

U020-P01

Room:Convention Hall

Time:May 24 10:30-13:00

## Mineralogical and geochemical characteristics of pyrite spherulites found in the Nishi Kannondou Kuroko deposit

Miki Hasegawa<sup>1\*</sup>, Ryoichi Yamada<sup>1</sup>, Tsubasa Otake<sup>1</sup>, Takeshi Kakegawa<sup>1</sup>

<sup>1</sup>Graduate School of Science, Tohoku Univ.

Pyrite spherulites are often observed in modern seafloor hydrothermal vents as well as ancient hydrothermal systems. Sulfide spherulite has been proposed as an important material in the origin of life by catalyzing metabolisms or acting like a cell. However, formation processes of the pyrite and their association to biotic processes are not well understood due to a lack of detailed investigations on mineralogical and geochemical characteristics of the pyrite. We have recently found a possible fossil chimney and abundant pyrite spherulites in a small sulfides deposit (Nishi Kannondo deposit), an ancient (ca. 13Ma) seafloor hydrothermal system, in Hokuroku district, Akita Prefecture, Japan. Objectives of this study are (1) to compare the mineralogical and geochemical characteristics of spherulitic pyrite and non-spherulitic pyrite found in the Nishi Kannondo deposit, and (2) to investigate the relationship of the formation of spherulitic pyrite and biological activities.

We collected various ore samples. Pyrite-rich ores are commonly found in western and northern side of the ore deposit. Black ores containing sphalerite and galena are found in the center of the ore deposit, and barite ores are from southern side of the deposit. These lithological variations correspond to the paleo-structures of chimney and mounds. Pyrite spherulites are found in barite-rich ores which may be located at the chimney out wall or mound inside: those were formed in low temperature and sulfate-rich environments, thus in distant from black smoker activities.

Based on microscopic observations, an individual pyrite spherulite, a few mm in diameter, is divided into (a) central, (b) middle, and (c) outer parts. Central and middle parts are mostly composed of radial pyrite crystals. Other sulfide minerals (e.g., chalcopyrite, tennantite and molybdenite) were also observed in the central part. Middle parts are composed of concentric layers of radial pyrite crystals and other minor minerals (e.g., chalcopyrite, tennantite and molybdenite). In chemical mapping of the pyrite layers, concentric zonings of As and Cu were observed from central to middle parts. Outer parts are composed of cubical pyrite aggregates. These characteristics of pyrite spherulites indicate that the pyrites record periodical rapid and slow precipitation processes. We also propose that these characteristics of pyrite spherulite reflect changes in surrounding environments during the formation of pyrite spherulites, such as repeated dissolution and precipitation of sulfates in chimney or mounds.

Samples containing abundant pyrite spherulites are also enriched in organic carbon content (up to 1.6 wt%), compared to those mostly containing non-spherulitic pyrite. S isotope analyses of these samples showed that S isotope compositions of pyrite spherulites were about 15 per mil lighter than those of non-spherulitic pyrites. This indicates that hydrogen sulfide for the formation of pyrite spherulites was supplied through bacterial sulfate reduction. Therefore, our preliminary investigation suggested that biological activities were related to the formation of pyrite spherulites.

Keywords: pyrite, spherulite, kuroko, organic carbon, bacterial sulfate reduction

U020-P02

Room:Convention Hall

Time:May 24 10:30-13:00

## Sedimentary environments after Kuroko deposits around 13 Ma: mineralogical and geochemical studies on pyrite framboids

Misato Endo<sup>1\*</sup>, Ryoichi Yamada<sup>1</sup>, Tsubasa Otake<sup>1</sup>, Takeshi Kakegawa<sup>1</sup>

<sup>1</sup>Graduate School of Science, Tohoku Univ.

In the Hokuroku district of Akita Prefecture, Kuroko deposits were formed at ~13 Ma by submarine hydrothermal activities. Previous study (e.g., Komuro et al., 2004) suggested that, during the formation of Kuroko deposits bottom of an ocean water become anoxic locally. When an ocean becomes anoxic, it may further become euxinic by either hydrothermal or microbial activities. Extents of anoxic or euxinic ocean and their duration have been poorly understood during and after the formation of Kuroko deposits. In this study, geological, geochemical, and mineralogical investigations, including the size measurements of pyrite framboids, were carried out on mudstones in the Hokuroku district. Size distribution of pyrite framboids in sedimentary rocks has been used as indicators for distinguishing oxic and euxinic ocean water (Wilkin et al., 1996). Sulfur isotope ratios of pyrite in the rocks were also analyzed to evaluate activities of sulfate reducers.

Mudstones, named M3, M2b, M2a and M1 were collected from outcrops in the Hokuroku district. The size and chemical compositions of pyrite framboids in the samples were examined by standard petrographic microscopy, SEM, and EPMA. Contents of organic carbon and pyrite sulfur of the samples were determined by an elemental analyzer (EA). The sulfur isotope compositions of the samples were determined by EA-IRMS.

Detailed size analyses of the pyrite framboids showed that mean sizes of pyrite framboids in the lower M2b mudstones (~5.2 micro meters) were smaller than those of the upper M2b, M2a and M1 mudstones (~6.3 micro meters). This trend indicates that the lower M2b mudstones were deposited under euxinic conditions, and that the upper M2b, M2a and M1 mudstones were deposited under oxic conditions. Therefore, the bottom oceans were euxinic soon after the Kuroko formation, and the euxinic water overlaid the entire Hokuroku basin. Here we propose that such euxinic conditions prevent the oxidation of Kuroko deposits and contributed to their preservation. Then the bottom oceans became oxic a few million years after the Kuroko formation. The sulfur isotope compositions of pyrites in the mudstones deposited in euxinic environments range from -50 to -30 per mil, which indicates that redox sulfur cycling were driven by sulfate-reducing and sulfur-oxidizing bacteria at the redox boundary in a water column. Interestingly, there is no signs of hydrothermal sulfur in pyrites in the lower M2b, suggesting the euxinic condition was generated by microbial activities. The results of sulfur isotope analyses suggest that microbial activities were involved in the change of oceanic environments to euxinic, even near submarine hydrothermal activities. On the other hand, the sulfur isotope compositions of pyrites in the M2a and M1 mudstones range from -30 to -15 per mil, which suggests that only sulfate reducing bacteria were active in the sediments a few million years after the Kuroko formation.

### References

Komuro K., Kubota H., Sato T., Kajiwara Y. and Tanimura S. (2004) Trace fossils and sulfur isotopes in mudstones around the Kuroko deposits in Hokuroku basin, northeast Japan: an attempt to delineate the depositional environment. *Resource Geology*, 54, 4, 425-436

Wilkin R. T., Barnes H. L. and Brantley S. L. (1996) The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta*, 60, 20, 3897-3912

Keywords: pyrite framboids, Kuroko deposits, bacterial activity, euxinic

# Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

©2011. Japan Geoscience Union. All Rights Reserved.



U020-P03

Room:Convention Hall

Time:May 24 10:30-13:00

## Evolution of water chemistry of paleolake recorded in the mineral compositions of the lake sediment from Darhad basin

Madoka Fuchizaki<sup>1\*</sup>, Keisuke Fukushi<sup>2</sup>, Kenji Kashiwaya<sup>2</sup>, Hitomi Abe<sup>1</sup>

<sup>1</sup>Kanazawa University, <sup>2</sup>Kanazawa University

Darhad basin in northern Mongolia is located in the continent where is sensitive to the climate change. Hydrologic events with climate changes occurred in this area. For example, according to data from previous study, it is suggest that Darhad basin formed ice dam lake by Pleistocene glaciers and the lake repeated drainage and impounded water.

Disturbance of equilibria between minerals and solution in Lake caused by climatic changes leads to the water-mineral reaction. In consequence, The records of biological and chemical reaction resulted from such reactions are preserved in the mineral compositions in lake sediments. Therefore, it is expected that lake sediments from Darhad basin would have record of evolution of water chemistry over the past a few million years.

We tried to reconstruct evolution of water chemistry of the paleolake by mineralogy analysis of lacustrine sediment from Darhad basin. We also tried to clarify the contributing factors which affected evolution of water chemistry.

# Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

©2011. Japan Geoscience Union. All Rights Reserved.



U020-P04

Room:Convention Hall

Time:May 24 10:30-13:00

## Formation condition of monohydrocalcite

Risa Nishiyama<sup>1\*</sup>, Takashi Munemoto<sup>2</sup>, Keisuke Fukushi<sup>3</sup>

<sup>1</sup>Kanazawa University, <sup>2</sup>Tokyo University, <sup>3</sup>Kanazawa University

Monohydrocalcite ( $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ : MHC) was found from sediment core at lake Hovsgol, Mongolia. It is estimated that MHC was formed during the cold periods. It may be possible to estimate water quality condition of lake Hovsgol during the cold periods by understanding the formation condition of MHC. Synthesis experiments of carbonate minerals from various concentration of Ca, Mg  $\text{CO}_3$  were conducted to find the formation condition of MHC. MHC was produced when the original solution condition was  $\text{Ca} < \text{CO}_3$  and Mg existed. Crystal morphology of MHC was observed by scanning electron microscope. The morphology of MHC was spherocrystal that aggregate acicular or long column crystal, and bow-tie-shaped crystal depending on Mg/Ca ratio in original solution. In present study, the equilibrium constant of MHC formation reaction was estimated from the reaction solutions.

U020-P05

Room:Convention Hall

Time:May 24 10:30-13:00

## Surface complexation modeling for Eu adsorption on granite

Koshi Maeda<sup>1\*</sup>, Yusuke Hasegawa<sup>1</sup>, Keisuke Fukushi<sup>1</sup>, Yuhei Yamamoto<sup>2</sup>, Daisuke Aosai<sup>2</sup>, Takashi Mizuno<sup>2</sup>

<sup>1</sup>Kanazawa University, <sup>2</sup>Japan Atomic Energy Agency

It is planned that the high-level nuclear waste caused by nuclear electricity generation is isolated deep underground from the human environment by the geological disposal. AThe radionuclide Migration of radioactive nuclidetransfer to the human environmentbiosphere is prevented by the multi-barrier system which is composed of the artificial engineered barrier and the natural barrier. The artificial barrier is composed of the steel overpack and the bentonite.The natural barrier is composed of laying underground to underground many hundreds of meter restoration. After disposal of the high-level nuclear waste, the function of the artificial engineered barrier will lose the desired functionsis seemed to last probably up to one thousand years. Adsorption of the radionuclide on a rock bed is expected to play an important role in afor the retardation migration retardant of it when the artificial barrier becomes depleted and the radionuclide is released into a native environmentfrom the engineered barrier. Although aAdsorption of the radionuclide on a rock bed is an important process to value a safety offor the safety assessment of the geological disposal. Adsorption of the radionuclide is influenced by solution conditions such as pH, ionic strength, adsorbent and adsorbate. So to value to predict thea safety of the adsorption characteristics of adsorption radionuclide on a rock bed, it is needed to predict thean adsorption behavior is needed to be expected in various water quality environment. Surface complexation models modeling are is the suitable method to handle quantitatively absorption of solute to on a the rock bed (minerals).

This study is aimed at ato building construct the method which is based on surface complexation models to predict expept the an absorption behavior of unclear radionuclide species on a rock bed based on surface complexation modeling. In present study, granite is used for tThe adsorbent, while europium which has strong adsorptive property like some actinides species is selected to the solute granite and the adsorbate is Eu which has strong adsorptive property. The calculation model of adsorption is tried to lie, based on the analysis of the surface charge of a granite and the adsorption behavior of Eu.A granite which was stamped in Mizunami Underground Research Laboratory is used.

This study is the collaboration with the Japan Atomic Energy Agency.

Keywords: adsorption

U020-P06

Room:Convention Hall

Time:May 24 10:30-13:00

## The identification of a bioalteration texture occurred in low-grade metamorphosed green-rocks

Hisanari Sugawara<sup>1\*</sup>, Masayuki Sakakibara<sup>1</sup>

<sup>1</sup>Earth Sciences, Ehime University

Bioalteration textures found within greenrocks of ancient oceanic crusts outcropped on-land are the keys to characterize ancient microbial activity within oceanic crusts before the Jurassic. However, there is difficulty with identifying those textures as a bioalteration texture because most of them have experienced metamorphism and often recrystallized. The aim of this study is, therefore, bioalteration textures found within metabasalts from early to middle Permian Ibara dismembered ophiolite from the Maizuru tectonic belt, southwest Japan are examined to discuss the identification as a bioalteration texture by means of morphology, mineralogy, and elemental mapping analysis. Original structures and textures are well-preserved in the Ibara greenrocks. The Ibara greenrocks are divided into four zones based on their metamorphic mineral assemblages; zone I for prehnite-pumpellyite facies, zone II for prehnite-actinolite facies, zone III for greenschist facies, and zone IV for amphibolite facies. The mineral assemblages and chemistry suggest that all zones have experienced a low-pressure metamorphism, and the distribution of metamorphic mineral assemblages indicates it as the ocean-floor metamorphism. Granular and tubular bioalteration textures are found within quench glass of the basaltic pillow lavas in three locations. Granular bioalteration textures occur from irregular clusters along either veins or clacks within altered basaltic glass, and they are approximately less than 10 micrometers in diameter and consist of titanite. Tubular bioalteration textures occur from clacks or veins extended into altered basaltic glass, and are less than 20 micrometers in width and less than 400 micrometers in length. Tubular bioalteration textures are morphologically divided into four types; (1) unbranched tube with spiral tube, (2) unbranched tube with larger diameter at the end of tube, (3) branched tube with larger diameter at the end of tube, and (4) others. Although minute original textures are often not well-preserved, but the occurrence and preserved morphology resemble the bioalteration textures found within in-situ oceanic crust in previous study. Based on diagnosis of bioalteration textures (McLoughlin et al., 2009), granular texture and tubular textures from (1) to (3) could correspond to *Granulohyalichnus vulgaris* isp., *Tubulohyalichnus spiralis* isp., *Tubulohyalichnus annularis* isp., and undefined, respectively. Elemental mapping analysis performed by SEM-EDS on a tubular bioalteration texture showed a significant concentration of C at some parts within the tube and at the rim of the tube. The concentrated C within tube shows positive correlations with Si, Al, and K. On the other hand, the carbon concentrated part at the rim of tube do not exhibit significant concentration of Si, Al, K, Ca, Fe, and Mg. The concentration of P is also observed at the rim of tube. The elemental mapping analysis exhibited significant concentrations of biophile elements C and P within a tubular bioalteration texture. Because the observed C at the rim of tube does not show positive correlations with Ca, Fe, and Mg, it could not be originated from carbonates. This result suggests that the C could be originated from microbes at the rim of tubular texture. Also, phosphate minerals observed within the tube would be possibly originated from microbes. Based on our study, the bioalteration textures occurred in the Ibara greenrocks have disfeatured their minute textures of original morphology because of recrystallization by ocean-floor metamorphism. These facts suggest that bioalteration textures in the greenrocks experienced higher metamorphism than prehnite-pumpellyite facies could lose their original morphology. However, this study suggests that bioalteration textures within low-grade metamorphic greenrocks could be identified by occurrence, morphology, and mapping analysis of biophile elements.

Keywords: bioalteration texture, greenrock, criteria, Maizuru belt, biophile elements, elemental mapping analysis

U020-P07

Room:Convention Hall

Time:May 24 10:30-13:00

## Experimental study on hydrogen production through hydrothermal alteration of komatiite

Motoko Yoshizaki<sup>1\*</sup>, Takazo Shibuya<sup>2</sup>, Katsuhiko Suzuki<sup>3</sup>, Kenji Shimizu<sup>3</sup>, Kentaro Nakamura<sup>2</sup>, Soichi Omori<sup>1</sup>, Ken Takai<sup>4</sup>, Shigenori Maruyama<sup>1</sup>

<sup>1</sup>Department of Earth & Planetary Sciences, <sup>2</sup>JAMSTEC, Precambrian Ecosystem Lab., <sup>3</sup>JAMSTEC, IFREE, <sup>4</sup>JAMSTEC, SUGAR

Hydration of komatiite can be a source of significant amount of hydrogen in the Hadean and early Archean ocean floor. We report the direct evidence for this process based on the results of our hydrothermal alteration experiments on the synthetic komatiitic glass and spinifex komatiite at 300 degree C and 500 bars. Starting materials were synthesized by dehydration and remelting of weathered Al-depleted komatiite collected from the early Archean Komati Formation, the Barberton Greenstone Belt, South Africa. The komatiitic glass contained 10% aluminum and the spinifex komatiite contained 5% aluminum.

Since the composition of seawater in Hadean ocean have not been known, we use pure water and NaCl fluid for reaction water to examine the salt concentration dependence. In the experiment of komatiitic glass with pure water, accumulation of hydrogen (2.4 mmol/kg) over 2,600 hours is observed. This amount of hydrogen is truly significant and is comparable to those observed by hydration of peridotitic rocks. Another experiment was performed using komatiitic glass with NaCl fluid at 300 degree C and 500 bars. This experiment is conducted to compare H<sub>2</sub> generation process with alkalinity. The run is still continuing in our lab, and the concentration of H<sub>2</sub> was up to 2.8 mmol/kg after 1000 hours. The H<sub>2</sub> concentration and the trend of H<sub>2</sub> accumulation are comparable to experiment using pure water.

In contrast, 21 mmol/kg of hydrogen was produced in the experiment of spinifex texture with NaCl fluid at 300 degree C and 500 bars. The different of textures were reflected in the quantitative ratio of glass and olivine crystal in the starting materials. This result indicates that the amount of hydrogen production is not so much by controlled by the seawater composition but by the texture and the amount of aluminum.

Our results suggest that hydrothermal alteration of komatiite may have provided the H<sub>2</sub> in the vicinity of hydrothermal vents that fueled the early evolution of living ecosystems in the Hadean and early Archean.

Keywords: hydrothermal experiment, early Earth, komatiite, hydrothermal alteration, hydrogen



U020-P08

Room:Convention Hall

Time:May 24 10:30-13:00

## Solid-water distribution of molybdenum and tungsten under reducing ocean

Yoshio Takahashi<sup>1</sup>, Teruhiko Kashiwabara<sup>1</sup>, Eriko Omori<sup>1\*</sup>, Yuka Yokoyama<sup>1</sup>, Youko Miyoshi<sup>2</sup>, Shinsuke Kawagucci<sup>3</sup>, Jun-ichiro Ishibashi<sup>2</sup>

<sup>1</sup>Hiroshima University, <sup>2</sup>Kyusyu University, <sup>3</sup>JAMSTEC

The concentrations of trace elements in the ocean are controlled by their adsorption onto ferromanganese oxide. Molybdenum (Mo) and Tungsten (W) have similar chemical characteristics since they are congener of belonging to Group 6 family, so they have similar chemical feature. However, the concentration of the dissolved W in the ocean is considerably smaller lower than that of Mo, since the concentration of trace elements in the ocean is dominated by adsorption to ferromanganese oxides. Tungsten is easier adsorbed significantly onto the ferromanganese oxides and is removed from seawater, while Mo is difficult to be adsorbed on the ferromanganese oxides and is readily dissolved in seawater. On the other hand, under the reductive ocean like early earth, the concentration of these trace elements in the ocean might be dominated by adsorption on sulfides. In other words, by changes in redox status condition due to the Earth's evolution, the water solubility of Mo and W are expected to be reverse to the present ocean. However, the solubility of Mo and W under reductive ocean is largely unknown. Therefore, in this study, adsorption experiments were conducted under various systems conditions to simulate reductive ocean in order to investigate the solid phase-liquid phase distribution behaviors of Mo and W under these systems. Adsorption structure and distribution coefficients of Mo and W were determined by using X-ray adsorption fine structure (XAFS) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. The measurement results showed that adsorption distribution coefficient of Mo is about 8 times larger than that of W, and the two elements can be readily adsorbed onto pyrite under low-pH condition. Although their adsorbed chemical species are also sulfide, while the formation of Mo sulfide is did not affected by the pH, while formation of W sulfide did not proceed under high pH condition, where W sulfide was not generated. Thus, the water solubility of W is more likely greater than that of Mo under reductive condition where the solubility is dominated sulfide.



# Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

©2011. Japan Geoscience Union. All Rights Reserved.



U020-P09

Room:Convention Hall

Time:May 24 10:30-13:00

## Mineralogy of natural and synthesized Bacteriogenic Iron Oxides (BIOS)

Sakiko kikuchi<sup>1\*</sup>, Makita Hiroko<sup>2</sup>, Mitsunobu Satoshi<sup>3</sup>, Takai Ken<sup>2</sup>, Takahashi Yoshio<sup>1</sup>

<sup>1</sup>Hiroshima University, <sup>2</sup>JAMSTEC, <sup>3</sup>University of Shizuoka

Mineralogy of natural and synthesized bacteriogenic iron oxides (BIOS) was studied using XAFS, micro-XAFS, SEM and EPMA. Natural BIOS were collected at 2 sampling sites: seafloor at Mariana trough and at stream from groundwater discharge at Sambe hot spring in Shimane prefecture. BIOS synthesis was carried out using diffusion cell which can simulate BIOS precipitation in natural condition. Chemoautotrophic bacteria (*M. ferrooxydans*) or heterotrophic bacteria (*L. discophora*) were cultured in one side of the diffusion cell. SEM and EPMA analysis showed similar precipitation morphology to all samples where iron oxides precipitate around bacterial-induced organic materials. Although each natural BIOS were precipitated at different environments, XAFS showed similar spectrum. Synthesized BIOS also show similar spectrum to natural samples regardless of the species of iron oxidizing bacteria and the medium employed in the culture. XANES fitting suggested that BIOS consist of ferrihydrite and iron-organic complex. This mineralogy will affect adsorption behavior of trace minerals onto BIOS.

U020-P10

Room:Convention Hall

Time:May 24 10:30-13:00

## Abundance, diversity, function and composition of microbial community on oceanic Mn crusts from Takuyo-Daigo Seamount

Shouta Nitahara<sup>1\*</sup>, Shingo Kato<sup>1</sup>, Akihiko Yamagishi<sup>1</sup>

<sup>1</sup>Department of Molecular Biology, Tokyo U

### Background and Purpose

Ferro-manganese oxide deposits are often observed on the seafloor. Rocks covered with these ferro-manganese oxide deposits are called Mn crust or Mn nodule. Oceanic Mn crusts grow slowly (1-10 mm/ Myr), and are observed mainly on old seamounts. These Mn crusts are expected to cover 70 % of seafloor at water depth of 5 km to 6km (Rona, 2003).

Microbes on Mn crusts may play a role in geochemical cycling between hydrosphere and lithosphere, and in accumulation of ferro-manganese oxides. However, little is known about microbes on oceanic Mn crust. In this study, our purpose is to clarify composition, diversity, abundance and function of microbes and spatial distribution in each depth on Mn crust in Takuyo-Daigo seamount by 16S rRNA gene and *amoA* gene analyses.

### Method

We collected Mn crusts and nodules, sediments and ambient seawater from Takuyo-Daigo Seamount on NT09-02 cruise in Feb 2009. The water depth of each sampling point was 1200 m, 1419 m, 2209 m and 2991 m, respectively. DNA was extracted from each sample. We amplified 16S rRNA gene and *amoA* gene by PCR with prokaryote-universal and archaea-specific primer sets and archaeal and bacterial *amoA* specific primer sets. We constructed the clone libraries and determined the nucleotide sequences of clones in the libraries. The microbial community compositions were determined by phylogenetic analyses. And diversities of microbial community were determined by statistical analysis. We also estimated the copy number of 16S rRNA genes and *amoA* genes of bacteria and archaea by quantitative PCR.

### Result and Discussion

Bacterial and archaeal cell numbers were estimated to be  $10^7$  to  $10^8$  cells/g in the ferro-manganese samples, respectively. Archaea dominated in three of four Mn crust samples (50~83 % of total cell numbers). The copy numbers of bacterial and archaeal *amoA* gene were  $10^6$  copy/g in both samples. In contrast, the copy numbers of bacterial and archaeal *amoA* genes were  $10^7$  copy/g and  $10^6$  copy/g, respectively.

Phylotypes closely related to *Nitrosospira* and Marine crenarchaeota Group I (MGI) were detected from four Mn crust samples. These groups include ammonia-oxidizing chemoautotrophs. Furthermore, *amoA* genes, encoding an ammonia-oxidizing enzyme, were also detected from Mn crust samples. These results suggest that these putative ammonia-oxidizing microbes play a role as primary producers in the microbial ecosystem of the Mn crust.

Few phylotypes (1-8 species) were shared between the solid samples (Mn crust and sediment) and seawater sample of the same depth, as shown by comparative analysis. Phylotypes of MGI detected from the solid samples and seawater sample were separated into distinct clusters in the phylogenetic tree. Furthermore, Phylotypes of MGI in the solid samples formed several distinct clusters. The detected *amoA* genes in the solid samples and seawater samples were also separated into distinct clusters in the phylogenetic tree. These results suggest that several subgroups of phylotypes of MGI, which distinguished from those in seawater sample, exist on Mn crusts.

The detected archaeal *amoA* genes were related to *amoA* genes of uncultured crenarchaeota (95 -98 %) and to that of cultivated *Nitrosopumilus maritimus* (79-83 %). The detected bacterial *amoA* genes were most closely related to *amoA* gene from cultivated species of *Nitrosolobus multiformis* and *Nitrosospira* sp. (78 % respectively). These results suggest that uncultivated and novel ammonia oxidizing bacteria and archaea exist on the Mn crusts.

Keywords: Ferro-manganese crust, 16S rRNA gene, *amoA* gene, ammonia oxidizing bacteria

U020-P11

Room:Convention Hall

Time:May 24 10:30-13:00

## Snow algae and mineral particles on the snow surface in the Tateyama Mountains in Toyama Prefecture, Japan

Tomoko Umino<sup>1\*</sup>, Nozomu Takeuchi<sup>1</sup>

<sup>1</sup>Chiba University Graduate School

Snow algae are photosynthetic microorganisms living on snow and ice and are specialized to harsh cold environment. Red snow is a well-known phenomenon due to bloom of red colored snow algae on the thawing snow surface. Since snow surface is usually extremely nutrient-poor condition, it is question how algae acquire nutrients on the snow. Wind-blown mineral particles such as clay particles, which are relatively abundant on snow surface, may play a role in acquirement of nutrients for algae. The purpose of this study is to describe how snow algae are associated with mineral particles on the surface in the Tateyama Mountains in Toyama Prefecture, Japan. In September, 2010, snow samples were collected in Kuranosuke and Hamaguri snow valleys in the Tateyama Mountains. The snow algae in the snow samples were examined with an optical microscope, and the mineral particles were analyzed by X-ray diffraction.

X-ray diffraction analysis showed that the snow samples contained quartz, plagioclase and clay minerals including chlorite and illite. These mineral particles are assumed to be derived from Kosa, which is a dust event from distant continental desert. Hornblende was also contained in the samples of Hamaguri snow valley. It is probably derived from debris derived from rock cliffs around the snow surface.

Microscopic observation revealed the abundant snow algal cells in the samples. Four types of algal cells were observed (1) a round cell with 15 micro-m diameter, (2) a small round cell with <10 micro-m diameter, (3) a spindle shape cell 20 micro-m long, (4) a round cell with red pigments (hypnozygote of *Clamdomonas* sp.). In Kuranosuke snow valley, type (1) accounted for 70% and type (4) for about 5%. In Hamaguri snow valley, type (2) accounted for 90% and types (1) and (3) for the rest. A part of algal cells formed aggregations of algal cells and mineral particles. Size of the aggregations were approximately 50 micro-m x 50 micro-m. The aggregations were more abundant in the surface samples compared to the samples collected about 10 cm below the surface. Mineral particles in the aggregations may support the algae to acquire nutrients on the snow surface.

Keywords: mineral particles, snow algae, nutrient, clay minerals

U020-P12

Room:Convention Hall

Time:May 24 10:30-13:00

## Effects of calcium chloride on the dimerization rate of glycine in aqueous solution

Kasumi Sakata<sup>1\*</sup>, Hikaru Yabuta<sup>1</sup>

<sup>1</sup>Earth and Space, Osaka Univ.

### Introduction:

The Lost City hydrothermal field has been recently discovered in 2000 and known for its characteristic conditions that differs from the typical hydrothermal vents, such as basic pH, low temperature ( $> \sim 90^{\circ}\text{C}$ ), metal ion compositions (Kelley et al. 2001; 2005). The hydrothermal system is suggested as a plausible environment for the origin and evolution of life in the early Earth (Russell, 2003). In our previous study, it was revealed that the dimerization of glycine (Gly) in aqueous solution reached the maximum rate in basic solution at pH 9.8 (Sakata et al., 2010), supporting the above hypothesis. In this study, the heating experiments of Gly solution containing calcium chloride were conducted under various pH conditions, in order to evaluate the effects of calcium chloride on the kinetics of the formation of glycyglycine (GlyGly) and diketopiperazine (DKP).

### Experimental:

Half milliliter of 100 mM aqueous solutions of Gly at pH 2.3, 6.0 and 9.8 with 200 and 400 mM  $\text{CaCl}_2$  and without  $\text{CaCl}_2$  were put into pyrex glass tubes, vacuumed and replaced with Ar gas. Each solution was heated at  $140^{\circ}\text{C}$  for 1 to 14 days. Each sample was 10 times diluted and analyzed by High Performance Liquid Chromatography (HPLC). In this experiment, the four reaction pathways were considered: 2 Gly to GlyGly (the second order), GlyGly to DKP (the first order), DKP to GlyGly (the first order), GlyGly to 2 Gly (the first order). The rate constants were determined by fitting the changes of the concentrations of Gly, GlyGly, and DKP with increasing heating time.

### Results and discussion:

Equilibrium concentration of GlyGly decreased with increasing concentration of calcium ion at acidic and basic pH. At neutral condition, concentration of GlyGly was almost constant. Dimerization rates of Gly ( $k_1$ ) were decreased by  $\text{CaCl}_2$  at pH 2.3, 6.0, while at pH 9.8, that slightly increased with increasing concentration of calcium ion. The same way as Gly solution without  $\text{CaCl}_2$ ,  $k_1$  was fastest at pH 9.8 in Gly solution with  $\text{CaCl}_2$ .

However, at pH 9.8, hydrolysis rate of GlyGly ( $k_{-1}$ ) was much larger than that of  $k_1$ , which likely caused the lower concentration of GlyGly. Thus, in particular at basic pH,  $\text{CaCl}_2$  drives hydrolysis of GlyGly. This is probably due to the complex formation of GlyGly with calcium ion where hydroxyl ion easily hydrolyzes the peptide link.

### References:

- Kelley et al. (2001) Nature 412:145-149
- Kelley et al. (2005) Science 307:1428-1434
- Russell (2003) Science 302:580-581
- Sakata et al. (2010) Geochim Cosmochim. Acta 74, 6841-6851.

Keywords: glycine, reaction rate, metal salt, hydrothermal vent, alkaline