

## Changes in lead uptake during transformation of monohydrocalcite to aragonite

MUNEMOTO, Takashi<sup>1\*</sup>, MURAKAMI, Takashi<sup>1</sup>

<sup>1</sup>The university of Tokyo

### INTRODUCTION

Monohydrocalcite is metastable and transformed to aragonite in aqueous solutions [1]. The uptake of phosphate and arsenate, oxyanions, by monohydrocalcite has shown that it depends on the concentration of sorbate whether or not the transformation occurs, and in addition, that the uptake characteristics may vary with the presence or absence of the transformation [2]. This strongly suggests the uptake of oxyanions by monohydrocalcite is not a simple process. On the other hand, there have been few studies for the uptake of cations by monohydrocalcite. We conducted uptake experiments of lead ion by monohydrocalcite to examine changes in uptake behavior of lead ion during transformation of monohydrocalcite to aragonite.

### METHODS

To minimize changes in concentrations of carbonate ions and pH, buffer solutions were equilibrated with atmospheric CO<sub>2</sub> using Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and NaNO<sub>3</sub>; the solution pHs were adjusted to pH 8.50, 9.00 and 9.50 by NaOH and HNO<sub>3</sub>. 2 g/L of synthesized monohydrocalcite was added to each solution for the experiments. The transformation kinetics was examined at 1 μM of initial Pb<sup>2+</sup> and pH 8.50, 9.00 and 9.50. The apparent sorption isotherm experiments were conducted at 0.5 to 100 μM of initial Pb<sup>2+</sup> and pH 9.50. The concentrations of Pb were measured at the end of each batch experiment. The durations of the kinetic experiments were up to 15 hours, while all isotherm experiments were carried out for 24 hours.

### RESULTS AND DISCUSSION

Monohydrocalcite was transformed to aragonite in several hours in aqueous solutions. Aragonite increased in amount gradually while monohydrocalcite decreased with time. Monohydrocalcite was almost completely replaced by aragonite in 15 hours. The growth rates of aragonite were almost the same between the three different pH conditions. Before, during and after the phase transformation, the amounts of uptake of Pb<sup>2+</sup> were almost the same at different pH.

The solutions with more than 3 μM of Pb<sup>2+</sup> were supersaturated with respect to cerussite (lead carbonate) which was, however, not identified by X-ray powder diffraction. Therefore, the precipitation of lead carbonate was not predicted in solutions with less than 3 μM of Pb<sup>2+</sup>. Despite the supersaturation in 10 μM initial-Pb<sup>2+</sup> solution, SEM observation of the reacted solid showed that the contrast of BSE image was homogeneous, suggesting Pb was associated with aragonite probably by sorption or coprecipitation. At 100 μM of initial Pb<sup>2+</sup>, fine grains with high contrast were observed by BSE, showing the formation of lead carbonate. Some amount of Pb was considered to be associated with aragonite because of the reasons as follows: (1) the Pb<sup>2+</sup> concentration at the end of the experiment at 100 μM of initial Pb<sup>2+</sup> was about 4 μM, of which the concentration was similar to that for the 5 μM initial-Pb<sup>2+</sup> experiment where about a half of Pb was associated with aragonite and (2) the transformation was completed in 15 hours.

The transformation mechanisms of monohydrocalcite to aragonite are dissolution and precipitation [1]. Depending on the initial Pb<sup>2+</sup> concentrations, portion of Pb forms lead carbonate and some other portion is associated with aragonite after the transformation. Because aragonite increases in amount gradually and because aragonite and cerussite are isostructural to one another, it is possible that the Pb with aragonite forms solid solution during the transformation, which will be clarified in the near future.

### REFERENCE

- [1], Munemoto and Fukushi, 2008, Journal of Mineralogical and Petrological Sciences, 103, 345-349
- [2], Fukushi, et al., 2011, Science and Technology of Advanced Materials, 12, 064702

Keywords: monohydrocalcite, aragonite, transformation, lead

## Iodine uptake by calcium carbonate polymorphs

ANRAKU, Sohtaro<sup>1\*</sup>, Jun HOSHINO<sup>1</sup>, MATSUBARA, Isamu<sup>1</sup>, SATO, Tsutomu<sup>2</sup>, Tetsuro YONEDA<sup>2</sup>

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

Iodine has high radioactivity for long term in geological repository, which will be planned as transuranic(TRU) waste repository. Therefore, the immobilization of iodine must be investigated.

Naturally-occurring calcium carbonate, discovered in hyperalkaline spring (pH<12) in Oman, has high distribution coefficient of iodine, especially aragonite. The uptake of iodine on calcium carbonate is effective, because it is possible to form calcium carbonate. Therefore iodine interaction with calcium carbonate must be investigated.

In this study, I conducted some experiments, coprecipitation, adsorption, and desorption, to understand incorporation of iodide and iodate on calcium carbonate, calcite and aragonite.

Coprecipitation was conducted by synthesis of calcium carbonate in the presence of iodide or iodate ion in water. Adsorption was also conducted by synthesis of calcium carbonate, but iodide or iodate ion is not in water. Synthesis calcium carbonate put into iodide or iodate solution (solid/liquid = 400mg/40mL). Iodide and iodate concentrations were 50, 100, 500, 1000, 5000, 10000 ppm respectively both experiments. Then, this solution was open air and stirred with a magnetic stirrer at 25°C for about 24h.

The phase of calcium carbonate was effected by iodate not iodide, and then vaterite and monohydrocalcite were generated instead of calcite and aragonite, respectively. Aragonite has relatively high distribution coefficient than calcite in the experiments of adsorption and coprecipitation in laboratory as the field in Oman. The coprecipitation process of iodide by aragonite was dominant than the adsorption process.

Keywords: calcium carbonate, polymorphs, iodine, adsorption, coprecipitation, natural analogue

## Geochemical reaction modeling of $\text{CaCO}_3$ polymorphs formation at hyperalkaline springs in Oman.

MATSUBARA, Isamu<sup>1\*</sup>, Jun Hoshino<sup>1</sup>, ANRAKU, Sohtarō<sup>1</sup>, SATO, Tsutomu<sup>2</sup>, Teturo Yoneda<sup>2</sup>

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

In Japanese transuranic (TRU) waste disposal facilities, <sup>129</sup>I is the most important key nuclide for the long-term safety assessment. Thus, the  $K_d$  values of I to natural minerals are important factor in the safety assessment. However, the degradation of cement materials in the repositories can produce high pH pore fluid which can affect to anion transport behavior. Therefore, it should be necessary to understand behavior of anions such as I<sup>-</sup> under the hyperalkaline conditions.

Natural hyperalkaline spring water (pH>11) has known to generate from the partly serpentinized peridotite in the Oman ophiolite. The spring water is characteristically hyperalkaline, reducing, low-Mg, Si and  $\text{HCO}_3^-$ , and high Ca, while the river water is moderately alkaline, oxidizing, high-Mg and  $\text{HCO}_3^-$ . The mixing of these spring and river water caused the formation of secondary minerals. Naturally-occurring hyperalkaline conditions near the springs in Oman were used as natural analogue for the interaction between cement pore fluid and natural Mg- $\text{HCO}_3^-$  groundwater.

Anraku *et al.* (2009) said that calcite ( $\text{CaCO}_3$ ), aragonite ( $\text{CaCO}_3$ ), hydrotalcite [ $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}$ ] were observed in the precipitates, and their mineral compositions were varied depending on the difference of sampling points. Moreover, Anraku *et al.* (2009) also said that Iodine can be remarkably fixed in aragonite. If aragonite can also form in disposal condition, safety ratio in the long-term safety assessment will be increased by generation of aragonite.

The main goal of this work is to incorporate the effect of fixing iodine by aragonite into safety assessment. With this aim, we carried out the in-situ synthesis experiment in order to simplify the condition of secondary minerals formation in Oman. Moreover, we tried to model which can express the reaction of the in-situ synthesis experiment.

The in-situ synthesis experiment was conducted by mixing different ratios between spring and river water. The precipitates were synthesized by letting mixing solutions stand for 2 days. The mineralogy of the precipitates was determined by X-ray diffractometer (XRD), scanning electron microscope (SEM). In addition, mass of minerals in the precipitates were obtained by Rietveld method. In the result of this experiment, aragonite formed in all precipitates, and increasing the percentage of river water caused decreasing the percentage of calcite in the precipitates.

The geochemical reaction modeling was performed by using Geochemist's workbench R8.0 based on the result of the in-situ synthesis experiment. Aragonite is well-known as more unstable phase than calcite in earth's surface condition. In equilibrium state, aragonite will not form. Berner (1975) said that Magnesium ion is a inhibitor of calcite growth kinetics. And there is no inhibition of aragonite growth by magnesium ion. Our result showed the same tendency with Berner (1975). Thus, We incorporated Mg inhibition model calculated by Lin and Singer (2009) into our models. the percentage of calcite/aragonite in modeling results corresponded approximately to experimental results. Since generation of aragonite can be possible to calculate, safety ratio in the long-term safety assessment can be increased by generation of aragonite.

Keywords: Calcium carbonate mineral, Polymorphs, Geochemical reaction modeling, Kinetics, Radioactive waste disposal, Natural analogue

## Desorption of Cs from Cs contaminated smectite by major cations

Yuki Yamashina<sup>1</sup>, FUKUSHI, Keisuke<sup>2\*</sup>

<sup>1</sup>School of Natural System, College of Science and Engineering, Kanazawa University, <sup>2</sup>Institute of Nature and Environmental Tehcnology, Kanazawa University

Expandable clay mineral can fix Cs strongly on the inter layer position. However, the fixed Cs can be desorbed by reaction with other cationic species, if the concentrations of the species are especially high. Although it is very important to know the desorption behavior of Cs fixed in expandable clay minerals by major cations, there are very few studies to systematically examine the desorption behaviors. The purposes of the study are (1) to examine the desorption behavior of Cs on smectite by major cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>) as function of the cation concentrations and (2) to construct the predictive model for the Cs desorption on smectite by the major cations.

Keywords: cesium, smectite, cation exchange, major cations

## Cation Exchange Capacity Measurement for Bentonite by Spectrophotometry

HORIUCHI, Yu<sup>1\*</sup>, TAKAGI, Tetsuichi<sup>1</sup>

<sup>1</sup>Geological Survey of Japan, AIST

The cation exchange capacity (CEC) of bentonite is commonly measured by the method JBAS-106-77, provided by Japan Bentonite Manufacturers Association. JBAS-106-77 instructs the use of ammonium acetate for cation exchange, and recommends the Kjeldahl method for the quantification of ammonium ions. Though this procedure is a general method for the CEC measurement, it is often time-consuming and laborious. There are several other methods for the quantification of ammonia nitrogen, such as spectrophotometry, ionic electrode method, and ion chromatography. Of these methods, the spectrophotometry seems to be most favorable for the CEC measurement, in the point of accuracy, simplicity and quickness. In this study, we have tried to experiment spectrophotometry by using indophenol color development for attempting of convenient CEC measurement. Indophenol represents blue color, which is generated by the reaction of ammonium ions with phenol and hypochlorite.

As a result of the experiment, color development of samples started immediately after the mixture of reagent. The absorbance had stabilized after 4-5 hours, without regard to the concentration of ammonia nitrogen. The CEC value of standard bentonite, measured by the absorbance after 5 hours, represented lower values than expected value of this sample by the Kjeldahl method. This inconsistency is probably resulted from inappropriate conditions of color development, such as pH. In the future, it is necessary to improve the accuracy and reproducibility of this CEC measurement.

## Origin of manganese oxide in cold spring, Saga Prefecture.

TAKASHIMA, Chizuru<sup>1\*</sup>, HIGASHI, Yuka<sup>1</sup>, MORI, Taiki<sup>1</sup>, OKUMURA, Tomoyo<sup>2</sup>

<sup>1</sup>Faculty of Culture and Education, Saga Univ., <sup>2</sup>Graduate School of Social and Cultural Studies, Kyushu Univ.

Manganese oxide plays an important role in material cycling and has been reported from fresh water, hot springs and deep-sea hydrothermal vents (e.g., Mita et al., 1994; Fitzgerald and Gillis, 2006). In this study, we focused on manganese oxide in cold spring and discussed about the origin and the water chemistries.

Study site is Hiramatsu cold spring in Saga City, Ssga Prefecture, and is used for bathing at Hiramatsu welfare center located ~60 m from the spring. The water emit from a well naturally and is first stored in a tank close to the spring (tank 1). Then, the water in tank 1 is transported by pomp to another tank next to the welfare center (tank 2) and used in bathtub after heating. Manganese-rich precipitate was prominent at the tank 2, but also seen in the spring, tank 1, and the bathtub,

We collected water samples from the spring, tank 1 and tank 2. They were used for analysis of water chemistries with XRF and oxygen and carbon isotopic ratio with a mass-spectrometer. For the manganese precipitate collected from the tank 2, we observed textures and microbes with optical and fluorescence microscope and SEM. Moreover, identification of mineralogy was performed by XRD.

The water at the spring was about 18 degrees and shows neutral or faintly alkaline pH. The springwater was microaerophilic, containing dissolved oxygen (DO) of about 0.6 mg/L. It is rich in Mg (about 50 mg/L), Ca (about 35 mg/L), Na (about 30 mg/L), Cl (about 17 mg/L). Mn concentration was about 2 mg/L, and Fe was hardly detected (below 0.1 mg/L). Concentration of Mn decreased from the vent to tank 2. Oxygen isotopic values were -6.9 to -6.0 permill and consistent with a value of meteoric water in north Kyushu area (-7.0 to -6.0 permill; Mizota and Kusakabe, 1994). Low carbon isotopic value (-17.6 permill) of the dissolved inorganic carbon indicates contribution of organic carbon in soil.

Manganese oxide of black to dark brown in color was very soft and unconsolidated. Mineralogy analysis conformed that it was manganese oxide, but shows a broad peak indicating the amorphous MnO<sub>2</sub>. The precipitate contained numerous brown colored filaments of 3-4 micrometers in width, which were covered with mineral precipitates. This showed that bacteria induced precipitation of MnO<sub>2</sub>. Inorganic oxidation reaction of manganese under neutral pH is slow even in an O<sub>2</sub> saturated setting, but is largely enhanced by bacterial activity (Zhang et al., 2002). It is known *Psuedomonas* sp. and *Leptothrix discophora* as manganese oxide bacteria, but at present, type of bacteria in this manganese oxide are not specified. Further examination is needed to identify the bacteria with detailed observation and phylotype analysis.

### [References]

Fitzgerald, C.E. and Gillis, K.M. (2006) Hydrothermal manganese oxide deposits from Baby Bare seamount in the Northeast Pacific Ocean. *Marine Geology*, 225, p. 145-156.

Mita, N., Maruyama, A., Usui, A., Higashihara, T and Hariya, Y. (1994) A growing deposit of hydrous manganese oxide produced by microbial mediation at a hot spring, Japan. *Geochemical Journal*, 28, p. 71-80.

Mizota, C. and Kusakabe, M. (1994) Spatial distribution of dD-d<sup>18</sup>O values of surface and shallow groundwaters from Japan, south Korea and east China. *Geochemical Journal*, 28, p.387-410.

Zhang, J., Lion, L.W., Nelson, Y.M., Shuler, M.L., and Ghiorse, W.C. (2002) Kinetics of Mn(II) oxidation by *Leptothrix discophora* SS1. *Geochimica et Cosmochimica Acta*, 65, p.773-781.

Keywords: Manganese oxide, bacteria, cold spring

## Estimation of chemical weathering rates using a process-based chemical weathering model

NOZU, Taichi<sup>1\*</sup>, TAJIKA, Eiichi<sup>2</sup>

<sup>1</sup>Dept. EPS, Sch. Sci., Univ. Tokyo, <sup>2</sup>Dept. Complex. Sci. Eng., Univ. Tokyo

Chemical weathering of silicate minerals has been recognized as one of the most important processes in the long-term geochemical cycles in the Earth system. However, field-based studies on different spatial-scale watersheds have shown that the chemical weathering rates are different according to the scale of observations. Long-term mineral dissolution experiments and compilation of chemical weathering rates estimated for different weathering durations suggested that the chemical weathering rates decline significantly with time. The discrepancy may be explained as a sum effect of several phenomena such as increase in surface roughness with time and difference in reaction affinities between natural and experimental conditions.

We are developing a process-based chemical weathering model to study behaviors of the geochemical cycle system in response to changes in modern- and paleo-environment. This model consists of soil physics (heat, moisture, and gas transport) modules, chemical reaction (mineral dissolution/precipitation and aqueous speciation) modules, and a simplified soil biological activity module. We consider difference and variation in hydraulic parameters depending on soil texture and moisture content. The model has been applied to several different small (< 10 km<sup>2</sup>) watersheds to verify the model to reproduce major ion concentrations of modern streams. We introduced a free parameter which represents a ratio of field-scale weathering rate to mineralogical dissolution rate to fit the observational data. Sensitivity analyses show that riverine ionic concentrations of base cations are well reproduced from the model by tuning this parameter alone. This parameter may represent erosional effect which, in turn, controls age of the weathering environment. That is, the time dependency of silicate weathering can explain the difference in this parameter. The obtained parameter is also comparable with the ratio of the effective surface area to the BET surface area estimated in previous studies. Methods of determination of the effective surface area from environmental parameters such as an erosion rate and lithology will be discussed.

Keywords: chemical weathering, effective surface area, numerical model

## Rapid change of sedimentary environments in ca. 13Ma at Hokuroku area: mineralogical and geochemical studies on pyrite

ENDO, Misato<sup>1\*</sup>, Ryoichi Yamada<sup>1</sup>, Takeshi Kakegawa<sup>1</sup>

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

Previous study suggested that the bottom water locally become anoxic after the formation of Kuroko deposits in the Hokuroku district, Akita in Japan (Komuro et al., 2004). However, the temporal and spatial distribution of anoxic water during 15 to 10 Ma are still poorly understood. Anoxic bottom water may be a critical factor in the initial preservation of volcanogenic massive sulfide deposit (VMS) (Eastoe and Gustin, 1996). Therefore, the importance exists as to if the Kuroko deposits were also preserved in anoxic conditions or not.

Size distribution of pyrite framboids in carbonaceous sedimentary rocks is one indicator to identify the presence of anoxic ocean water. Carbonaceous sedimentary rocks, which age range from 15 to 10 Ma, are available in the Hokuroku district. In addition to age distribution, the same-aged carbonaceous sedimentary rocks are largely extended. Therefore, those carbonaceous sedimentary rocks have potential to examine temporal and spatial distribution of anoxic water in the past Hokuroku district.

In this study, geological, geochemical, and mineralogical investigations were carried out on mudstones in the Hokuroku district. In particular, the size distributions of pyrite framboids were analyzed using SEM. The mudstones from M3, M2 Ma and M1 were collected from outcrops in the large area of the Hokuroku district. The M3 mudstone, which age is most likely between 15 to 14 Ma, was deposited before the formation of Kuroko deposits. M2 mudstone was deposited soon after Kuroko hydrothermal activity (ca.14 to 13 Ma). M1 and M1 mudstones, which ages are ranging from 13 to 10 Ma were deposited with no relation to Kuroko hydrothermal activity.

Detailed size analyses showed that mean sizes of pyrite framboids in the M2 mudstones (5.0 to 5.2 micro meters) were smaller than those of M3, M1 and M1 mudstones (5.0 to 9.7 micro meters). The standard deviation of pyrite framboids in the M2 (2.0), were also smaller than those of others (2.4 to 4.2). These results above indicate that M2 mudstones were deposited under euxinic conditions, and M3, M1 and M1 mudstones were deposited under oxic conditions. The examined M2 mudstones were collected both near and far from the ore bodies and all show the same size distribution of framboidal pyrite. This suggests that anoxic water were rather widespread at the bottom of the Hokuroku ocean between 14 to 13 Ma. On the other hand, anoxia of bottom ocean water only restricted during sedimentation of M2 mudstones. The total range of sulfur isotopic compositions of pyrites were range from -44 to -15 per mil. In particular, the sulfur isotope compositions of pyrites in M2 were range from -37 to -34 per mil. Such light values indicate microbial sulfur cycling by sulfate-reducing, sulfur-oxidizing and/or sulfur-disproportionating bacteria in the anoxic water column. On the other hand, S(pyrite)/C(organiacs) in M2 mudstone is not high compared to Black Sea sediments, which deposited in euxinic conditions and redox boundary reached to photic zone. Those facts indicate that euxinic bottom water at the pale-Hokuroku ocean were created by microbial activities, not submarine hydrothermal activities. The anoxic water at this age was limited at the bottom of deep ocean and did not reached to photic zone, so that the magnitude of microbial productivities (and pyrite precipitation) at redox boundary were limited.

On the other hand, the sulfur isotope compositions of pyrites in the upper part of M1 and M1 range from -30 to -15 per mil. M1 mudstones contain the secondary pyrite (e.g., pyrite overgrowth on primary framboidal pyrite). Such secondary pyrite often contain unusual amounts of Mn. Texture and chemistry of secondary pyrite suggest that those were formed during late diagenetic stage by dissolving and reprecipitating primary framboidal pyrite. Such diagenetic process, accompanied with change of clastic sediments and sedimentation rates, may affected on sulfur isotope compositions of M1 and M1.

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



## Microbial sulfate reduction within the Iheya North subseafloor hydrothermal system constrained by quadruple sulfur isoto

AOYAMA, Shinnosuke<sup>1\*</sup>, NISHIZAWA, Manabu<sup>2</sup>, TAKAI, Ken<sup>2</sup>, UENO, Yuichiro<sup>1</sup>

<sup>1</sup>Tokyo Institute of Technology Department of Earth and Planetary Sciences Tokyo Institute of Technolo, <sup>2</sup>JAMSTEC

Subseafloor hydrothermal system may host active and abundant microbial community. Sulfate reduction may be one of the dominant microbial metabolisms among the subseafloor ecosystem. In order to demonstrate and quantify the potential sulfate reducing activity, we analyzed sulfur isotopes ( $^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$ ) of pore water sulfate extracted from core samples at the Iheya North hydrothermal system in the Okinawa drilled by CHIKYU, 2009 (IODP Leg 331). After drilling, core samples were divided into several sections. Then, pore water was extracted on board, and stored with cadmium chloride for fixing hydrogen sulfide. In our laboratory, the samples were first divided into sulfide precipitate and supernatant liquid by centrifugation. Then, dissolved sulfate was precipitated as  $\text{BaSO}_4$  by addition of barium chloride into the supernatant liquid. After weighing, the barium sulfate was converted into silver sulfide and subsequently sulfur hexafluoride, which was purified by GC and then introduced into mass spectrometer (MAT253) through newly developed microvolume inlet for precisely determining quadruple sulfur isotopic composition.

Based on pore water chemistry and temperature profile, the subseafloor environment are divided into Unit-1, -2 and -3 with depth below surface. In Unit-1 (0-10 mbsf), fresh seawater is circulated, whereas in Unit-3 (>40 mbsf), hot hydrothermal fluid (>150°C) is stored below anhydrite cap. The Unit-2 is the mixing zone between the hydrothermal fluid and seawater.

We found that the  $\delta^{34}\text{S}$  value of sulfate in the mixing zone was higher than those expected by simple mixing between seawater sulfate in Unit-1 (-20 permil) and the hydrothermal component in Unit-3 (-16 permil). The observed  $^{34}\text{S}$ -enrichment and decreased sulfate concentration suggest sulfate reduction took place in this hydrothermal system. Based on our model calculation assuming the mixing and reduction, apparent isotope effect for  $^{33}\text{S}$ ,  $^{34}\text{S}$  and  $^{36}\text{S}$  are estimated to be -16.5 permil, -32.2 permil and -62.5 permil, respectively. These large fractionations together with slight  $\text{D}^{33}\text{S}$  enrichment and  $\text{D}^{36}\text{S}$  depletion all suggest that the sulfate reduction is microbial and not thermochemical process. Our numerical simulation also indicates that the sulfate is reduced before mixing with high temperature fluid, probably within the recharge zone of seawater. Based on these results, we will discuss microbial sulfur cycling in this subseafloor environment.

**Keywords:** Microbial sulfate reduction, quadruple sulfur isotope, subseafloor hydrothermal system, Iheya North hydrothermal system in the Okinawa

## Impact Chemical Evolution Processes for Simple Amino Acids (Glycine and Alanine) Formed by Oceanic Impact

UMEDA, Yuhei<sup>1\*</sup>, FUKUNAGA, Nao<sup>1</sup>, SEKINE, Toshimori<sup>1</sup>, FURUKAWA, Yoshihiro<sup>2</sup>, KAKEGAWA, Takeshi<sup>2</sup>, Kobayashi Takamishi<sup>3</sup>, NAKAZAWA, Hiromoto<sup>3</sup>

<sup>1</sup>Graduate School of Science, Hiroshima University, <sup>2</sup>Graduate School of Science, Tohoku University, <sup>3</sup>National Institute for Materials Science

The biomolecules on Earth are thought either to have come from the extraterrestrial parts carried with flying meteorites or to have been formed on Earth from the inorganic materials through given energy. From the standpoint to address the importance of impact energy, it is required to simulate experimentally the chemical reactions during impacts, because violent impacts may have occurred 38-40 years ago to create biomolecules initially. Shock reactions between ocean and meteoritic constitutions can induce locally reduction environment to form bioorganic molecules such as amino acid.

We need to know possible processes how the chemical evolution proceeds further by impacts and how complicated biomolecules are formed. In this study we prepared aqueous solutions of the two simplest amino acids (glycine and alanine) labeled by <sup>13</sup>C and investigated the reactions. Shock recovery experiments were carried out with a propellant gun. Sample of aqueous solution immersed in olivine powders sealed in a stainless steel container was used as a target. The sample space has air gap behind the mixture of olivine and solution. In some shots we added ammonia solution and so on to model the old ocean composition. The recovered samples were analyzed with LC/MS for water soluble components and XRD and TEM for solids. The analytical results indicate the formations of alanine from glycine, glycine from alanine, and amines from the both and that the residual glycine and alanine in each solution are very small less than 1%. There is no evidence for formation of complicated amino acids even if benzene was added. The starting olivine particles became fine-grained and some grains had reaction rims of hydration. According to the present results, simple amino acids of glycine and alanine can change one another, but they decompose amines and others mostly. So, these results imply not only that the impact-induced process is not so simple to proceed the chemical evolution just to one way, but also that there are complicated and multi-process ways. In meteorite impacts, it also must be taken into account the heterogeneous distribution of impact energy in an impact that may cause a significant effect on the chemical evolution.

## Chirality change of valine by marine bolide impacts

TAKASE, Atsushi<sup>1\*</sup>, SEKINE, Toshimori<sup>1</sup>, FURUKAWA, Yoshihiro<sup>2</sup>, KAKEGAWA, Takeshi<sup>2</sup>, Takamichi Kobayashi<sup>3</sup>, NAKAZAWA, Hiromoto<sup>3</sup>

<sup>1</sup>Graduate School of Science, Hiroshima University, <sup>2</sup>Graduate School of Science, Tohoku University, <sup>3</sup>National Institute for Materials Science

The chirality of terrestrial amino acids consisting of biomolecules is only L-type. In order to make clear the origin of life from the standpoint that biomolecules are formed by oceanic impacts of meteorites, it is crucial to determine the chirality change of amino acids through impact process that have been considered to have occurred at early Earth. Each aqueous solution (~100 mmole/l) of L- and D-valine was prepared separately and used as reactants. Samples after shock recovery experiments on mixtures of powdered olivine and the solution were analyzed by LC/MS for the contents of L- and D-valines. The present results indicate that valine survives significantly (~10%) and that the aqueous L- and D-valines transform partially (~5%) to D- and L-valines, respectively. Although further studies need to define how the final chirality changes by shock processes, marine bolide impact may have significant effects on the chirality and the chemical evolution of biomolecule.

## Causes of recent increased aeolian dust productions over East Asia - An analysis using meteorological observatory data

KUROSAKI, Yasunori<sup>1\*</sup>, SHINODA, Masato<sup>1</sup>, MIKAMI, Masao<sup>2</sup>

<sup>1</sup>Arid Land Research Center, Tottori University, <sup>2</sup>Meteorological Research Institute

Production of aeolian dust (i.e., wind erosion) depends on aeolian erosivity and erodibility. The erosivity is an ability of wind to cause wind erosion, and it can be represented by one parameter, which is wind friction speed or simplistically wind speed. On the other hand, the erodibility is characterized as the sensitivity of a surface to wind erosion, which is influenced by an infinite number of soil and land surface characteristics, particularly the soil particle size distribution, soil water content, soil freeze/thaw processes, snow cover, vegetation coverage, vegetation type, and we do not clarify most relations between these parameters and erodibility. Even though all of these will be clarified, we will still have difficulties in monitoring the all erodibility factors. The above means monitoring erosivity is relatively easy but monitoring erodibility is difficult.

We can recognize the minimum wind speed initiating an dust production (hereafter, threshold wind speed) as an index of erodibility. Estimations of threshold wind speed have been conducted by a combination of anemometers and devices which measure instantaneous soil particles motions, such as SENSIT (Stout, 2004, Earth Surf. Processes Landforms) and SPC (Mikami et al., 2005, J. Geophys. Res.). However long-term erodibility monitoring by such devices in a broad area is not realistic due to problems of manpower and fund.

We can monitor a dust production in a broad area for a long term using synoptic data whose observation is made at meteorological observatories, which are widely distributed in the world. A meteorological observation is conducted at every 3-hour at many of synoptic observatories. A dust production is recorded in a present weather observation. Regarding erosivity, we have a wind speed observation. However, we have no observation of erodibility.

In this presentation, we will show a methodology of statistical estimate of threshold wind speed (Kurosaki et al., 2011, Geophys. Res. Lett.). We will show dust production frequency, strong wind frequency, and 5-percentile of threshold wind speed on April for 1990s (1990-1999) and 2000s (2000-2009) over East Asia, and we will discuss the contribution of erosivity and erodibility on changes in dust production from 1990s to 2000s from changes in strong wind frequency and 5-percentile of threshold wind speed. Here, a strong wind is defined as a wind whose wind speed exceeds 5-percentile of threshold wind speed on April for 1970-2009. We will also show analyses of precipitation for June-August (hereafter, summer precipitation) and annual maximum NDVI (Normalized Difference Vegetation Index) in order to examine dead-leaf hypothesis (Shinoda et al., 2010, SOLA). In this hypothesis, the precipitation amount during the vegetation growing season predominantly controls plant production in summer, the vegetation in summer remains as dead leaves until spring of the following year, and consequently the dead leaves chiefly control the erodibility in spring. Our main results are as below:

1. The dust production frequency increased at many observatories in Mongolia, Inner Mongolia, and northeastern China, whose land cover types are grassland and cultivated land, from the 1990s to the 2000s due to changes in erodibility.
2. We have some observatories where the dust production frequency increased for the period in the Gobi Desert in China and a western part of the Loess Plateau, whose land cover type is desert, due to changes in erosivity.
3. Both summer precipitation and annual maximum NDVI decreased at some observatories in Mongolia, but no such relationship is seen in other regions. This result suggests that the dead-leaf hypothesis can be applied to such observatories in Mongolia, but not to the other regions.

Keywords: aeolian dust, Asian dust, wind erosion, erosivity, erodibility

## Precipitation rate and isotopic composition of calcium carbonate under conditions induced by degassing of carbon dioxide

KANO, Akihiro<sup>1\*</sup>, Tomoyo Okumura<sup>1</sup>

<sup>1</sup>Kyushu University

It has been well known that degassing of carbon dioxide increases the saturation state and induces precipitation of calcium carbonate. Representative natural examples of this phenomenon are fluvial tufa in a limestone area, and travertine in carbonate hot-spring environments. These two examples largely differ in the precipitation rate. The difference is likely related with the differences in equilibrate partial pressure of carbon dioxide, alkalinity, and calcium concentration, however it has not been fully understand with a theoretical principle. In general, the carbonate precipitation has been treated as adjunction of carbonate and calcium ions on the mineral/water interface, which was often formulated by activity product of the two ions. The previous formulas are consistent with the rates in tufa environments, but fail to reproduce high precipitation rates of the travertines.

This study will propose a new rate formula based on the sum of chain-reactions, in which the degassing induces the carbonate precipitation. A prominent feature of this is that three ions (bicarbonate, hydroxide, and calcium) are captured on the mineral surface. The formulated rate is proportional to the product of the calcium carbonate saturation and the carbon dioxide partial pressure, and well reproduces the actual precipitation rates of tufas and travertines. In addition, the proposed model is consistent with an apparent disequilibrium of oxygen isotopic composition of travertine, which is variable with pH. The model can be more comprehensive than the previous ones in terms of reproducing the overall phenomena of carbonate precipitation.

Keywords: travertine, tufa

## Change of host phase of REE and preservation of REE pattern during the diagenesis of marine sediments

TAKAHASHI, Yoshio<sup>1\*</sup>

<sup>1</sup>Hiroshima University

Relative abundances of rare earth elements (REE) in geological materials are used widely to investigate geochemical problems such as the origins of sedimentary rocks and REE behavior during processes such as weathering and diagenesis. One of the REE, cerium (Ce), can exist in either trivalent or tetravalent form depending on the redox condition. Thus, knowledge of the oxidation state of Ce in rocks and minerals could potentially be used to constrain the redox states of past and present geological environments. In this study, we examined validity of REE pattern as geochemical indicators reflecting sedimentary paleoenvironment.

For this aim, we discussed the behavior of REE under diagenetic environment by using Ce and Mn distributions in sediments, and oxidation states of Ce and Mn determined in X-ray absorption near edge structure (XANES). Sediment core samples used in this study were recovered from North Pacific at Site 1179, ODP Leg 191. Sediment at these core sites consists of siliceous ooze, clay, and thin volcanic ash layer. According to XRF data, the concentration depth profiles of Fe and Mn show that they have high concentration peaks. Manganese is accumulated at 0.20 m, and then decreases toward deep due to reductive dissolution of MnO<sub>2</sub>. The oxidation state of Mn from 0.60 m to 7.18 m is mostly divalent, which is consistent with the low concentration of Mn layer. Marine ferromanganese nodule is known to have a high absorption capacity for REE. Among the REE, Ce tends to accumulate in Mn oxide due to oxidation from soluble Ce<sup>III</sup> to insoluble Ce<sup>IV</sup>. Cerium concentration in sediments is relatively constant from top to bottom of the core, but Mn concentration is not. These results imply that the host phase of Ce changed from Mn-oxides to the other phase.

We confirmed that host phase of Ce changed from Mn oxide to phosphate based on the chemical leaching experiments. Additionally, positive Ce anomaly were observed in both Mn and P phases determined by laser ablation (LA)-ICP-MS, suggesting that the anomaly was conserved during change in the host phase of Ce. Micro-XANES study also showed that Ce in Mn oxides is tetravalent, but trivalent in apatite found at the depths of 0.70 m and 0.80 m.

Overall, the shapes of REE patterns were similar from the surface to the depths studied here, though the host phase of REE changed from Mn oxides to phosphate. Thus, the phosphate having high affinity for REE is important to keep the initial REE pattern during the diagenesis.