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

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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 $\delta^{15}N$ 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 $\delta^{15}N$ 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

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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

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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

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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

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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

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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.

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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.