

## Hydration and hardening process of iron and steel slags used for roadbed material

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Steel slag is a by-product of the steel manufacturing process and produced in large quantities every year. Steel slag is expected to reuse in Japan. However, it was observed that the uniaxial compressive strength (UCS) differs among mixed slag for roadbed materials produced from different factories including even with the same mixing ratio of DCS and GBFS. In particular, the difference between the UCS of slag produced from K ironworks and N ironworks was remarkable. The reason for these differences has not yet been clarified. To extend the market of steel slag, it is essential to clarify the relationship between secondary minerals formed after hydration and the UCS of the slag.

This study firstly investigated the UCS of the MIX slag ( DCS / GBFS = 4 ) from K ironworks and N ironworks. Based on the UCS tests, the slag from N ironworks is stronger than the slag from K ironworks.

Batch experiments were then conducted for samples from K ironworks and N ironworks to investigate and compare the evolution of solution chemistry and precipitation of secondary minerals during slag hydration. Based on the XRD analysis for the samples after the batch experiments, the main product of the MIX sample from K ironworks is  $\alpha$ -C<sub>2</sub>SH while the MIX sample from N ironworks produced mainly CSH. The difference in mineralogy could be related to the UCS of the slag because of the difference in volume of secondary minerals. Based on the solution analysis of the samples, it is observed that the main source of Ca ion is DCS, while the main source of Si ion is GBFS. In addition, it is possible that the concentration of H<sub>4</sub>SiO<sub>4</sub> in the solution, which is present in the form of calcium silicate hydrates, is determined by GBFS. Kinetic model was constructed. The model represent the mineral evolution during slag hydration in the both MIX slags.

Keywords: Slag, Hydration

## Shock-induced Strecker Reactions for prebiotic amino acid formation: Experimental simulations

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Amino acid is thought to be one of the most primary biomolecules related to the origin of life. The prebiotic syntheses of amino acids under early Earth condition were simulated in experiments using by several energies such as electric discharge, light, heat and shock wave. According to a previous study by Aubrey et al., 2009, it is considered that amino acid formation from ammonium formate ( $\text{NH}_4\text{HCO}_2$ ) depends mainly on concentration of starting materials. It has been known that ammonium formate can produce HCN above 180 °C, and that HCN is a necessary material in order to synthesize amino acid via strecker reaction. Strecker reaction is used for syntheses of amino acids in the presence of  $\text{NH}_3$  and HCN. These molecules can be easily formed from ammonium formate at high temperature. They performed hydrothermal experiments at concentrations of 0.1 M and 0.001 M. Then, amino acids such as glycine and alanine were formed from only a high concentration sample (0.1 M). However, this concentration is unrealistically too high for natural marine conditions. We need to know the effect of shock energy on the formation.

In this study, we carried out shock recovery experiments using a propellant gun for aqueous solutions of ammonium formate and formamide. Starting material, encapsulated in steel container as a target, was ammonium formate or formamide aqueous solution immersed in the pressed olivine powder. We used two concentrations (5 mM and 100 mM) to compare with the results of hydrothermal experiments. Olivine was simulated as ordinary chondrite. The peak pressure in this study was about 5 GPa. Recovered solutions were analyzed by using hybrid/MS for biomolecules of the m/z values between 50 and 500 with analytical errors within 3 mmu (0.003). The results indicated that glycine and glycyglycine were detected in all samples and that benzoic acid as carboxylic acid was detected in only formamide samples. Present results suggest that glycine formation by shock reaction might be more effective than that of hydrothermal reaction because glycine was formed from low concentration samples. Detailed discussions will be given as poster.

Keywords: Marine meteorite impact, Amino acids, Strecker reactions

## The Study on Removal Efficiency of Ammonium Nitrogen by Four Herbaceous Plants in Artificial Rainwater

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The Study on Removal Efficiency of Ammonium Nitrogen by Four Herbaceous Plants in Artificial Rainwater

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**Abstract:** To select the best herbaceous plant for ammonium nitrogen removal in a bioretention, the ammonium nitrogen removal efficiency by four herbaceous in bioretention were explicated through a pot experiment. This experiment simultaneously set two scenarios, namely analyzing and measuring the removal efficiency of plants on ammonium nitrogen under the circumstance of different inflow concentration and different soil mediums. The results show that the four herbaceous plants have good removal effects on ammonium nitrogen in the artificial rainwater, and the average removal efficiency of ammonium nitrogen is between 93.90%~99.90%. The ranks of capabilities of different herbaceous plants removing ammonium nitrogen in artificial rainwater from high to low are: *lolium perenne* > *axonopus compressus* > *poa annua* > *festuca elat*. Four herbaceous plants have different removal efficiency on the ammonium nitrogen in the artificial rainwater with different concentrations. In the artificial rainwater, with the increase of inflow concentration of ammonium nitrogen, the removal efficiency of four herbaceous plants on ammonium nitrogen have also enhanced. For the same herbaceous plants with same inflow concentration, soil II is the optimum soil medium, possessing relatively good capacity of removing ammonium nitrogen.

**Key words:** Bioretention; Herbaceous Plants; Ammonium Nitrogen; Removal Efficiency

## Immobilization of hazardous anions in andosol and alluvial soil using magnesium oxide

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Soil contamination by hazardous anions is a significant problem in Japan. Magnesium oxide (MgO) has been used as an immobilization agent for hazardous anions such as fluoride and boron. However, it is difficult to optimize the immobilization process because the immobilization depends on the type of soil and the long-term elution behavior of hazardous substances is uncertain.

In this study, to investigate whether MgO can be applied to immobilize fluoride and boron in andosol and alluvial soil and to clarify the immobilization mechanism, the following experiments were conducted; 1) characterization of different types of soil (andosol, alluvial soil), 2) MgO hydration rate determination, 3) interactions between soils and MgO, 4) fluoride and boron sorption behavior onto MgO, 5) immobilization experiments using the soils under several pH and anion loading.

The possible mechanisms of immobilization of fluoride and boron in andosol and alluvial soil using MgO are as follows. Fluoride is immobilized via incorporation into the magnesium hydroxide (Mg(OH)<sub>2</sub>) structure during the MgO hydration reaction. On the other hand, boron is immobilized by coprecipitation with magnesium following the formation of a magnesium borate complex. To summarize, proposals for carrying out immobilization were made. To immobilize the anions, MgO should be added into the soils to establish the above mechanisms. One significant point is that MgO addition should take the pH buffering capacity of soils into account.

Keywords: Fluorine, Boron, Soil, Magnesium oxide, Immobilization

## TEM observations of clay minerals in Lake Tega sediment

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### **1. Introduction**

Like minerals and rocks, microbes are ubiquitous in soils and aquatic sediments. It is well known that the interaction between minerals and microbes contribute to mineral dissolution and precipitation (Dong and Lu, 2012). For example, dissimilatory iron reducing bacteria (DIRB), which are widely distributed in natural environment, transform  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  at the surface of an iron oxide particle (Lovley et al., 2004). Thus, the minerals-microbes interaction plays an important role in biogeochemistry on the earth's surface. Transmission electron microscopy (TEM) is commonly used as an experimental technique to analyze the interplay between minerals and microbes (Kawano and Tomita, 2001; Tazaki, 2005). Although, detailed mineralogical researches are highly important to elucidate the minerals-microbes interaction, there is little studies of TEM observation on aquatic sediments. This study is focused to describe compositional and crystal chemical features of minerals in lake sediments by using HRTEM observation.

### **2. Materials and Methods**

Sediment samples were collected from a ca. 20 cm core drilled at Lake Tega in Abiko city, Chiba in Japan. The sample core was divided into two types, upper and lower sediments. The samples were examined for mineralogical details with scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and fourier transform infrared spectroscopy (FT-IR).

### **3. Results and Discussion**

The powder XRD patterns of upper and lower layer sediments showed that quartz, orthoclase, plagioclase, and kaolin (kaolinite and halloysite) were included, but clay minerals were mainly composed of the lower layer sediment. The SEM images revealed that organism fragments ranging from 10 to 30  $\mu\text{m}$  in size were widely observable in both upper and lower layer sediments. FT-IR spectroscopy showed that the weak bands derived from organics were observed from the both sediments, indicating that the deposits included the minerals and organic compounds which probably originates from organisms.

The TEM analysis showed that kaolinites in the sediments had plate shape with 1-4  $\mu\text{m}$  in width, which is compatible with previous studies (Sudo et al., 1980; Bergaya et al., 1996). The forms of halloysites with 50-100 nm in length lath-like shape and with ca. 100 nm in width spherical shape are also consistent with those of previous studies (Sudo et al., 1980; Singh and Gilkes, 1992). The EDS analysis of individual particles revealed that kaolinites and halloysites contained not only Si, Al, O but also K, Na, Fe, although the electron diffractions showed clear diffraction spots with their symmetries.

In kaolin minerals, very small amount of  $\text{Fe}^{2+}$  can be substituted for  $\text{Al}^{3+}$ , which results in slightly negative charge (Detellier and Schoonheydt, 2014). Therefore, it is likely that substitution of  $\text{Fe}^{2+}$  for  $\text{Al}^{3+}$  in the kaolin minerals gives rise to absorption of  $\text{K}^+$  and  $\text{Na}^+$  to stabilize the charge balance.

Keywords: lake sediment, TEM, clay mineral, kaolinite, halloysite

## Study on molecular structure of diatoms frustule by synchrotron X-ray Diffraction and Infrared spectroscopy

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### 1. INTRODUCTION

The diatoms in ocean, a lake, and a river are responsible for almost a quarter of the photosynthesis of the whole earth (Nelson, et al. 1995). They have a great influence on the element movement of the Earth's surface by absorbing different metal ions selectively (Morel and Price 2003). The diatoms with complicated surface structure have a property to adsorb various substances to their frustules, but the adsorption characteristic depends on the structures of the frustule surface. Furthermore, whether perished diatoms' frustules are stored or not is determined by the structures of the frustules. However, the surface structures of the diatoms' frustules are still unknown very well. Kamatani (1974) researched on the structure of the diatom's frustules by Infrared spectroscopic analysis, but the author didn't separately analyze the collected samples. Recently, Gelibert et al. (2004) classified every species of diatom and studied the structure of the frustules by using the small angle scattering method and Infrared spectroscopic analysis. Because the frustules would be heavily damaged by their samples treatment process, the results of the study have little credibility. This study is aimed to elucidate the molecular structures using Infrared spectroscopic analyses and X-ray diffraction analysis for the diatom's frustules which were collected and cultivated separately in the laboratory.

### 2. MATERIALS AND METHODS

#### 1) Collection and cultivation processes of diatoms

Diatoms were collected from three sites in Lake Yogo, Siga prefecture, Japan, and in Obitsu River tideland, Chiba prefecture, Japan, and at the northern part of Thailand. They were cultured in nutrient medium f/2 and harvested under red and green LED light at 25 degree C. After multiplying moderately, each species of diatom was carefully transferred into separate Petri dishes and multiplied under a same condition. As a result, 19 species of diatom were isolated and finally three species were successfully obtained in enough quantity for the following experiments.

#### 2) Sample treatments

The each diatom multiplied was filtered through a membrane filter and removed from salts and organic matters by centrifugal separation. After rinsed with acetone, the diatom's frustules were dried at 50 degree C in an oven for three days.

#### 3) The measurement

The synchrotron radiation X-ray diffraction analysis was performed at High Energy Accelerator Research Organization(KEK), Photon Factory(PF), beam line BL8B.

### 3. RESULT AND DISCUSSION

Gomphonema sp. in the northern part of Thailand, and Nitzschia cf. Frustrum in the Lake Yogo, Siga prefecture form a wedge shape and a spindle shape, respectively. Cyllindrotheca sp. in Obitsu River tideland has a long extended needle shape. The form is characterized by the twisted spindle shape composed of thinly frustules. The SEM observation showed that the Gomphonema sp. and Nitzschia cf. Frustrum maintained their forms during the sample treatment. With centrifugal separation, on the other hand, most of the forms of Cyllindrotheca sp. were destroyed except the spiculums at the both ends, maintained. Synchrotron radiation X-ray diffraction analysis showed that Gomphonema sp. and Nitzschia cf. Frustrum gave basically similar broad diffraction pattern to that of amorphous silica. However, Cyllindrotheca sp. , unlike other two species, showed sharp peaks at the position of  $d = 3.920, 2.603, 1.545\text{\AA}$  and a few weak peaks. The results of the Infrared spectroscopic analysis on Gomphonema sp. and Nitzschia cf. Frustrum showed that the absorption spectra were similar to those of amorphous silica, which is consistent with the result of the X-ray diffraction patterns. On the other hand, Cyllindrotheca sp. showed a spectrum similar to that of opal-CT.

Keywords: diatoms, molecular structure, X-ray diffraction, IR spectroscopy

## Microbial zonation observed on travertines: a case in northern Sumatra

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Travertines, carbonate developed in calcareous hot springs, often exhibit laminated structures of the ancient stromatolites. Cyanobacteria play a central role to form laminated structures (e.g., Okumura et al. 2013), other microbial groups can be associated with the travertines. An example is the case in Dolok Tinggi Raja in northern Sumatra. Distinct microbial zonation was observed along the flow passage of the two major spring sites. At proximal locations besides the hot spring at 60 degrees, sulfur turf inhabited a high concentration of hydrogen sulfide. Purple sulfur bacteria become dominant from several meters below the spring. The sulfur bacteria that form a biofilm of 1 mm thick have potential to develop laminated structure. Water chemistry indicates that aragonite precipitation was activated from this location. In the lower portion of the flow passage where the temperature is declined below 50 degree, microbial community was replaced by cyanobacteria that formed a biofilm of similar thickness. Decreases in hydrogen sulfide and temperature are responsible factors for this microbial zonation.



## Mobilization of manganese and iron in marine sediments and tuffs by dolerite in Hokuroku District.

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Mn rich sediments are often used to evaluate the presence of submarine hydrothermal activities and the redox state of paleoenvironment in the sea. The oldest Mn ore deposit occurs 2.4 billion years ago as the banded manganese formation, corresponded to oxidation of Precambrian ocean water. Those studies suggest that Mn geochemistry is important to consider not only the Earth history but also paleoenvironment evaluation.

Hokuroku district is famous for Kuroko deposits which is rich in metals such as Zn, Cu, and Pb. During the hydrothermal activities, metals of forming Kuroko precipitated in closed area around ores, on the other hand Mn and Fe can be transported in distal by hydrothermal plume, as a result of formation of Mn and Fe rich sediments on the Kuroko horizon without heavy metal deposition. Therefore, the first purpose of this research is to evaluate the exploration potential of Kuroko deposits using Mn, thus the examination of spatial relationship between Mn and Kuroko ores. Presence of Mn rich layers is also known in the Hokuroku district. Their origin was completely unknown. Mn rich layers were potentially formed submarine hydrothermal activities related post Kuroko ore forming activities. Therefore, the second purpose of this research is to discuss whether the submarine hydrothermal activity was present even after Kuroko ore formation and if they are responsible for Mn enrichment in post Kuroko mudstone.

I have investigated the "M2" mudstone which is often overlaid with Kuroko deposits. For the first purposes, 6 Samples of "M2" mudstones were collected from 3 areas. Moreover, I have investigated the Mn rich layer to discuss the second purpose. 31 Samples of "R2", "T2", dolerite, and mudstone were collected from Koyukizawa areas. The mineral and chemical compositions of the samples were examined by standard petrographic microscopy, SEM, and EPMA. Chemical composition of samples were determined by energy dispersive X-ray spectrometry, and EDXRF. Mineral assemblage is determined by X-ray diffraction (XRD).

For the first purpose, Mn concentrations in "M2" mudstones are found to be about 0.04 wt%, which is low concentrations. I can't find the change of Mn concentrations according to the distance from ores. Therefore, it suggested that Mn is not the exploration index of Kuroko deposits at this stage. For the second purpose, the geological survey was performed in the area of Koyukizawa (route A and route B). Tuff breccia and pumice tuff are abundant in this area associated with mudstones. Those were intruded by dolerite. Red to brown alteration are common even in dolerite representing hydrothermal alterations in route A. I could find the Mn rich layers (3.7 wt%, 1.8 wt%) by chemical analyses. Partial Mn enrichments were also found in rocks on the boundary between "T2" and dolerite. On the other hand, I can't find the red alteration in dolerite route B. From those findings, Mn rich layer was formed by the recycle of Mn by heat generated from the intruding dolerite. Mn was enriched in rocks when circulated hydrothermal water was oxidic enough. Moreover, by EDXRF, Mn and Fe have similar behavior, and Mn was oxidized prior to Fe on the oxidative environment.

Keywords: banded manganese deposit, Hokuroku district, Kuroko, hydrothermal activity, redox state



## Role(s) of microorganisms on the formation of manganese deposits in hot springs

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The natural manganese distributed widely during environment. The +II, +III, and +IV are the most prevalent oxidation states of Mn in nature, in particular, +III and +IV manganese exist as oxides mainly. It is considered that the manganese oxide (MnO<sub>2</sub>) formation is attained by 1) inorganic process including autocatalysis and 2) organic process by microbial oxidation. The latter is further classified into two groups, the direct process and indirect process. In general, it seems the organic process is more important than the inorganic process. The organic direct process with the Mn-oxidizing bacteria attracts attention particularly recently. On the other hand, it has been published the experiment with isolated and cultured photosynthesis microorganisms indicates the Mn-oxidation reaction promoted by photosynthesis. However, those most were speculated by culture experiments and simulations, therefore, the relative importance of above these processes and mechanisms in the natural Mn-oxidation reaction does not yet become clear. In this study, it is intended to clarify an elementary process of the Mn oxides formation based on an in situ evaluation in the environment. The subject of this study is Sanbe hot spring (in Shimane, Japan) and Onneto yuno-taki (in Hokkaido, Japan), the representative example of the terrestrial large-scale Mn oxides deposit.

At the Sanbe hot spring, Mn oxides layer form at thickness up to approximately 1 cm in the lower area by 150 m from the spring site. According to thin section observation, many photosynthetic organisms inhabit in the surface, and it is confirmed most of them are buried in the oxides. In addition, *Hyphomicrobium* sp. was detected by 16S rDNA Analysis. In this study, through four kinds in total of microelectrode-measurement (pH, Eh, dissolved oxygen DO, Mn<sup>2+</sup>), the chemical profiles in the vicinity of the oxide surface were evaluated. Under the light condition, DO, Eh, pH rose in the oxides surface, and Mn<sup>2+</sup> showed decrease. Under the dark condition, DO decreased, and the tendency to increase or decrease of Eh, pH, Mn<sup>2+</sup> profiles were remain unchanged in comparison with them under the light condition, but each flux was all smaller than it under the light condition. From the result, it was found the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, and MnO<sub>2</sub> change into the dissolved chemical species (Mn<sup>3+</sup>), by the oxidation-reduction reaction in Mn<sup>2+</sup> and MnO<sub>2</sub> under the dark condition. This is supported by the observation with the Mn oxides layer being thin for the decrement amount of Mn<sup>2+</sup> in the surface. Furthermore, regardless of difference of light or dark condition, the contribution to manganese oxidation by Mn-oxidizing bacteria was likely small so that cannot be detected by microelectrode-measurement.

At the Onneto yuno-taki, the manganese deposit layer distribute respectively about 100 m from two spring site and is thick relatively (about 10 cm). Onneto yuno-taki has also many photosynthetic organisms inhabiting in the surface, and it is confirmed by thin section, most of them are buried in the oxides by thin section observation. According to the result of microelectrode-measurement, DO, Eh, pH rose in the oxides surface, and Mn<sup>2+</sup> showed decrease under the light condition. Under the dark condition, all profile has tendency to decrease. Mn<sup>2+</sup> flux was especially smaller than its under the light condition. Therefore, it was suggested that the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, on the other hand, it may occur the Mn-oxidation reaction by Mn-oxidizing bacteria (organic direct process) It was also thought that the effect of dissolution of MnO<sub>2</sub> was respectively small. In fact, the manganese deposit of Onneto yuno-taki is very thick.

## Establishment of iron microelectrode measurement and its application to iron deposit re-sembling BIF

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Precambrian banded iron formation (BIF) is important for estimating the redox state of the global environment during that period, and many studies have been conducted until now. In the traditional model, BIF had been considered to be formed by oxidation of Fe(II) by cyanobacteria-released oxygen. However, it has been recently suggested that other microbial metabolisms, such as direct iron oxidation associated with carbon fixation of non-oxygenic Fe(II)-oxidizing phototrophic bacteria, were also involved in the formation. Therefore, its formation process is considered to be complicated much more than previously thought, and detailed investigation about the microbial processes that can potentially form BIF is required. This study aimed to reveal the formation processes of iron deposits found in Sambe hot spring in Shimane Prefecture, and applied both geochemical and geomicrobiological techniques. In previous study, it have been described that this deposit is mainly composed of iron hydroxide (ferrihydrite), and microbial composition at the deposit surface is dominated by iron-oxidizing bacteria (*Gallionella* sp.) with minor cyanobacteria. In this study, we applied the Fe(II) microelectrode in addition to the pH, redox, O<sub>2</sub> microelectrodes in order to accurately evaluate the microbial and inorganic precipitation occurring in the surface. By these microelectrodes, we measured the chemical profiles at the vicinity of deposit surface (about 1 mm from the surface) and found that all chemical profiles were almost the same both in light and dark conditions, indicating that contribution of photosynthesis was negligible. Fe(II) and O<sub>2</sub> consumption at the deposit surface implied that iron-oxidizing bacteria (*Gallionella* sp.) oxidized Fe(II) by using oxygen. This kind of iron precipitation process would provide an important knowledge about the formation process of BIF deposited when the ocean gradually became oxidative by cyanobacteria released oxygen. In addition, measurement method of Fe(II) microelectrode established in this study will be applicative to other types of BIF modern analogs, and it is expected that further details of BIF formation processes will be revealed.

## Nitrogen and noble gas isotopes of Eoarchean Nuvvuagittuq rocks

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The Nuvvuagittuq greenstone belt is an Eoarchean volcano-sedimentary sequence located in northern Quebec. Rocks are gabbroic intrusions, volcano-sedimentary silicic rocks and banded iron formation (BIFs), enclosed by 3.66 Ga tonalitic gneiss. Rocks are metamorphosed to amphibolite facies and zircon U-Pb ages give a minimum age of 3.75-3.82 Ga to the belt. A deficit in <sup>142</sup>Nd compared to the terrestrial Nd standard found in some igneous rock which were dated possibly at 4.28 billion years ago, making this rock suite one of the oldest on Earth. Characterization of the fluids in silicic rocks and BIFs, identified by previous works as chemical precipitates in seawater, might give precious constraints on the Earth superficial conditions in Late Hadean, following the Late Heavy Bombardment.

A preliminary survey intended to analyze the fluids trapped into several lithologies of the belt on the noble gas and nitrogen isotopic compositions. Selected samples are an ultramafic intrusion (POR21), a tonalitic gneiss (POR23), three felsic to intermediate silicic volcanoclastic rocks (POR27b, 28c, 28h), a meta-conglomerate (POR29) and a plagioclase-rich amphibolite (POR30). Preliminary noble gas isotopes were carried out at GEOTOP by using a quadrupole mass spectrometer. <sup>4</sup>He, <sup>22</sup>Ne, <sup>36-40</sup>Ar, <sup>84</sup>Kr and <sup>129,132,136</sup>Xe were analyzed after crushing bulk rock and recovering gases in a purification line. All samples contain radiogenic <sup>4</sup>He, from  $3.7 \times 10^{-8}$  to  $2.5 \times 10^{-7}$  cm<sup>3</sup>STP/g<sub>rock</sub>, although the calculated radiogenic <sup>4</sup>He/<sup>40</sup>Ar\* ratio is only 0.01 to 0.03 against the expected crustal ratio of 4.2. This could indicate large loss of helium during time (which is often observed in Archean rocks) or poor potassium content, the parent element of radiogenic <sup>40</sup>Ar\*. The measured <sup>40</sup>Ar/<sup>36</sup>Ar ratios range from 403 to 9635, higher than the atmospheric value of 295.5. The sample that contains most radiogenic noble gas <sup>4</sup>He and <sup>136</sup>Xe (from U fission and alpha decay) and <sup>40</sup>Ar\* is the tonalitic gneiss (POR23). All other samples show atmospheric composition of noble gases (except <sup>4</sup>He and <sup>40</sup>Ar\*) or slight <sup>136</sup>Xe anomalies.

A new series of noble gas and nitrogen isotopic measurements are under way at Osaka University to determine the origin of gases into the Nuvvuagittuq fluids and try to constrain crustal and igneous sources possibly feeding them.

Keywords: Eoarchean, Atmosphere, Nitrogen, Noble gas

## Geological and geochemical studies of sedimentary rocks at the Wagon Road gold mine, Barberton Greenstone Belt.

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Banded iron formations (BIFs) are common in Archean to early Proterozoic cratons. The formation processes of BIF are controversy as to if a variety of microbes (e.g., cyanobacteria and Fe-oxidizing bacteria) were involved or inorganic oxidation was responsible. Detailed studies on BIF and the surrounding sedimentary rocks may constrain factors to oxidize Fe and the role of microbial activities. Therefore, the BIF and the surrounding sedimentary rocks in the Fig Tree Group (~3.2 Ga in age) in the Barberton Greenstone Belt, South Africa, are investigated in the present study. The studied area is called Euryca syncline area, and abandon Au mine (Waggon Road mine) is located. Sandstone, shale, black chert, and BIF are found in the studied area. Besides petrographic characterization, SEM-EDS analyses were performed on the representative rocks. Concentrations of organic carbon and their  $\delta^{13}\text{C}$  values were determined by EA and IR-MS. Siderite and hematite were found as ferruginous minerals in BIF and black chert samples. The grain size of siderite was larger (30-200  $\mu\text{m}$ ) than the surrounding quartz (<10  $\mu\text{m}$ ). Siderite is interpreted as a secondary mineral formed during early diagenesis. Euhedral hematite crystals (<5  $\mu\text{m}$ ) were found. Hematite is interpreted as a primary mineral, although some hematite, normally larger and more red color, are supergene origin. Black chert samples show separated features of organic-rich layers and Fe-rich layers. Therefore, it is considered that the source of organic carbon is not related to Fe-oxidizing bacteria. The  $\delta^{13}\text{C}$  values of all analyzed samples were range from -27.7 to -23.5 ‰. These values are made by metabolisms by Calvin cycle using atmospheric  $\text{CO}_2$ . Overall results of this study indicated that presence of 3.2 Ga oxygenic shallow oceans in where cyanobacteria were active.

## Geological and geochemical study of lower-Fig Tree Group in Josefsdal, South Africa

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Understanding extent of Archean biosphere and conditions of surface environments is important subject to understand evolution of the Earth. Accumulating more geological and geochemical data on Archean sedimentary rocks is necessary to approach the above problem. Therefore, geological and geochemical studies are performed on Fig Tree Group (~3.2 Ga) and Onverwacht Group (~3.4 Ga) in the Barberton Greenstone Belt, South Africa in the present study. The objectives of this study were (1) to survey lower-Fig Tree Group and upper-Onverwacht Group, which were not described in previous literatures and (2) to constrain paragenesis of minerals, including sulfides, in the sediments, and (3) to investigate the carbonaceous matter (CM) in the black chert in the Fig Tree Group using the raman geothermometer of Beysac et al (2002) and to discuss microbial ecosystem through stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ).

Result of the outcrop survey revealed that our research areas correspond to stratigraphy to that of Hoffman (2005), who studied area in the Fig Tree Group in the BGB. Mineralogical investigations showed that Ni-rich sulfide minerals were abundant and some of them were chemically zoned in the black chert. These observations suggest that represent carbonaceous sediments in the lower-Fig Tree Group were silicified by later hydrothermal fluids which contain abundant Ni, most likely coming from ultramafic rocks. Using the raman geothermometer, the peak temperature about CM in the black chert in the Fig Tree Group is estimated to be approximately lower than  $330 \pm 50$  °C, suggesting very low metamorphic grade (lower green schist).

Additionally,  $\delta^{13}\text{C}$  values of the examined samples in the Fig Tree Group ranged from -28.9 ‰ to -23.2 ‰. Carbon isotope compositions of Onverwacht Group samples are ranged from -30.63 ‰ to -26.5 ‰ (PDB), which is within a range of organic matter produced by Calvin cycle using atmospheric  $\text{CO}_2$ , such as cyanobacteria.

Keywords: Carbonaceous sedimentary rock, Hydrothermal process, Barberton Greenstone Belt, Fig Tree Group

## The hydrothermal activity and host rock alteration of 2.7Ga VMS deposit in Potter mine, Abitibi greenstone belt.

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Volcanogenic massive sulfide (VMS) deposits are formed near the seafloor, where high temperature fluid in hydrothermal system contacts with seawater. Potter Mine, in Abitibi greenstone belt, is the one where sulfides were mined from a VMS deposit. A thin komatiite (lower komatiitic unit) underlays the ore deposit's host rock, mostly hyaloclastite or lappilli stones from tholeiitic basalt. Black shales are often interbedded in those hyaloclastite. Ores are found as disseminated sulfides and/or sulfide veins in hyaloclastite or sediments. Stratified ores are also seen. Those are overlain by upper komatiite sequence. The feature of host rock, its mineralization near the deposit and origin of organic matter associated with ores are still unknown, since no research related to the host rocks mineral and organic carbon has been performed. In this report, the chemical composition measurement of host rock minerals and organic carbon analysis at the drill core samples near the sulfide deposit were performed. By surface geological survey, the evidence of hydrothermal altered komatiite (lower komatiitic unit) was not found in Potter mine. On the other hand, serpentinization of upper komatiite was significant just above ore location. This may suggest continuous hydrothermal activities from ore deposition age to post-ore deposition age. But there is no evidence that if lower komatiite was involved in hydrothermal circulation. The result suggests that ores were composed of chalcopyrite, sphalerite and pyrrhotite mainly. Pyrrhotite and sphalerite were precipitated in non-equilibrium condition. Hyaloclastite and black shales contain different altered minerals; talc is more abundant in hyaloclastite and black shale contains more Fe-rich chlorite. Carbon isotope compositions of organic matter suggest a methanotrophic biological activity during the sulfide mineralization, in addition to thermogenic degradation of organic matter. In addition to these results, evidence of carbonate mineralization accompanied with hydrothermal activity was observed in some samples, which indicates the rise in pH. Thus, This mineralization feature should be difference between Potter mine and other VMS deposits.

Keywords: volcanogenic massive sulfide deposits, Abitibi greenstone Belt, komatiite, methanotroph, hydrothermal alteration

## Mineralogical and geochemical study of marine sedimentary rocks of Gunflint Formation(1.9 Ga), Ontario, Canada

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Gunflint Formation is composed of marine sedimentary rocks, which deposited at ca.1.9 to 1.8 Ga. Disappearance of banded iron formation and Sudbury meteorite impact occurred during the sedimentation of Gunflint Formation. However, impacts of those geological events on ecology were not evaluated in past. Therefore, in the present study, geochemical studies are performed.

Concentration patterns of Fe are different from lowermost to upper sections. Such change is corresponded to disappearance of BIF, thus decrease of Fe flux in shallow sediments. Compositions of kerogen were similar through the entire sections. However, a section which recorded Sudbury impact shows variable N/C ratios of kerogen. This may suggest that nitrogen cycle through atmosphere, hydrosphere and biosphere changed temporarily right after meteorite impact.