Exploring the hydrogen isotopic composition of deep-sea corals

*Samuel Hallett Davin[1], Claude Hillaire-Marcel[1], Yves Gelinas[2]

1. Université du Québec àMontréal, 2. Concordia University

Despite the widespread use of hydrogen isotopic analyses in environmental investigations, no previously-published work has attempted to measure or utilize the hydrogen isotopic composition (δ D) of deep-sea corals. Geographically widespread, forming annual growth rings, and having lifespans on the scale of hundreds of years, δ D measurements of deep-sea coral skeletons have the potential to elucidate oceanographic parameters at well-resolved spatial and temporal resolutions.

We present a method for the determination of annually-resolved δ D in gorgonin, a complex proteinaceous material making up the horny skeletal component of gorgonian corals. We address the issue of exchangeable hydrogen in gorgonin by controlling the isotopic composition of the exchangeable fraction of the total hydrogen pool using a heated batch equilibration technique. Coupled with seawater δ D profiles, the δ D of particulate organic matter (POM) filtered from seawater, and the δ D of plankton trawl samples, we attempt to identify the relationships between trophic exchange, physical oceanographic parameters, and the δ D of gorgonin from 3 species of live-collected coral.

Results include a 43-year record from a Primnoa pacifica colony collected from the Gulf of Alaska, three 10-year records from Primnoa resedaeformis colonies collected from the Labrador Sea, and a 40-year record from a Keratoisis grayii colony collected from southern Baffin Bay. Preliminary data show an unprecedented range of δ D values in all three species, ranging from -40‰ to -110‰. Final results will determine the suitability of gorgonin δ D as a potential marine environmental proxy by testing the reproducibility of δ D values between adjacent colonies.

Keywords: Deep-sea, Coral, Hydrogen, Isotopes, Experimental, Geochemistry

Evaluation of heterogeneity of reaction-transport phenomenon in rock by sequential pore water extraction

*Tadashi Yokoyama[1]

1. Graduate School of Integrated Arts and Sciences, Hiroshima University

Heterogeneity of dissolution/precipitation and solute transport in rock pores has been drawing attention in recent years. This phenomenon has been often studied using numerical calculation, but direct analysis of pore water is important to know what is actually occurring in pores. However, most previous studies have analysed the composition of bulk pore solution and it is difficult to discuss the detail of reactive-transport behaviour in pores using the bulk composition. In the present study, an experimental technique to sequentially extract pore water by applying various gas pressures to wet sample was used. With this technique, pore water can be extracted for each pore radius, which provides information on the heterogeneity of reaction and transport in pores. In the experiment, pure water was first passed through a sandstone core to induce dissolution in pores (flow-through reaction), then pore water was extracted for each pore size and solute concentrations were measured. The result of the experiment showed that the concentrations of Na, Ca, Mg, and Si increased with decreasing pore radius and that the concentration increases of Ca, Mg, and Na were greater than that of Si. Qualitatively, this result can be explained by a numerical model of the advection and dissolution in a single tube for different pore radii. However, the observed concentration increases were significantly greater than the model calculation, and it seems possible to evaluate the extent of the mixing of solutions in narrow pore and large pore by comparing the model calculation and experimental result.

Keywords: pore water, dissolution, advection

Subseafloor weathering of cretaceous basaltic basement revealed by nanomineralogical and conventional clay characterizations

*Yamashita Seiya[1], Hiroki Mukai[1], Yohey Suzuki[1]

1. Graduate School of Science, The University of Tokyo

Areal coverage of basaltic ocean crust overlain by oxygenated sediments reaches up to 25% on Earth. During 10 million years after formation, porous basaltic lava erupted at mid-ocean ridges generally become impermeable due to infilling of secondary minerals formed by hydrothermal alteration. Although chemical reactions between basalt and seawater might continue to influence the elemental distribution between ocean and crust around the globe, it remains unknown whether or not porous fractions filled with secondary minerals are susceptible of low-temperature rock water interactions collectively referred to as weathering. By integrated ocean drilling program (IODP), 84-120-Ma basaltic basement covered by 70-m-thick oxygenated sediment was drilled down to 121 meters below seafloor, and nanomineralogical and conventional clay characterizations were conducted for three basaltic core samples with different fracture-filling secondary minerals (Ca carbonate in U1365E7R-2, celadonite in U1365E8R-4, Fe oxyhydroxides in U1365E12R-2). X-ray diffraction (XRD) pattern analysis of clay fractions collected from powdered core samples after particle dispersion in water revealed that the presence of clay minerals with basal spacings (d_{001}) of 1.5 nm after air dry and d_{001} of 1.7 nm after glycolation in all samples. As (060) reflections of the clay minerals are characteristics of trioctahedral smectite in U1365E7R-2, Fe-rich dioctahedral smectite in U1365E12R-2, and both the smectite clays in U1365E8R-4. Scanning electron microscopic (SEM) observations with energy dispersive X-ray spectroscopic (EDS) analysis clarified that chemical compositions of the trioctahedral and dioctahedral smectite clays are identical to those of saponite and notronite, respectively. SEM-EDS analysis of thin sections across the basalt-fracture transect revealed the infilling of Ca carbonate-bearing fractures with saponite in U1365E7R-2, whereas nontronite, which was located at the rim of celadonite in U1365E8R-4 and randomly in the partially filled fracture in U1365E12R-2, was highly enriched with Fe. By focused ion beam (FIB) milling coupled to high- resolution transmission electron microscopy (HR-TEM), it was revealed that the excess Fe is resulted from the co-occurrence of goethite nanoparticles. As the occurrence of nontronite is clearly correlated with textural features that indicate the high porosity and permeability around grain boundaries, it is suggested that notronite was likely formed by weathering. Furthermore, the K enrichment in notronite agrees with downward diffusional K flux from seawater to the basaltic basement through overlying sediments, which supports the inference that subsefloor weathering is ongoing and associated with microbial colonization. From this study, it is concluded that the upper oceanic crust might be globally reactive to control the chemical composition of seawater.

Keywords: nontronite, oceanic crust, weathering, FIB-TEM

Microstructure and geochemistry of organic matters associated with iron minerals in 3.2 Ga banded iron formations, Moodies Group, Barberton Green stone Belt, South Africa

*Ryo Nakajima[1], Yoko Ohtomo[3], Tsubasa Otake[2], Takeshi Kakegawa[4], Tsutomu Sato[2]

1. Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, 2. Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, 3. Faculty of Engineering, Hokkaido University, 4. Graduate School of Science, Tohoku University

The iron oxidation process in Banded iron formations (BIFs) is still controversial especially before the Great Oxidation Event. Previous studies suggest that microbial activity, either free oxygen produced by cyanobacteria or anoxygenic iron-oxidizing bacteria was involved in the formation of BIFs. Therefore, geochemical characteristics and occurrence of organic matters relating to the iron mineralogy may give an insight to the oxidation process. Here, we performed geological, petrological, and geochemical investigations on ~3.2Ga BIFs deposited in a shallow ocean, where high microbial productivity were expected, in the Sheba gold mine, Moodies Group, Barberton Green stone Belt, South Africa. Rock samples were classified into the MT type (magnetite-rich sandstone, 13-50 wt% Fe_2O_3) and SD type (magnetite-poor silty clastics, 10-30 wt% Fe_2O_3) based on the dominant iron mineral. MT type consists of alternating magnetite-rich layers and silicate-rich layers, containing euhedral magnetite, carbonates, quartz, biotite and chlorite. SD type is subdivided into SD-1, which consists of alternating carbonates (siderite, ankerite and dolomite)-quartz-rich layers and biotite-chlorite-rich layer, and SD-2, which contains the smaller grains of quartz, chlorite and biotite.

These samples contain 0.03-0.29 wt% of carbonaceous matters, which are observed as aggregates of 20 μm round or oval flakes in diameter. Wrinkles and folding structure are often observed on the surface of the flake structures. Carbon stable isotope ratio of the carbonaceous matters shows -26~-27‰, suggesting that it is likely to be derived from organisms. Microfossil-like strucstures in Moodies shales observed by Javaux et al., (2010) have the similar characteristics to this study, though they shows the wider range in the size distribution (31-298 μm in diameter). Organic matters extracted by acid dissolution has ~0.002 of N/C ratio, which is consistent with that of kerogen in Archean rocks that were subjected to a similar metamorphic grade. Raman microspectroscopy of the extracted organic matters indicates that they have experienced ~500 °C metamorphic temperature, which is slightly higher than the regional metamorphism in Moodies group. This may be due to an influence by the later hydrothermal fluids involving gold mineralization.

In both sample types, the iron content show a negative correlation with the organic carbon content, but a positive correlation with the carbonate carbon content. Most SD-1 samples show higher carbonate carbon to iron ratios than that of siderite. The carbon stable isotope ratios of carbonates in MT and SD-1 samples were ~-4‰. These results suggest that most carbonates in SD-1 and MT samples were ankerite and/or dolomite derived from mineralizing fluids. Previous studies indicate that organic matters in BIFs can be consumed as CO_2 or converted to siderite by a reaction with primary iron oxides during diagenetic and metamorphic process (Perry et al., 1973, Kohler et al., 2013). However, SD-2 samples showing high organic carbon contents are poor in carbonates and iron. Moreover, considering carbonate carbon stable isotope ratio in MT and SD-1 type samples and relatively high organic carbon contents in MT type samples (0.03-0.26 wt%), we suggest that the negative correlation between the organic carbon and iron contents is a primary signature during the deposition of BIFs. Assuming that a model proposed by Kohler et al. (2013) can be applied to this study, SD-2 samples, which are organic carbon-rich and iron-poor, and MT samples, which are carbon-poor and iron-rich, may reflect the activities of cyanobacteria and iron-oxidizing bacteria, respectively, in different depositional settings. Then, our results imply that cyanobacteria would flourish nearby coast, whereas iron-oxidizing bacteria would be active relatively far from the coast, or below the cyanobacteria in 3.2Ga shallow ocean.

Keywords: Banded Iron Formations, Barberton Green stone Belt, organic matters

Depositional environment of graphite-bearing metasedimentary rocks and banded iron formations in >3.7 Ga Isua Supracrustal Belt, West Greenland

*Yoko Ohtomo[1], Takenori Kato[2], Tsubasa Otake[1], Takeshi Kakegawa[3]

1. Faculty of Engineering, Hokkaido University, 2. Division for Chronological Research, Institute for Space-Earth Environmental Research, Nagoya University, 3. Graduate School of Science and Faculty of Science, Tohoku University

Biogenic graphite in > 3.7 Ga metasedimenrary rocks, Isua Supracrustal Belt (ISB), West Greenland, has been reported as the oldest remnants of life (Rosing, 1999; Ohtomo et al., 2014). However, ecosystem spreaded in the >3.7Ga ocean is still poorly understood. Depositional environments of metasedimentary rocks containing biogenic graphite and surrounding banded iron formations (BIFs) could give an insight into microbial activities in the >3.7Ga ocean. Graphite-rich schist reported by Ohtomo et al. (2014) contains rare earth element (REE) minerals such as monazite, zircon and xenotime. These REE minerals could have been deriven by one or some of the following processes: detrital transport, precipitation from a seafloor hydrothermal fluid, generation during diagenesis and precipitation from a metamorphic fluid. Occurrence, geochemical composition and chronological information of the REE minerals might constrain their origin and provide information of depositional and/or alteration process of the graphite-rich schist. Here, we performed a geological survey in the west side of the ISB and investigated the petrographic and geochemical characteristics of sedimentary rocks to reconstract the depositional environment. Chemical Th-U-total Pb Isochron Method (CHIME) was conducted on monazite to determine the age.

Samples collected in the whole west side of the ISB consist of alternate layers of magnetite-amphibote-chlorite-rich and quartz-rich layers. The samples were roughly divided into magnetite-rich type, which distributed at northeast to south, and silicate-rich type, mostly distributed at northwest, based on the dominant minerals. Bulk chemical compositions of the examined samples showed that magnetite-rich type are abundant in Fe, whereas silicate-type are rich in Mg. Magnetite-rich type primarly composed of Fe-rich amphibole, grunerite, whereas silicate-rich type contains more Mg or Ca-rich amphibole. Similarly, chemical compositions of chlorite in magnetite-rich type are Fe-rich, whereas that of silicate-rich type are Mg-rich. Amphibole and chlorite compositions in graphite-rich metasedimentary rocks are Mg-rich, which is similar to silicate-type BIF samples. The results suggest that Mg-rich characteristics of BIFs and graphite-rich metasedimentary rocks at north west, and Fe-rich characteristics of BIFs at north east to south are a primary signature. Ti and Al concentrations in BIFs and graphite-rich sedimentary rocks showed a positive correlation, indicating contribution of detrital components to them. Graphite-rich schist sample consisted of graphite-chlorite- and quartz-cummingtonite-dominated microlayers, containing high amounts of REE compared to samples showing low graphite content. The graphite-rich sample contained euhedral monazite, zircon and minor xenotime 2-10 μm in diameter, which were accumulated in graphite-chlorite microlayers and concordant with orientation of lamination, whereas most of the monazite in samples showing low graphite content were anhedral. CHIME age of the monazite in graphite-rich schist samples indicated 3630±91Ma, which ranges in the ages of prograde metamorphism and detrital zircon in previous report (Nutman et al., 2009). Considering monazite occurrence concordant with lamination of the graphite-rich schist, it is most likely that monazite was syngenetic with host rocks, probably derived from detritus and the age was modified during metamorphism, or crystalized during diagenesis to early metamorphism. Our results suggest that BIFs and graphite-rich schist at north west of west side of the ISB deposited where clastic components such as Mg, Al, Ti and REE were supplemented at a relatively high rate, evoking that photosynthetic microorganisms might have been flourished in >3.7Ga shallow ocean.

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Keywords: Isua Supracrustal Belt, rare earth element, monazite, graphite

Abiotic Nitrogen Fixation and Organic Synthesis by Photochemistry on Early Mars

*Zang Xiaofeng[1], Waka Kawade[1], Norio Kitadai[1,2], Yuichiro Ueno[1,2]

1. Tokyo Institute of Technology Department of Earth and Planetary Sciences, 2. Tokyo Institute of Technology Earth-Life Science Institute

Detailed studies of Mars in recent years have provided many progress on understanding the possible view of environment on early Mars. With the fact that liquid water was present on early Mars, and the discovery of organic molecules as well as nitrogen-bearing compounds on Mars, there is possibility that life could have emerged on early Mars. Thus, it is important to understand the abiotic organic synthesis and nitrogen fixation process to evaluate the possible origin of life on Mars or other terrestrial planet. Previous studies suggested that organic matters can be produced by photochemistry. Total pressure of Martian atmosphere is lower than Earth. Thus, UV may penetrated down to the surface and can directly photolyze liquid water. This suggests that UV-induced photochemistry may have been more important. However, little is known about abiotic nitrogen fixation by UV light. This experimental study examines the nitrogen photochemistry at the surface of water. In the experiment, initial gas contains N_2O or N_2 with or without CO under the presence of liquid water. The starting condition may have existed on early Mars. The results showed that NH_3, methylamine, glycine and other amino acids was produced from N_2O + CO + H_2O, whereas only trace amount of NH_3 was formed from N_2 + CO + H_2O. When gas phase do not contain CO, nitrate and nitrite were produced instead of NH_3. A numerical model including 296 photochemical reactions was constructed, and can qualitatively explain the formation of NH_3 from N_2O. However, the concentration of NH_3 in the model is order of magnitude lower than the observed amount in the experiment, suggesting that current photochemical model still lack some possible reactions to generate NH_3. The results provide important insights on chemical evolution theory that lead to the origin of life and the atmospheric evolution on Mars when the reaction pathway of NH_3 starting from N_2O and N_2 by UV light is confirmed.

Keywords: Mars, Nitrogen fixation, amino acid synthesis, UV

Distribution of Ammonium-Bearing Clay Minerals and their δ^{15}N values Occurred in Shallow-Seafloor Hydrothermal System in Kagoshima bay, Southern Kyushu, Japan.

*Jaeguk Jo[1], Toshiro Yamanaka[2], Youko Miyoshi[3], Jun-ichiro Ishibashi[4], Yoshihiro Kuwahara[4], Hitoshi Chiba[1], Tomoki Kashimura[1]

1. Graduate School of Science, okayama University, 2. Tokyo University of Marine Science and Technology, 3. The National Institute of Advanced Industrial Science and Technology (AIST), 4. Department of Earth and Planetary Sciences, Graduate School of Sciences, Kyushu University, Japan

The seafloor hydrothermal fluids occurred in the arc and back-arc systems where are often covered with thick sediments contained organic matter are characterized by a high concentration of ammonium which is considered to originate from decomposition of the sedimentary organic matter. Under these conditions, ammonium cation can be fixed in interlayer space of 2:1 clay mineral during their formation associated with hydrothermal mineralization. However, the role of this process with respect to the nitrogen cycle around the Earth' s surface has not been well understood until today. In this study, we measured ammonium concentrations and their isotopic ratios in the venting hydrothermal fluids and clay fraction in the hydrothermal altered sediments obtained from Kagoshima Bay, southern Kyushu, Japan.

The submarine volcano, Wakamiko, located in the submerged Aira Caldera, which formed during the late Pleistocene (ca. 29 ka) resulting from the huge eruption of the Ito pyroclastic flow, and about 200 m in water depth of depression area as well as it is filled with thick unconsolidated sediment layer up to 80 m. The hydrothermal activity of this area is associated with the Aira magmatism, and the emitting fluid has been characterized by a high ammonium concentration up to 17 mM, respectively.

All of samples were collected around vent expect for typical marine sediments of PC-4 site. Clay minerals were recovered as a clay size fraction (2 μm) by hydraulic elutriation from the core sediments and then samples repeatedly treated by 30 % hydrogen peroxide solution and finally KOBr-KCl solution to remove organic matter and exchangeable ammonium. After that clay fractions were measured by XRD for identification of clay minerals as well as their chemical composition were measured by EPMA. And NH group were detected by FT-IR. Nitrogen contents and their isotopic ratios were measured by EA/irMS. Total nitrogen (TN) contents and inorganic nitrogen (IN) contents were ranging from 0.03 to 0.28 μg/g and from 0.002 to 0.01 μg/g, respectively. And $\delta^{15}N_{TN}$ and $\delta^{15}N_{IN}$ values were ranging from -6.2 to +4.6 ‰(av. +0.3 ‰) and from -1.7 to +5.1 ‰(av. +1.2 ‰), respectively. The δ^{15}N values of venting hydrothermal fluids and porefluids were ranging from -1.8 to +1.9 ‰(av. -0.2 ‰) and from +2.4 to +2.9 ‰ (av. +2.7 ‰), respectively. Particularly, $\delta^{15}N_{IN}$ values can be divided two groups, relatively 15N-enriched and 15N-depleted. And those trends were consistent with the difference of δ^{15}N values between hydrothermal fluids and pore fluids. Further study, it is required that understanding of nitrogen fractionation between fluid and mineral in hydrothermal system through the synthesis of ammonium-smectite.

Keywords: seafloor hydrothermal system, nitrogen cycle, 2:1 clay mineral, ammonium, nitrogen isotope

The uptake behavior of antimony with earth surface materials at Ichinokawa mine in Saijo city in Ehime prefecture

*Akitoshi Akehi[1], Satoshi Mitsunobu[2], Keisuke Fukushi[1]

1. Kanazawa University, 2. Ehime University

Antimony (Sb) is element which come into Periodic table 15 group, and this chemical behavior is similar to arsenic (As). These elements have toxic for human, so we hope to understand about these elements behavior at earth surface. These elements are sorbed by earth surface materials which is formed secondary minerals at earth surface and is considered to be good sorbents (Fukushi 2017), because many earth surface materials are produced fine grain so its specific surface area become large (Tsukimura and Nakazawa 1994) and it is produced metastable phase. Typical earth materials are clay minerals (smectite, vermiculite and so on), metal (hydroxide)oxide materials (ferrihhydrite, goethite and so on), carbonate minerals (calcite, aragonite and so on) and so on. There are number of studies about As uptake behavior with earth surface materials from field observations and laboratory studies. On the other hand, the investigation of Sb uptake behaviors are very limited. So we hope to understand Sb behavior by earth surface materials. In order to investigate Sb behavior, we should focus on the site with high Sb concentration. The purpose of the study is to understand the Sb uptake behaviors with iron oxide or carbonate minerals of which occurrences can be observed at the tunnel at Ichinokawa mine.

In situ AFM study on crystal growth and dissolution of calcite at a nano-level

*Keisuke Otsuka[1], Yoshihiro Kuwahara[2]

1. Graduate School of Integrated Sciences for Global Society, Kyushu University, 2. Faculty of Social and Cultural Studies, Kyushu University

Calcite is one of useful indicator minerals for environmental changes and occurs in a wide variety of geologic environments. The processes and kinetics of dissolution and crystal growth of calcite easily change with slight variations of temperature and concentration of solutions. Most global-scale geochemical phenomena begin with atomic-scale growth and dissolution reactions at the mineral-water interface. In situ Atomic Force Microscopy (AFM) allows direct observation of the growth and dissolution processes at the mineral-water interface at the site or step level. Here we report the results of an experiment performed by in situ AFM observations of the dissolution and growth behaviors on the (10-14) surface of calcite in under- and supersaturated $CaCO_3$ solutions at 25°C.

The calcite sample was obtained from the Stonehem Barite Deposit in Colorado, USA in the form of a single optically clear crystal. The calcite crystal was cleaved parallel to the (10-14) cleavage plane with a sharp knife blade immediately before the AFM observations. The $CaCO_3$ aqueous solution ($Ca^{2+} : CO_3^{2-}$ = 1:1) was prepared by mixing Na_2CO_3 and $CaCl_2$ solutions consisting of analytical grade chemicals and deionized water immediately before the AFM observations. The degree of super- (or under-) saturation (*SI*) and ionic strength were calculated using the program PHREEQC. In situ observations of the calcite dissolution and growth were performed by a Nanoscope III with a Multimode SPM unit (Digital Instruments) operating in contact-mode AFM (CMAFM) on a vibration isolation platform in a temperature- and humidity-controlled room. The cleaved calcite crystals were first reacted with deionized water to ensure stable AFM scanning conditions and obtain reliable AFM images. We then replaced the water with $CaCO_3$ solution in the fluid cell and began observing the growth process on the calcite (10-14) surface at 25(±0.2)°C. Deionized water and $CaCO_3$ solution flowed through the fluid cell at a constant rate of 10 ml/h, controlled by a syringe pump.

In pure water and all undersaturated solutions, inverted pyramidal-shaped etch pits which were defined by [-441] and [48-1] steps were formed during the dissolution. However, a pair of [-441] and [48-1] steps of a quadrangular pyramid tended to curve with higher undersaturations. The two pairs of [-441] and [48-1] steps in etch pits showed the anisotropic retreat behavior, that is, the steps having higher retreat rates showed the higher effect of the undersaturation of the solution on the retreat rates. The retreat rate of the (10-14) plane was much slower than those of the [-441] and [48-1] steps in etch pits.

In supersaturated solutions, pyramidal-shaped growth spirals which were defined by [-441] and [48-1] steps were formed during the growth. The pyramidal-shaped growth spirals showed clear ridgelines. The [-441] and [48-1] steps on the growth spirals have a height of approximately 0.3 nm which corresponds to a monomolecular of $CaCO_3$ but showed mostly two layer periodicity. The advance rates of the steps during the growth tended to be faster than the retreat rates of those during the dissolution, while the growth rates of growth spirals toward the direction perpendicular to the (10-14) plane were slower than the retreat rates of (10-14) plane in etch pits.

Keywords: calcite, crystal growth, dissolution, AFM

Role of amorphous silica in forming calcium silicate hydrate for strength development of steel slag-dredged soil mixtures

*Kanako Toda[1], Yu Arai[1], Tsubasa Otake[2], Tsutomu Sato[2], Haruna Sato[1], Nilan Weerakoon[1], Nishimura Satoshi[2]

1. Graduate School of Engineering, Hokkaido University, 2. Faculty of Engineering, Hokkaido University

Dredged soils consists of minerals including clays, organic debris and seawater, and are excavated beneath ports to maintain the waterways. Partially they are landfilled due to its soft physical properties disabling its usage as construction materials. Indeed its characteristics differ greatly depending on the sampling areas due to the variation in its composition. Recently, it is discovered that mixing dredged soil with steel slag, that is also partially treated as waste produced as iron smelting process’ s by-products, develops strength. This discovery may turn dumped fraction of both materials to resources by expanding their application into building materials for undersea constructions. Nonetheless, different combinations of a type of steel slag and dredged soil from various areas show gaps in the strength development even in under the identical mixing condition. The relationship between mixing condition and strength development is not yet clarified, making it difficult to be utilized for the above application.

Clarifying the hardening mechanism of the steel slag-dredged soil mixture will enable prediction of the strength with a particular combination of steel slag and dredged soil. In order to achieve it, clarifying the secondary mineral formation that contributes to hardening is essential. Previous studies suggest that the strength development is related to the pozzolanic reaction, which results in cementation by the formation of calcium silicate hydrates (C-S-H). Key factors in the pozzolanic reaction include the increase in pH of the pore water, and the supply of calcium and silica ions to pore water. Steel slag contains $Ca(OH)_2$, which supplies calcium and increases pH of the mixture. Silica is said to be supplied from the dredged soils, but it is not clarified what is being the silica supply.

Focusing on the variation of dredged soil affecting the strength development, the objective of this study is to understand the effects of amorphous silica in dredged soils, which has faster dissolution rate compared to crystalline silica phases, to the early strength development of steel slag-dredged soil mixture.

In this study, dredged soils from various sampling locations (A, B, C and D) and steel slag from iron works 1 were mixed for the investigation. XRD analysis showed no significant difference between the mineralogical compositions of all the dredged soils. The unconfined compressive strength showed mixtures with soil A exhibits the highest strength, followed by those with B, C and D. Formation of C-S-H in mixture A was found to be denser than mixture D through scanning electron microscope, filling up pores in the mixture. In addition, the measurement of mixture’ s pore water pH transition showed decreasing trend in pH from 12.5 in only mixtures A and B but not C and D from 1 day curing onward. This suggests stronger mixtures’ (A and B) pore water’ s pH were influenced by formed secondary minerals, such as C-S-H which expels H^+ when it forms, indicating that its formation was notably greater in stronger mixture. In our mixtures, the silica ion was most likely supplied from dredged soils. The silica concentration dissolved from diatom frustules were measured. Soils A and B showed higher dissolved silica concentration compared to C and D. Inorganic amorphous silica such as volcanic glass content is also discussed. From geochemical modelling which treats amorphous silica dissolution kinetically, it was clarified that stronger and weaker mixtures show significant difference in the volume of C-S-H forming. We suggest that the silica supply from amorphous silica in dredged soils may be the driving force for the pozzolanic reaction for early strength development.

Keywords: pozzolanic reaction, dredged soil, steel slag, Amorphous silica

Localization of magnetite from Fe-rich brucite induced by pH changes during serpentinization

*kohdai homma[1], Atsushi Okamoto[1], Ryosuke Oyanagi[1], Masaoki Uno[1], Masakazu Fujii[2], Nobuo Hirano[1], Noriyoshi Tsuchiya[1]

1. Graduate School of Environmental Studies, Tohoku University, 2. National Institute of Polar Research and SOKENDAI

H_2-rich fluids from ultramafic-hosted hydrothermal vent is important for understanding generation of hydrocarbon and biosphere in deep sea floor. Key to the formation of hydrogen in such system is magnetite formed serpentinization reaction. Magnetite distribution in serpentinized peridotite is usually heterogeneous; randomly scatted, and/or localized at former olivine-grain boundaries. However, formation mechanism of magnetite segregation during serpentinization remain poorly understood.
In this study, hydrothermal experiment of olivine –H_2O system was conducted with varying initial solution pH from under conditions of 250 °C and vapor-saturated pressure of 3.98 MPa. In the autoclave, 1.0 g of olivine powder (Fo91;38-75 μm) were set with solutions. Six solutions with varying initial solution pH at room temperature were used; pH at room temperature is 5.7, 6.8, 9.0, 10, 11, and 12. pH were adjusted by diluting NaOH solutions. The run time up to 63 days.
After the experiments, for solutions of initial pH = 5.7-9.0, pH increased to around 10. In contrast, for solutions of initial pH >10, the pH after experiments weren’t changed. SEM observation revealed that Serpentine + Brucite + Magnetite were formed and no significant difference was not observed by changing pH of initial solution. Magnetite occurred with 5-10 μm, and seems that no localization of magnetite occur. After 63 days experiments, amount of serpentine and brucite, measured by thermogravity, were increased with increasing the pH of initial solutions. Amount of magnetite, which was measured by Alternating Gradient force Magnetometer, was increased with increased with increased with increasing initial pH up to 11. At initial pH = 12, the amount of magnetite after 63 days reaction was lower than that of initital pH = 11.
From EPMA analysis, the presence of ferric ion in serpentine and brucite were not observed. the iron content of the serpentine was almost similar with varying initial pH. In contrast, the iron content of the brucite roughly increased as pH was increased. The amount of products were almost proportional to reaction progress, indicating that reaction rates were approximately constant during the experiments.
Mass balance calculation revealed that iron partitioning varies with pH; at initial pH = 6.8, the Fe partition ratio ween brucite and magnetite was 3:7. With increasing the initial pH, the ratio gradually decreased to 6:4 at initial pH = 12.
Klein et al. (2013) suggests that magnetite was formed at >200 °C by breakdown of Fe-rich brucite formed at <200 °C. Our experiments revealed that Fe-rich brucite could be formed by reaction with alkaline solution (pH>11). This indicates that pH changes from alkaline to neutral could from magnetite from Fe-rich brucite. To test this hypothesis, further hydrothermal experiments were conducted. The solid samples, which reacted with initial pH = 12 for 27 days, was reacted with water for 14 days. As a result, two type of magnetite were observed; magnetite with 5-10 micro and magnetite with < 1 μm. The later magnetite was occur within brucite grains, which was not observed reaction with initial pH = 12 for 27 days.
Our experiments revealed that, by changing pH in solution from alkaline to neutral, magnetite were formed from Fe-rich brucite. Two stage process of magnetite formation were suggested; (1) low fluid-flux serpentinization of olivine changes the fluid to alkaline to form serpentine and Fe-rich brucite. (2) Reaction with fresh fluid which were transported via newly-formed cracks to form magnetite and hydrogen

is generated.

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Keywords: serpentine, magnetite, hydrothermal experiment, hydrogen

Nano-scale observation of interface between lichen and basaltic lava by TEM and STXM

*Tomoya Tamura[1], Atsushi Kyono[1], Yoko Kebukawa[2], Motoo Ito[3], Yuki Nishimiya[4]

1. Graduate School of Life and Environmental Sciences, University of Tsukuba, 2. Faculty of Engineering, Yokohama National University, 3. Kochi Institute for Core Sample Research JAMSTEC, 4. Transmission Electron Microscopy Station, National Institute for Materials Science

Introduction: Lava extruded during a volcanic eruption moves downslope and covers huge areas. Living plants are destroyed by the lava flow over a wide area. The surface lava has been exposed to the weathering and erosion at the Earth's surface for a long time, which is responsible for the formation of soils. Recently, lichens as the earliest colonizers of terrestrial habitats are recognized to accelerate the degradation of minerals. Much interest has been therefore devoted in recent years to the weathering induced by the lichen colonization. Here, we report the nano-scale observation of the interface between lichen and basaltic lava by TEM and STXM techniques.

Materials and Methods: Basaltic lavas totally covered by lichens were collected from the 1986 lava flows on the northwest part of Izu-Oshima volcano, Japan. To prepare specimens for the nano-scale observation, we utilized the focused ion beam (FIB) system (JEOL: FIB-4000; JEOL: JEM-9320FIB) at National Institute for Materials Science (NIMS), Tsukuba, Japan. The specimens were thoroughly investigated by TEM (JEOL: JEM 2100F) equipped with energy-dispersive X-ray spectroscopy (EDX) at NIMS. Chemical components and chemical heterogeneity at the interface were observed by synchrotron scanning transmission X-ray microscopy (STXM) at Advanced Light Source (ALS) branch line 5.3.2.2.

Results and Discussion: The collected lava is augite-pigeonite-bronzite basalt, with 6 to 8% plagioclase phenocrysts. Mafic phenocrysts, orthopyroxene, clinopyroxene, and titano-magnetite, are less than 1%. The basaltic lava can be characterized to be chemically homogeneous with 52.2 to 52.5% SiO_2 and 15.2 to 15.6% Al_2O_3. Species of the lichens adhering to the lava was mainly *S. vesuvianum*, fruticose lichen, which are widespread over the area of investigation. The STEM-EDX observations for all the lichen-lava interfaces showed there are numerous small particles of amorphous alumino-silicate, goethite (α-FeOOH), and α-quartz within micrometer size. Since no α-quartz was observed in the collected basaltic lava, it is of exogenous origin. A small amount of Mg, Fe, and K are detected from the amorphous alumino-silicate. Poorly ordered alumino-silicates, iron oxides, and iron hydroxides have been already observed as biological weathering products (Adamo and Violante 2000). It is therefore certain that the small particles at the interface between the *S. vesuvianum* and basaltic lava were produced by the biological weathering process. Taking into consideration that the *S. vesuvianum* can readily produce organic compounds such as fatty acids, phenolics and carotenes, the amorphous alumino-silicate and goethite observed at the interface were produced by dissolution of plagioclase, augite, and pegionite.

Keywords: lichen-rock interaction, TEM, STXM, nano-scale

Distribution of arsenic and uranium between lake waters and sediments in saline lakes in south Mongolia.

*Eigo Imai[1], Baasansuren Gankhurel[1], Uyangaa Udaanjargal[1], Keisuke Fukushi[1], Davaasuren Davaadorjd[2], Noriko Hasebe[1], Kenji Kashiwaya[1]

1. Kanazawa University, 2. National University of Mongolia

The health risks associated with toxic chemicals in saline lake become environmental problems (Barber et al. 2009). In saline lakes, the dissolved matters are enriched in solutions because of the evaporation of lake water. The enrichments result in the formation of the contaminated lake water and salts deposits containing high levels of the toxic chemicals (Barber et al. 2009).

The toxic elements distribution between the sediments and lake water are essential for the understandings of the enrichment processes and the mobility of toxic species in surrounding environments. In present study, we investigated the distribution processes of arsenic and uranium by analyzing the lake waters, suspended matters and sediments in saline lakes (Olgoi, Boon Tsagaan and Orog lake) in south Mongolia.

The solid and liquid samples from the lake waters were separated by centrifugation. The solid phases were measured by XRD. Morgan and Tao extraction were conducted for solid phases and the extracts were analyzed by ICP-OES and ICP-MS. XRD profile shows that each sample has authigenic minerals, including calcite and Monohydrocalcite. The extraction experiment showed that arsenic and uranium are distributed into calcium carbonates rather than amorphous iron oxide.