Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-01 Room:105 Time:May 26 12:00-12:15

Indigenous Microbial Populations Dominantly Thriving in Deep Terrestrial Crust

INO, Kohei[1*] ; KOUDUKA, Mariko[1] ; SUZUKI, Yohey[1]

[1]Graduate School of Science the University of Tokyo

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 Nitrosiprae 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 Nitrosprirae 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 seqeuncing, Mizunami underground research laboratory, Grimsel Test Site, deep biosphere

BCG28-02 Room:105 Time:May 26 12:15-12:30

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

FURUTANI, Hitoshi[1*] ; KOUDUKA, Mariko[1] ; SUNAMURA, Michinari[1] ; KATO, Shingo[2] ; NAKAMURA, Kentaro[3] ; SUZUKI, Yohey[1]

[1]Graduate School of Science, The University of Tokyo, [2]Japan Collection of Microorganisms, RIKEN BioResource Center, [3]Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

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

BCG28-03 Room:105 Time:May 26 12:30-12:45

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

KAKEGAWA, Takeshi[1*] ; TERAJIMA, Shogo[1] ; NARA, Fumiko[1]

[1]Graduate School of Science, Tohoku University, [2]tohoku, [3]tohoku

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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-04 Room:105 Time:May 26 14:15-14:30

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

KATAOKA, Tomoyasu[1*] ; YOSHIOKA, Hideyoshi[2] ; KOUDUKA, Mariko[1] ; FUKUDA, Akari[3] ; MATSUMOTO, Ryo[3] ; SUZUKI, Yohey[1]

[1]Graduate School of Science, The University of Tokyo, [2]National Institute of Advanced Industrial Science and Technology, [3]Organiization for the Strategic Coordination, Meiji University

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 gammaproteobacteiral 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 CO_2 reduction were measured by sediment slurry incubation with 14C-labbeled aceatate and bicarbonate, respectively. Although acetate fermentation was greatly influenced by drilling contamination, CO_2 reduction was not apparently influenced. Interestingly, the rate of CO_2 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

BCG28-05 Room:105 Time:May 26 14:30-14:45

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

SHIRAISHI, Fumito[1*] ; MITSUNOBU, Satoshi[2] ; MORONO, Yuki[3] ; SUZUKI, Katsuhiko[3] ; INAGAKI, Fumio[3]

[1]Hiroshima University, [2]University of Shizuoka, [3]JAMSTEC

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-MnO_2 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 archea) 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 archea 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 archea, and its metabolism requires malticopper 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 malticopper 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.

BCG28-06 Room:105 Time:May 26 14:45-15:00

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

YOSHINISHI, Haruka[1]* ; FUCHIDA, Shigeshi[1] ; MASUDA, Harue[1] ; TOKI, Tomohiro[2]

[1]Department of Geosciences, Faculty of Science, Osaka City University, [2]Faculty of Science, University of the Ryukyus

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 recordedat 200 mbsf (100 ppb). Arsenic concentration of sediments was 5-10ppm down to 150 mbsf, and peaked at 400 mbsf (23 ppm).

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

The arsenic concentration of porewater was higher than that of sea water (1.7 ppb) and varied with depth, suggesting thatarsenic 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 ($\mathrm{As}^{\text{客}}$) 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 ℃). 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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-07 Room:105 Time:May 26 15:00-15:15

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

TOKUNAGA, Kohei[1]* ; TAKAHASHI, Yoshio[2]

[1]Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, [2]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo

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 H3AsO30 from pH 2.0 to pH 8.0, and H2AsO3- at pH 11.0, while (ii) As(V) are mainly dissolved as H3AsO40, H2AsO4-, HAsO42- 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 μg/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

©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-08 Room:105 Time:May 26 15:15-15:45

Formation condition of monohydrocalcite (CaCO3.H2O)

FUKUSHI, Keisuke[1*] ; NISHIYAMA, Risa[1] ; SUZUKI, Yuma[1] ; FUKUMOTO, Hiroto[1] ; MUNEMOTO, Takashi[2]

[1]Kanazawa University, [2]JAEA

Monohydrocacite (MHC: $CaCO_3.H_2O$) 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: $MgCO_3.3H_2O$). 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.

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-09 Room:105 Time:May 26 15:45-16:00

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

ISHIKAWA, Ko[1*] ; OTAKE, Tsubasa[1] ; SATO, Tsutomu[1] ; KAKEGAWA, Takeshi[2]

[1]Division of Sustainable Resource Engineering, Graduate School of Engineering, Hokkaido University, [2]Department of Earth Science, Graduate School of Science, Tohoku University

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 (˜15μm), and that the black layers are composed of large grains of magnetite (˜50μm). 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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-10 Room:105 Time:May 26 16:15-16:30

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

WATANABE, Yusuke[1*] ; TAKAHASHI, Yoshio[1]

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

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 unnder 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 absorbed 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 degreee 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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-11 Room:105 Time:May 26 16:30-16:45

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

KIKUCHI, Ryosuke[1]* ; KURAMATA, Chisaki[1] ; INOUE, Sayako[1] ; KOGURE, Toshihiro[1]

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

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

BCG28-12 Room:105 Time:May 26 16:45-17:00

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

YOKOYAMA, Tadashi[1]*

[1] Dept. Earth & Space Science, Osaka Univ.

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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-13 Room:105 Time:May 26 17:00-17:15

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

NAGASAKI, Sagakuni[1*] ; YOKOYAMA, Tadashi[1] ; NAKASHIMA, Satoru[1]

[1]Department of Earth and Space Science, Graduate School of Science, Osaka University

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 ℃. At 25 ℃ 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^+) → formation of dissolved $Fe(OH)_3$ → formation of solid $Fe(OH)_3$ (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 $Fe(OH)_3$ decreased slowly presumably due to nucleation, first-order-like decrease of $Fe(OH)_3$ 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 3.3E-5 - 1.1E-2 s^{-1} were obtained at 15-55 ℃. Good linearity was confirmed in an Arrhenius plot of these rate constants, and an activation energy (Ea) of 118 ± 5 kJ/mol was obtained.

Secondly, solutions of Fe^{3+} 100 ppm were prepared by dissolving $Fe(NO_3)_3$ nonahydrate and $Fe_2(SO_4)_3$ 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 ℃ in the nitrate system, and 25, 35, 45, and 55 ℃ in the sulfate system. At 25 ℃, 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 2.7E-5 - 3.6E-3 s^{-1} in the nitrate system and 6.7E-5 - 5.9E-3 s^{-1} in the sulfate system, again showed good linearity in Arrhenius plots. Ea = 122 ± 4 kJ/mol for the nitrate system and Ea = 119 ± 4 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 ℃. At 25 ℃, pH of the solution decreased from ˜3.8 to ˜3.3 as reaction time passed. The rate constants obtained was 2.7E-5 - 2.9E-3 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 Ea = 162 ± 3 kJ/mol and higher than that at pH 2.2-2.7.

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

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)
©2015. Japan Geoscience Union. All Rights Reserved.

BCG28-14 Room:105 Time:May 26 17:15-17:30

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

TSUNAZAWA, Yuya[1*] ; YOKOYAMA, Tadashi[2] ; NISHIYAMA, Naoki[2]

[1]Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, [2]Department of Earth and Space Science, Graduate School of Science, Osaka University

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