An unexpected mineral in reef-building massive coral

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Coral reefs are important for marine ecosystem by providing habitat to many animals in tropical and subtropical zones. Coral skeletons are also mineralogically interesting, because they consist of aragonite ($CaCO_3$) which is a thermodynamically metastable mineral phase under growth environments of corals. So far, the calcification process has been still unknown. It is generally known that XRD patterns of reef coral skeletons show only aragonite phase peaks, although chemical analyses reveal that coral skeletons contain various elements. Recently it was suggested that such elements directly break into calcification medium from seawater. This indicates that abundant elements in seawater, such as Na^+, Cl^-, SO_4^- may precipitate in coral skeleton during calcification as halite and gypsum. To confirm these mineral phases, we observed massive coral skeleton of Porites lobata by Analysis Transmission Electron Microscope (ATEM) and Fourier Transform Infrared spectrometer (FT-IR) which are powerful tools to detect small amount of mineral phases. In this observation, we found an evidence that halite precipitates almost simultaneously with aragonite during calcification. The existence of halite is one of strong supports for the supporting a model of extracellular calcification. On the other hand, gypsum could not be observed. This suggests that coral have ion selectivity from seawater to calcification medium. The halite phase in coral skeleton will provide a new perception for understanding the process of coral calcification.

Keywords: coral skeleton, aragonite, trace element

U03-02　　　　　　　　　Room:302　　　　　　　　　Time:May 20 10:15-10:30

Behavior of nickel in wastewater during the precipitation of layered double hydroxide

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Nickel is one of the most valuable heavy metals used in the electronics and metal plating industries. The demand has been increasing year by year due to the advances in technology. Some industrial wastewater contains a large amount of Ni. Generally, the removal of Ni from contaminated wastewater is accomplished by adding an antalkaline reagent to increase the pH to 10 or above, which would result in the generation of Ni-hydroxides and oxides after treatment. After that, it is necessary to adjust the pH below 8.6(effluent standard is pH5.8 to 8.6). However, this method has some disadvantages, such as the high cost of chemical reagents and problems in the disposal of alkali sludge. Therefore, a more efficient remediation method is required to achieve a more sustainable wastewater treatment technology. On the contrary, natural attenuation processes can reduce the mass, concentration, and mobility of contaminants, such via neutralization, adsorption, and mineral precipitation. They are safer, cost-effective and more environmentally friendly than traditional methods. Therefore, a sustainable remediation method may be developed by understanding and applying the mechanisms involved in the natural attenuation process. For example, mine drainage at Dougamaru abandoned mine at Shimane Prefecture, Japan contains concentration of Cu and Zn exceeding water standard, but Cu- and Zn-bearing mine drainage was naturally attenuated by the formation of green precipitates composed of Cu-bearing layered double hydroxide (LDH), hydrowoodwardite (Okamoto et al., 2010). Because a LDH has hydroxide structure, six-coordinate heavy metals such as not only Cu but also Ni and Co can be incorporated into the structure.

In this context, to check the applicability of LDH in Ni-bearing wastewater treatment, synthesis experiments were carried out by coprecipitation method to synthesize Ni-bearing LDHs with different concentration of dissolved Al. The results of ICP-AES measurements showed that the removal efficiencies of Ni from the synthetic wastewaters by the precipitation have increased with adding Al. Al addition method selected LDH as a precipitated phase can remove Ni at pH lower than previous methods which precipitated Ni-hydroxides. From the extraction experiments, the most of all Ni should be incorporated in to the structure of LDH. However, spectroscopic data is necessary to know about the bonding state and bond distance between Ni and Ni, or Ni and the other ions. XAFS analysis was conducted to evaluate those for the precipitate qualitatively. In this presentation, the results of XAFS analysis will be involved to show chemical behavior of Ni in the precipitation process.

Keywords: Remediation, Layered double hydroxide, Nickel

Imaging of microbial cells in niches of marine sediment using in situ DNA and electron staining

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   Ubiquitous presence of microbes and their inherent activity make them extremely important for a better understanding of physical, chemical, and biological processes in the subsurface environments. In situ detection of submicron microbial cells in the marine sediments is initial steps towards the detailed understanding of microbial life in subseafloor biosphere. However, there are almost no adequate techniques to observe microbes in their in situ condition. Here, we developed a technique that enables the observation of in situ microbes within subseafloor sediments. The technique includes resin-embedding followed by thin sectioning of marine sediments to fix the microbes as well as microstructures in the sediments. Microbial cells in the sediment are visualized under a fluorescent microscopy by staining with SYBR Green I. Then, cells are also visualized with a scanning electron microscopy/energy dispersive spectrometry (SEM-EDS) by applying electron staining of microbial cells. Under SEM-EDS observation, we could match the points where heavy elements used for electron staining are concentrated with the points where SYBR Green I-stained cells were observed in fluorescent microscopy, indicating the microbial cells are selectively recognized in SEM-EDS observation. The coupled SYBR Green staining and electron staining method facilitate the observation of in situ microbes and their interaction with sedimentary minerals even in soft sediment samples with high spatial resolution.

Keywords: electron staining, microbe, SYBR Green staining

Effect of water film on weathering of rock under unsaturated condition

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The pores in rocks near the Earth's surface often become unsaturated as the result of intermittent rainfall, drying, and drainage. There are several possible ways by which the weathering of rock progresses under unsaturated conditions: (1) The surfaces of the pores filled with air do not react at all. (2) Wetting (as water film) spreads to all the pore surfaces even for the pores filled with air, and reaction occurs as with the case of fully saturated condition. (3) Whether or not the wetting and reaction occur depends on pores. To understand the weathering of rocks near the Earth's surface, it is important to evaluate various factors under unsaturated conditions, such as the reactive surface area, the rates of dissolution, precipitation, and solute transport, and the thickness of water film. In this study, the effect of water film on water-rock reaction under unsaturated condition was studied.

A core was cut from a porous rhyolite (porosity 18%, mineral composition: glass 87%, plagioclase 9%, quartz 4%), and water was passed into the cores under a constant water head difference. Dissolution of Si occurred from the rock, and the solution containing dissolved Si was discharged from the rock. By measuring the concentration of Si in the solution discharged, the amount of dissolution was determined. To compare the amount of dissolution under unsaturated and saturated conditions, the experiments were conducted using both the saturated sample and dried sample. When water was passed into the dried rock, water saturation quickly increased with elapsed time and became 30% after 2 hour, but after that the increase was small, and the water saturation after 6 days was 41%. The relationship between the flow rate Q (cm^3/s), the concentration of Si in the solution discharged C (mol/cm^3), the mineral-water reactive surface area A (cm^2), and the dissolution rate of mineral R (mol/cm^2/s) is given by

$$Q_{sat}C_{sat} = A_{sat}R_{sat}$$

$$Q_{unsat}C_{unsat} = A_{unsat}R_{unsat}$$

Because R_{sat} is equal to R_{unsat} when the Si concentration is low, A_{unsat}/A_{sat} can be determined by measuring Q_{sat}, C_{sat}, Q_{unsat}, and C_{unsat}. The results of the experiment showed that A_{unsat}/A_{sat} was similar to the value of water saturation in the early period of the experiment but increased with elapsed time, and approached to 1 after 6 days passed. Similar results were obtained also for a sandstone (porosity 6%, quartz ~100%). For the case of the sandstone, A_{unsat}/A_{sat} was almost equal to 1 over the entire period of the experiment. These results showed that almost all the pore surfaces under unsaturated condition were covered with water film and dissolution occurs, even though the rhyolite and sandstone have different pore structure and mineral composition.

Keywords: weathering, dissolution, water film

Reactive-transport modeling in water film in rock pores: Implication to the dissolution of water-unsaturated rock

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Mineral-water reactive surface area is essential for considering water-rock interaction. Because water and air often coexist in rock pores in the vadose zone, the reactive surface area in the rock under water-unsaturated conditions may be smaller than that under saturated condition. However, our experiments using Fontainebleau sandstone (porosity: 6%, mineral composition: quartz ~100%) and porous rhyolite (porosity: 18%, glass 87%, plagioclase 9%, quartz 4%) demonstrated that almost the same amounts of dissolved element (= [dissolution rate constant $(mol/m^2/s)$] x [reactive surface area (m^2)] x [reaction time (s)]) were obtained under saturated and unsaturated conditions, which shows that the reactive surface area was unaffected by the decrease of water saturation. This result indicates that almost all the surfaces of air-containing pores were wetted with water film and thereby dissolution occurred. The results also suggest that the rate of flushing of dissolved element to the outside of the water film was fast enough to keep the concentration in the film far lower than the equilibrium concentration of the mineral, because the mineral dissolution rate usually decreases if the concentration approaches equilibrium. To quantitatively understand the reaction and the transport in water film and to elucidate the factors that may affect these phenomena, we constructed a reactive-transport model considering the dissolution and diffusion occurring in the water film.

First, we estimated the water film thickness h (m) that is an important parameter for modeling reactive transport in the film. Theories for estimating the relationship between film thickness and relative humidity have been developed on the basis of van der Waals force and electric double layer force acting between air-water film-mineral. We applied the theories and derived the expression for predicting the thickness of water film in equilibrium with the relative humidity in air-containing pores. By using the expression, the film thickness was revealed to depend mainly on pore diameter d_{pore} (m). For Fontainebleau sandstone having pore diameters of 6-42 micrometers, the film thicknesses were estimated to be 7-20 nm. Next, by considering the mass balance in the water film, the following formula is obtained:

$$dc/dt = D(d^2c/dx^2) + k(A/V_{film})(1 - c/c_{eq})$$

where c (mol/m^3) is the solute concentration in the film, t (s) is the time, x (m) is the position, D (m^2/s) is the diffusion coefficient, k $(mol/m^2/s)$ is the dissolution rate constant, A (m^2) is the reactive surface area, V_{film} (m^3) is the volume of the film, and c_{eq} (mol/m^3) is the equilibrium concentration. By analytically solving the above formula, we obtained the expression of the concentration profile formed in the water film at the steady-state. It was found that the concentration depends on film thickness, diffusion length (~grain size), surface roughness, diffusion coefficient, and type of mineral (k and c_{eq}). The thicker the water film, the faster the flushing rate and the lower the concentration in the film. The concentrations of Si in water film calculated for Fontainebleau sandstone were found to be significantly lower than c_{eq} of quartz (<0.03 c_{eq}), which is consistent with the experimental result.

Finally, by applying the model presented in this study to sedimentary rocks with various pore structure and mineral composition, we evaluated the condition of the film thickness (pore diameter) and the grain size required for keeping the concentration in the water film to be far lower than equilibrium concentration. If a rock of interest has pore diameters and grain sizes that satisfy the required condition, the surface areas available for dissolution are the same between water-saturated and unsaturated conditions. Such criteria would be useful to evaluate the reactive surface area under unsaturated conditions.

Keywords: reactive surface area, reactive-transport modeling, water film, unsaturated condition, dissolution

U03-06　　　　　　　　Room:302　　　　　　　　Time:May 20 11:30-12:00

Structure of mica and calcite/water intefaces

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Mineral/liquid interfaces are ubiquitous in the Earth's surface and control a range of processes such as ion exchange, contaminant migration, biomineralization, oil reservoir, and many others. These processes occur in the atomic scale and therefore we need techniques having atomic scale resolution for observing and analyzing the interfaces. A combination of x-ray crystal truncation rods (CTR) method and molecular dynamics (MD) simulations are powerful methods for observing the structure and dynamics of these interfaces [1]. The pioneered works of X-ray CTR scattering measurements on the mineral/liquid interfaces by Fenter group [2] revealed the electron-density distribution of the interfaces with sub-angstrom resolutions. A limitation of the CTR scattering technique is the lack of identification of atomic species. The MD simulation is a candidate that overcomes this limitation by comparing the results with those of the X-ray CTR scattering measurements.

Here we talk about the recent results of mica/salt solutions and calcite/artificial sea water (ASW) interfaces. Mica is a good model mineral for clay minerals and the interaction with water should be important for understanding the frictional strength of faults. The X-ray CTR scattering and MD simulations revealed the structure of electrical double layer for mica/NaCl solution interface [3] and the presence of the hydrated Na^+ on the interface can be the high lubrication among mica surfaces [4]. Calcite is a biomineral preferred by many organisms and plays an important role in the carbon and oxygen cycles. It is the main constituent of chalk and limestone, which serve as hosts for oil reservoirs and water aquifers in Europe. The modification of the affinity of the surface for water and the attachment of organic molecules is critical for enhancing oil recovery and the crystal growth. Can dissolved ions in water change the affinity of the calcite surface? The X-ray CTR measurements may give some clues to understand the effects and the underlying mechanism.

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Keywords: X-ray CTR scattering, MD simulation, hydration, surface, friction, oil

Submerged atomic resolution imaging of hydration structure on calcite in the presence of the synthetic polypeptide

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Dehydration is an important growth rate-determining process in solution growth (Bennema, 1967). Recently, it has been suggested that hydration was eased by hydrophilic organic material from the result that the step velocity of calcite was increased by the addition of hydrophilic peptide(Elhadj et al., 2006). However, the influence of organic material on hydration has not been revealed. In order to verify the influence of the organic material on the hydration of the crystal surface visually, we tried in situ observation of hydration structure on calcite surface in atomic level during solution growth.

The observation was conducted by a recently developed high-resolution and low-thermal-drift Frequency Modulation AFM (FM-AFM) working in liquids (Fukuma et al., 2005). Hydration imaging was realized by force mapping of FM-AFM (Kimura et al., 2010) . The prove is scanned on the vertical line to the crystal surface. Hydration layer is detected by the frequency shift due to the interaction of tip and water molecule. The supersaturated solution of CaCO3 was prepared to be supersaturated for both calcite and aragonite at pH 8.1 and room temperature. A cleaved calcite crystal was glued to the bottom of an open fluid cell, and the solution was put on the surface. The synthetic polypeptide was adopted as organic material in our experiment. The synthetic polypeptide consists of fifteen amino acid residues including six aspartic acids periodically (Takagi and Miyashita, 2010). This polypeptide is considered as important material to control the polymorph of calcium carbonate in the field of biomineralization.

We obtained atomically image of lacy network of hydration on calcite (104) face. Water molecule formed four layers to be piled up alternately in the vertical direction of calcite surface. Water molecules were above gaps between calcium ions on calcite surface in the first and third layer. In the case of the second and fourth layer, water molecules were located above calcium ions. Furthermore, 3D hydration structure was constructed by multiple 2D hydration images which were taken at interval of 0.15 nm to the one direction. The hydration structure on each layer was described after construction of 3D image. As a result, it was confirmed that water molecules keep stable structure corresponding to the calcite surface structure until the height 0.5 nm above calcite surface.

Our result shows that the hydration can be visualized in the level that we can compare the structure in atomic resolution. It is strongly expected that the influence of organic material on hydration structure would be revealed.

Factors controlling barite-water distribution of selenium

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Geochemical behavior of trace elements in water is controlled by their interaction with major minerals through ion exchange, sorption/desorption, and coprecipitation/dissolution processes, which finally govern the concentrations of trace elements in natural water. Especially, the coprecipitation into the structure of mineral is potentially important because trace elements is less available and can be immobilized in the crystal lattice at least until the dissolution of the minerals. Previous studies showed that the partitioning behaviors of the trace elements to such minerals were controlled many complex factors, such as crystal constraints of ion substitution, complexation effects in water, crystallization rate, and changes in temperature and/or pressure. For instance, Yokoyama et al. [2011, 2012] demonstrated that, in the case of arsenic (As) and selenium (Se) incorporation into calcite, calcite selectively incorporated arsenate rather than arsenite, and selenite rather than selenate because of their high stability of calcium arsenate and calcium selenite complexes compared with those for arsenite and selenate. In this study, we focused on the Se incorporation mechanism to barite to examine the influence of or chemical effect and structural effect to the solid-water distribution behaviors.

The coprecipitation experiments of Se with barite were conducted to examine the influence of (a) the chemical effect at various pH conditions (pH = 3-8), and (b) structural effect of ion substitution as a function of the reaction time (0-42 days). Barite was precipitated from a mixture of artificial seawater (ASW) and $BaCl_2 2H_2O$ solution in the presence of selenite or selenate solution. The total concentration and valence ratios of Se in barite were measured by ICP-MS and X-ray absorption near-edge structure (XANES) at Se K-edge, respectively.

[Chemical effect]

The results showed that Se(IV) was preferentially incorporated into barite at 7<pH<8 whereas Se(VI) at 3<pH<6, which reveals its correlation with the pH dependence of Se(IV) and Se(VI) speciation. These results suggest that the pH has a strong influence on the coprecipitation of trace elements into barite. Thus, the chemical affinity is an important factor controlling the species of Se incorporated into barite, as also found in Se and As incorporation into calcite.

[Structural effect]

The results showed that both the Se(VI)/Se(IV) ratio and total Se concentration in barite increased at first, and reached constant as time passed, suggesting a strong correlation between the Se(VI)/Se(IV) ratio in barite and crystallinity. The correlation indicates that the aging effect in the first stage was dominated by the chemical effect, or larger affinity of Se(IV) than Se(VI), while the aging in the second stage was influenced by the structural similarity between sulfate (SO_4^{2-}) and selenate (SeO_4^{2-}). It is considered that the Se(IV) was dissociated at barite due to the low structural affinity, thus, the Se(VI)/Se(IV) ratios in barite relatively increased through crystallization.

Keywords: distribution behavior, selenium, barirte, chemical effect, stracture effect, XAFS

U03-09   Room:302   Time:May 20 14:15-14:30

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

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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 (32S/33S/34S/36S) of pore water sulfate extracted from core samples and mineralized sulfide at the Iheya North hydrothermal system in the Okinawa drilled by CHIKYU, 2009 (IODP Leg 331). Based on pore water chemistry and temperature profile, the subseafloor environment is divided into Unit-1, -2 and -3 from top to bottom. In the Unit-1, fresh seawater is circulated, whereas in Unit-3, hot hydrothermal fluid (>300?C) is stored below anhydrite cap rock. The Unit-2 is a mixing zone between the hydrothermal fluid and seawater. We found that the d34S value of sulfate in the Unit-2 was higher than those expected by simple mixing between seawater sulfate and the hydrothermal component. The observed 34S-enrichment and decreased sulfate concentration suggest sulfate reduction took place in this hydrothermal system. Based on our model calculation, apparent isotope effect 34e is estimated to be -32.2 permil. The large fractionations together with slight D33S enrichment and D36S depletion all suggest that the sulfate reduction is not thermochemical process but microbial reduction with high reaction rate. Our numerical simulation indicates that the sulfate is reduced probably within the recharge zone of seawater before mixing with high temperature fluid. Additionally, we estimate the contribution of microbial sulfate reduction from mineralized sulfide. In spites of sulfide dominantly deposited from hydrothermal fluid, deep (>16 m) sulfide sulfur shows characteristic isotopic composition suggesting incorporation of microbial sulfide, roughly ~50%. Consequently, rapid seawater circulation in the Iheya North hydrothermal system may support active microbial sulfate reduction below the seafloor.

Ecophysiology of microaerophilic iron-oxidizing bacteria

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Iron-oxidizing bacteria (FeOB) gain energy for their growth by oxidation of ferrous iron. Many FeOB are chemolithoautotrophs that can fix inorganic carbon into organic carbon. They play a role as primary producers in chemosynthetic ecosystems. Some species of FeOB produce unique extracellular structures such as twisted ribbon-like stalks or tube-like sheaths (Emerson et al., 2010). Iron oxides attached to these structures are called biogenic iron oxides (BIOS). BIOS accumulate metals on their surface (e.g., Langley et al., 2009). Thus, FeOB are likely to play an important role in elemental cycling in environments. Furthermore, microbial ecosystems supported by FeOB are expected to be widely distributed on the oceanic crusts (Bach and Edwards, 2003). However, little is known about ecophysiology of FeOB because of few cultivated species. In this presentation, recent studies of FeOB are reviewed, and then the ecophysiology of microaerophilic FeOB is discussed based on the results of my FeOB isolate.

Keywords: Iron-oxidizing bacteria, Microaerophiles, Chemolithoautotrophs, Ecophysiology, BIOS

Inner-structural and microbiological comparison on hydrothermal sulfides

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Around deep-sea hydrothermal vents, the characteristic ecosystem thrives, which is different from the one on shallow-sea. This ecosystem is based on primary production of chemolithoautotrophs using metal sulfide deposition precipitated in response to mixing of hot fluids with cold seawater, such as "chimney". Because inactive chimney is potential hydrothermal deposits, it is in the spot light not only in geochemistry but in aspect of utilization as resource. For the purpose to reveal microbial community of inactive chimney, Suzuki et al.(2004), Kato et al.(2004), and Sylvan et al.(2012) powdered inactive chimney to extract 16S rRNA gene. However, at the same time, it becomes too difficult to clarify microorganisms' distribution within the chimney structures on that method.

To explore that comparison, I collected five inactive sulfide chimneys and divided them into altered and unaltered portions for microbiological and mineralogical analyses at the South Mariana Trough. For shore-based study, the powdered altered (-EX) and unaltered (-FI) portions were subjected to total cell counting and powder X-ray diffraction (XRD) pattern analysis conducted for identification of mineral constitutes. For the thin sections of intact subsamples, fluorescence in-situ hybridization (FISH) with probes targeting bacteria was performed to clarify their distribution within the chimney structures. In addition, optical microscopy with transmitted and reflected light and scanning electron microscopy (SEM) coupled to energy-dispersive spectroscopy (EDS) was conducted to correlate the extent of alteration and mineral assemblage to the distribution pattern of microorganisms.

Total cell counting revealed that cell densities ranged from 2.8×10^6 cells/ml to 1.9×10^8 cells/ml. And XRD revealed samples in which many microorganisms were harbored was majored by calcopyrite, pyrite, and marcasite. Then #1435-5 and #1437-2, that has 10^8 and 10^{6-7} scale in total cells, respectively, selected to more research by the thin section. At #1437-2-exterior, EDS revealed the main mineral component was silica and there were fewer microorganisms than #1435-5-exterior and -interior referring fluorescence. Interestingly, although metal sulfide was dominant at #1437-2-interior, there were the least total cells in all subsamples. Compared #1437-2-middle with #1435-5-middle, it was the fact that porosity on the former was apparently lower.

These results suggest that both mineral composition and porosity play important roles on total cells within inactive sulfide chimney. Specifically, microorganisms prefer living metal-sulfide-rich and high porosity section.

Keywords: hydrothermal vents, metal sulfides, microorganisms

U03-12   Room:302   Time:May 20 15:15-15:30

Fe retention fraction of paleosol as a barometer of atmospheric oxygen level

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Although various geological records indicate that there was a great rise of oxygen in the Paleoproterozoic (2.5 - 1.6 Ga) (the Great Oxidation Event, Holland, 2006), the quantitative knowledge about how oxygen increased is still unclear. The paleosols formed during the Neoarchean-Paleoproterozoic (2.8 - 1.6 Ga) can be used to strongly constrain the atmospheric oxygen levels, because they are formed by direct interactions with the contemporary atmosphere and water. Quantification of oxygen levels has been tried using Fe records, because iron is redox-sensitive element (Holland, 1984; Murakami et al., 2011). Recently, Murakami et al. (2011) demonstrated that the amount ratio of precipitated Fe(III) to dissolved Fe(II) in weathering process (the phi ratio) can be used to quantify the atmospheric levels, because the phi ratio can be converted to Fe(II) oxidation rate, which is a definite function of oxygen concentration. Although the phi ratios are useful, all the literatures of the Neoarchean-Paleoproterozoic paleosols have not always reported both Fe(II) and Fe(III) contents required to calculate the phi ratios; some literatures report only total iron contents (Fe(II) + Fe(III)), from which only the Fe retention fraction can be calculated. Although the time-transition of Fe retention fraction levels throughout the Neoarchean-Paleoproterozoic paleosols indicates qualitatively the gradual rise of oxygen (Murakami et al., 2011), quantitative use of Fe retention fraction is more desirable but not yet attempted.

Using Fe retention fraction along with those of the other major cations (Mg, Ca, Na and K) and Si, we attempted to estimate Fe(II) oxidation rate at the time of weathering. The estimation is based on (1) the mass balance of elements (Fe, Mg, Na, K and Si) between the solid and water phases and (2) the volume balance during chemical weathering, with an assumption that Fe(III) oxyhydroxides are the dominant secondary minerals of iron. The validity of the method is confirmed by reasonable agreement of the estimated Fe(II) oxidation rates based on the method with those calculated from measured phi ratios in olivine dissolution experiment under various oxygen levels conducted by Sugimori et al. (2012), although, when oxygen level is decreased, the method tends to calculate the oxidation rate higher than that calculated from the phi ratio. By application to the paleosols with known phi ratios (Cooper Lake, Pronto/NAN, Gaborone, Drakenstein and Flin Flon paleosols), we further assessed the validity. For the ~2.2 Ga Gaborne, ~2.1-Ga Drakenstein and ~1.8-Ga Flin Flon paleosols, oxidation rates estimated by phi ratios and Fe retention fractions are consistent, while for the ~2.5-Ga Cooper Lake and Pronto/NAN paleosols, again the Fe retention fraction method calculated Fe(II) oxidation rates higher than those calculated from the phi ratios. The deviation of Fe(II) oxidation rates derived from Fe retention fractions are attributed to the violation of the assumption that Fe(III) oxyhydroxides are the major secondary minerals of Fe. Under low O_2 conditions, some Fe(II)-bearing clay minerals can be also secondary minerals of Fe (MacFarlane et al., 1994). Therefore, although Fe retention fraction method cannot calculate Fe(II) oxidation rates as precisely as phi ratios when oxygen level is low, it still can give strong upper constraints on Fe(II) oxidation rates and therefore oxygen levels at the time of weathering, even for the paleosols with phi ratios unavailable.

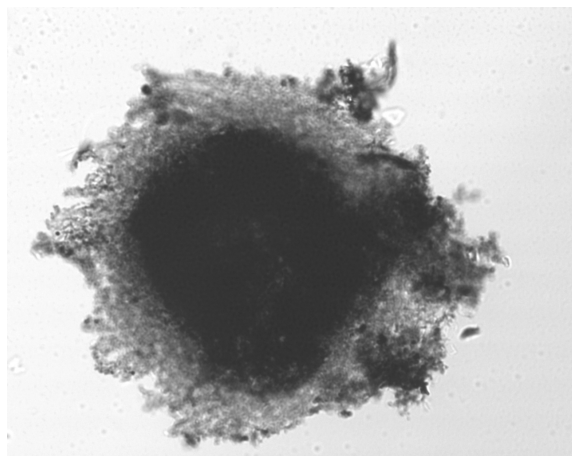Keywords: paleosol, weathering, oxygen

U03-13   Room:302   Time:May 20 15:30-16:00

Organic-walled flanged microfossils from the 3.4 Ga Strelley Pool Formation in the Pilbara Craton, Western Australia

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The Strelley Pool Formation (SPF) in the Pilbara Craton, Western Australia is known to contain well-preserved and morphologically diverse stromatolites. Recently we discovered fossil-like microstructures from the four remote localities of this formation. The structures are present in carbonaceous black chert associated with evaporite and stromatolite, at the upper horizon of SPF. They are morphologically diverse, including film-like structures (possible fragmented biofilm), spheres, filaments, and lenses. Another assemblage of possible microfossils, which are morphologically distinct from ours, was reported also from sandstones at the lower unit of SPF. The most enigmatic and thus most important microfossil type among them is the lens-like one with flange-like appendage along the equatorial plane (the photo shows the polar view). Many of them are 40 to 60 microns along the major dimension and rarely up to 120 microns, and have thickness at the center is generally 2/3 of the major dimension. Their sizes are significantly larger than those of the majority of prokaryotic cells. In addition to the solitary occurrence, the structures more commonly occur as colony-like clusters and chain-like composite structures, probably corresponding to their reproducing, one of fundamental functions of life. Carbon isotopic values of individual structures range -35 to -29 per mil. These lines of evidence indicate that the structures are genuine microfossils. More recently, we successfully extract the lens-like microfossils by acid (HF-HCl) maceration. This indicates that the microfossils have acid-resistant organic wall, which has been paleontologically regarded as an important feature of eukaryotic algae and cyanobacteria. Such the microfossils extracted by acid-maceration are called "acritarchs". Since the oldest-known acritarchs are carbonaceous spheroids discovered from 3.2 Ga siliciclastic rocks in South Africa, our study put the oldest record of acritarch back 2 billion-years. At present, unfortunately, it is difficult to specify the biological affinity of these lens-like microfossils. However, it may be mentioned that the very ancient microfossils are morphologically quite similar to "phycoma" of Prasinophyte (gleen algae) and similar microcfossils have been reported from the Paleozoic and the Proterozoic.

Keywords: Archean, Strelley Pool Formation, microfossils, chert

U03-14 Room:302 Time:May 20 16:15-16:45

Bioenergy production using subterranean microbial community associated with the accretionary prism in Southwest Japan

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The accretionary prism situated along the Pacific side of Southwest Japan is traceable laterally for some 1,800 km and forms thick sediment that accretes onto the non-subducting tectonic plate at a convergent plate boundary. The sediment is composed mainly of non- to weakly metamorphosed sequences of sandstone, shale, alternating beds of both, and local associations of chert and greenstone. The materials are derived from marine sediment scraped from the subducting oceanic crust; therefore, they are rich in complex organic matter. The sediment contains layers of water-bearing permeable sandstone and no water-bearing impermeable shale. Groundwater is mainly recharged by rainfall infiltrating into outcrops or faults. The water flows down through the permeable sandstone and is reserved in a deep aquifer. In addition to the groundwater, it has been reported that dissolved natural gases are present in the deep aquifer associated with the accretionary prism in Southwest Japan.

It is generally believed that natural gas in subsurface environments is formed by microbial production (biogenic origin), nonbiological thermal decomposition of organic matter (thermogenic origin), or geochemical reaction in hydrothermal systems during water-rock interactions (abiogenic origin). These origins have been interpreted based on chemical compositions of gaseous alkanes and stable carbon and hydrogen isotope ratios of methane.

To identify the methane production pathways present in a deep aquifer associated with an accretionary prism in Southwest Japan, a series of geochemical and microbiological studies of natural gas and groundwater derived from a deep aquifer were performed. Stable carbon isotopic analysis of methane in the natural gas and dissolved inorganic carbon in groundwater suggested that the methane was derived from both thermogenic and biogenic processes. Archaeal 16S rRNA gene analysis revealed the dominance of H_2-utilizing methanogens in the groundwater. Furthermore, the high potential of methane production by H_2-utilizing methanogens was demonstrated in enrichments using groundwater amended with H_2 and CO_2. Bacterial 16S rRNA gene analysis showed fermentative bacteria inhabited the deep aquifer. Anaerobic incubations using groundwater amended with organic substrates and methanogen inhibitor suggested a high potential of H_2 and CO_2 generation by fermentative bacteria. To confirm whether or not methane is produced by a syntrophic consortium of H_2-producing fermentative bacteria and H_2-utilizing methanogens, anaerobic incubations using the groundwater amended with organic substrates were performed. Consequently, H_2 accumulation and rapid methane production were observed in these enrichments incubated at 55^oC and 65^oC. Thus, the results suggested that past and ongoing syntrophic biodegradation of organic compounds by H_2-producing fermentative bacteria and H_2-utilizing methanogens contributes to the significant methane reserves in the deep aquifer associated with the accretionary prism in Southwest Japan.

We are currently conducting research to develop the CH_4 and H_2 production system using the groundwater and the microbial community associated with the accretionary prism in Southwest Japan. In this paper, we describe the potential and future plan of the bioenergy production system.

Keywords: accretionary prism, subterranean microbial community, methanogen, fermentative bacteria, bioenergy

Daily lamina formation by a moderately thermophilic unicellular cyanobacteria

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Travertines are calcite or aragonite precipitates from hot spring water and generally exhibit sub-mm order laminations. The lamination has been considered to be formed daily cycle by comparison between lamina thickness and depositional rate (1). Our previous investigations of day/night monitoring of texture, water chemistry and distribution of microbes suggested two processes forming the lamination by daily activities of filamentous cyanobacteria (2, 3). The different processes were confirmed from a calcite and an aragonite travertine, in which exhibit different micro-textures. Further case studies are needed to identify the variation in processes controlling the diversified travertine textures. In this study, we investigated a laminated travertine in Myoken hot spring, Kagoshima Prefecture, southwestern Japan, for specify the processes forming the sub-mm order lamination.

Myoken hot spring is one of the springs discharging along the Amori River, where is located 10 km away from Kirishima volcanoes in northern Kagoshima Prefecture. Investigated travertine at Rakuenso occurred in a mound shape with 15 m width, which was precipitated from spring water directly flowing from a vent. Following procedures of the previous studies, eight series of water and sediment samples were collected every 4 hours from November 25-26, 2012 for describing the variation in texture, water chemistry and distribution of cyanobacteria trough a day and night.

Lamination of Rakuenso travertine consisted of the light colored layers of dendritic calcite crystals with 150-250 micrometer in thickness and the dark colored layers of micritic aragonite crystals with 50-100 micrometer in thickness. Sequence of the samples showed that the dark micrite layer was formed during daytime in 50-micrometer-thick biofilm of dominated by a unicellular cyanobacterium. The biofilm covered the travertine surface only during daytime, while embedded dendritic crystals during nighttime. The embedded cyanobacteria climbing to surface at next morning and started forming a new biofilm. Phylogenetic analysis on 16S rRNA gene showed that the unicellular cyanobacterium was relatives of *Thermosynechococcus elongatus* BP-1 that is moderately thermophile having phototactic motility (4, 5). Water at the sampling point had been stable in temperature (around 55 degree C), pH and ion concentration including Mg/Ca ratio, one of the controlling factors of $CaCO_3$ polymorph. Thus, the lamination in Rakuenso travertine was formed principally by daily activities of the unicellular cyanobacteria. Precipitation of aragonite in the cyanobacterial biofilm was consistent with the results of a previous study that showed the induction of aragonite precipitation by extracellular polymeric substances (6).

Microtexture, composition of the lamination, and cyanobacterial taxa in Rakuenso travertine were different from that in the previously reported travertines under lower temperature (<40 degree C). Travertine is a potential modern analog for some ancient stromatolites due to textural similarities (7). Geomicrobiological processes demonstrated in this study will provide new insights for understanding the ancient stromatolites.

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Keywords: travertine, daily lamination, unicellular cyanobacteria

Direct observation of microbe-metal-mineral interaction by micro-XAFS-FISH technique

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Microorganisms in the environment critically impact global geochemical cycles and redox reactions of various elements. Many geochemically important redox reactions (e.g., sulfate reduction and Fe(II) oxidation) are largely associated with microbial activity. In addition, microbes can mediate mineral formation by a process called biomineralization. Recent studies suggest a significant relationship between Fe(II)-oxidizing bacteria and ancient Banded Iron Formation, one of the large geochemical events in Earth's history. The general ecological importance of environmental microbial reaction and biomineralization has been well recognized; however, the specific mechanisms of the reactions in the environments such as the reaction rate and spatial dynamics are poorly understood. In the environment such as soils, microbial reactions and habitability vary locally and form complicated geochemical networks, which makes it difficult to characterize the specific biogenic reactions in detail.

In the present study, we developed a novel method using synchrotron microprobe (micro-XAFS) combined with fluorescence in situ hybridization (FISH) to determine directly microbial communities and chemical species with high spatial resolution (XAFS-FISH), and applied it to bacteriogenic Fe oxidation in natural hot spring. We successfully conducted in situ visualization of potential Fe(II) oxidizers in Fe mats and characterization of Fe biominerals with 1-5 micrometer spatial resolution by the XAFS-FISH technique. The present study shows that coupled XAFS-FISH could be a potential technique to provide direct information on specific biogenic reaction mediated by target microorganism, even if the microbe is uncultivable species.

In my presentation, I'll talk about not only details of the XAFS-FISH technique but also its application into biogeochemical reactions of trace metal(loid)s such as arsenic in the natural environments.

Keywords: micro-XAFS, FISH, Iron-oxidizing bacteria, arsenic

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A study on the adsorption mechanism of organoarsenic compounds in soil

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Inorganic arsenic compounds are predominant cause of water-related disease of arsenic in natural systems. In addition, organoarsenic compounds, phenylarsonic acid (PAA) and diphenylarsinic acid (DPAA) were detected in well water, which is suggested to cause serious health problems in Kizaki region of Kamisu City, Japan [1]. These phenyl arsenic compounds are considered as a product of decomposition of chemical warfare agents during World Wars I and II. Recently, adsorption and mobility of these aromatic arsenic compounds in agricultural soils have been investigated [2]. However, their adsorption mechanisms on soil particles are still unknown. In general, the adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. Thus, it is important to understand the adsorption mechanism of the arsenic compounds to predict future fate of them in environment. In this study, we conducted As K-edge XAFS measurements and ab initio MO calculations for PAA and DPAA as well as methylarsonic acid (MMA) and dimethylarsenic acid (DMA) adsorbed on ferrihydrite, a strong absorbent of arsenic compounds, to determine their adsorption structures and understand the effects of substitution of organic functional groups on their adsorption. EXAFS analysis suggests that all organic arsenic compounds in this study form the inner-sphere complex with ferrihydrite regardless of the organic functional groups and the number of substitution. The As-Fe distances are ca. 3.25 A which agree with the results of ab initio MO calculations. The coordination number (CN) of the As-Fe shell was less than 2 indicating the formation of bidentate structure which was reported for the adsorption of arsenate [3]. This fact implies that the ratio of monodentate structure increases due to steric hindrance.

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Keywords: organoarsenic compound, adsorption, XAFS, quantum chemical calculation