.5. The sample that contains most radiogenic noble gas ⁴He and ¹³⁶Xe (from U fission and alpha decay) and ⁴⁰Ar* is the tonalitic gneiss (POR23). All other samples show atmospheric composition of noble gases (except ⁴He and ⁴⁰Ar*) or slight ¹³⁶Xe anomalies.

A new series of noble gas and nitrogen isotopic measurements are under way at Osaka University to determine the origin of gases into the Nuvvuagittuq fluids and try to constrain crustal and igneous sources possibly feeding them.

Keywords: Eoarchean, Atmosphere, Nitrogen, Noble gas

Geological and geochemical studies of sedimentary rocks at the Wagon Road gold mine, Barberton Greenstone Belt.

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Banded iron formations (BIFs) are common in Archean to early Proterozoic cratons. The formation processes of BIF are controversy as to if a variety of microbes (e.g., cyanobacteria and Fe-oxidizing bacteria) were involved or inorganic oxidation was responsible. Detailed studies on BIF and the surrounding sedimentary rocks may constrain factors to oxidize Fe and the role of microbial activities. Therefore, the BIF and the surrounding sedimentary rocks in the Fig Tree Group (~3.2 Ga in age) in the Barberton Greenstone Belt, South Africa, are investigated in the present study. The studied area is called Euryca syncline area, and abandon Au mine (Waggon Road mine) is located. Sandstone, shale, black chert, and BIF are found in the studied area. Besides petrographic characterization, SEM-EDS analyses were performed on the representative rocks. Concentrations of organic carbon and their $\delta^{13}\text{C}$ values were determined by EA and IR-MS. Siderite and hematite were found as ferruginous minerals in BIF and black chert samples. The grain size of siderite was larger (30-200 μm) than the surrounding quartz (<10 μm). Siderite is interpreted as a secondary mineral formed during early diagenesis. Euhedral hematite crystals (<5 μm) were found. Hematite is interpreted as a primary mineral, although some hematite, normally larger and more red color, are supergene origin. Black chert samples show separated features of organic-rich layers and Fe-rich layers. Therefore, it is considered that the source of organic carbon is not related to Fe-oxidizing bacteria. The $\delta^{13}\text{C}$ values of all analyzed samples were range from -27.7 to -23.5 ‰. These values are made by metabolisms by Calvin cycle using atmospheric CO_2 . Overall results of this study indicated that presence of 3.2 Ga oxygenic shallow oceans in where cyanobacteria were active.

Geological and geochemical study of lower-Fig Tree Group in Josefsdal, South Africa

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Understanding extent of Archean biosphere and conditions of surface environments is important subject to understand evolution of the Earth. Accumulating more geological and geochemical data on Archean sedimentary rocks is necessary to approach the above problem. Therefore, geological and geochemical studies are performed on Fig Tree Group (~3.2 Ga) and Onverwacht Group (~3.4 Ga) in the Barberton Greenstone Belt, South Africa in the present study. The objectives of this study were (1) to survey lower-Fig Tree Group and upper-Onverwacht Group, which were not described in previous literatures and (2) to constrain paragenesis of minerals, including sulfides, in the sediments, and (3) to investigate the carbonaceous matter (CM) in the black chert in the Fig Tree Group using the raman geothermometer of Beysac et al (2002) and to discuss microbial ecosystem through stable carbon isotopic compositions ($\delta^{13}\text{C}$).

Result of the outcrop survey revealed that our research areas correspond to stratigraphy to that of Hoffman (2005), who studied area in the Fig Tree Group in the BGB. Mineralogical investigations showed that Ni-rich sulfide minerals were abundant and some of them were chemically zoned in the black chert. These observations suggest that represent carbonaceous sediments in the lower-Fig Tree Group were silicified by later hydrothermal fluids which contain abundant Ni, most likely coming from ultramafic rocks. Using the raman geothermometer, the peak temperature about CM in the black chert in the Fig Tree Group is estimated to be approximately lower than 330 ± 50 °C, suggesting very low metamorphic grade (lower green schist).

Additionally, $\delta^{13}\text{C}$ values of the examined samples in the Fig Tree Group ranged from -28.9 ‰ to -23.2 ‰. Carbon isotope compositions of Onverwacht Group samples are ranged from -30.63 ‰ to -26.5 ‰ (PDB), which is within a range of organic matter produced by Calvin cycle using atmospheric CO_2 , such as cyanobacteria.

Keywords: Carbonaceous sedimentary rock, Hydrothermal process, Barberton Greenstone Belt, Fig Tree Group

The hydrothermal activity and host rock alteration of 2.7Ga VMS deposit in Potter mine, Abitibi greenstone belt.

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Volcanogenic massive sulfide (VMS) deposits are formed near the seafloor, where high temperature fluid in hydrothermal system contacts with seawater. Potter Mine, in Abitibi greenstone belt, is the one where sulfides were mined from a VMS deposit. A thin komatiite (lower komatiitic unit) underlays the ore deposit's host rock, mostly hyaloclastite or lappilli stones from tholeiitic basalt. Black shales are often interbedded in those hyaloclastite. Ores are found as disseminated sulfides and/or sulfide veins in hyaloclastite or sediments. Stratified ores are also seen. Those are overlain by upper komatiite sequence. The feature of host rock, its mineralization near the deposit and origin of organic matter associated with ores are still unknown, since no research related to the host rocks mineral and organic carbon has been performed. In this report, the chemical composition measurement of host rock minerals and organic carbon analysis at the drill core samples near the sulfide deposit were performed. By surface geological survey, the evidence of hydrothermal altered komatiite (lower komatiitic unit) was not found in Potter mine. On the other hand, serpentinization of upper komatiite was significant just above ore location. This may suggest continuous hydrothermal activities from ore deposition age to post-ore deposition age. But there is no evidence that if lower komatiite was involved in hydrothermal circulation. The result suggests that ores were composed of chalcopyrite, sphalerite and pyrrhotite mainly. Pyrrhotite and sphalerite were precipitated in non-equilibrium condition. Hyaloclastite and black shales contain different altered minerals; talc is more abundant in hyaloclastite and black shale contains more Fe-rich chlorite. Carbon isotope compositions of organic matter suggest a methanotrophic biological activity during the sulfide mineralization, in addition to thermogenic degradation of organic matter. In addition to these results, evidence of carbonate mineralization accompanied with hydrothermal activity was observed in some samples, which indicates the rise in pH. Thus, This mineralization feature should be difference between Potter mine and other VMS deposits.

Keywords: volcanogenic massive sulfide deposits, Abitibi greenstone Belt, komatiite, methanotroph, hydrothermal alteration

Mineralogical and geochemical study of marine sedimentary rocks of Gunflint Formation(1.9 Ga), Ontario, Canada

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Gunflint Formation is composed of marine sedimentary rocks, which deposited at ca.1.9 to 1.8 Ga. Disappearance of banded iron formation and Sudbury meteorite impact occurred during the sedimentation of Gunflint Formation. However, impacts of those geological events on ecology were not evaluated in past. Therefore, in the present study, geochemical studies are performed.

Concentration patterns of Fe are different from lowermost to upper sections. Such change is corresponded to disappearance of BIF, thus decrease of Fe flux in shallow sediments. Compositions of kerogen were similar through the entire sections. However, a section which recorded Sudbury impact shows variable N/C ratios of kerogen. This may suggest that nitrogen cycle through atmosphere, hydrosphere and biosphere changed temporarily right after meteorite impact.