

## Impact-induced products from glycine polymers in early Earth's oceans

SEKINE, Toshimori<sup>1\*</sup> ; KATSUKI, Yuto<sup>1</sup> ; SUGUMURA, Kousuke<sup>1</sup> ; KOBAYASHI, Takamichi<sup>2</sup>

<sup>1</sup>Hiroshima University, <sup>2</sup>National Institute for Materials Science

Early oceans may have contained appreciable amounts of prebiotic organic molecules, since previous studies have indicated that simple organic molecules are capable to be formed through oceanic impact processes by meteorites. Geologic evidence suggests that the root for the origin of life materials occurred just after or during the heavy bombardment period. At that time the impact energy is considered to have been important for molecules present in oceans to react. Shock reactions of organic molecules in aqueous solutions have been subject to few studies.

Here we investigate the reactions for glycine polymers (dimer G2, trimer G3, and tetramer G4) and alanilglycine (AG) in aqueous solutions in order to know their stability and reaction products during impacts. The starting G2 (>99.0% Tokyo Chemical Industry Co. Ltd), G3 (>98.0%, Tokyo Chemical Industry Co. Ltd), G4 (>95%, Tokyo Chemical Industry Co. Ltd), and AG (>98.0%, Tokyo Chemical Industry Co. Ltd) were used in the present study. Hypervelocity plane impact experiments were carried out using a propellant gun. Sample solutions of glycine polymers in sealed steel containers were subjected to impact at velocities of about 1 km/s. The calculated shock pressures are 5-6 GPa by the impedance match solution. The recovered solutions were analyzed with a hybrid Fourier transform mass spectrometer (Thermo Fisher Scientific LTQ Orbitrap XL) at Hiroshima University.

The analytical results for the recovered samples were compared with those for the initial sample. Limited numbers of amino acids of Glycine, alanine, and their polymers, amines from propylamine to octylamine, and carboxylic acids from acetic acid to decanoic acid were selected due to a measured range of their m/z values. The identification of a molecule was done by the presence of a peak with the calculated m/z value ( $\pm 0.002$ ). The results are discussed.

Keywords: Glycine polymers in early Earth's oceans, Impact-induced products

## Effect of mineral species on the glycine polymerization

ONISHI, Hiroyuki<sup>1\*</sup> ; KITADAI, Norio<sup>2</sup> ; FUKUSHI, Keisuke<sup>3</sup>

<sup>1</sup>Department of Nature System, Kanazawa Univ., <sup>2</sup>Earth Life Science Institute, Tokyokogyo Univ., <sup>3</sup>Inst Nature and Environmental Technology, Sci., Kanazawa Univ.

Protein is a major constituent of life on the earth, and is produced by polymerization due to dehydration condensation of amino acids. Polymerization of amino acids is an important process for the origin of life. The understanding of amino acid polymerization process in the earth surface environment is important for the origin of life. It is well known that polymerization of amino acids under the ambient condition is thermodynamically difficult. Therefore, how the amino acids polymerization in the early earth environment proceeded is still under debates.

Many model experiments for amino acid polymerization had been designed so far. Among them, one of the promising method is mixing the mineral powder with glycine solution with heating (e.g., Bujdak and Rode, 1997a). Bujdak and Rode, (1997b) was confirmed that alumina could promote alanine polymerization than Quartz. They suggested that the effect of mineral type is important on the polymerization of amino acids. However, it is not known which functions of the mineral affect the amino acid polymerization. After Bujdak and Rode, (1997b), amino acid polymerization experiments by using various type of mineral species has been widely examined. However, the experiment condition has not been unified among the studies. We cannot compare the effect of amino acid polymerization on each mineral. In present study, we conducted the experiments of amino acid polymerization using t various types of minerals (Rutile, Anatase, Amorphous silica, Quartz, gamma-Al<sub>2</sub>O<sub>3</sub>, Corundum, Hematite, Magnetite, Forsterite) under the unified experimental conditions. The purpose of the study is to clarify the factors for promoting the amino acid polymerization in mineral species.

Keywords: amino acid, polymerization, mineral

## Role of minerals for hydrogen generation in the interaction between ultramafic rocks and water

FUKUHARA, Naoki<sup>1\*</sup> ; SATO, Tsutomu<sup>1</sup> ; OTAKE, Tsubasa<sup>1</sup>

<sup>1</sup>Laboratory of Environmental Geology, Hokkaido university, Graduate School of Engineering, Hokkaido U

Hydrogen generation by high temperature serpentinization is understood as hydration of mafic and ultramafic rocks, owing to the oxidation of reduced iron present in the olivine or pyroxene. On the other hand, in the Oman Ophiolite and Lost City Hydrothermal Field (LCHF) in the Mid-Atlantic Ridge, hydrogen is generated via low temperature serpentinization. Moreover, previous experimental study shown generating hydrogen at low temperatures (<100 degrees C). However, since even the rate of hydrogen generation by high temperature serpentinization is slow, the mechanism of hydrogen generation by low temperature in short period is yet to be explained. Therefore, the objective of this study is to clarify the mechanism of hydrogen generation via low temperature serpentinization for a short period. Batch experiments were conducted at 30 degrees C, 60 degrees C and 90 degrees C using minerals which constitute ultramafic rocks (olivine, Magnetite, Fe-Ni alloy), and serpentinite. Samples were taken after various reaction times (3h, 6h, 12h, 24h, and 1week). Liquid samples were analyzed by ICP-AES, ion chromatography, UV-Vis, pH, and ORP. Mineral phase changes in the solid samples were characterized by TG-DTA, SEM-EDX and XRD. The concentration of hydrogen gas was determined by GC-RGD.

Hydrogen generation was observed in all samples. Highest concentration of hydrogen gas was observed in the experiment using Fe-Ni alloy. In the experiment using Fe-Ni alloy, apparent surface change was not observed at the surface of Fe-Ni alloy. Therefore, hydrogen gas was generated by catalysis of Fe-Ni. The generation of hydrogen gas by this catalysis would be higher than that of generated hydrogen accomplished by the dissolution of olivine, which is the dominant mineral in the ultramafic rocks.

In this study, the hydrogen generation was confirmed at a temperature of less than 90 degrees C. The hydrogen generation process is catalyzed by Fe-Ni alloys or magnetite present in secondary minerals by serpentinization.

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

ISHIKAWA, Ko<sup>1\*</sup> ; OTAKE, Tsubasa<sup>1</sup> ; KAWAI, Shohji<sup>2</sup> ; SATO, Tsutomu<sup>1</sup> ; KAKEGAWA, Takeshi<sup>2</sup>

<sup>1</sup>Division of Sustainable Resource Engineering, Graduate School of Engineering, Hokkaido University, K, <sup>2</sup>Department of Earth Science, Graduate School of Science, Tohoku University, Aoba 6-3, Aoba-ku, Senda

Geochemical data for ferruginous chemical sedimentary rocks (e.g., Banded Iron Formation: BIF) have been used to understand surface environments on early Earth. For example, enrichment of Cr relative to Ti in BIFs that occurred ~2.48 billion years ago has been considered as a result of the chemical mobilization of Cr in acidic aqueous environments due to sulfide oxidation after the oxygenation of atmosphere. While the Archean sedimentary environments studied in most previous works are limited to deeper settings, the 3.2 Ga Moodies BIF in the Barberton Greenstone Belt, South Africa also indicated that Cr was enriched in the BIF and was therefore chemically mobile in a shallow marine environments. This finding could be significant because it may indicate the oxidation of, at least, some parts of the ocean and therefore, imply the emergence of oxygenic photosynthesis. However, spatial distribution of Cr enrichment in the BIF has not been well understood because the data were obtained from an outcrop and an underground mine. Therefore, the objective of this study is to investigate sedimentary environments and Cr enrichment of the Moodies BIF at another locality.

We conducted a geological survey of another outcrop of the Moodies BIF in the Eureka syncline located ~10 km northeast of Barberton. The section of the BIF exposed in the outcrop was underlain by a conglomeratic quartzite, which is stratigraphically correlated with the BIF at Moodies Hills block in the previous study. Whereas the BIF at Moodies Hills block are 22m in the thickness and overlain by 122m thick silty sandstone and sandstone, the BIF in this study has a thickness of 36m and is overlain by a 103m thick layer of greywacke and silty sandstone. Petrographic observation of the BIF samples shows that the reddish layers are composed of microcrystalline quartz and fine grains of hematite (~15 $\mu$ m), and that the black layers are composed of large grains of magnetite (~50 $\mu$ m). These observations indicate that they are typical oxide-type BIF and therefore were originally formed as precipitates from seawater. Although chromite, which is a host mineral for Cr, was found in both BIF and clastic sedimentary rock (e.g., silty sandstone) samples, chromite in the BIF was always overgrown by magnetite. This observation is also consistent with results from previous studies. The chemical compositions of the chromite determined by FE-EPMA were low Mg# (0.001~0.01) and high Cr# (0.76~0.89). No significant difference in chemistry was observed in chromite between BIF and clastic sedimentary rock samples. Bulk chemical compositions of the samples were also analyzed by XRF. The results show that the Cr/Ti ratio was not significantly different between BIF and clastic sedimentary rock samples. Therefore, Cr enrichment was not observed in the BIF in this study. The apparent contradiction to the previous study at Moodies Hills block can be explained by the difference in (1) analytical method used or (2) the sedimentary environment. The Ti contents of BIF at Moodies Hills block were determined by ICP-MS after acid decomposition, by which the detection limit is one order of magnitude lower than XRF used in this study. Therefore, the high detection limit in this study may lose the sensitivity for Cr enrichment in samples in which Ti content was low. Alternatively, the BIF in this study could have been deposited in a deeper setting than that at the Moodies Hills block. Therefore, the results may suggest that oxygenated seawater was only localized in very shallow parts.

Keywords: Banded Iron Formation, chromium, chromite, Barberton Greenstone Belt, surface environments on early Earth

## Change by a diagenesis of first minerals in 1.9 Ga sedimentary rocks of the Gunflint Formation

NIKAIDO, Emi<sup>1\*</sup> ; KAKEGAWA, Takeshi<sup>1</sup>

<sup>1</sup>Graduate School of Science, Tohoku University

Some microfossils in the 1.9 Ga Gunflint Formation show clear morphology of aerobic microorganisms. However, carbon isotope compositions of microfossils and other geochemical characteristics suggest the activity of anaerobic microorganisms in the same rock sample. This leads to the skepticism if the 1.9 Ga surface ocean environments were essentially anoxic and oxic environments were very limited.

In order to examine if oxic world were more common or anoxic world were more common, shallow water sedimentary rocks were collected from Kakabeka (the bottom of the Gunflint) and Telly Fox (the top of the Gunflint) areas. The following features were found in the present study. (1) Chemistry of carbonate change into either Fe-rich or Mg-rich from calcite during diagenesis. Fe-rich feature is only found at the bottom of the Gunflint Formation, suggesting wide injection of reduced fluids in sediments. (2) Carbon isotope compositions were similar to cyanobacteria value, and feature of anaerobic bacteria were not detected. This suggests that previous report of carbon isotope compositions of anaerobic bacteria was limited in a few places and not widespread in the Gunflint Formation. Therefore, aerobic microorganism was the major life forms. (3) Sulfur isotope compositions of pyrite range from -2 to +15 per mil, suggesting closed system sulfate reduction. The closed system was most likely isolated oxic seawater from anoxic sediments, probably high sedimentation of SiO<sub>2</sub> and CaCO<sub>3</sub>. In addition, isolated sediments were anaerobic bacterial world, where organic matter from the oxic world was largely consumed.

Keywords: diagenesis, oxic, anoxic, closed system

## Origin of phosphate stromatolite formed after the snowball Earth

SHIRAISHI, Fumito<sup>1\*</sup>; OKUMURA, Tomoyo<sup>2</sup>; TAKASHIMA, Chizuru<sup>3</sup>; KANO, Akihiro<sup>4</sup>

<sup>1</sup>Hiroshima University, <sup>2</sup>JAMSTEC, <sup>3</sup>Saga University, <sup>4</sup>Kyushu University

The sedimentary rocks formed after Neoproterozoic snowball Earth distribute near Irece, Bahia, Brazil. Salitre Formation is one of them, and contains unique phosphate (apatite) stromatolites. They show dense columnar shape, and are surrounded by laminated dolomite. The relationship between stromatolite and dolomite is mostly sharply bounded, although some parts appear transitional. Stromatolite contains various shape of microfossils. Filamentous microfossil (5-10  $\mu\text{m}$  diameter, about 300  $\mu\text{m}$  long) is most abundant and resembles to filamentous cyanobacteria, and thus, photosynthetic microorganisms such as cyanobacteria are considered to be involved in the formation of stromatolite.

In order to understand the influence of microbial photosynthesis on apatite precipitation, saturation state of apatite after removing 200  $\mu\text{M}$  of  $\text{CO}_2$  from seawater was calculated by Phreeqc. The result indicated that photosynthesis can significantly increase saturation state of apatite, when the concentration of dissolved phosphate is at least 1  $\mu\text{M}$ . Although the saturation state of  $\text{CaCO}_3$  is also increased by photosynthesis, its degree is much smaller than that of apatite. As a result, apatite is more likely to precipitate than carbonate, and phosphate stromatolite is formed.

The concentration of dissolved phosphate is extremely low at the surface ocean due to the uptake by phytoplankton, and its concentration is as high as several  $\mu\text{M}$  even at the deep ocean. At the time of post-snowball Earth, similar situation is expected for the surface ocean, while the concentration of phosphate in the deep ocean is considered to be much higher than today. If occasional upwelling transported such water mass to the shallow sedimentary basin where cyanobacterial mat is developed, phosphate stromatolite will be formed even if dissolved phosphate concentration is several  $\mu\text{M}$ .

## Large Fe isotope fractionations in ferruginous sedimentary rocks above Kuroko deposits in the Hokuroku district

SUZUKI, Ryohei<sup>1\*</sup>; TSUBASA, Otake<sup>1</sup>; YAMADA, Ryoichi<sup>2</sup>; SHIN, Ki-cheoul<sup>3</sup>; KON, Yoshiaki<sup>4</sup>; YONEDA, Tetsuro<sup>1</sup>; SATO, Tsutomu<sup>1</sup>

<sup>1</sup>Laboratory of Environmental Geology, Graduate School of Engineering, Hokkaido University, <sup>2</sup>Tohoku Univ., <sup>3</sup>Research Institute for Humanity and Nature, <sup>4</sup>National Institute of Advanced Industrial Science and Technology

The Hokuroku district in Akita Prefecture, Japan, hosts many large volcanogenic massive sulfide (VMS) deposits called Kuroko deposits formed around 15.3 million years ago by ancient submarine hydrothermal activity. VMS deposits were formed by the precipitation of metals from hydrothermal fluids and could have contacted with seawater in geological timescales. Because they are composed of sulfide minerals that are stable in a reducing environment, such as pyrite and chalcopyrite, an anoxic environment in the Hokuroku basin may play an important role in the preservation of the sulfide ores containing valuable metals in Kuroko deposits. However, geochemical evidence of such an environment occurring in Hokuroku district is currently lacking. Therefore, objective of this study is to investigate the distribution of REEs and the variation of Fe isotope compositions in the Fe-Mn-rich sedimentary rocks associated with VMS deposits in the Hokuroku district to understand the depositional environments and ancient sea-floor hydrothermal systems in the Hokuroku basin. Sedimentary rock samples obtained from both outcrops and mines in the Hokuroku district include ferruginous cherts occurring directly on or above a Kuroko deposit, manganese-rich siliceous mudstone, and amber in mudstone or tuff. Samples were analyzed by XRD, petrography, and SEM-EDS for mineralogy, by XRF and LA-ICPMS for chemical composition and MC-ICPMS for iron isotope composition ( $\delta^{56}\text{Fe}$  (‰) =  $1000 * [(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}} / (^{56}\text{Fe}/^{54}\text{Fe})_{\text{IRMM-14}} - 1]$ ).

The results of these analyses show the  $\delta^{56}\text{Fe}$  values of mine samples occurring directly on and above Kuroko deposits were -1.5 to 0.5 ‰. These values are largely fractionated from  $\delta^{56}\text{Fe}$  value that is similar with igneous rock's  $\delta^{56}\text{Fe}$ . Iron isotopic fractionation occurs when ferrioxide precipitate part of the bivalent iron present in the reservoir. These values are largely fractionated from the  $\delta^{56}\text{Fe}$  value of the standard (i.e., 0 ‰), which is similar to that of igneous rocks. The samples that have a large negative value also bears negative Ce anomaly. These signatures indicate that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the sea-floor of the Hokuroku Basin was anoxic. On the other hand,  $\delta^{56}\text{Fe}$  values of chemical sedimentary rocks formed during 2 -3 Ma after Kuroko deposits formed ranges from -0.8 to -0.3 ‰. These values are similar to that of dissolved ferrous ion in a modern sea-floor hydrothermal fluid. Therefore, the  $\delta^{56}\text{Fe}$  values of the samples indicate near complete oxidation of dissolved ferrous iron in an oxic environment. Therefore, the results of this Fe isotope study suggest that the depositional environment in the Hokuroku basin shifted from anoxic to oxic after the formation of Kuroko deposit.

Keywords: iron isotope, rare earth pattern, anoxic environment, Volcanogenic massive sulfide, hydrothermal system

## SEM and TEM observations of carbonate, Fe-oxide and silica minerals in Okuoku-hachikuro hot spring, Akita Prefecture

TERAJIMA, Shogo<sup>1\*</sup> ; KAKEGAWA, Takeshi<sup>1</sup>

<sup>1</sup>Graduate School of Science, Tohoku University

Recent studies of biomineralization mainly treated biominerals produced by evolved life. It is uncertain if primordial microbes are capable to precipitate biominerals. If biomineralization by early life is well documented, it will help to understand the Precambrian environments more in details.

Abundant carbonates are precipitating at Okuoku-hachikuro hot spring, located in Kosaka, Akita Prefecture, Japan. We collected sinters, soft to solidified sediments and microbial mats. Then, those constituents were observed using field emission-scanning electron microscopy (FE-SEM). Minerals around microbial sheath were also observed by transmitted electron microscopy (TEM). Analyses of X-ray diffraction, pH, DO, dissolved amino acids, carbon isotope compositions and chlorophyll compositions were also performed.

Hot spring water does not contain appreciable amounts of dissolved oxygen, but Fe-oxides immediately precipitated after discharge. Chlorophyll analyses indicate no presence of anoxygenic photosynthesizing bacteria. These results suggest that Fe were precipitated by Fe-oxidizing bacteria dominantly, supported by SEM observation of characteristic morphology of the sheath. Cyanobacteria become more dominant in the distance.

Most samples contain radial aggregates of needle-shape aragonite. Such morphology was found in bubble in the "first" discharging fluid. 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, Fe-oxide covering sheath are found locally. Using dilute hydrochloric acid etching, Fe-oxide is observed clearly, especially in zone 1. It has 3 morphological types: sheath-like, agglomerated and needle in radial aggregates. It is noteworthy that Fe-oxides never grow in large crystals. This can possibly because microbial activities or organic molecules may prohibit the growth of Fe-oxides. Furthermore Si was detected in Fe-oxide. This result suggests that Fe-oxide probably adsorbs amorphous silica selectively. Such unique morphology may help to interpret the origin of hematite in Precambrian banded iron formations.

Keywords: aragonite, Fe-oxide, Fe-oxidizing bacteria, SEM, TEM



## Microbial processes forming lamination in hot spring stromatolites by sulfur oxidizing bacteria and cyanobacteria.

OKUMURA, Tomoyo<sup>1\*</sup>; TAKASHIMA, Chizuru<sup>2</sup>; HIRANO, Misa<sup>2</sup>; KANO, Akihiro<sup>3</sup>

<sup>1</sup>JAMSTEC, <sup>2</sup>Faculty of Culture and Education, Saga Univ., <sup>3</sup>SCS, Kyushu Univ.

Travertines are carbonate precipitates from hot-spring water containing a sufficient amount of calcium and carbon dioxide. Most of travertines show sub-mm order laminations that were resemble to ancient stromatolites. Recently, daily microbial processes were identified in some travertines precipitated from some sulfide-poor and moderate temperature (<55 degree C) springs. In the process, daily growth of biofilms consisting cyanobacteria or heterotrophic bacteria, which inhibited inorganic mineral precipitation (1,2). While, lamination is less common in the travertines at higher temperature (>60 degree C) and sulfide-rich springs (3) likely because such daily microbe-mineral interaction might not be occurred. In order to understand the geomicrobiological system in high temperature and sulfide-rich spring, this study investigates a travertine in Sipoholon, Northern Sumatra, Indonesia.

Sipoholon hot spring forms the hugest travertine mound among the hot springs in Tarutung area located about 30 km south from the Lake Toba. The travertine mound spread in total area of 50,000 km<sup>2</sup>. The actively precipitated region was separated 3 areas; A is natural mound without artificial effect, B is the mounds in a quarry, C is exposes the rim pools behind spa facilities. In all area, sulfur-rich yellow sediments were formed near the vents, while white laminated sediment was formed from midstream to downstream. The surface color of the laminated travertine was changed with water temperature; pale pink around 55 degree C and green below 50 degree C. Lamination in the green travertine consisted of light colored crystalline layer and dark colored biofilm-rich porous layer in the interval of 0.5-1.0 mm. While, some lamination in the pink travertine was not clear.

12 sequences of water and travertine samples were collected at a green travertine and a pink travertine in Area C every 4 hours during 48 hours. Samples of both types of the travertine showed that the dark layer was formed during daytime and light colored layer was formed during nighttime without variation in pH, water temperature, Ca ion concentration, alkalinity, and flow. Only dissolved oxygen concentration showed the daily variation in the water chemistry, which was higher during the daytime and lower during the nighttime. Phylogenetic analysis on 16S rRNA gene showed that the pink and green travertines have a microbial composition dominated by obligatory chemolithoautotrophic sulfur-oxidizing bacteria. Phototrophs, cyanobacteria and chloroflexus were more diverse in the green travertine than in the pink one. Epifluorescence microscopy showed that phototrophs were concentrated in the diurnal dark layer in the green travertine, while sparsely distributed near the surface in the pink travertine.

These results suggest that formation of phototroph biofilm in daily cycle was responsible for lamina formation in the green travertine same as previous study. On the other hand, formation of sulfur-oxidizer biofilm stimulated daytime increment of oxygen concentration was likely responsible for lamina formation in the pink travertine. The obscure lamination in the pink travertine possibly due to growth of chemolithoautotrophs stimulated by extrinsic factor that is daily supplement of oxygen, in contrast to intrinsic daily growth of phototrophs. This novel microbial process could be occurred in ancient stromatolites formed under the anoxic sulfide-rich ancient ocean.

[Ref]

(1) Takashima, C. & Kano, A. (2008) *Sediment. Geol.* 208, 114-119.

(2) Okumura, T., Takashima, C., Shiraishi, F., Nishida, S., Kano, A. (2013) *Geomicrobiol. J.* 30, 910-927.

(3) Fouke, B.W., Farmer, J.D., Des Marais, D.J., Pratt, L., Sturchio, N.C., Burns, P.C., Discipulo, M.K. (2000) *J. Sediment. Res.* 70, 565-585.

Keywords: travertine, lamination, stromatolite, cyanobacteria, sulfur-oxidizing bacteria

## Influences of silica and embedding on thermal alteration of aliphatic hydrocarbons in cyanobacteria as evaluated by FTIR

IGISU, Motoko<sup>1\*</sup> ; YOKOYAMA, Tadashi<sup>2</sup> ; UENO, Yuichiro<sup>3</sup> ; NAKASHIMA, Satoru<sup>2</sup> ; MARUYAMA, Shigenori<sup>3</sup>

<sup>1</sup>JAMSTEC, <sup>2</sup>Osaka University, <sup>3</sup>Tokyo Institute of Technology

To study influences of the presence of silica and embedding on thermal changes of aliphatic hydrocarbons in prokaryotic cells, cyanobacteria *Synechocystis* sp. PCC6803 were isothermally heated at 250-400 °C and the changes in IR signals were monitored by micro-Fourier transform infrared (FTIR) spectroscopy. The absorbance of aliphatic C-H decreased with heating time, indicating the degradation of aliphatic hydrocarbons. Both the presence of silica and embedding delayed the degradation of the aliphatic C-H. The absorbance ratios of 2960 cm<sup>-1</sup> band (aliphatic CH<sub>3</sub>) to 2925 cm<sup>-1</sup> band (aliphatic CH<sub>2</sub>) (R<sub>3/2</sub> values) increased or changed little by the heating. Raman spectral features showed that some experimental products had a structural ordering similar to the Proterozoic microfossils, indicating that they were carbonized to a degree similar to the microfossils. These results reveal that the presence of silica and embedding affect the thermal degradation rate of aliphatic C-H in cyanobacteria but do not lead to the decrease in R<sub>3/2</sub> values. The low R<sub>3/2</sub> values of Proterozoic prokaryotic fossils from Bitter Springs and Gunflint Formations are not considered to be due to thermal degradation upon fossilization during diagenesis. Although other possibility cannot be ruled out, the results suggest that precursor lipids, having low R<sub>3/2</sub> values, were selectively preserved in microfossils.

Keywords: micro-FTIR, cyanobacteria, silica, thermal alteration, aliphatic hydrocarbon

## Role(s) of extracellular polymeric substance in microbial mineralization

NAKAMURA, Yuki<sup>1\*</sup> ; SHIRAIISHI, Fumito<sup>1</sup>

<sup>1</sup>Hiroshima University

Microbialites are defined as organosedimentary deposits that have accreted as a result of benthic microbial community binding detrital sediment or forming the locus of mineral precipitation. Most of microbialites are consisted of carbonate minerals, and considered to be formed by microorganism, such as cyanobacteria and sulfate reducing bacteria. Microbialite records the history of interaction between life and Earth environment, and therefore, it is important to understand their formation. Microbialites are formed mainly by three processes, including grain-trapping, mineral precipitation by metabolism and mineral nucleation by extracellular polymeric substances (EPS). Grain-trapping is locally important, but key processes are precipitation and nucleation. The knowledge of precipitation process by bacterial metabolism has increased, while that of EPS is still limited. Therefore, this study aims to investigate the influences of EPS on microbialite formation. We examined carbonate deposit developed at Kibedani hot spring, Shimane Prefecture. Calcite was despite of undersaturation in bulk water. Microelectrode measurement revealed that this deposit is formed as a result of photosynthesis-induced  $\text{CaCO}_3$  precipitation. The result of EPS staining observation by Confocal Laser Scanning Microscope revealed that this deposit contains abundant acidic EPS, which is generally considered to have important roles in mineral nucleation. This deposit composed of two layers: the upper layer is consisted of empty EPS sheaths and the lower layer is of cyanobacteria with EPS sheaths. Both layers contain acidic EPS, while only lower layer was mineralized. This observation implies that acidic EPS cannot solely cause nucleation, and requires high mineral saturation state induced e.g. by photosynthesis.

## Controlling factors of microbialite textures inferred by a tufa deposit

HANZAWA, Yuhsaku<sup>1\*</sup>; OKUMURA, Tomoyo<sup>2</sup>; SHIRAIISHI, Fumito<sup>1</sup>

<sup>1</sup>Hiroshima university, <sup>2</sup>Japan Agency for Marine-Earth Science and Technology

Microbialite is organosedimentary deposits that are formed by the interaction between life, water and mineral. It has accreted as a result of a benthic microbial community trapping and binding detrital sediment and/or forming the locus of mineral precipitation. Typical examples of microbialite are laminated stromatolite, and clotted thrombolite. In the Earth history, stromatolite appeared from about 3500 Ma, followed by its peak at 1300 Ma. At about 500 Ma, stromatolite rapidly declined, and thrombolite appeared. Although this transition is considered to reflect evolution of life and Earth environment, its detail is still not well understood. To understand the basic mechanisms forming microbialites, the geomicrobiological studies of recent samples are essential. While microbialite in modern marine environment is scarce, it is relatively common at freshwater environment as a tufa. The present study focuses on tufa for investigating the relationship between depositional structure and microbial composition. Tufa deposit usually has laminated structure resembling stromatolite. However, tufa deposit developed in Takahashi city (Okayama prefecture) exhibits both stromatolitic and thrombolitic structures by reflecting the difference of hydrodynamic condition. The chemical compositions of creek water at the sites where stromatolitic and thrombolitic tufa are depositing are almost the same, and similar to that of common tufa-depositing creek. Extracellular polymeric substances (EPS) staining observation applied for deposits surface by Conforcal Laser Scanning Microscope (CLSM) showed that the distribution patterns of phototrophs and EPS were different between stromatolitic and thrombolitic tufa. At the surface of thrombolitic tufa, coccoid cyanobacteria densely colonized to form small mounds (500  $\mu\text{m}$  in diameter) and EPS located inner and marginal part of the mounds. On the other hand, at the surface of stromatolitic tufa, filamentous cyanobacteria distributed sparsely with EPS, and calcite was widely exposed. Vertical thin section observation revealed that there were large calcite crystals (500  $\mu\text{m}$  in diameter) at the surface of thrombolitic tufa, and filamentous one colonized around them. Stromatolitic tufa, on the other hand, was consisted of fine grained calcite (10  $\mu\text{m}$  in diameter) with filamentous cyanobacteria colonized perpendicular to the lamination. Microbial composition of both deposits was examined by 16S rRNA gene analysis. The result indicated that cyanobacteria were abundant and some strains were common between thrombolitic and stromatolitic tufa. However, the diversity of microbial population microbial population was higher in thrombolitic tufa than stromatolitic ones.

From the results above, it is inferred that the transition from stromatolite to thrombolite in  $\sim 500$  Ma was caused by microbial diversification and resultant EPS composition change.

Keywords: microbialite, stromatolite, thrombolite, tufa, carbonate rock

## Soil micromorphology and the effect of biotic activity

SUZUKI, Shigeyuki<sup>1\*</sup> ; HATTORI, Tsutomu<sup>2</sup> ; HATTORI, Reiko<sup>2</sup> ; MIMURA, Kaori<sup>3</sup> ; ISHIGURO, Munchide<sup>4</sup>

<sup>1</sup>Okayama University, <sup>2</sup>Atic Laboratory, <sup>3</sup>Kanematsu-NNK Corporation, <sup>4</sup>Hokkaido University

Soil is formed on a boundary between geosphere and biosphere in relation with hydrosphere and atmosphere. The major component is quite very fine-grained particles which are not still unknown in detail. A great variety of microbes are associated in soil (e.g., Hattori, 1987). Hattori (2006) suggests that there is a possibility some bacteria produce very fine-grained mineral particles, silica-nano particle as a part of soil material. Micromorphology is observed under petrological microscope. The technique for preparation to make thin section from unconsolidated soil is followed by method in FitzPatrick (1993). Soil fragments are examined by scanning electron microscope. Samples are collected from recent cultivated soil (Okayama University Farm), fluvial soil (Sendai City), rice field soil (150 to 2000 years old fluvial soil from Okayama University), paleosol (about 3000 years old organic rich fluvial soil from Dhaka City, Bangladesh).

The formation of microaggregates: The structure of soil macroaggregate (1~2mm) which is composed of microaggregates (0.05~0.3mm) and sand grains of mineral and rock fragments is observed in the recent cultivated soil from Okayama University Farm. Similar microaggregates (0.1~0.5mm), structure with heterogeneous granular domains is observed in rice field soil from Okayama University. A paleosol from Dhaka, which is not considered to have artificial effects, also consists of microaggregate. The aggregates do not have distinctive boundary but are distinguished by different compositions (content of organic materials, deposited ferri-hydrate and manganese dioxide, particles of mineral and rock fragment). Root pipes and cracks are associated in the soil. The compound structure is interpreted to be formed under effects of microorganisms, root and physical process as demonstrated by previous soil research (e.g., FitzPatrick, 1993).

The formation of silica-nano particle: Under scanning electron microscope, surface of mineral grain has structures caused by weathering, for example embayment, fracture and etch pit. Crystallized nano-sized minerals are formed on weathered surface of a mineral. A bacterial cell surrounded by radiate fibrous mineral is found. The feature indicates a possibility that some bacteria promote to form minerals. And also there is a possibility that a part of inorganic soil materials might be formed relation with organism.

FitzPatrick, E.A. (1993) *Soil Microscopy and Micromorphology*, Wiley

Hattori, T. (1987) *Microbial life in the soil*, Iwanami

Hattori, T. (2006) *Soil Microorganisms*, 60(2), 105-107

Keywords: soil, microaggregate, silica-nano particle, bacteria

## A novel remediation method for nickel-bearing wastewater at neutral conditions

OKAHASHI, Haruko<sup>1\*</sup> ; NISHIUCHI, Toru<sup>1</sup> ; SATO, Tsutomu<sup>2</sup> ; OTAKE, Tsubasa<sup>2</sup> ; YONEDA, Tetsuro<sup>2</sup>

<sup>1</sup>Graduate School of Engineering, Hokkaido University, <sup>2</sup>Faculty of Engineering, Hokkaido University

Advances in technology such as the electronics and metal plating industries have increased the demand of Ni year by year. On the other hand, the resources are unevenly distributed in a few countries and the supply is highly dependent on strategic policies. Moreover, since Ni is not produced in Japan and it is dependent on imports from foreign countries, the supply structures of Ni are vulnerable. Because of this, the necessity of recovering Ni from wastewaters and other waste forms has been increasing. Some industrial wastewaters contain large amounts of Ni. Generally, the removal of Ni from contaminated wastewater by adding antalkaline and flocculants to increase the pH to 10 or above would result in the generation of Ni-hydroxides after treatment. After that, it is necessary to adjust the pH below the effluent standard (pH 5.8~8.6). However, this method suffers from some disadvantages, such as the high cost for chemical reagents, problems in the disposal of alkali sludge and inefficient treatment system. Therefore, a more sustainable remediation method must be developed to achieve sustainable wastewater treatment operations. This study focused on natural attenuation processes which are safer, cost-effective and more environmentally friendly than traditional methods. For example, at Dougamaru abandoned mine in Japan, high concentrations of Cu and Zn in wastewater are naturally incorporated in the structure of layered double hydroxides (LDH), which forms in the presence of Al ions, hence, natural attenuation of Cu and Zn occurs (Okamoto et al., 2010). Because LDH has the hydroxide structure, six-coordinated heavy metals such as Cu, Ni and Co can be incorporated into the structure during the formation process. Therefore the objective of this study is to develop a remediation method for Ni-bearing wastewaters at neutral conditions, and to clarify the behavior of Ni in the neutralization and precipitation process.

In this context, to check the applicability of LDH in the treatment of Ni-bearing wastewaters, synthesis experiments were carried out by co-precipitation of Ni-bearing LDHs containing  $\text{SO}_4^{2-}$  as the interlayer anion with different concentrations of dissolved Al ions. Analysis of water chemistry before and after the co-precipitation show that the removal efficiencies of Ni from the synthetic wastewaters increased with increasing dissolved Al concentration. The results further show that the presence of Al in the formation of LDH removed Ni at pH values lower than previous methods which precipitated Ni-hydroxides. It is expected that treatment costs will be reduced in actual wastewater treatment systems because Al addition leads to the reduction of antalkaline use and the neutralization process.

Ni adsorption experiments and extraction experiments were conducted to investigate the sorption behavior of Ni. Only a small amount of Ni was adsorbed to LDH and basaluminite (major minerals in coprecipitation experiments) as inner- and outer-sphere complexes. From the result of XAFS analysis, Ni was incorporated into the structure by being able to precipitate LDH selectively. This shows Ni is fixed securely in the structure of LDH and that the mobility of Ni will be governed by the solubility of LDH. Thermodynamic modeling suggests that the precipitation of LDHs with the optimum Al/Ni molar ratio (0.25~0.50) is determined by the initial conditions (e.g. pH, Al, Ni concentrations). Furthermore, modeling results reproduce the experimental results such as removal efficiency and mineral species well, opening the possibility of its application in actual wastewater treatment operations.

Keywords: Remediation, Layered double hydroxide, Nickel

## Changes in water properties and microbial facies along a flow path of a travertine developed in northern Sumatra Island,

TAKASHIMA, Chizuru<sup>1\*</sup>; HIRANO, Misa<sup>1</sup>; OKUMURA, Tomoyo<sup>2</sup>; KANO, Akihiro<sup>3</sup>

<sup>1</sup>Saga Univ., <sup>2</sup>JAMSTEC, <sup>3</sup>Kyushu Univ.

Sumatra Island has many hot springs related with volcanoes belonged to the Ring of fire. Geothermal studies for these hot springs have been performed actively, but hot spring sediments including travertines have rarely been reported. Travertine is a useful modern analog for the Precambrian stromatolites (Takashima and Kano, 2008; Okumura et al., 2013).

We studied travertines at Sipoholon hot spring located about 30 km south from the Lake Toba which is the largest caldera lake in the world. The travertines spread in total area of 50,000 km<sup>2</sup>, in which active deposition occurs mainly in three separated sites; Area A, B and C from north to south, respectively. This study focused on Area A that lacks artificial effect.

In this study, we measured chemical components and stable isotopes of water and observed textures and bacteria of the travertine. Based on these results, we cleared that relationship between water properties, travertine textures and distribution of bacteria.

The travertine deposit occurs along ~35-m-long flow path. The water from the vent first flows 15 m on a narrow (50 cm) and gentle passage and then widely on a steep slope on the travertine dome. Below the dome, the water passes on terrace-like rim pools and finally flows into a pool about 5 m in diameter.

The water with sulfurous smell emits from a vent at a rate of 286 L/min. This water is high temperature (61.4 degree Celsius), neutral pH (6.48) and microaerobic (DO of 0.6 mg/L). The water is rich in Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, and poor in Mg<sup>2+</sup> and Cl<sup>-</sup>. To the downstream, the water temperature decreases, pH increase, and conversely alkalinity and Ca<sup>2+</sup> concentration decrease. These and increased carbon isotope of dissolved inorganic carbon indicate that CO<sub>2</sub> degassing increased supersaturation and induced deposition of calcium.

The travertine in Sipoholon hot spring is mainly composed of aragonite, but in one place, calcite coexists. It tends to become softer from the upstream to the downstream. This may reflect difference in crystal shape and texture. The harder travertines consist of tightly packed spherical aggregates of aragonite needles, while softer travertines have loose textures containing dumbbell-shape crystals.

Microbial facies on the travertine surface changes obviously from the upstream to the downstream. A white sulfur-turf in upper stream is composed of sulfur oxidizing bacteria with sulfur particles (Maki et al., 2004). It is known that the sulfur-turf prefers in high temperature, neutral pH and rich in hydrogen sulfide, which corresponds the conditions of the upstream. On high flow parts of the travertine dome, the travertine colored in pale pink likely due to the occurrence of purple sulfur bacteria. Green microbial mat covers the travertine deposited in in lower part with low flow rate. The mat is composed of filamentous bacteria with photosynthesis pigment identified in fluorescence observation. These are cyanobacteria. Water temperatures on the mat are all below 45 degree Celsius. Thus, color change of travertine surface reflect that of microbial composition responded to water properties, such as water temperature, flow rate, flow volume, nutrient.

### [References]

Takashima, C. and Kano, A. (2008) Microbial processes forming daily lamination in a stromatolitic travertine. *Sedimentary Geology*, 208, 114-119.

Okumura, T., Takashima, C., Shiraishi, F., Nishida, S., Kano, A. (2013) Processes forming daily lamination in a microbe-rich travertine under low flow condition at the Nagano-yu Hot Spring, Southwestern Japan. *Geomicrobiology Journal*, 30, 910-927.

Maki, Y., Ogawa, K. and Shimizu, A. (2004) A model for syntrophic cooperations in microbial mats on pristine Earth: Structure-function relationship of sulfur-oxidation in sulfur-turf microbial mat vegetating in hot spring effluents. *Viva Origino*, 32, 96-108.

Keywords: travertine, aragonite, sulfur oxidizing bacteria, cyanobacteria

## A study of irregular shaped tests formation of planktonic foraminifera

HORI, Masako<sup>1\*</sup> ; SHIRAI, Kotaro<sup>1</sup> ; TAKAHATA, Naoto<sup>1</sup> ; SANO, Yuji<sup>1</sup> ; KURASAWA, Atsushi<sup>2</sup> ; KIMOTO, Katsunori<sup>2</sup>

<sup>1</sup>Atmosphere and Ocean Research Institute, The University of Tokyo, <sup>2</sup>Japan Agency for Marine-Earth Science and Technology

Planktonic foraminifera are protist forming carbonate tests. They are used as useful index fossils, and moreover, the oxygen isotopic and trace element compositions in their calcite tests are recognized as a promised archive representing paleo-ocean environments. Foraminifera generally consist of multipul chambers, and each chamber forms spirally for the center of the first chamber. Culturing observations have contributed for understanding relationships between trace elements and isotopic indices, and environmental factors. However, the transfer of elements and trigger of test formation are poorly understood. Cultured specimens sometimes show irregular-shaped tests, which are unlikely formed under natural condition in the ocean.

In this study, we focused the test formation of planktonic foraminifera, and cultured two species (*Globigerina bulloides*, *Globigerinoides ruber*) collected at Sagami bay. Culturing temperature was controlled at 19, 21, 23 and 25 °C. Calcium isotopic reagents were added to the culturing seawater to mark the timing of test formation. Moreover, we also investigated the other specimens cultured with seawater, whose calcium concentration was raised for 10% respective to the original concentration. In those cases, the pH of calcium reagents were adjusted to appropriate pH, and therefore, the seawater pH was kept at constant during the observation.

As a result, three of ten specimens of *G. ruber* have newly formed a regular test at 19, 21 and 23 °C. On the other hand, 5 of 7 specimens of *G. bulloides* have formed new tests, three of which have formed irregular shaped tests. These three specimens are ones survived more than a couple of weeks after sampling. The water temperature of irregular test formation was 21 or 25 °C, suggesting that the temperature was not a direct controlling factor of irregular test formation. Potential factors are concentrations of dissolved oxygen or dissolved organic matters. Foraminifera first forms organic layer called POM at the beginning of test formation. Anomalously high organic concentration in crystallization liquid may impede the regular formation of POM, consequently resulting in the formation of irregular-shaped tests.

For the specimens with increasing calcium concentration of seawater, the spines fell out within 12 hours. Because calcium is an essential element not only for test formation but also various biological reactions, rapid increase of calcium concentration might disturb the biofunction of planktonic foraminifera.

Keywords: planktonic foraminifera, laboratory culture



## Anion adsorption and post-adsorption behavior of metastable iron hydroxides

KODAMA, Ritsu<sup>1\*</sup> ; OKAHASHI, Haruko<sup>1</sup> ; YAMAMOTO, Takato<sup>1</sup> ; SATO, Tsutomu<sup>1</sup> ; OTAKE, Tsubasa<sup>1</sup> ; YONEDA, Tetsuro<sup>1</sup>

<sup>1</sup>Laboratory of Environmental Geology, Hokkaido university, Graduate School of Engineering, Hokkaido U

Pollution by dissolved anions has been a pertinent environmental concern in many areas around the world. For example, acid mine drainage from abandoned mines and contaminated waters resulting from the Fukushima nuclear power plant accident emphasize the importance of predicting the behavior of the dissolved trace elements on Earth's surface environments. Iron minerals may play a potentially important role in the control of dissolved trace elements in the environment. In particular, poorly crystalline iron minerals exhibit excellent adsorption capacities for toxic anions due to their high specific surface areas and reactivity. In order to evaluate the potential of poorly crystalline iron minerals as stable sinks of dissolved hazardous ions, it is necessary to investigate the adsorption mechanism on these minerals and their post-adsorption behaviors.

Adsorption experiments using arsenate, phosphate, chromate, sulfate, selenate, fluoride, and chloride were performed to investigate the selectivity of Schwertmannite and Ferrihydrite for various anions. Adsorption selectivity decreases in the following order:  $\text{H}_2\text{AsO}_4^- > \text{H}_2\text{PO}_4^- > \text{HCrO}_4^- > \text{SeO}_4^{2-} \approx \text{SO}_4^{2-} \gg \text{F}^- \approx \text{Cl}^-$ . Schwertmannite and Ferrihydrite didn't have an ability to adsorb  $\text{F}^-$  and  $\text{Cl}^-$ . The adsorption mechanism of these anions was investigated using zeta potential measurements. The results indicated that  $\text{H}_2\text{AsO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HCrO}_4^-$  formed inner-sphere complexes while  $\text{SeO}_4^{2-}$  and  $\text{SO}_4^{2-}$  formed outer-sphere complexes. The adsorption mechanism of these anions to both Schwertmannite and Ferrihydrite is generally similar, except in the case of  $\text{HCrO}_4^-$ .

Accelerated alteration experiments were performed to observe post-adsorption behaviors of Schwertmannite and Ferrihydrite. Oriented specimens loaded with varying amounts of adsorbed anions were aged under saturated water vapor pressure conditions at 50 °C for 30 days and analyzed by XRD. Results show that larger amounts of adsorbed anions delay the transformation of Schwertmannite and Ferrihydrite into more stable phases, indicating that adsorption of anions, particularly as inner-sphere complexes, stabilizes poorly crystalline iron minerals.

These results show that poorly crystalline iron minerals are capable of taking up a range of toxic anions from contaminated waters and that the stability of these minerals will be affected by the amount of anions sorbed on the surface. These suggest that poorly crystalline iron minerals may serve as stable, long-term sinks for toxic anions.

## Anion adsorption and post-adsorption behavior of metastable calcium carbonate polymorph

YAMAMOTO, Takato<sup>1\*</sup> ; KODAMA, Ritsu<sup>1</sup> ; SATO, Tsutomu<sup>1</sup> ; OTAKE, Tsubasa<sup>1</sup>

<sup>1</sup>Laboratory of Environmental Geology, Hokkaido University

In Japanese transuranic (TRU) waste disposal facilities, I-129 is the most important radionuclide that must be considered in long-term safety assessments of the repository. However, the degradation of cement materials used in the repositories can produce high pH pore fluids that can affect to anion transport behavior. Therefore, it is necessary to understand the behavior of anions such as I<sup>-</sup> in hyperalkaline conditions. Examples of I<sup>-</sup> behavior in natural hyperalkaline environments, such as in Oman, show that I<sup>-</sup> is taken up by aragonite, opening up the possibility of calcium carbonates as inhibitors of I<sup>-</sup> migration. This concept is currently being applied in the development of the Advanced Liquid Processing System (ALPS), which employs carbonate coprecipitation to treat contaminated waters resulting from the Fukushima Daiichi nuclear power plant accident. However, the stability of the carbonate phases precipitated in this system as well as the anion uptake capacities of these phases are poorly understood. In a previous study, (Kasahara, 2012), it was found that monohydrocalcite (MHC), a precursor of aragonite, affects the iodine capacity of aragonite, making it a possibly important material that can control the behavior of anions. The objective of this study therefore, is to investigate the sorption capacity of MHC for anions and its stability. MHC ( $Mg^{2+}/Ca^{2+}=6$ ;  $Ca^{2+}/CO_3^{2-}=1$ ) was synthesized and used for sorption experiments involving  $F^-$ ,  $Br^-$ ,  $I^-$ ,  $IO_3^-$ ,  $SO_4^{2-}$ ,  $CrO_4^{2-}$ ,  $HAsO_4^{2-}$ , and phase transformation experiments. Results show that Kd values of  $HAsO_4^{2-}$  and  $F^-$  on MHC are high, while  $IO_3^-$ ,  $SO_4^{2-}$  are relatively low. On the other hand,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $CrO_4^{2-}$  were not taken up. It is because MHC has high chemical reactivity and high specific surface (4 times large of aragonite, 15 times large of calcite), in addition MHC is most low density of calcium carbonate, so MHC can take up relatively large amount of anions than other calcium carbonate. And other thing, MHC involves  $Mg^{2+}$  abundantly. This study indicates that  $Mg^{2+}$  form fluoride adsorption site. Results of the transformation experiments show that MHC with no adsorbed anions easily transforms into a stable phase, whereas MHC loaded with increasing amounts of anions transform after longer durations. It is because the driving force for the transformation decreases with the anions content in the solution. In conclusion, MHC can take up fluoride and oxyanions that ionic radii is similar to carbonate but larger than that. In addition, MHC is stabilized as a function of uptake amount of anions.