Interactions among mineral, water and biomolecule by shock wave: morphological changes of olivine grains reacted with amino acid solutions by impact process

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Early oceans on Earth might have contained a certain amount of biomolecules such as amino acids, and were subjected to meteorite impacts, especially during the late heavy bombardment. When hypervelocity meteorites impact to oceans on Earth, some minerals contained in meteorite may react with solutes in oceans under high pressure and temperature conditions and subsequent pressure release processes induced by impact process. We performed shock recovery experiments to simulate shock reactions of marine meteorite impacts among olivine as meteorite components, water and biomolecules as oceanic components. Olivine is one of the most typical minerals in ordinary chondrites that represent about 90% of flying meteorites to Earth. In the present study, we investigate reactions between olivine and amino acids in water during impact process. We present the results of changes of olivine grains. We conducted shock recovery experiments by using a propellant gun at National Institute for Materials Science. Shock recovery experiments were performed that a metal flyer as projectile accelerated by a propellant gun impacted to the metal sample container after sealed with two screws as targets. Amino acid solutions (130 μl) were set with olivine powders (200 mg) and air gap in the sample room in sample containers. Impact velocities measured by using the magnetoflyer method were about 0.9 km/s. Shock pressure was calculated with the measured impact velocity using the impedance match method. After experiments, experimental products were collected from holes drilled on the impact surfaces of the recovered containers. Recovered solid samples were analyzed using X-ray powder diffraction method (XRD), scanning electron microscopy (SEM), electron probe microanalyser (EPMA), and transmission electron microscopy (TEM) with energy dispersive X-ray spectrometry (EDX). The analytical results on the shocked sample of water-amino acid-olivine mixtures demonstrated the metallic material, shocked olivine grain affected by water and carbon rich material like spike as experimental products. Analytical result of EPMA indicated the metallic material derived from stainless 304 of sample container, and a detectable decreasing deviation in the atomic ratio of Mg/Si in shocked olivine relative to that of the starting olivine. The shocked olivine was shown the traces of water molecule impacting on surface by TEM observation. The results of TEM observation and EDX analysis indicated the carbon rich material derived from amino acids. The present study suggests the water-amino acid-olivine system under shock reaction is able to interact with each other. Especially, organic compounds related to origin of life in early ocean might transform to solid state by meteorite impacts. Hence, it is necessary to consider the phase change of initial materials on pre-biotic experiments simulated natural condition.

Keywords: Meteorite impact, Olivine, Amino acid

Experimental study of adsorbed methane in a methane-seep carbonate from the upper Miocene in Joetsu City, Niigata Prefecture

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Submarine methane seeps where methane-charged fluids seep out of the seafloor have been regarded as major sources of methane which is a main component of natural gases and a potent greenhouse gas. In methane seeps, anaerobic oxidation of methane (AOM) by microbial consortia increases alkalinity and induces methane-derived authigenic carbonate precipitation. Ancient methane seeps can be recognized from low stable carbon isotopic compositions derived from methane and lipid biomarkers of microbes performing AOM recorded in carbonate rocks hosted in sedimentary strata. They have a great significance as direct evidences of generation, migration, and emission of methane in the geological past. Methane is generated by microbial or thermal degradation of organic matter in shallow or deep sediment depths, respectively, and the origins of methane can be distinguished by proxies such as carbon isotopic compositions of methane. Identifying the origin of methane in ancient seep fluids can provide an insight into origin and pathway of seep fluid, and oil and natural gas generation in the past, but the way to directly estimate origins of methane in ancient seeps has not been established yet. Authigenic carbonates are reported to adsorb hydrocarbon gases in surrounding sediments (Ijiri et al., 2009). If ancient seep carbonates could also adsorb “paleo-methane” dissolved in seep fluids, it may be possible to estimate the origins of methane in ancient seeps by analyzing isotopic compositions of the adsorbed methane. This study attempted to extract adsorbed gas from an ancient seep carbonate and analyze stable carbon isotopic compositions ($\delta^{13}C$ values) of methane to estimate its origin. Studied material is a methane-seep carbonate collected from the upper Miocene Nodani Formation in Joetsu City, Niigata Prefecture, central Japan. This carbonate mainly consists of dark-grey matrix of micritic aragonite and has abundant void spaces rimmed with creamy-colored acicular aragonite cements. Both of the micritic part and acicular aragonite have low $\delta^{13}C$ values (−42.6 to −15.4‰ vs. PDB), and the former contains lipid biomarkers of anaerobic methanotrophic archaea, pentamethylicosane and crocetane, showing that the carbonate was precipitated in a methane seep. Adsorbed methane was liberated by dissolution of carbonate powders by adding phosphoric acid, and then introduced into GC-IRMS to analyze concentration and $\delta^{13}C$ values of methane. Methane was successfully extracted from all samples, and the $\delta^{13}C$ values of methane ranged widely from −60.7 to −40.0‰. This suggests that the extracted methane is composed of a mixture of biogenic and thermogenic methane in various ratios and/or contains biogenic methane enriched in ^{13}C due to fractionation through AOM. The $\delta^{13}C$ values of the extracted methane and those of the carbonate powders from which gases were extracted showed a weak positive correlation, and void-filling acicular aragonite mostly have lower $\delta^{13}C$ values of extracted methane and carbonate than those of micritic parts. This result implies that the methane contained in the seep fluid could be trapped in the host carbonate phases during their precipitation, and there was some relation between precipitation of each carbonate phase, either in sediment or void, and origin and/or flux of methane trapped in it. Because it is also possible that the methane was adsorbed after precipitation and during burial of the carbonate, further investigation of the preservation state of the gases in the seep carbonate is required to elucidate where and how the methane was trapped within the carbonate.

Keywords: Methane seep, Carbonate, Miocene, Joetsu City, Adsorbed gas

Hydrothermal experiments between basalt and H_2O at 130°C and 230°C

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Water-rock interaction occurs during weathering on ground surface, hydrothermal alteration around hot spring on continental crust, and reaction in oceanic crust. Many hydrothermal experiments have been conducted to examine the rock alteration and/or chemical composition of solution under various reaction temperature conditions, but most of them were focused on compositional variation after reactions between seawater and rock samples. In this study, as a primary, pure water was reacted as solvent with basalts samples under 130°C and 230°C conditions to understand the temporal evolution of composition of the basalts and solution under simple reaction in different temperature conditions.

In the experiments at 230°C, many kind of elements were dissolved in the solvent from basalts after reactions. Especially, concentrations of SiO_2 and Na_2O decreased by their dissolutions, on the other hand, Fe_2O_3 and MgO increased by their insolubility, relatively. The run products at 230°C experiments changed their compositions from starting materials more greatly than those at 130°C. In such run products, coarse grains(>200μm) were more outstanding at 230°C experiments, on the other hand, fine grains(<200μm) were kept leaving after long-term experiments at 130°C. It is suggested that groundmass as glass components and fine crystals dissolved precedingly at 230°C during reactions.

Solubility in the solvent showed different temporal variations every element. However, they can be classified into three major patterns. First, concentration of element increased primary and then decreased (pattern I). Secondly, concentration increased primary, decreased secondly, and then increased again (pattern II). Thirdly, concentrations repeated increasing and then decreasing twice (pattern III). Decreasing of elemental concentrations shows its precipitation by saturation after dissolution of starting material. Concentration increasing after decreasing suggests that the precipitated materials dissolved again under unsaturated situation by over precipitation. In the experiments at 130°C, behavior of Fe, Mg and Al, which are classified into pattern I, suggest immediate precipitation unless redissolution after reactions. In contrast, behavior of Si, Na, K, Ca, and Nb, pattern II, suggest that such elements redissolve it easily by the situation of the solution changing even if they were precipitated by oversaturation. Such elemental behaviors in solution are consistent with temporal variations of compositions of solid materials modified after basalt samples: increasing Fe and Mg, decreasing SiO_2, progressively. On the other hand, experiments at 230°C showed immediate precipitations of Fe, Na, K and Nb (pattern I) and re-precipitations of Si, Mg, Ca, and Al after redissolution(pattern III). It is expected that the degree of dissolution and variation of elements in the solution depend on temperature. And then, such factors changed basalt compositions variously detailed in different run products, caused by difference of elemental precipitation or dissolution during reactions.

Keywords: Hydrothermal experiments, Basalt , Alteration

Lichen-substratum interactions in severe environment polluted by heavy metals

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Heavy metal pollution is a worldwide problem. The use of native organisms for assessment and monitoring of polluted sites is an approach that could contribute to a reduction on costs and secondary environmental impacts. Because several fruticose lichens occur even in areas highly polluted by heavy metals, lichens may meet the requirements. Therefore, interactions between lichens and substrata is an important key to determine the behavior of heavy metals in surface environment polluted by heavy metals.

Although, no studies have investigated interactions of fruticose lichens and the corresponding substrata comprehensively from the aspect of biogeochemical behavior of heavy metals. Therefore, several fruticose lichens, including *Stereocaulon exutum* and several *Cladonia* Spp., from contaminated abandoned mine sites and the corresponding substrata were investigated (1) to determine the behavior of heavy metals during the weathering of slag mediated by *S. exutum*, (2) to determine the distribution of the heavy metals in the thalli of *S. exutum*, and (3) to determine the correlations between the heavy metal concentrations of lichens and those of the corresponding substrata.

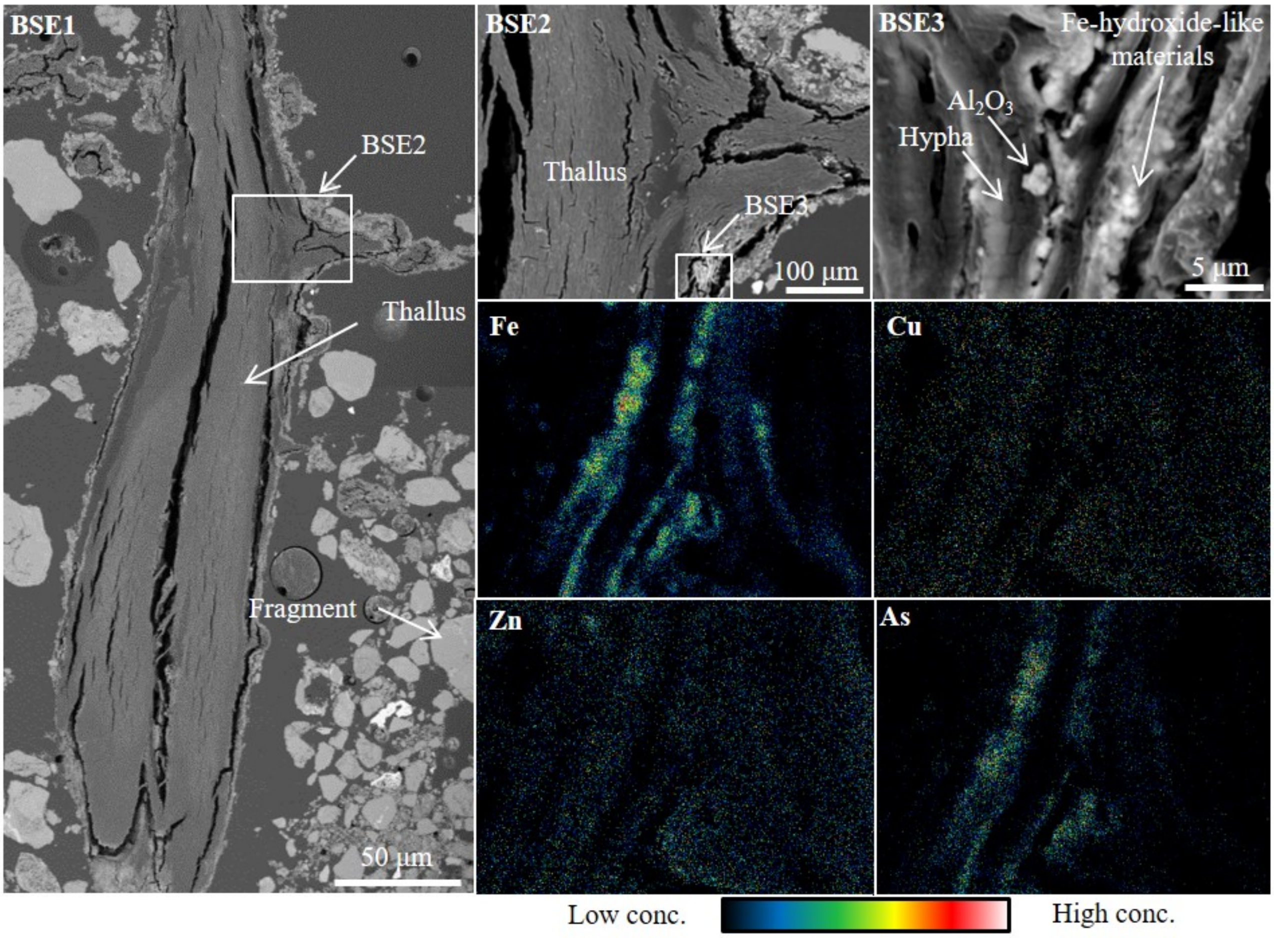
The slag that is a substratum of *S. exutum* consists primarily of willemite, fayalite, and/or magnetite and contains matte drops, which are mainly Cu-metals, -alloys, and -sulfides. The willemite and matte drops are ultimately converted to Fe-hydroxides during the weathering process. In addition to abiotic weathering, the heavy metals are dissolved during the biotic weathering by substances from the lichen and hyphal penetration. The dissolved heavy metals are absorbed into the lichen thalli. Absorbed Cu and Zn are distributed within the cells of hyphae, whereas Fe and As are distributed on the surface of hyphae. Fe-hydroxide-like materials are occur on the surface of hyphae (Fig).

Based on previous studies, cations in thalli are distributed into four fractions, e.g. the intercellular and surface, ion exchange site, intercellular, and residual fractions. Although the form of the ions was not identified in this study, the distribution of elements in the hyphal cells may indicated the possible absorption of ions into the cytoplasm through ion exchange sites from external solutions. For the Fe and As concentrated on the surface of hyphae as Fe-hydroxide-like materials, this distribution could be explained by elemental precipitation or the formation of compounds on the hyphae.

The concentrations of Cu, Zn, As, and Pb of *Cladonia* Spp. thalli were positively correlated with those of the corresponding substrata. Distribution maps of the average heavy metal concentrations of the lichens and the corresponding substrata were made to determine the practical applications of the lichens as a biomarker. The maps for the distribution of Cu, Zn, and As in the lichens had very similar distributions to those of the corresponding substrata at the scale of all study sites in southwest Japan. Therefore, a large-scale analysis of lichens with many samples successfully detected the distribution of heavy metal pollution of soil.

In conclusion, *C.ladonia* Spp. lichens can be used in practical applications for biomonitoring and assessment of heavy metal pollution of soil. Because lichen is a pioneer organism in polluted areas by heavy metals worldwide, the investigation of interactions between lichens and substrata could contribute to determine the elemental cycle between biosphere and lithosphere during natural recovery process of polluted areas.

Keywords: abandoned mine site, weathering of slag, fruticose lichen, absorption of heavy metals, biomarker



Back-scattered electron images and elemental maps of the medulla inside the cortex of thallus (Sueoka *et al*., 2015).

Reaction rate of ferric hydroxide formation at pH 2-4

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Iron hydroxides widely exist in the Earth's environment, and their formation processes, adsorption properties, and transport behavior have been attracting great attention. Dissolved Fe^{3+} reacts with water and transforms to ferric hydroxide ($Fe(OH)_3$) as time passes. We focused on the early process of ferric hydroxides formation and evaluated the reaction rate constants and activation energies under a wide range of solution conditions (pH 2-4, initial Fe concentration 5-300 ppm, temperature 5-55 °C, and dissolved anion species Cl^-, NO_3^-, SO_4^{2-}). Aqueous solutions containing ferric ions were prepared by dissolving one of the following $FeCl_3$, $Fe(NO_3)_3 \cdot 9H_2O$, and $Fe_2(SO_4)_3 \cdot nH_2O$ in pure water. As dissolved ferric ions change to ferric hydroxide, the pH of the solution gradually decreases. The time variation of pH was monitored under the constant temperature, and the rate constant k was determined by converting the pH change to the change in the concentration of dissolved ferric species (assumed to be a 1st order reaction as with Grundl and Delwiche, 1993) using a geochemical code PHREEQC (Parkhurst and Appelo, 1999). Comparison of the k values of ferric hydroxide formation at pH 2-3 under the presence of the different anion species revealed that the k values for Cl^- and NO_3^- were almost the same and that for SO_4^{2-} was approximately one half to one fourth of the values for Cl^- and NO_3^-. Despite the dependence of the rate constants on the anion species, activation energies were almost the same between Cl^-, NO_3^-, and SO_4^{2-} (~120 kJ/mol). In the experiment using $FeCl_3$ solution, the k value increased as the initial pH increased from 2 to 4. On the basis of the pH dependence of k at 25 °C, an equation to predict k for various pH was obtained.

Keywords: Ferric hydroxide, Reaction rate

Distribution of arsenic and uranium between lake waters and sediments in saline lakes in Southern 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 Lake, Boon Tsagaan Lake and Orog Lake) in Southern Mongolia.

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Keywords: Saline lakes, mongolia, arsenic, uranium

Laminated textures of deposits in Shiohitari hot spring, Kagoshima Prefecture

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Fe-rich deposits and travertine (carbonate-rich deposits) are precipitated from hot springs containing amount of minerals. Some of these deposits have laminated textures and origins of laminated textures are explained by several papers. In terms of Fe-rich deposits, metabolism of iron-oxidizing bacteria and symbiosis of cyanobacteria and iron-oxidizing bacteria forms laminated textures (Takashima et al., 2008; Takashima et al., 2011). On the other hand, lamination of travertine are contributed by photosynthetic bacteria showing daily cycle (Takashima and Kano,, 2008; Okumura et al., 2013). This study focuses on laminated deposits in Shiohitari hot spring. Shiohitari hot spring is located at Kirishima city, Kagoshima Prefecture and emit naturally without artificial effects. This is registered in Kirishima Geopark.

The hot spring deposit occur along10-m-long flow path. The water from the vent first flows about 2 m on a narrow (30 cm) and gentle passage and then widely on a steep slope on the travertine dome. Below the dome, the water flows into Amafuri River. Unconsolidated Fe-rich deposit is precipitated at the vent is, and in the lower part, travertine covered by green colored biofilm is. Both deposits have laminated texture.

This water is 51.2 degree celsius, neutral pH and microaerobic. The water is rich in Ca^{2+}, Na^{+} and Cl^{-}, and poor in Mg^{2+} and SO_4^{2-}. To the downstream, the water temperature decreases, pH increase, and conversely alkalinity and Ca^{2+} concentration decrease. This is consisted with travertine deposition. Because an oxygen isotopic ratio of the water (-6.8 per mill) is similar to that of surface and shallow groundwater in southern Kyushu area (-7~-6 per mill; Mizota and Kusakabe, 1997), the origin of water may be fresh water. A carbon isotopic ratio of the water is -6.8 per mill which is similar in that of magmatic gases.

Mineralogy of the Fe-rich deposits in Shiohitari hot spring is ferrihydrite and exhibit micron order laminations which alternate with a dense part and a not dense part. The dense part is composed of dendritic structure ferrihydrite. In addition, meshwork atructure like organic matter is observed from specimens treated with citric acid. This possibly shows that precipitation of ferrihydrite is induced by bacterial metabolism.

The travertine in Shiohitari hot spring is mainly composed of aragonite forming dumbbell-shape and spherical crystals. Between crystals, organic matter like EPS is observed. The lamination of the travertine is likely formed by photosynthetic bacteria same as other travertine.

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