

Distribution of carbonate minerals and morphological observation by SEM in Okuoku-hachikuro hot spring, Akita Prefecture

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Recent studies of biomineralization mainly treated biominerals produced by evolved organisms. There exist uncertainties if primordial microbes are precipitating biominerals. In addition, importance exists to examine interaction between primordial microbes and minerals to constrain the pre- to early- biotic mineral-organic interactions.

Okuoku-hachikuro hot spring, located in Kosaka, Akita Prefecture, Japan, is a hot springs where carbonate minerals are precipitating. In this hot spring, aragonite is dominating minerals in entire area. Color of hot spring precipitates change from red to mixture of red and green, corresponded to difference in microbial type: Fe-oxidizing bacteria to cyanobacteria. We collected sinters, soft to solidified sediments and microbial mats then constituents were observed using field emission-scanning electron microscopy (FE-SEM). Analyses of X-ray diffraction, pH, DO, dissolved amino acids and carbon isotope compositions were also performed.

Most samples contain radial aggregates of needle-shape aragonite. Such morphology was found in bubble in the first discharging fluid, which is not influenced by microbial activities. Each needle in radial aggregates seems to be bigger depending on a distance from the discharging point. Aggregates of coarser and random orientated needles of aragonite are found in lower stream zone, where evaporation and cooling of hot spring water are more visible. Because of no systematic correlation to biological activities (microbial mat, amino acid, organic carbon, etc.) to those morphological changes, all aragonites are formed inorganically. On the other hand, ferrihydrite covering sheath of Fe-oxidizing bacteria and cyanobacteria are found locally. It is noteworthy that no ferrihydrite showed perfect crystalline signature or conversion to hematite. They can possibly be influenced by microbes or organic molecules. Furthermore Si was detected in ferrihydrite. This result suggests that ferrihydrite probably adsorbs amorphous silica selectively.

Keywords: aragonite, ferrihydrite, Fe-oxidizing bacteria, cyanobacteria, biomineralization, FE-SEM

Seasonal changes of physical and chemical properties in Mn-rich cold spring

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Hiramatsu cold spring contains about 2 mg/L of manganese and precipitates unconsolidated manganese oxide in its tanks and bathtub (Takashima et al., 2012). But, origin of Mn in the cold spring is not clear. This study identifies origin of Mn-rich cold spring and causes of seasonal changes in the water chemistry from a continuous observation for a year.

This spring is located at Saga city, Saga Prefecture. Depth of this spring source is very shallow, about 7.5 m, from the altitude of about 2 m. Jizou River flows about 150 m west from the spring. Geology of Saga plain on the basal granite consists of the Nakahara Formation, Takagise Formation, Aso-4, Mitagawa Formation including sands and gravels, Ariake Clay, sands and gravels, rich of the lower Hasuike Formation, clay-rich upper Hasuike lower formation, in ascending order (Miura et al., 1996). A continuous observation was performed from January 2012 to January 2013. Samples were collected from the spring source and Jizou River after measuring water temperature, pH and dissolved oxygen concentration (DO). Collected water samples were analyzed of alkalinity, water chemistries and stable oxygen isotope.

Results of the continuous observation indicate distinct seasonal changes of each parameter in the spring and the river water, especially in a period from June to August. The spring water temperature is stable at about 18 degree from January to May and increases to August, and then decrease to 18 degree from September to next January. On the other hand, the river water temperature increases continuously until August, and decreases during next winter. The spring water tends to be stable in slightly alkaline, but in July and August, it was neutral pH. DO concentration of the spring water is less 1.5 mg/L during winter, and keep high level (above 1.5 mg/L) during summer. Concentrations of Mg, Na, Cl, Mn clearly decreased in summer. Oxygen stable isotope values of the spring water show lighter values in summer.

Depth of the spring source is very shallow and probably comes out sand and gravel rich Hasuike lower formation located about -5 m below the sea level. Given shallow depth source and geology around the cold spring, meteoric water should be the origin of the cold spring water. But seasonal changes of the spring water temperature and dissolved component concentration cannot be explained by such a simple origin. The Mg-rich spring water does not consistent with Ca-HCO₃ type groundwater in granite area (Sasaki, 2008). Moreover, because the spring water temperature is very stable excepting for summer period, the spring water contains likely groundwater in aquifer. Candidate of an aquifer is the Ariake Clay lying below the lower Hasuike Formation, which contains much Mg and Mn. Therefore, the cold spring is consists of mineral-rich groundwater in the Ariake Clay and meteoric water.

Seasonal changes of each parameter in the cold spring during summer reflect dilution effect by meteoric water. During summer, meteoric water of high temperature and lower density flows above the Ariake Clay, and, the cold spring also becomes high temperature of lowered concentration of dissolved components. In contrast, during winter, fractions of mineral-rich groundwater increase due to raising the aquifer, because higher density meteoric water flows under the aquifer.

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Keywords: groundwater, Ariake Clay Formation, precipitating water, tide

The composition of mineral particles on snow surface and their possible effect on microbes in Tateyama Mountains, Japan

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Snow algae are autotrophic microbes and play an important role as primary producers in food chain of glaciers and snowfield. Although their reproduction requires nutrients, snow and ice is extremely poor in nutrients. One of the possible sources of nutrients is mineral particles blown by wind and deposited on the snow. They may contain variable elements and provide nutrients for snow algae. However, we scarcely know about the relationship between mineral particles and snow algae. In this study, we described spatial and seasonal variations in mineral particle composition and snow algae on the snow surface in the Tateyama Mountains, Japan. We discussed the possible effect of mineral particles on snow algae.

Tateyama Mountains are located in the middle-north part of Japan ranging from 2000 ? 3000 m above sea level and have heavy snow fall in winter due to strong monsoon wind from Siberia. The snow starts to thaw in April and remains until late summer as perennial snow patches in some valleys. Kosa eolian dust is known to be blown from Chinese deserts and deposited on the snow every spring. Also, snow algal bloom is often observed as red-colored snow in summer. Samples were collected from the snow surface during summer in 2008 - 2011 at four different sites (A ? D) in this area. We analyzed them by X-ray diffractometer (XRD) and inductively coupled plasma (ICP) to obtain elements and composition of mineral particles, and we examined them with microscope to describe structure of snow algal community.

XRD analysis revealed mineral particles on the snow surface were mainly composed of quartz, plagioclase, hornblende, mica, chlorite, and amorphous. In April, mineral compositions of all sites were almost similar to that of Kosa eolian dust, indicating that these mineral particles were derived from Chinese arid regions. After May, the mineral compositions changed according to sites. The proportion of hornblende at the site C significantly increased. Since the site C was located near geological features mainly composed of hornblende, the supply of mineral particles from local sources is likely to increase after snow began to disappear. These results indicate mineral particles on the snow surface were blown from distant Chinese deserts in April when snow covered entire ground surface, and they may change to be supplied from the local exposed ground surface after May.

ICP analysis revealed mineral particles at the site C contained significantly more manganese than the site D.

Microscopy revealed that algal community structure was different among study sites. The community structure at the site C showed the cyanobacteria were dominate, and that at the site D showed green algae were dominate. Mineral particles at the site C contained more hornblende and manganese than the site D. Hornblende contains Fe and/or Mg. Fe, Mg, and manganese are essential trace elements for plants. This suggests that mineral particles may affect algal community.

In order to reveal direct relationship between mineral particles and snow algae, further analysis is necessary such as electron microscope.

Keywords: mineral particles, snow algae

Controlling factors on depositional fabrics of stromatolite and thrombolite

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Tufa is carbonate deposit in freshwater environment, and usually has laminations similar to fossil stromatolites. However, tufa depositing at Ueno, Takahashi City, Okayama Prefecture has thrombolite-like texture, exhibiting unusual appearance. The present study aims to find out the cause of thrombolite-like texture by comparing stromatolite-like tufa in Shimokuraida, Nimi City, and thrombolite-like tufa in Ueno. Based on this comparison, it is expected to get new insight about thrombolite divergence and stromatolite decline events in early Paleozoic era. First, in the composition of water chemistry at Ueno and Shimokuraida, there was no significant difference between two sites. Chemical profiles at the vicinity of deposit surface, also did not show significant difference between two sites: they both were formed by photosynthesis-induced CaCO₃ precipitation. On the other hand, there were obvious differences in the appearance of deposit surfaces observed by Confocal Laser Scanning Microscopy. At the surface of Ueno deposit, numerous small mounds were formed by coccoid cyanobacteria, and their periphery was surrounded by exopolymeric substances (EPS). At the surface of Shimokuraida deposit, in contrast, erect filament of cyanobacteria is at flat surface, and EPS distributed only near the bacteria. In addition, some of differences were also recognized by observing at vertical section of deposits. At Ueno deposit, filamentous cyanobacteria located around the surface mounds, concentrated at 2-3 mm depth, and scatteredly distributed at 0-2 mm depth. At Shimokuraida deposit, in contrast, had only two layers composed of filamentous cyanobacteria growing vertically. Therefore, the differences between these two deposits might be due to the differences of EPS distribution and/or growth pattern of cyanobacteria. In addition, iron-reducing bacteria were found at Ueno deposit by genetic analysis, which closely related to class Deltaproteobacteria, families Desulfuromonadales, genera Geobacter. The result of CARD-FISH indicated that they distributed where photosynthetic bacteria were scarce, which indicating the possibility that Geobacter-induced dissolution and recrystallization minerals form thrombolite-like texture. In future, it is necessary to reveal the relationships between minerals and microbes.

Microbial roles on the formation of manganese deposits at Sambe hot spring

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Manganese oxides have various chemical characteristics. For instance, MnO_2 particle, already present, catalytically oxidizes Mn^{2+} to form new MnO_2 . Many geochemists have been attracted by oxidation reaction of manganese for a long-years, and many experimentations being related to manganese oxidation has operated. According to the result, biological manganese oxidation is generally fast relative to abiotic manganese oxidation process, including surface-catalyzed reactions. However, environmental and biological oxidation reaction of manganese is not understood enough to evaluate it. In the present study, Sambe hot spring, which is forming manganese oxides is researched. On the result of on-the-spot investigation, manganese oxide is formed along hot spring water stream. Following the course of the stream upward, iron oxides is observed at the upper area. A lot of algae is observed on manganese oxide surface, by the observation of CLSM. According to previous report, the bacteria being able to oxidize manganese are lively in the environment with algae.

On the result of genetic analysis, diatom is observed. This result supports biological manganese oxidation.

Hydrogen generation by interaction between ultramafic rocks and water

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Hydrogen is generated by the interaction between ultramafic rocks and ground water in the Oman Ophiolite and Lost City in the Atlantic Ocean. Previous studies have shown that hydrogen is generated via low temperature serpentinization. However, this process has not been verified experimentally. Previous experimental studies have succeeded in generating hydrogen only at high temperatures (>200 degree C). Therefore, the objective of this study is to clarify the mechanism of hydrogen generation by low temperature serpentinization.

In order to clarify the process of hydrogen generation by low temperature serpentinization, batch experiments were conducted at 90 degree C and 180 degree C using three different ultramafic rocks, (dunite, harzburgite and wehrlite) from the Oman ophiolite reacted with deionized water. Samples were taken at various reaction times. Liquid samples were analyzed by ICP-AES, ion chromatography, UV-Vis, and pH and ORP meters. Mineral phase changes in the solid samples were characterized by SEM-EDX and XRD. The concentration of dissolved hydrogen was determined by GC-TCD. A geochemical reaction model of the hydrogen generation process was then constructed.

Hydrogen generation was observed only at 90 degree C because the experiment utilized a system designed to minimize hydrogen loss. In the experiment at 180 degree C, the generated hydrogen would be loss during experimental procedure. The solutions after the interaction with dunite and harzburgite at 90 degree C showed higher concentrations of dissolved hydrogen than that of wehrlite. Eh and pH of all the solutions decreased and increased, respectively, indicating the occurrence of serpentinization. However, the changes in Eh and pH are inconsistent with the observations in Oman. XRD analysis of the solids did not show significant changes in the amounts of olivine, magnetite and serpentine. Geochemical modeling of the reaction showed that hydrogen generation was accomplished by the dissolution of olivine, which is the dominant mineral in the ultramafic rocks.

However, the amount of hydrogen produced calculated by the geochemical model is lower than the amount observed in this experiments. This discrepancy would be attributed to the catalytic effect of the other components such as Fe-Ni alloy mineral in the samples. This also explains the higher hydrogen amounts generated by dunite and harzburgite, both of which contain the higher amounts of Ni.

In this study, the hydrogen generation has been confirmed at a temperature of less than 100 degree C using experimental techniques. The hydrogen generation process catalyzed by the Fe-Ni alloy mineral would be checked by the experiments using materials composed by mono-mineral such as olivine, pyroxene and Fe-Ni alloy mineral.

Keywords: hydrogen, ultramafic rocks, Oman ophiolite, serpentinization, Fe-Ni alloys

Hydrogen isotopic composition of ca. 3.5 Ga seawater estimated from Archean MORB in South Africa

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Origin of Earth's seawater and its subsequent evolution are still poorly understood. Hydrogen isotopic composition is a key to constrain secular change of seawater volume through hydrogen escape and degassing from mantle, and thus critical to estimate the original isotopic composition of the primitive ocean. A fragment of the Archean seafloor is well preserved in Barberton Greenstone Belt, South Africa. We have systematically analyzed hydrogen and oxygen isotopic compositions of sub-greenschist facies pillow basalts in upper part of Hoogenoeg Complex. Petrographic observation together with XRD analysis showed that almost hydrous mineral in the sample is composed of chlorite with minor amounts of epidote and actinolite. Chlorite is useful to deduce seawater isotopic composition because of little temperature dependence both for hydrogen and oxygen isotope fractionations against H₂O. Based on the relationship between isotopic composition and water contents, we have concluded that the 3.5 Ga seawater was depleted in deuterium by more than 20‰ compared to modern seawater. These results indicate the seawater volume may have decreased by hydrogen escape into space through the Earth's history.

Keywords: South Africa, basalt, chlorite, isotope fractionation, sea water, hydrogen isotope