

## Superflares on Solar-Type Stars

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Stellar flares emit harmful UV and high-energy particles such as protons. Although the atmosphere protects the surface of the planets, certain amount of UV penetrates the atmosphere and high-energy particles reach the ground as secondary radiation. These radiations are thought to affect habitability and evolution of life.

High precision photometry of Kepler spacecraft enables us to detect superflares on G-type dwarfs. By extending Maehara et al. (2012, Nature), we found 1547 superflares on 279 G-type dwarfs detected from light curves of 500 days (Shibayama et al., 2013, ApJS). In the case of the Sun-like stars (with surface temperature 5600 - 6000 K and slowly rotating with a period longer than 10 days), the frequency of superflares with energy of  $10^{34}$  -  $10^{35}$  erg (100 - 1,000 times larger than the largest solar flare) is once in 800 - 5000 years. No hot Jupiters were found in these superflare stars. These superflare stars often show quasi-periodic brightness variation, which might be evidence of the large star spot. Rotational period can be estimated from the brightness variation period. It is interesting that superflares are detected on slowly rotating stars ( $P > 10$  days) like the Sun. Using these data, we studied the statistical properties of superflares. We compare the flare frequency distribution of the superflare and solar flare, and study the similarity of them. We also found that some G-type dwarfs show very high activity and exhibit superflares once in  $\sim 10$  days. In the case of Sun-like stars, the most active stars show one superflare in  $\sim 100$  days.

Keywords: Stellar flare, Solar flare, Habitability, Evolution

## Survey Observations of A Glycine Precursor, Methylenimine (CH<sub>2</sub>NH)

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It is widely thought that prebiotic chemical evolution from small to large and complex molecules would have resulted in the Origin of Life. The interstellar medium (ISM), where more than 170 molecules ranging from simple linear molecules to COMs were detected, show chemically rich environment. Ehrenfreund et al. (2002) argued that exogenous delivery of COMs to the early Earth by comets and/or asteroids could be more than their terrestrial formation by two orders of magnitude; molecules delivered from the Universe might have played an important role in early Earth chemistry. From this point of view, many observations were conducted to search for prebiotic molecules in the ISM, which might turn into the “ Seeds of Life ” when delivered to planetary surface. Especially, great attention was paid to amino acids, essential building blocks of terrestrial life; many surveys were made unsuccessfully to search for the simplest amino acid, glycine (NH<sub>2</sub>CH<sub>2</sub>COOH), towards Sagittarius B2 and other high-mass star forming regions (e.g., Brown et al. 1979; Snyder et al. 1983; Combes et al. 1996, ...).

In these days, the Atacama Large Millimeter/submillimeter Array (ALMA) is expected to break through such difficulties associated with glycine survey. Garrod (2013) used her chemical reaction network simulation and argued the possibility in detecting glycine with very high spatial resolution (~0.1 ″) and the collecting power of ALMA. It would be important to know which are potential glycine-rich sources for future surveys. However, the chemical evolution of N-bearing molecules, including glycine, is poorly known. We would need to better understand formation mechanisms of N-bearing COMs including amino acids and to have carefully selected good candidate sources for amino acids before conducting searches for amino acids by ALMA.

Although the chemical evolution of interstellar N-bearing COMs is poorly known, methylamine (CH<sub>3</sub>NH<sub>2</sub>) has been proposed as a precursor to glycine. Theoretical and laboratory studies have demonstrated that glycine is formed on icy grain surface from CH<sub>3</sub>NH<sub>2</sub> and CO<sub>2</sub> under UV irradiation (Holtom et al. 2005). It is suggested that CH<sub>3</sub>NH<sub>2</sub> can be formed from abundant species, CH<sub>4</sub> and NH<sub>3</sub>, on icy dust surface (Kim & Kaiser 2011). Further methyleneimine (CH<sub>2</sub>NH) would be related to CH<sub>3</sub>NH<sub>2</sub>. Another possible route to form these species is hydrogenation to HCN on the dust surface (Dickens et al. 1997; Theule et al. 2011).

However, a source number of such precursor molecules is very limited. In order to increase the number of CH<sub>2</sub>NH sources and to better understand formation paths to CH<sub>2</sub>NH, we conducted survey observations of CH<sub>2</sub>NH, with the NRO 45 m telescope and the SMT telescope towards 11 high-mass and three low-mass star-forming regions. As a result, CH<sub>2</sub>NH was detected in eight sources, including four new sources. The estimated column densities were roughly 10<sup>14</sup>-10<sup>15</sup>, 10<sup>15</sup>-10<sup>16</sup>, and 10<sup>16</sup>-10<sup>17</sup> cm<sup>-2</sup>, respectively, for extended, 10 ″, and 2 ″ sources. G10.47+0.03 and Orion KL are found to be especially CH<sub>2</sub>NH-rich sources. We used chemical reaction network simulations to investigate formation process of CH<sub>2</sub>NH in the ISM. Under the dark cloud condition, the simulated CH<sub>2</sub>NH abundance in the gas phase is more than 10 times lower than our observations even if we conservatively estimate the CH<sub>2</sub>NH abundance with an extended source. On the other hand, if we include hydrogenation reaction to HCN in our model, the CH<sub>2</sub>NH abundance increased about by two orders of magnitude, enabling us to reconcile the observed abundance of CH<sub>2</sub>NH. We also showed that this reaction is dominant in the early, low temperature phase of cloud evolution.

Keywords: Origin of Life, Chemical Evolution, Interstellar Medium, Glycine

## Formation, alteration and delivery of interstellar organics: Verification with experiments on ground and in space

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As a wide variety of organic compounds have been found in meteorites and comets, their relevance to the origin of life is discussed. Many kinds of amino acids have been identified in extracts of carbonaceous chondrites, their origin is controversial. Possible carriers of organic compounds to the Earth were meteorites, comets and interplanetary dust particles (IDPs). It is said that IDPs could deliver organics more safely than meteorites and comets, the nature of organics in IDPs are little known since they have been collected usually in terrestrial biosphere. In addition, IDPs are directly exposed to cosmic and solar radiation, which might destroy organics in IDPs.

When possible interstellar media (a mixture of carbon monoxide or methanol, ammonia and water) was irradiated with high-energy particles, amino acid precursors were formed in high energy yields. We are planning to irradiate possible interstellar media with high energy heavy ions from a newly developed Digital Accelerator in KEK to confirm it. It suggested that amino acid precursors could be formed in interstellar space in prior to the formation of the solar system. Before the incorporation of interstellar organic compounds into comets or parent bodies of meteorites, they could be altered with high energy photons from the young Sun. Soft X-rays irradiation of simulated interstellar organics resulted in the formation of hydrophobic compounds as seen in comets.

We are planning a novel astrobiology mission named Tanpopo by utilizing the Exposed Facility of Japan Experimental Module (JEM/EF) of the International Space Station (ISS). Two types of experiments will be done: Capture experiments and exposure experiments. In the exposure experiments, organics and microbes will be exposed to the space environments to examine possible alteration of organic compounds and survivability of microbes. Selected targets for the exposure experiments of organic compounds are as follows: Amino acids (glycine and isovaline), their possible precursors (hydantoin and 5-ethyl-5-methyl hydantoin) and complex precursors (CAW) synthesized from a mixture of carbon monoxide, ammonia and water by proton irradiation. In capture experiments, we will collect space dusts by using ultra-low density silica gel (aerogel), and will analyze them after returning them to the Earth. Amino acid enantiomers will be analyzed after HF digestion and acid hydrolysis, as well as characterization of complex organic compounds in space dusts. The mission is planned to be started in 2015.

Keywords: origins of life, interstellar organic compounds, cosmic rays, interplanetary dust particles, Tanpopo Mission, particles irradiation

## Polymerization of methionine: Ignition of sulfur metabolism?

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Methionine, sulfur-bearing amino acid, is one of protein-forming 20 amino acids. On the other hand, peptide formation using methionine is known to be difficult, because of large thermal stability of methionine. Incorporation of methionine into peptide has importance to form metal-sulfur-cluster in protein or other biologically important molecules, such as taurine. In order to overcome difficulties to make methionine-bearing peptide, new series of experiments were performed in the present study. Experiments were performed at 175 C and 150 MPa, using various mixtures. Methionine-trimers, which were not formed by previous investigators, were produced in the present study. Surprisingly a part of methionine was converted into glycine and then glycine-methionine peptide was newly formed. Those results demonstrated that high T and P conditions were suitable for not only methionine-peptide formation but also making multi-component peptide. Sulfur isotope compositions were determined on run products of the present study. Run products were enriched or depleted in <sup>32</sup>S compared to starting materials. Hydrogen sulfides were preferentially released from methionine for the <sup>32</sup>S-depleted samples. The <sup>32</sup>S-enriched samples are explained by loss of sulfate from methionine, although oxidants of methionine-sulfur are still unclear. Modern living organisms metabolically produce sulfide and sulfate from methionine and cysteine. Such metabolic path is similar to the abiological production of sulfide and sulfate in the present study. This may imply that course of sulfur metabolism was most likely established early in the prebiotic age when methionine was incorporated in prebiotic protein.

Keywords: prebiotic, methionine, peptide, sulfur

## Formation of extraterrestrial oceans: Cradles of life

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As one of research groups on "Astrobiology in the Solar System" (a proposal submitted to MEXT), our group will study the origin of icy satellites around giant planets, and the origin and evolution of the interior ocean(s) of those icy bodies and their universality. Outside the so-called snowline of H<sub>2</sub>O, the mass of protoplanets could be large enough to collect surrounding gas rapidly to form massive gaseous giant planets. Icy satellites would have been formed or trapped by the circumplanetary gas disks around giant planets. In multisatellite cases, orbital resonances may stabilize satellite migration and tidal dissipation would provide heat for sustaining interior oceans. Even when surface temperature is lower at a further distance from the sun, additional ice component (NH<sub>3</sub>, CH<sub>4</sub>, CO, etc.) would decrease the melting temperature. As a result, the more extended condition for presence of liquid water can be considered in comparison with the conventional habitable zone (with surface water).

Keywords: icy satellites, habitability, interior ocean, habitable zone, gas giant planets, origin of planetary systems

## Tanpopo: Astrobiology Exposure and Micrometeoroid Capture Experiments - Experiments at the Exposure Facility of ISS-JEM

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Tanpopo, a dandelion in Japanese, is a plant species whose seeds with floss are spread by wind. We propose this mission to examine possible interplanetary migration of microbes, and organic compounds at the Exposure Facility of Japan Experimental Module (JEM: KIBO) of the International Space Station (ISS). The Tanpopo mission consists of six subthemes: Capture of microbes in space (Subtheme 1), exposure of microbes in space (Subtheme 2), analysis of organic compounds in interplanetary dust (Subtheme 3), exposure of organic compounds in space (Subtheme 4), measurement of space debris at the ISS orbit (Subtheme 5), and evaluation of ultra low-density aerogel developed for the Tanpopo mission (Subtheme 6). 'Exposure Panel' for exposure of microbes and organic materials and 'Capture Panels' for capturing micro particles with aerogel will be launched. The panels will be placed on the Exposed Experiment Handrail Attachment Mechanism (ExHAM) in the ISS. The ExHAM with the panels will be placed on the Exposure Facility of KIBO (JEM) with the Japanese robotic arms through the airlock of KIBO. The panels will be exposed for more than one year and will be retrieved and returned to the ground for the analyses.

Keywords: Panspermia hypothesis, Microbes, Organic compounds, Aerogel, Space exposure experiments

## Rock Magnetic Constraints on the origin of putative biological magnetite in the Martian ALH84001 Carbonates

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McKay et al. (1996) discussed 4 lines of evidence that were consistent with the possible presence of ancient life on Mars. Although none of these have been falsified, the one that has triggered the most intense debate concerns the claim that some of the fine-grained magnetite crystals embedded in small carbonate deposits might have been formed by the magnetotactic bacteria. These magnetite particles, when examined by high-resolution transmission electron microscopy, are indistinguishable from particles only produced by magnetotactic bacteria on Earth (Thomas-Keprta et al., 2001). Unfortunately, the magnetic and microscopic analyses done to date do not allow us to provide a direct statistical test of the probability that these particles are of biological origin, vs. the hypothesis they form from high-temperature decomposition of siderite (FeCO<sub>3</sub>).

In the past decade, developments in superconducting magnetometry and electron microscopy now provide new experimental approaches that can be applied to this problem. First, the new Ultra-High Resolution Scanning Magnetic Microscopes (UHRSMs) can detect magnetic moments 3 to 4 orders of magnitude below the sensitivity of the best superconducting rock magnetometers, and robust dipole-fitting routines allow the 3-D vector magnetic moment of tiny particles to be resolved quantitatively. We have shown recently that individual fragments of the famous ALH84001 carbonate blebs can be imaged clearly using this technique, opening the possibility of experimental tests that should distinguish low-temperature (biological) from high-temperature (thermal decomposition) magnetite. Magnetite produced by thermal decomposition of carbonate during shock heating should carry a relatively strong Thermo-Remanent Magnetization (TRM), whereas biological magnetite trapped during carbonate growth should have a much weaker detrital magnetization (DRM). Fuller et al. (1988) reported a simple technique that compares the relative intensities of the Natural Remanent Magnetizations (NRMs) to Isothermal and Anhyseretic magnetizations (IRMs and ARMs) that can easily distinguish TRMs from DRMs; this new sensitivity now be applied to these particles. Second, because the magnetotactic bacteria use genetic control to manufacture their magnetite crystals, particles within the same cell are of very similar size and shape. When these cells die and leave their magnetite crystals in the sedimentary record as magnetofossils, they produce clumps of similarly-sized crystals because they stick together magnetically with very strong force (Kobayashi et al., 2006). Sediment transport and removal processes cannot disaggregate them, but they do get scrambled together during extraction and high-resolution TEM studies. We therefore need to do very high-resolution studies that can demonstrate the position of these crystals within the carbonate matrix of the ALH 84001 carbonate precipitates. We propose to use the new focused ion-beam (FIB) milling techniques available at the Earth-Life Science Institute of TiTech to make 3-dimensional reconstructions, at a 5 to 10 nanometer scale, of rectangular chunks of the ALH84001 carbonate. At this resolution, the putative magnetosomes will be represented by up to 500 voxel elements, each with definitive elemental composition. We should be able to determine whether clusters of particles within these carbonates are of similar size and shape, as expected from collapsed magnetosome chains. It will then be very simple to do statistical tests to determine whether these clumps are non-random assemblages sampled from the background crystal size distribution. The debate about life on Mars may rise again!

Fuller et al.,1988, *Geophys. Res. Lett.*, v. 15, p. 518-521.

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Keywords: Martian Magnetofossils, Rock Magnetism, Panspermia, Carbonate

## Cu-Zn ores in 2.7 Ga komatiite-basalt assemblages in Abitibi Greenstone Belt, Canada, and their associations to microbes

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Archean greenstone belts are hosting many massive sulfide ores. In particular, komatiite-basalt sequences are hosting Ni-Cu ores, which are mostly considered as a magmatic in origin. Some Ni-Cu ores are associated with serpentinization near seafloor. Such serpentinization may have been important for early life as hydrogen donors with alkaline fluids. Cu-Zn-Pb ores are also reported from the same komatiite-basalt sequences, although the origin of these ores are still uncertain. One representative 2.7 Ga komatiite-basalt sequence appears in the Munro area of the Abitibi Greenstone Belt. In order to understand the origin of Cu-Zn-Pb ores, mineralogical and geochemical studies are performed on ores at Munro area. Sulfide ores are essentially developed in black shale zones, and some ores are disseminated in altered volcanic rocks. Chalcopyrite, sphalerite, pyrrhotite are major minerals associated with minor galena, electrum, pentlandite, etc. Sulfur isotope compositions of those sulfides are ranging are not magmatic values. Some ores are rich in Se and As. Host volcanic rocks are extensively hydrated (followed by metamorphism) forming tremolite, chlorite and talc. Those features are similar to the modern submarine hydrothermal deposits, rather than magmatic ore deposits. Therefore, Cu-Zn-Pb ores in komatiite-basalt sequences were formed by black smoker type submarine hydrothermal activities. Carbon isotope analyses of organic matter in ore-associated sediments suggest that methanogens were active when komatiite became serpentinite, followed by submarine hydrothermal activities.

Keywords: Komatiite, ore, submarine, Abitibi, microbe

## Microbial community development in deep-sea hydrothermal vents in the Earth, and the Enceladus

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Over the past 35 years, researchers have explored seafloor deep-sea hydrothermal vent environments around the globe and studied a number of microbial ecosystems. Bioinformatics and interdisciplinary geochemistry-microbiology approaches have provided new ideas on the diversity and community composition of microbial life living in deep-sea vents. In particular, recent investigations have revealed that the community structure and productivity of chemolithotrophic microbial communities in the deep-sea hydrothermal environments are controlled primarily by variations in the geochemical composition of hydrothermal fluids. This was originally predicted by a thermodynamic calculation of energy yield potential of various chemolithotrophic metabolisms in a simulated hydrothermal mixing zone. The prediction has been finally justified by the relatively quantitative geomicrobiological characterizations in various deep-sea hydrothermal vent environments all over the world. Thus, there should be a possible principle that the thermodynamic estimation of chemolithotrophic energy yield potentials could predict the realistic chemolithotrophic living community in any of the deep-sea hydrothermal vent environments in this planet. In 2005, a spacecraft Cassini discovered a water vapour jet plume from the sole pole area of the Saturnian moon Enceladus. The chemical composition analyses of Cassini's mass spectrometer strongly suggested that the Enceladus could host certain extent of extraterrestrial ocean beneath the surface ice sheet and possible ocean-rock hydrothermal systems. An experimental study simulating the reaction between chondritic material and alkaline seawater reveals that the formation of silica nanoparticles requires hydrothermal reaction at high temperatures. Based on these findings, we attempt to build a model of possible hydrothermal fluid-rock reactions and bioavailable energy composition in the mixing zones between the hydrothermal fluid and the seawater in the Enceladus subsurface ocean. The physical and chemical condition of the extraterrestrial ocean environments points that the abundant bioavailable energy is obtained maximally from redox reactions based on CO<sub>2</sub> and H<sub>2</sub> but not from with other electron acceptors such as sulfate and nitrate. In the low-temperature zones, the available energy of the Enceladus methanogenesis and acetogenesis is higher than those in any Earth's environment where the methanogens sustain the whole microbial ecosystem. Our model strongly suggests that the abundant living ecosystem sustained by hydrogenotrophic methanogenesis and acetogenesis using planetary inorganic energy sources should be present in the Enceladus hydrothermal vent systems and the ocean.

## Light absorption and energy transfer in photosynthesis: Toward extending our current biosignatures

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In the recent success in detecting for extrasolar planets, several habitable planets, which can sustain liquid water, have already been discovered. From reflection spectra on exoplanets, what and how to detect signs of life, biosignatures, have been controversial (Kiang et al. 2007). One of proposed biosignatures is vegetation red edge (VRE), which is observed from reflectance spectra on the Earth. VRE is identified as a sharp contrast in about 700 - 750 nm due to the absorption in visible region by photosynthetic pigments like chlorophylls and the reflection in NIR region. However, VRE is an effective as biosignature only if exovegetation shows the same spectral feature to that on the Earth (Seager et al. 2005). Therefore, the criterion as biosignature needs to be extended when the primary stars are totally different. Because in future missions searching for a second earth, the M type stars (cooler than Sun) will be the main targets, as the first step, we focused on the fundamental properties of purple bacteria which absorbs longer wavelength radiation (1025 nm).

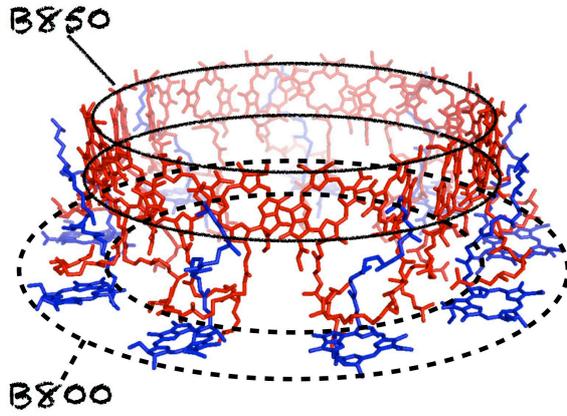
We investigated light absorptions and excitation energy transfers (EETs) based on quantum dynamics simulations for light harvesting complexes (LHCs), which contain array of photosynthetic pigments. After light reaches in LHCs, effective EET is accomplished by cooperative electronic excitation of the pigments. We used theoretical models for LHCs in purple bacteria (LH2s). LH2 is made of 2 rings: inner ring (B850) and the outer (B800), as shown in Figure. In our model, a dipole-dipole approximation was used for the electronic excitations. The low-lying electronic excited states of a LH2 were computed by using transition dipole moment of first excited state of each pigment calculated at time-dependent density functional theory. Corresponding to the light absorption process, the oscillator strength in the system could be computed. The oscillator strength of one LH2 was in a good agreement with the experimental value. Subsequently, quantum dynamics simulations were performed by Liouville equation to examine the EET process. In this model, the densities relaxed according to energy gradient. This treatment corresponded with the EET process. The relaxation parameters were determined based on the energy transfer time from B800 to B850 (0.8 ps). The calculated transfer time between two LH2s was determined to 2.72 - 3.67 ps in good agreement with the experiment values (2.0 - 10.0 ps). In order to deal with more realistic system, we calculated at a macro structural model. The calculated systems were composed of 7 LH2s and 19 LH2s, where LH2s were aligned in triangle lattice. As the system size increases, the oscillator strength shifted longer and the transfer velocity became faster. In photosynthesis, collected energies are efficiently transferred to lower energy sites where redox reactions take place, very efficiently by EET. When two pigments in central LH2 in the system were exchanged to pigments absorbed longer wavelength radiation (850 nm to 890 nm), the transfer velocities became faster. Moreover, in order to examine for what environments the absorption spectra of purple bacteria were optimized, the absorption efficiency was calculated from blackbody spectra expected in typical extrasolar planets. As a result, the absorption efficiency was maximum at the emission spectrum of a black body at around 200 K. Furthermore, the Light absorptions and EETs in purple bacteria, cyanobacteria and plants will be examined by using our methodology.

Keywords: biosignatures, extrasolar planets, photosynthesis, quantum chemical calculation, light harvesting, purple bacteria

BAO01-10

Room:502

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## Ancient Habitable-Trinity Mars and Future Targeting of potential Signs of Life

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Mars, the most Earth-like planet in our solar system, once had Habitable-Trinity conditions: an interfacing ocean, atmosphere, and nutrient-enriched primordial crustal materials with energy circulation driven by the Sun. Mars is thus considered the best target to search for life beyond Earth, as there are no other planetary bodies in our solar system that record Habitable-Trinity conditions. Following the termination of Habitable Trinity conditions nearly 4.0 Ga, when a strong dynamo shut down prior to the post-heavy-bombardment Hellas and Argyre impact events, the atmosphere was thinning, and plate tectonism was ongoing though waning, life would have found it increasingly difficult to survive at or near the surface, and thus would have migrated to the subterranean to persist. Vent structures, such as those located in the western part of Elysium Planitia where oceans once occupied the Martian surface and long-term magma-water interactions (billions of years) may be still ongoing, as evidenced through pristine lavas, faults that cut youthful surfaces, and geologically-recent flood events, are thus considered to be optimal targets to search for signs of life on Mars. The vent structures were formed by the transferal of subterranean materials to the surface likely due to magma-water interactions. The geologically youthful vent structures could be readily investigated in situ through current mission design.

Keywords: Habitable Trinity, potential signs of life

## Origin of life component of the Earth

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The Earth is highly depleted in volatile in general. Water is one of them and only 0.023wt% among mass of the solid Earth. If the parental chondrite is carbonaceous with 2.3wt% water, the Earth must have been covered by 380km thick ocean, where too much amount of water was present, hence no life was born because of no supply of nutrients (Maruyama et al., 2013). Origin of water is critical to control the birth of life on rocky planet. Snowline is a concept of the boundary whether solid ice or vapor (gas) is stable at 2.7AU. If the Earth was formed at 1.0AU, the Earth must have been dry, no atmosphere and no ocean.

By this reason, there are several ideas to make the Earth with thinly covering ocean. One of such ideas is that Earth was born as a dry planet with Moon at 4.5-4.6Ga, followed by late bombardments to transport water components to the Earth at 4.4Ga (Maruyama et al., 2013).

Here we propose that late bombardment delivered not only water component but also carbon and nitrogen together at 4.4Ga. The organic lines are present within a narrow region around 2.1AU which is much closer to the Earth than the snowline. Asteroids derived from chondritic materials were transported to the Earth at 4.4Ga, and their organic matters turned to be primordial atmosphere from which primordial ocean was born. C and N with respect to O and H are enriched to make reduced atmospheric composition which could be favorable to synthesize complex organic compounds at the interface between atmosphere and ocean.

## Theoretical investigation of amino acid formations on interstellar dusts

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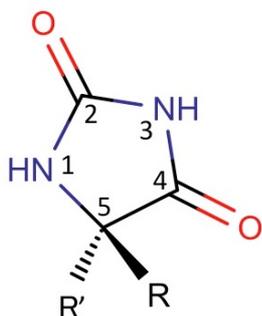
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Molecular evolution in the interstellar space remains unsolved. Formations of molecules in space have been extensively studied by experiments and space observations. Formations of complex organic molecules are expected in the interstellar space. In fact, some amino acids were found in meteorites and amino acids were detected after UV irradiation of interstellar ice analogs.

In the amino acid formation in space, many precursors and molecular evolution pathways are expected. Among these possible pathways, it is very important to know the energy profiles and molecular structures in the major formation pathways. In this study, possible amino acid formation pathways are investigated by using accurate quantum chemistry methods at the density functional theory levels.

Two formation pathways of glycine and alanine were examined: (1) hydrolysis of aminoacetonitrile and (2) hydrolysis of hydantoin derivatives. In the aqueous solution model, Polarizable Continuum Model was used.

Calculated formation energy of glycine is the most stable in the formation pathway in vacuum and no excessively stable intermediates existed. In aqueous solution, hydantoin pathway was slightly unstabilized. In conclusion, glycine production is considered to be occurred easily if the components exist. Similar trend is expected for the alanine production.



## Cosmic dusts capture on the International Space Station: Progress of the ground-based experiment

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**Introduction:** Organic matter in interplanetary dust particles (IDPs) records the primitive chemical history in the early Solar System as well as it is thought to have delivered the building blocks of life to the early Earth (Chyba and Sagan, 1992). The Japanese Astrobiology working group, Tanpopo, is planning to collect the IDPs using a low-density silica aerogel (0.01 g/cm<sup>3</sup>) (Tabata et al. 2011) on the International Space Station (Yamagishi et al. 2009). The mission has a great advantage that collection of the pristine IDPs without atmospheric entry heating and terrestrial contamination will be expected. One thing that has to be considered is a possible modification of the chemical composition of organic matter in IDPs upon their high velocity impact to the aerogel. This issue has been also concerned in the Stardust cometary dust sample return mission. Although the laboratory simulations have been conducted to study the alteration of minerals (Okudaira et al. 2004; Noguchi et al. 2007), the alteration of organics under a realistic condition has not been well understood. As a ground-based experiment, we have conducted a laboratory experiment of aerogel capture of Murchison meteorite powder at 4 km/s using a two-stage light gas gun, in order to evaluate the extent of modification of organic matter in the meteorite.

**Experimental:** The Murchison meteorite powder (~500 ug) of a particle diameter of 30-100 um in a polycarbonate sabot was shot at ~4 km/s using a two-stage light gas gun at JAXA/ISAS. The penetrations of the meteorite powder formed ~70 tracks of ~10 mm length in aerogel. Six terminal particles were extracted from the aerogel tracks using a tungsten needle and were pressed between two Al foils. The particles on the Al foils were analyzed by micro-Fourier transmission infrared (FTIR) spectroscopy at the beamline 43IR, Spring-8 and Osaka Univ., and micro-Raman spectroscopy at Osaka Univ. For a comparison, pre-shot Murchison meteorite powder was analyzed by these micro-spectrometers.

**Results and discussion:** The IR imaging detected the regions of absorptions of aliphatic carbons, CH<sub>3</sub> at 2960cm<sup>-1</sup> and CH<sub>2</sub> at 2920cm<sup>-1</sup> within the two Murchison terminal particles captured by aerogel. Thus, organic matter is survived through the high velocity impact at 4 km/s. The spectral intensities of aliphatic carbons in the terminal particles are slightly lower than those in the pre-shot Murchison meteorite. CH<sub>2</sub>/CH<sub>3</sub> ratios obtained from the IR spectra of the terminal particles were 0.3 ? 3, while those of the pre-shot sample were 1.3 ? 2. The difference in the ratios may be reflected by modification of aliphatic chains of organic macromolecules in the meteorite, e.g., demethylation, methylation, or cracking, due to the high velocity impact heating. From the two terminal particles, D- and G- bands, which are derived from carbonaceous matter, were detected by micro-Raman analyses. Peak widths and positions of the two bands showed similar values to those for pre-shot Murchison meteorite. Thus, modification of aromatic structures after the aerogel capture is unlikely. Although relative amounts of organics were low in the four other terminal particles, this may be reflected by original heterogeneity of the meteorite.

**Keywords:** International Space Station, Cosmic dusts, Organic matter, Astrobiology, Origin of life, Aerogel

## Possibility of production of amino acids by impact reaction using a light-gas gun as a simulation of asteroid impacts

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We are interested in the production process of amino acids in space. Especially, asteroids coming to Titan satellite have made impact reaction on the surface including nitrogen gas, water ice and methane. On the Titan surface, various material, produced by the impact reactions, have been stored under low temperature and dark condition. To do the simulation experiment, a JAXA 2-stage light-gas gun has been used. A projectile with 6.5km/s of speed hits a water + iron target in 1 atm of nitrogen gas, causing an impact reaction. Figure 1 shows a crater on the target. Figure 2 shows produced black soot which deposited onto the aluminum sheet. The samples produced are carefully collected and analyzed by HPLC, FTIR, TOF-MS. As a result of HPLC, peaks suggesting the existence of glycine and alanine in the samples produced were confirmed.

Keywords: impact reaction, gas gun, Titan, asteroid, amino acid, HPLC



Fig.1 A crater on the target.



Fig.2 Produced black soot deposited onto the aluminum sheet.

## Amino acid formation from simulated mildly-reducing primitive atmospheres by spark discharges and proton irradiation

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Miller (1953) reported that amino acids were abiotically formed in a gas mixture of methane, ammonia, hydrogen and water. However, it is suggested that the primitive Earth atmosphere was less reducing, and its major components were carbon dioxide and nitrogen. It is quite difficult to form amino acids from such non-reducing gas mixtures. If it is mildly reducing, i.e. it contained some carbon monoxide or methane, amino acid production could be expected.

We examined possible formation of amino acids from mildly reducing gas mixtures by spark discharges or by proton irradiation. A mixture of carbon dioxide and methane (total 50 %) and nitrogen (50 %) was introduced into a glass tube with liquid water. Spark discharges in the gas mixtures were performed with a Tesla coil for 12 hours. Proton beams (2.5 MeV, 2 mC) were irradiated to the gas mixtures from a Tandem accelerator (TIT). The resulting products were acid-hydrolyzed, and amino acids were determined by ion-exchange HPLC with post-derivatization with o-phthalaldehyde and N-acetyl-L-cystein.

A mixture of methane and nitrogen gave amino acids in high yields by either spark discharges or proton irradiation. When carbon dioxide was added to the gas mixture, amino acid yields decreased. In the case of spark discharges, amino acids could not be detected when methane ratio in total carbon sources (carbon dioxide + methane) was less than 30 %. In the case of proton irradiation, the mixture with the methane ratio was 5 % still gave amino acids. Thus, it was suggested that, in the case that the primitive Earth atmosphere was only slightly reducing, a major energy source for the production of amino acids was not thundering but cosmic rays.

Keywords: mildly-reducing primitive atmospheres, spark discharge, proton irradiation, origins of life, amino acids

## Stability and reactions of amino acids in simulated submarine hydrothermal systems

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The discovery of hydrothermal systems in the late 70s brought a new hypothesis to the origin of life. Previously, the Urey-Miller experiment had made waves in this new field, indicating that a reducing atmosphere could form amino acids from basic chemicals. The further discovery of hydrothermal systems with earth prebiotic conditions added another notion to the field. Since then, different kinds of simulation were conducted to test the hypothesis. Initially and autoclave was extensively used due to its robustness and durability, however this system was not an ideal system, hence a flow-type simulator was proposed instead. We tested the stability and reaction of several amino acids using a flow reactor simulating submarine hydrothermal systems at 200—250 °C. This study generally showed that there is a variation in the individual amino acids survivability in the simulators. This is mainly attributed to the following factors; heat time, cold quenching exposure, metal ions and also silica. We observed that, in a rapid heating flow reactor, high aggregation and/or condensation of amino acids could occur even during a heat exposure of 2 min. We also monitored their stability in a reflow-type of simulator for 120 min at 20 min intervals. The non-hydrolyzed and hydrolyzed samples for this system showed a similar degradation only in the absence of metal ions. We also tested the possible condensation that could be forming peptide bonds among the amino acids in one of the flow reactors. We utilized the Lowry protocol to determine the concentration of the peptide bonds in several hydrothermal temperatures. Concentration of peptide bonds was significantly higher when the temperature was at 300 °C. This is despite the decomposition of amino acids by more than half. However, the contribution of peptide bonds in the combined amino acids was less than 10%, even in the 300 °C sample, which showed the highest contribution of peptides. The major heat products were non-peptide amino acid condensates (NPACs) that only possess partial peptide bonds. The role of NPACs should be examined though they were often ignored in the classical chemical evolution scenario so far.

We experimented with Gly, Ala, Asp and Val in the SCWFR at 200 °C, 250 °C and 300 °C. We recorded the recovery of the samples and performed the Lowry method to quantify the peptide bond concentration. Peptide bonds' concentrations are significantly higher when the temperature is at 300 °C. This is despite the decomposition of amino acids by more than half. The highest peptide bond concentration among the samples constitute only about 10% of the total product yield of the amino acid mixture.

We also examined possible formation of amino acid condensates by using single amino acid (Gly, Ala, Asp or Val) and compared the results with those with all of four amino acids.

Keywords: submarine hydrothermal systems, amino acids, origins of life, flow reactor

## Scanning electron microscopic observation of organic microspherules formed by Maillard-type reaction

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It has been suggested that organic microspherules played a role as a physical container to maintain catalytic molecules and their reaction intermediates at concentrations high enough to sustain catalysis in prebiotic chemistry on the early Earth (Weber, 2005). Experimental studies on the formation of organic microspherules from a variety of organic compounds, such as amino acids (Fox and Harada, 1958), gelatin and gum arabic (Oparin, 1976), organic extracts from meteorite (Deamer, 1985; Deamer and Pashley, 1989), interstellar organic analogue (Dworkin et al. 2001), fatty acids and polycyclic aromatic hydrocarbons (Groen et al. 2012), formaldehyde and ammonia (Cody et al. 2009; Kebukawa et al. 2013) have been reported. However, the formation process and stability of these organic microspherules have been unexplored. In this study, sizes, shapes, and distributions of organic microspherules formed during the progress of Maillard-type reaction of formaldehyde and ammonia were investigated.

### Experimental:

Paraformaldehyde (120mg), glycolaldehyde (120mg), ammonium hydroxide (54ul), calcium hydroxide (30mg) in 2ml of water in a glass tube was heated at 50-90 degrees C for 71-720 hours. For comparison, the samples without ammonium hydroxide were heated under the same conditions. After heating, the sample solutions were centrifuged. The precipitated material were rinsed with 2N HCl to dissolve calcium, and dried at 50 degrees C to obtain organic solids. The organic solid samples were pressed on a indium plate, gold-coated, and observed by a scanning electron microscopy (SEM).

### Results and discussion:

After several minutes in heating, all the sample solutions turned yellow and eventually turned brown to black. Organic solids were produced at 90 degrees C but 50 degrees C. The yields of organic solids from sample solutions with ammonia were 10 times higher than those without ammonia. The yields gradually increased during heating. While distorted-shaped aggregates are produced from the samples heated for 71-120 hours, micron-sized organic microspherules (0.4-4.0 um) were observed from those heated for 240-720 hours. The samples with ammonia show perfectly round shapes of microspherules. Some microspherules are large and oval in the sample heated for 480 hours. The sizes of the microspherules increased with heating time. Organic solids produced by the same reaction as this study's at 90 degrees C for 72 hours consist of approximately equal abundances of aromatic and aliphatic carbons (Kebukawa et al. 2013). This molecular composition could result in amphiphilicity that is related to formation of the stable microspherules observed in this study. Formaldehyde and ammonia are thought to have been commonly present on the early Earth, and thus the organic microspherules formed by these molecules which proceed polymerization efficiently under mild conditions, could have played a role as a precursor of prebiotic cell membrane.

Keywords: organic microspherules, Maillard reaction, prebiotic cell membrane

## Fluorescence imaging of microbe-containing micro-particles that had been shot from a two-stage light-gas gun into an ult

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We previously proposed an experiment (the Tanpopo mission) to capture microbes and organic compounds on the Japan Experimental Module of the International Space Station. An ultra low-density silica aerogel will be exposed to space for one year. After retrieving the aerogel, particle tracks and particles found in it will be visualized by fluorescence microscopy after staining it with a DNA-specific fluorescence dye. In preparation for this study, we simulated particle trapping in the aerogel so that methods could be developed to visualize the particles and their tracks. During the Tanpopo mission, particles that have an orbital velocity of about 8 km/s are expected to collide with the aerogel. To simulate these collisions, we shot *Deinococcus radiodurans*-containing Lucentite particles into an aerogel from a two-stage light-gas gun (acceleration 4.2 km/s). The shapes of the captured particles and their tracks and entrance holes were recorded with a microscope/camera system for further analysis. The size distribution of the captured particles was smaller than the original distribution, suggesting that the particles had fragmented. We were able to distinguish between microbial DNA and inorganic compounds after staining the aerogel with the DNA-specific fluorescence dye SYBR green I as the fluorescence of the stained DNA and the autofluorescence of the inorganic particles decay at different rates. The developed methods are suitable to determine if microbes exist at the International Space Station altitude.

Keywords: Aerogel, Space experiment, Hypervelocity impact experiment, DNA-specific fluorescence dye.

Keywords: Aerogel, Space experiment, Hypervelocity impact experiment, DNA-specific fluorescence dye

## Studies on life detection methods by using enzymatic activities: Phosphatase and Catalase

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We have recognized that microorganisms can survive in such extreme environments as polar environments, deserts, hot springs and stratosphere. It is quite difficult to evaluate microbial activities in extreme environments, since most microorganisms in extreme environments are hard to cultivate. We are discussing how to detect microorganisms in extreme environments including Mars. In MELOS mission, a proposed Japanese Mars exploration, fluorescence microscope will be applied to life detection. In addition to the technique, we examined amino acid analysis and enzyme assay as possible chemical strategies for life detection in terrestrial and extraterrestrial extreme environment.

One of the most well studied enzymes in environments is phosphatase. Phosphatases hydrolyze phosphate esters to produce phosphate that is essential for terrestrial life, and they are known to be stable in environments. We assayed rocks and soils in extreme environments such as submarine hydrothermal core samples and Antarctic soil samples, and found that it can be a good indicator for microbial activity. Here we analyzed phosphatase activity in Atacama Desert soil samples. Atacama desert is known to be one of the driest and harshest environments on the Earth, and regarded as Mars simulant. Samples were collected in 2002 by USA-Mexico team. Phosphatase activity was correlated to precipitation rate.

Such extreme environments as Mars, Antarctica and deserts have commonalities. Strong UV causes formation of peroxides that will damage bioorganics. Thus, we supposed that catalase and peroxidase are quite important for the survival of organisms living there, and it would be a good biomarker. We are now studying the assay methods for catalase in soil samples.

Keywords: extreme environments, Mars, life detection, enzymatic activities, phosphatase, catalase

## Molecular approach to the characterisation of Sri Lanka red rain cells

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The recent mysterious phenomenon that has attracted much attention is that of the red rain which fell in Polonnaruwa, Sri Lanka, on 13 November 2012. The microbial content in red rain shows generic similarities to that of the Indian red rain which fell in 2001. The morphological property of those microbes has been well documented [1,2]. Various microscopic analyses of our Sri Lankan red rain sample indicate that the defining red rain cells (RRC) exist in the presence of other microorganisms including diatoms. In our past paper, the ultrastructure of RRC shows that it is possibly a spore-form and so allowing them to thrive in the extreme upper biosphere conditions [3]. We also show the presence of uranium in the abnormally thick cell wall of RRCs.

In this report, we present the molecular approach to the characterisation of microbial communities in red rain and reveal the genus of RRCs. A beads-beating protocol is carried out for the efficient extraction of DNA and denaturing gradient gel electrophoresis (DGGE) for the analysis of microbial communities.

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Keywords: Red rain, Extremophile, Polonnaruwa

## The mechanism that had formed the oldest organic carbon with the banded ironstone formations

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The band iron layers were formed about 3.8 billion years ago. M. T. Rosing reported that the oldest organic carbon was found in the sedimentary rock from west Greenland that formed at the same period [1]. That is, the value of carbon isotope ratio ( $^{12}\text{C}/^{13}\text{C}$ ) on 2- to 5-micrometers graphite globules in the rock is larger than that of inorganic carbon. Since photosynthesis is realized by a system of molecules with chain of reactions, the production of that carbon by the photosynthesis is difficult. The author proposes the mechanism that a slightly large amount of  $^{12}\text{C}$  was incorporated in the floating substances which were produced with the banded ironstone formations (BIF).

We can observe the phenomena by adding fine iron particles in carbonated water as shown in the [photograph 1]. Bubbles were produced at the surface of iron in the bottom of water. The bubbles transfer the fine particles of iron from the bottom to the surface. Since the electronegativity of carbon is larger than that of hydrogen, the carbon atom released from carbonated water by oxidation of iron was adhered to iron particle. The intermolecular bonding of iron with carbon becomes floating substance. The iron atom will be released from the floating substance as the form of iron oxide. So, the carbon atom that was released from the iron will constitute the floating substances [2].

At about 3.8 billions years ago, earth's surface was covered with compounds such as oxides, sulfides and carbonates. Although there were carbon dioxide gasses in the atmosphere, the seawater at mild temperature became dissolve the carbon dioxide. There occurred volcanic eruptions frequently. Iron particles were emitted by the volcanic eruption and the iron oxides were deposited at the bottom on the sea. that is the process of BIF. On the other hand, the carbon dioxide molecules in the sky smashed into surface of the sea water frequently. It is possible to produce an organization of molecules from the floating substance of intermolecular bonds by the energy that comes from outer world such as ultraviolet ray. The floating substances will accumulate at surface of water. At last, the substances deposited at bottom of the sea. That is, the carbon atoms those were included in sedimentary rocks from west Greenland had come from the sky.

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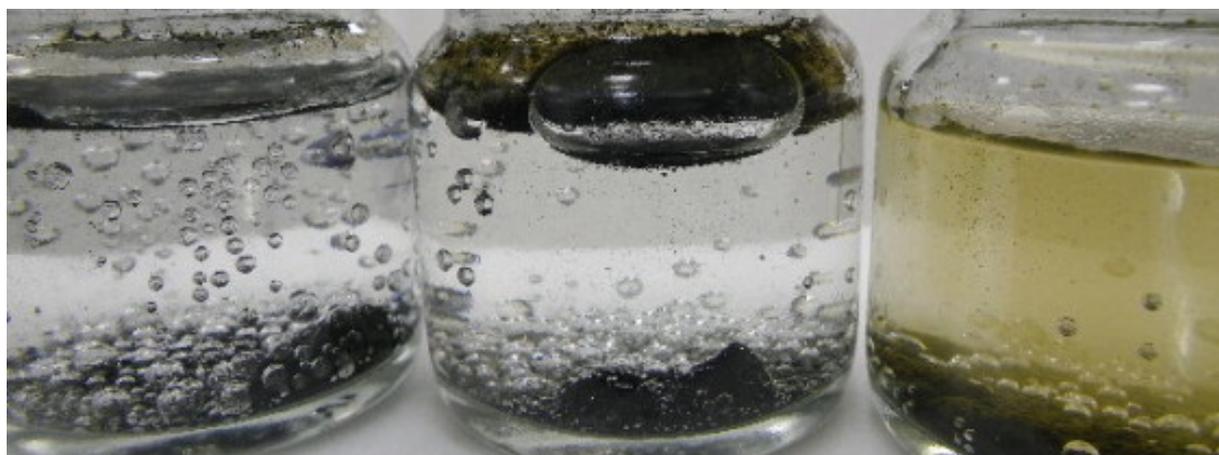
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### [Photograph 1]

Accumulation of the floating substances those are produced by adding fine iron particles in carbonated water (Left: old #300 meshed fine particles, Center: new #300 meshed fine particles, right: #200 meshed particles)

Keywords: 3.8 billion years ago, Banded iron formation, Organic carbon, Carbon dioxide, Carbon isotope ratio



## Ocean Acidification and its effect on calcification since the late 19th century revealed by $\delta^{11}\text{B}$ of Ogasawara coral

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Boron isotopes ( $\delta^{11}\text{B}$ ) of coral skeleton are known as a pH meter in the seawater. As pH of seawater is closely related to partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ) in the atmosphere, it is expected that  $\delta^{11}\text{B}$  becomes  $\text{pCO}_2$  indicator in the geological past too. However,  $\delta^{11}\text{B}$ -pH is under scrutinized since coral calcification itself probably affects the relationship. Although many studies have focused on  $\delta^{11}\text{B}$  measurements for cultured corals under pH-controlled aquarium, those for living corals outdoors have rarely measured, which are limited to, for example, Great Barrier Reef and Guam. Here we show 125 years-records (AD1873-1998) of  $\delta^{11}\text{B}$  and boron concentration (B/Ca ratio) for long-lived massive coral (*Porites* sp.) that was sampled at Chichi-jima, Ogasawara Islands, North West Pacific. They clearly reveal Ocean Acidification after the industrial revolution. We will discuss a relationship between ocean acidification and coral calcification from a slope of pH decline that is obtained from observational data. We will also discuss how B/Ca of calcium carbonate skeleton that is produced by marine calcifiers is reliable proxy for seawater pH, which is being paid a great attention mainly due to relative easiness to measure compared to isotopes.

Keywords: boron, Ogasawara, coral, calcification, Ocean Acidification

## Ocean acidification influences on coral growth of temperate species

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Carbon dioxide concentration in the atmosphere has steadily increased since the industrial revolution due to burning of fossil fuel and will cause the global warming and ocean acidification. It will raise the ocean temperature around Japan and reduce the seawater pH and then it may bring serious threat to corals dwelling around Honsyu Island, Japan. Last year, our research group did temperature-controlled culture experiments of temperate coral species from the Pacific side of Honsyu Island of Japan under the present level of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>). But, synergetic effect of the global warming and ocean acidification on these corals has not been tested yet in detail. In this study, we focus on the how the different pCO<sub>2</sub> levels (past, present, and future) can influence skeletal growth of temperate *Acropora* coral species under the different temperature setting using a precise control system. This system was used to generate six different pCO<sub>2</sub> levels: (i) pre-industrial, ~300 μatm, (ii) present-day pCO<sub>2</sub>, ~400 μatm, and at four near-future conditions, (iii) ~550 μatm, (iv) ~750 μatm, (v) ~1000 μatm and (vi) ~1200 μatm at three temperature conditions (17, 25, and 27 deg C). Our early results suggested a negative influence of higher pCO<sub>2</sub> levels on skeletal growth of temperate *Acropora* corals, but not so sensitive compared to tropical and subtropical *Acropora* corals.

Keywords: Ocean acidification, temperate coral, calcification, global warming

## Projecting impacts of rising water temperature on the distribution of seaweeds around Japan

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Using monthly mean sea surface temperature (SST) from 1950 to 2035 obtained by a high-resolution climate projection model (MIROC4h) and SST-based indices of the distribution of tropical-subtropical and temperate seaweeds (*Sargassum duplicatum* and *Ecklonia cava*, respectively), we evaluated the effects of SST rises on the potential distribution of the species in seas close to Japan. Estimated distributions from the 1950s to 2000s showed that the potential southern limit of the temperate seaweed shifted to higher latitudes due to rising water temperature-induced barren ground, while there was little change in the potential northern limit of them. In contrast, the tropical-subtropical seaweed *S. duplicatum* expanded their distribution polewards during the same period. Under the global warming scenario (RCP4.5), the potential distribution of *S. duplicatum* can replace the one of *E. cava* in coastal area of Kochi Prefecture by the 2010s. This replacement of the temperate seaweed species with the tropical-subtropical one could consequently change coastal productivity and food web structure, and therefore may affect ecosystem services around Japan.

Keywords: seaweed bed, global warming, climate model, *Ecklonia cava*, *Sargassum duplicatum*

## Standing genetic variation of coral populations under changing environments

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How genetic diversities affect ecosystem functions is one of key questions to understand the maintenance of genetic diversities and their roles in ecosystem. To evaluate the functional genetic diversities of corals which are main composers of coral reefs, I genotyped 20 colonies (collected in front of Sesoko Station) of *Acropora digitifera* which is one of dominant coral species around the Ryukyu Archipelago where is the northern peripheral area of coral reefs, and performed common garden experiment using five clonal fragments from each colony (to reduce accidental response in each genotype) to estimate variations of growth and photosynthetic efficiencies among colonies, namely, genotypes. Genotyping was performed with microsatellite markers for coral host and ITS2 direct sequencing for symbiotic algae, indicating that all host colonies were genetically distinct and belonging to major populations around the Ryukyu Archipelago and mainly maintaining clade C symbionts which are dominant around this region. In common garden experiment, all colonies showed different growth patterns whilst the photosynthetic efficiencies showed similar optimal peaks among colonies. The experimental approach above suggests that there are standing genetic variations in host itself of *A. digitifera*, which might guarantee the adaptive potential of coral population for future global warming in northern peripheral reef area. These genetic variations might also contribute to the change of material cycles in future coral reefs.

## Carbon flows in estuarine and shallow waters: blue carbon study

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Blue Carbon, which is carbon captured by marine living organisms, has recently been highlighted as a new option for climate change mitigation initiatives. In particular, coastal ecosystems have been recognized as significant carbon stocks because of their high burial rates and long-term sequestration of carbon. However, unlike sequestration in terrestrial ecosystems, coastal carbon burial does not lead directly to an uptake of atmospheric CO<sub>2</sub>. This is because the water column separates the atmosphere from benthic systems, and buried sedimentary carbon is composed of allochthonous sources in addition to autochthonous sources. Our research project is aiming to in situ measurements of carbon flows, including air-sea CO<sub>2</sub> fluxes, dissolved inorganic carbon changes, net ecosystem production, and carbon burial rates in estuarine and shallow waters.

Keywords: climate change, carbon sequestration, carbon storage, blue carbon, seagrass meadows, estuarine waters

## Field investigation and the path analysis of air-sea CO<sub>2</sub> flux in shallow waters of Ishigaki Island

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The Blue Carbon, which is carbon captured by marine living organism, is recently focused as an important option for climate change mitigation initiatives. The Blue Carbon is equivalent to approximately 55% of carbon fixed by photosynthesis activity of the earth. In particular, vegetated shallow waters have been recognized as significant carbon stocks due to the high burial rates and long term sequestration. However, the contribution of Blue Carbon sequestration to atmospheric CO<sub>2</sub> in subtropical shallow waters is unclear, because the investigation and analysis technologies are unmaturred.

In this study, using an approach combining field investigations and path analysis, we examined the mechanisms by which environmental factors directly and indirectly affecting air-sea CO<sub>2</sub> flux. Field investigations were performed to examine air-sea CO<sub>2</sub> flux and environmental factors (e.g., wind speed, water temperature, salinity, total alkalinity (TA), dissolved inorganic carbon (DIC)) in shallow waters (Fukido, Shiraho, Nagura, and Kabira) of Ishigaki Island, July 2013. In addition, we implemented the path analysis to infer important environmental factors and interactions affecting the air-sea CO<sub>2</sub> flux.

Keywords: blue carbon, coastal vegetation, air-sea CO<sub>2</sub> flux, path analysis

## Spatial distribution and its characteristics of stable nitrogen isotopic composition of macroalgae in Nagura Bay

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This study, focusing on Nagura Bay in the west of the Ishigaki Island, conducted a field sampling and measurement of  $\delta^{15}\text{N}$  values of macroalgae, *Padina* spp. and sea grass, *Thalassia hemprichii* in order to evaluate effects of land-derived nitrogen load on the coral reef ecosystem, and to discuss the reasons for the nitrogen load distribution in the bay.

In June 2013, 55 samples for each species were collected at about 50 m intervals on 7 transect lines, and their  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values were measured in the laboratory. At the same time, water samples at stream, spring and sea were collected and their water qualities were measured. Moreover, areas for each land use in related watershed were calculated using GIS to examine the relationship between the nitrate concentration in river water samples and land use, and to identify the source of land-derived nitrogen.

As a result, most of the  $\delta^{15}\text{N}$  values of macroalgae and sea grass linearly decreased from +6 to +2 ‰ with increasing distance from the shoreline. However, the transect lines around the river mouth of Nagura River relatively showed high  $\delta^{15}\text{N}$  values by about 1 km away from the shoreline comparing with the other transect lines. One of the reasons is probably water flow condition around the river mouth. Some previous studies had showed that the water flow stagnates around there due to the south monsoon wind in spring and summer. Before this field sampling, the mode of wind direction for 3 months was surely south wind. This is why the land-derived nitrogen loads through Nagura River remained around river mouth due to water stagnation and lower dilution in seawater, and the plants could have higher  $\delta^{15}\text{N}$  values.

On the other hand,  $\text{NO}_3\text{-N}$  concentrations have high correlations with ratios of farm land and cultivated areas. Thus, they were perhaps the main nitrogen sources in this study area. Additionally,  $\text{NO}_3\text{-N}$  flux [mg/s], which calculated by flow rate [m<sup>3</sup>/s] and  $\text{NO}_3\text{-N}$  concentration [mg/l], estimated 81.9 mg/s at the river mouth of Nagura River, and 59.4 mg/s at the upstream. Mangrove swamps and tidal flat exist between the two locations. Thus, the nitrogen source increasing the flux 22.5 mg/s could come from the swamps or their upstream.

Keywords: *Padina* spp., *Thalassia hemprichii*, Stable nitrogen isotopic composition, land-derived nitrogen, Nagura Bay, mangrove swamps and tidal flat

## Propagation of suspended matter from aquacultures as traced by stable C and N isotope ratios of bivalves

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Recently there is growing concern about the impact of densely-deployed aquacultures on coastal marine ecosystems in the Philippines. As suspension-feeding bivalves are expected to reflect local food sources, their effectiveness as an environmental indicator were examined by analyzing stable carbon and nitrogen isotope ratios of bivalves living in aquaculture and neighboring seagrass areas. As a whole, the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of bivalves collected in the seagrass areas ranged from -13.1 to -11.0 and from +4.0 to +6.6, respectively, but in seagrass area where water mass from aquaculture area passed through typically lower values (-18.9 ~ -16.1 and +2.7 ~ +5.2, respectively) were observed, and they were the lowest in the aquaculture area (-24.4 ~ -19.8 and +3.4 ~ +4.3, respectively). It suggests that bivalves mainly fed on sinking particles, and presumably also seagrass-derived particles in seagrass areas. Higher C/N ratio was observed at sites where impact of aquaculture was larger. Although the interspecies differences and food selectivity etc. may affect the variability of the bivalve  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  to some extent, these results demonstrated that stable isotope ratios of bivalves could be used as an effective indicator to evaluate propagation areas and actual effects of suspended matter resulting from anthropogenic source on ecosystems.

Keywords: suspension-feeding bivalve, seagrass, aquaculture, stable carbon and nitrogen isotope ratios

## Organic carbon preservation in tropical seagrass-bed sediments: importance of sorptive vs. non-sorptive mechanisms

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Large benthic primary producers such as seagrasses and seaweeds often exhibit extremely high CO<sub>2</sub>-fixing ability and are expected to have a potential to mitigate the deteriorative influence of ocean acidification on local communities. In particular, the seagrass community has also a capacity of accumulating and sequestering organic carbon (OC) in the sediment underlying it, which implies that it functions as a self-complete, long-term CO<sub>2</sub> sink in the biogeochemical carbon cycle. This feature has been recognized as one of the major ecosystem services of the coastal marine ecosystem. In this study, we investigated the distribution, the physical state, and the potential origins of OC stored in the sediments from tropical, subtropical, and temperate seagrass communities.

The concentration of OC per salt-corrected dry weight of sediment normally ranged between 500 and 1300  $\mu\text{mol C g}^{-1}$  in both temperate and subtropical seagrass beds, although extremely high values up to 4000  $\mu\text{mol C g}^{-1}$  have been found in some tropical seagrass sediments that were affected by OC inputs from adjacent mangrove forest. The carbon isotopic composition ( $\delta^{13}\text{C}$ ) of OC varied broadly from -28 ‰ to -12 ‰ (vs. VPDB), although the majority of seagrass bed sediments exhibited  $-20 \pm 3$  ‰. The variability in  $\delta^{13}\text{C}$  could be interpreted by varying contribution of multiple OC sources to the sediment, including seagrasses (c. -10 ‰), sinking particles derived from phytoplankton (c. -22 ‰), and allochthonous OC including terrestrial plant and mangrove detritus (c. -28 ‰).

The specific surface area (SSA) of sediment grains ranged between 1 - 20  $\text{m}^2 \text{g}^{-1}$  for seagrass bed sediments. In the case of temperate seagrass sediments, the concentration of OC was closely correlated to SSA ( $r = 0.9405$ ), with the average OC/SSA ratio being 0.72  $\text{mg C m}^{-2}$ . This trend, as well as the OC/SSA ratio, is consistent with the well-known sorptive preservation model of sediment OC originally proposed for shelf sediments (OC/SSA = 0.6 - 0.9  $\text{mg C m}^{-2}$ ; Keil et al. 1994, Mayer 1994). In contrast, no clear relationship between OC and SSA was detected for subtropical and tropical seagrass sediments. The OC/SSA ratio was generally higher for subtropical (up to 4.2) and tropical (up to 8.5) samples than temperate ones. Two clearly different trends of the  $\delta^{13}\text{C}$  of OC vs. the OC/SSA ratio could be distinguished for tropical and subtropical samples. In one trend, the  $\delta^{13}\text{C}$  converged to between -28 ‰ and -26 ‰ with increasing OC/SSA ratio. This trend was typically observed in mangrove-affected tropical seagrass beds and therefore could be ascribed to accumulation of mangrove-derived OC particles within seagrass sediments. The other trend, in which the  $\delta^{13}\text{C}$  gradually increased up to -12 ‰ with increasing OC/SSA, was found mainly in subtropical seagrass beds. This trend indicates an accumulation of OC particles of relatively high  $\delta^{13}\text{C}$ , putatively derived from the underground parts of seagrasses.

Overall, the above results demonstrated that the seagrass community actually has a large capacity to accumulate and store organic carbon of both autochthonous and allochthonous origins. However, the physical state of OC stored in the sediment seemed contrasting between temperate and tropical/subtropical seagrass communities. In the former, OC seemed to be stabilized by adsorption onto mineral particles as suggested by the consistent OC/SSA ratio. In the latter, accumulation of refractory detrital OC particles apparently played the major role in the OC storage in the sediment. The source of refractory OC particles could have been autochthonous (e.g. seagrass roots) or allochthonous (e.g. mangrove debris) depending on the environment. We are now investigating what causes such a difference in the accumulation state of OC depending on climatic and/or biological factors.

Keywords: carbon cycle, organic matter, coastal ocean, seagrass beds, sediment, specific surface area

## Inorganic carbon cycle at the Fukido estuary in Ishigaki Island

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“ Blue Carbon ” , which is carbon captured by marine living organisms and about 55 % of biological captured carbon in the world, is an important carbon budget in the global carbon cycle. The Blue Carbon in coastal regions is recently focused as an effective option for the climate change initiatives because the part of the Blue Carbon is separated from the atmosphere for long periods as the sediment in the soil. The potential of the carbon sequestration in tropical-subtropical coastal regions is expected to be high due to the abundant vegetations such as seagrass meadows and mangroves. Meanwhile, there is the potential that the coastal regions release CO<sub>2</sub> to the atmosphere due to the high decomposition rate of organic matters in vegetations and from land.

The precise measurement of the carbon cycle including the air-sea CO<sub>2</sub> flux is necessary for the evaluation of tropical-subtropical coastal regions related to atmospheric CO<sub>2</sub>. Because the temporal variation in tropical-subtropical regions is generally larger than that in other climate regions, the measurement should have a certain level of continuity for long periods. In this study, we analyzed the subtropical inorganic carbon flow base on the measurement of air-sea CO<sub>2</sub> flux by the eddy covariance method and the biomass of seagrass at an estuary in Ishigaki Island.

The measured air-sea CO<sub>2</sub> flux by the eddy covariance method ( $-1.00 \pm 0.11 \mu\text{mol}/\text{m}^2/\text{s}$ ; 95 % confidential limit) indicates that the estuary was atmospheric CO<sub>2</sub> sink during the measurement period; the value is almost the same as the flux measured by other method such as the bulk formula method or the floating chamber method. In addition, the measured flux shows different tendency before and after a typhoon approach at the site. Because the seagrass was autotrophic during the measurement period, the linkage between the Blue Carbon production and the absorption of atmospheric CO<sub>2</sub> was confirmed at the measurement site. The presentation will discuss about the potential of the Blue Carbon fixation at subtropical coastal regions based on the comparison of the carbon flow measurement in other climate zone.

Keywords: Carbon cycle, Blue Carbon, Air-sea CO<sub>2</sub> flux, Seagrass, Eddy covariance method

## Skeletal records in sclerosponges from Miyako-jima, Ryukyu Islands

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Sclerosponges, living in dark environments of tropical to subtropical shallow oceans, precipitate calcium carbonate skeleton with growth bands. They grow slowly at an approximate rate of <1 mm/year unlike corals (about 1 cm/year) but can be so long-lived for several decades to hundred years like corals (e.g., Benavides and Druffel, 1986). Skeletal oxygen isotopic ratios ( $\delta^{18}\text{O}$ ) reflect variations in sea surface temperature and seawater  $\delta^{18}\text{O}$  with the latter being closely related to salinity reflecting the precipitation-evaporation balance at the sea surface and changes in water mass transport (e.g., Wu and Grottoli, 2009). In contrast to zooxanthellate corals, which commonly show positive correlations between skeletal  $\delta^{18}\text{O}$  and carbon isotopic ratios ( $\delta^{13}\text{C}$ ), there do not exist vital effects in the secretion of sclerosponge skeleton (Druffel and Benavides, 1986). Previous studies showed significant decrease trends in the  $\delta^{13}\text{C}$  records toward the present, which is probably a result of  $^{12}\text{CO}_2$  added into the atmosphere/ocean from fossil fuel burning (e.g., Bohm et al. 1996). Therefore, sclerosponges are shown to provide annually resolved time series of proxy records of ocean environments since the Industrial Revolution. However, longer (>100 year) proxy records from sclerosponges were derived only from the Atlantic Ocean.

Here we present  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  records from high-Mg calcite skeleton of two sclerosponges (*Acanthochaetetes wellsi*) collected at a water depth of about 10 m from Miyako-jima, Ryukyu Islands in the North Pacific. The samples were slabbed to a thickness of 5 mm parallel to the skeletal growth and subsamples for stable isotope measurements were taken every 1 mm. External precision of replicate measurements of interlaboratory calcite material throughout the stable isotope analysis using a continuous flow isotope ratio mass spectrometer system (Delta V Advantage and Gasbench II: ThermoFisher Scientific Inc.) of Ryukyu University was  $\pm 0.05$  per mil for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ . Soft X-ray images showed highly developed skeletal growth bands with >100 high/low density layers. The secular changes in  $\delta^{13}\text{C}$  of the two sclerosponges were quite similar to previously reported  $\delta^{13}\text{C}$  records from Atlantic and Pacific corals and sclerosponges. The long-term  $\delta^{18}\text{O}$  trends of the two samples are characterized by slight depletions throughout their living periods, indicative of an overall trend toward warmer ocean environment around Miyako-jima. Our sclerosponge-based estimates of sea surface temperature and salinity may document thermal and hydrologic variations in the Ryukyu Islands, furthering a good understanding of northwestern tropical-subtropical Pacific climate change for the last several centuries in conjunction with coral-based long proxy records.

Keywords: sclerosponge, skeleton, oxygen isotope composition, carbon isotope composition, paleoenvironment, Ryukyu Islands

## Paleoenvironmental analysis using Tridacnidae shells from archaeological sites in Okinawa-jima, subtropical southwestern

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Symbiont-bearing Tridacnidae giant clams living in shallow waters of the Indo-Pacific tropical and subtropical regions can be used as an archive for documenting high-resolution record of thermal and hydrologic variations in coral reef environments for the past. Their shells, composed of dense aragonitic increments, are less sensitive to diagenetic alteration than porous skeleton of corals. They have annually and daily banded shells structure, providing chronological controls (e.g., Bonham 1965). The oxygen isotope composition ( $\delta^{18}\text{O}$ ) of shells, which are precipitated isotopically equilibrium with seawater, can reflect the temperature and seawater  $\delta^{18}\text{O}$  (e.g., Aharon & Chappell 1986). Several studies on paleoenvironmental reconstructions around the Ryukyu Islands were performed using geochemistry in fossil corals from Okinawa-jima (Mitsuguchi et al. 1998), Yonaguni-jima (Suzuki et al. 2001), Kikai-jima (Morimoto et al. 2007), and Kume-jima (Seki et al. 2012). However, only a  $\delta^{18}\text{O}$  record has been published from 6.2 ka giant clams from Kume-jima (Watanabe et al. 2004).

Here we present seasonally resolved  $\delta^{18}\text{O}$  time series of fossil Tridacnidae shells recovered from two archaeological sites (the Kogachibaru Shell Mound and the Second Aragusuku-Shichabaru Ruin) in Okinawa-jima, southwestern Japan to reconstruct subtropical coral reef environments of the past. The samples, mainly composed of aragonite shells with limited amounts of calcite cements, were selected for geochemical analyses. The radiocarbon dating results indicated that they lived during the early and middle Shell Mound periods in Okinawa-jima, corresponding to the middle-to-late Holocene, which is in good agreement with ages inferred from excavation (Okinawa Prefectural Board of Education 1987; Okinawa Prefectural Archaeological Center 2006). The shell  $\delta^{18}\text{O}$  values roughly showed seasonal variations, coincident with the occurrence of annual growth bands. The averages of annual, summer, and winter  $\delta^{18}\text{O}$  values of fossil shells were significantly lower than aragonite theoretically precipitated in present-day coral reef water of Okinawa-jima. These results demonstrate that the seawater temperature was higher and/or salinity was lower at the sites than today. It is likely that the giant clams lived in relatively small and/or closed coral-reef lagoons with less water circulation where seawater is highly susceptible to insolation-induced temperature increase and input of fresh water; the effect could be enhanced by the fisheries lifestyle that stonewalling would be constructed at shallow waters through the use of tidal variation during the Shell Mound period in Okinawa-jima.

Although it is extremely difficult to find well-preserved fossil Tridacnidae shells from carbonate sediments that are not fragmented, archaeological ruins and shell mounds can yield many fossils. Results of our study suggest that the use of fossil shells from archaeological sites can enable the reconstruction of temporal and spatial variations in coral reef environments and of the history of lifestyles and culture during prehistoric and protohistoric ages.

Keywords: coral reef, Tridacnidae, shells, fossil, oxygen isotopic composition, archaeological site

## Evaluation of natural break water of coral reefs affected by typhoons in the near future

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Tropical cyclones are one of the most extreme natural catastrophic events over the world and devastate coastal areas affected by floods and coastal erosions. Ryukyu Islands in the northwest Pacific is especially prone to many typhoons every year (Emanuel et al. 2008 Bull Amer Meteor Soc). However, the region is moderately protected from storm surge and wave during typhoons because coral reefs play a role in natural break water. For the last several decades, coral cover and species diversity on coral reef have shown dramatic declines in the region, influenced by global and local stresses (e.g., Hongo and Yamano 2013 PLoS ONE). According to the numerical modeling of global warming at the end of 21 st century, moreover, the mean intensity of tropical cyclones will probably increase significantly in the near future (Meehl et al. 2007 IPCC 4th Report). It is thus of some interest to understand the impact of tropical cyclones on the coastal areas in the region and the evaluation of coral reefs as natural break water.

To calculate a hydraulic force on a natural break water, we measured 9 transects using the echo sounder system (HFD-1000; Hongo et al. 2013 The Quat Res) on from the coast to the reef crest at Ishigaki Island in Ryukyu Islands during November 2013. To evaluate a contribution to reef formation by corals, moreover, we observed species abundance (cover) of tabular corals at the island. We shows that a change of role in natural break water of coral reefs in the island from present to end of 21 st century. Furthermore, we suggest necessary information of corals (e.g., cover and species) for maintenance of natural break water in the near future. The information are like to be one of basic criterion for determination of species in terms of direct transplantation of juvenile or adult corals, if the coral reefs will decline in the near future.

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Keywords: typhoon, coral reef, Ishigaki Island, Ryukyu Islands, natural break water

## Plant rhizosphere is a hotspot for greenhouse gas emissions

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Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas that also degrades stratosphere ozone. Marked N<sub>2</sub>O emission were detected from soybean root systems with degraded nodules during late growth stage in field-grown soybeans. A model system developed to produce N<sub>2</sub>O emissions from soybean fields. Soybean plants inoculated with *nosZ* mutant of *Bradyrhizobium japonicum* USDA110 (lacking N<sub>2</sub>O reductase) were grown in aseptic jars. After 30 days, shoot decapitation (D, to promote nodule degradation), soil addition (S, to supply soil microbes), or both (DS) were applied. N<sub>2</sub>O was emitted only in the DS treatment. Thus, both soil microbes and nodule degradation are required for the emission of N<sub>2</sub>O from the soybean rhizosphere. The N<sub>2</sub>O flux peaked at 15 days after DS treatment. A <sup>15</sup>N tracer experiment indicated that the N<sub>2</sub>O was derived from N fixed in the nodules. As for nitrification, the addition of nitrification inhibitors significantly reduced N<sub>2</sub>O flux. Both AOA and AOB were detected by PCR analysis with N<sub>2</sub>O emission profile in soybean rhizosphere. The N<sub>2</sub>O flux from the *nirKnosZ* mutant rhizosphere was significantly lower than that from *nosZ* mutant, but was still 30% to 60% of that of *nosZ* mutant, suggesting that N<sub>2</sub>O emission is due to both *B. japonicum* and other soil microorganisms. Only *B. japonicum nosZ+* strains could take up N<sub>2</sub>O. In particular, *Fusarium* spp., a soil fungus may contributed to N<sub>2</sub>O emission in soybean rhizosphere. From these results, the organic-N inside of the nodules was mineralized to NH<sub>4</sub><sup>+</sup>, and N<sub>2</sub>O producing processes (nitrification and denitrification) simultaneously occur in the soybean rhizosphere. We continue to examine which microbes really mediated N<sub>2</sub>O metabolism using isotopic techniques including <sup>15</sup>N site preference of N<sub>2</sub>O molecules. N<sub>2</sub>O emissions from soybeans ecosystems can be mitigated by inoculating *B. japonicum* mutants with increased N<sub>2</sub>O reductase activity (Nos<sup>++</sup> strains). The mutation of *nasS* gene is responsible for the Nos<sup>++</sup> phenotype. We propose that *nasS* mutation might be an effective strategy to induce higher Nos activities in N<sub>2</sub>O-reducing rhizobia, such as indigenous isolates from local soybean fields or even from other important leguminous crops such as alfalfa, and thus to mitigate N<sub>2</sub>O emission.

Plants have mutualistic symbiotic relationships with rhizobia and fungi by the common symbiosis pathway, in which Ca<sub>2</sub><sup>+</sup>/calmodulin-dependent protein kinase (encoded by *CCaMK*) is a central component. Although *OsCCaMK* is required for fungal accommodation in rice roots, little is known about the role of *OsCCaMK* in rice symbiosis with bacteria. Here, we report the effect of a *tos17*-induced *OsCCaMK* mutant (NE1115) on CH<sub>4</sub> flux in low-nitrogen (LN) and standard-nitrogen (SN) paddy fields as compared with wild-type (WT) Nipponbare. Growth of NE1115 was significantly decreased compared with that of WT, especially in the LN field. The CH<sub>4</sub> flux of NE1115 in the LN field was significantly higher (156?407% in 2011 and 170?816% in 2012) than that of WT, although no difference was observed in the SN field. The copy number of *pmoA* was significantly higher in the roots and rhizosphere soil of WT than those of NE1115. However, *mcrA* copy number did not differ between WT and NE1115. These results were supported by a <sup>13</sup>C-labeled CH<sub>4</sub>-feeding experiment. In addition, the natural abundance of <sup>15</sup>N in WT shoots (3.05 permille) was significantly lower than in NE1115 shoots (3.45 permille), suggesting higher N<sub>2</sub> fixation in WT due to dilution with atmospheric N<sub>2</sub> (0.00 permille). Thus, CH<sub>4</sub> oxidation and N<sub>2</sub> fixation were simultaneously activated in the root zone of WT rice in the LN field, and both processes are likely controlled by *OsCCaMK*.

Keywords: methane, nitrous oxide, rhizosphere, Bradyrhizobia, bacteria, stable isotope

## Does microbial ecology expand our understandings of nitrogen cycle in forests?

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Forests cover approximately 70% of Japan's total land area, representing a largest reservoir of diversity of organisms including plants, animals, fungi protists and prokaryotes on land. These organisms are closely associated each other in material cycles if not directly. Thus, we need to know how materials are cycling between the organisms in order to address a fundamental question in ecosystem ecology: why do forests have the richest biodiversity on land? However, it is not easy to understand the material cycles in a forest because the forest has the various environmental heterogeneity which greatly affect the cycle. For example, nitrogen dynamics can be different in soils around hills and valleys in forests. Such spatial heterogeneity of the dynamics in the soils has been explained mainly from phenomenological perspectives using abiotic information such as soil moisture, soil temperature or litter quality. However, these perspectives have not fully explained the dynamics. Here, we suggest that such heterogeneity need to be explained in the context of ecology of microbial communities which mediate the nitrogen dynamics. More specifically, we suggest that understanding the nitrogen dynamics based on the physiology, population dynamics and diversity of the microbial communities can provide the mechanistic insights into the nitrogen cycle in forests.

We analyzed the spatial heterogeneity of nitrogen dynamics and associated microbial communities in natural and planted forest soils in Asia. Specifically, we focused on nitrification in which ammonium are oxidized to nitrate and found the close association between gross nitrification rates and population size of nitrifiers in the soils. Additionally, nitrification rates cannot be fully explained by using environmental properties including substrate supply, soil moisture and litter quality, but can be explained by using the population size of nitrifiers. This shows that the better understandings of the microbial ecology allows us to more accurately explain and even predict the spatial heterogeneity of material cycles. In this presentation, we will discuss how information on microbial ecology expands our understandings of nitrogen cycle in forests.

Keywords: microbial ecology, nitrogen cycle, forest

## Diversity of microbial arsenic transformation pathways associated with arsenic cycling in the environment

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Arsenic (As) is a naturally occurring toxic element that is widely distributed in nature. Although the concentrations of As in natural systems are generally low ( $\sim 15 \mu\text{g g}^{-1}$  in soil and  $\sim 10 \mu\text{g L}^{-1}$  in surface waters), the elevated levels of As have been released via natural sources (i.e. volcanic activity) and anthropogenic activities due to its increasing industrial use. As can exist in four oxidation states (-III, 0, III and V), while they are mainly found as trivalent [arsenite; As(III)] and pentavalent [arsenate; As(V)] in natural systems. Depending on its oxidation state, As exhibit different mechanisms of toxicity to microorganisms and other biota. As(III) is highly reactive with thiol containing proteins and is considered more toxic than As(V). Despite its toxicity, microorganisms have developed mechanisms to tolerate As and/or utilize the element for respiratory metabolism. Although various microorganisms have been identified to catalyze As transformation including both oxidation and reduction, we have just began to unveil the full diversity of different microbial processes associated with the redox cycling of As in the environment.

To gain insight into microbial roles in the geochemical dynamics of As, the combined geochemical, physiological and molecular biological analyses were applied to examine As-impacted environments and microcosms. Microbial populations were analyzed using 16S rDNA-based molecular approach combined with metagenomic sequencing. The presence of indigenous microbial populations capable of As transformation was examined by using both molecular approach targeting As functional genes and cultivation approach. The genes coding for arsenite oxidase (*aiOA*), which catalyzes the oxidation of As(III) coupled to O<sub>2</sub> reduction, have been recovered from geochemically distinct geothermal habitats (pH 2.6-8) as well as the soils from mine tailing. Successful cultivation of various As(III)-oxidizing bacteria confirmed the microbial attribute in As oxidation *in situ*. In contrast, from the As impacted lake sediments and soils, diverse sequences of anaerobic arsenite oxidase (*arx*) and arsenate respiratory reductase (*arr*) genes were detected, while no *aiO* genes were recovered. The anaerobic arsenite oxidase, Arx, is known to catalyze arsenite-oxidation coupled to nitrate reduction or photosynthesis. Consistent with the molecular approach, the anaerobic arsenite-oxidizing nitrate reducer and arsenate-reducing bacteria were isolated from the lake sediments.

Our results showed that As redox metabolisms are widespread within phylogenetically and physiologically diverse bacteria, including both chemolithotrophic and organotrophic aerobes and anaerobes. This study revealed the diversity of As transformation pathways associated with geographically and geochemically distinct environments and presented the mechanisms behind microbial processes controlling the redox cycling of As.

Keywords: arsenite oxidase, arsenate reductase, microbial arsenic transformation, soil microbiology

## Biosignature found in iron oxide mineralogy of iron-oxidizing microbe origin?

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Recently, many iron mats have been discovered at deep-sea hydrothermal fields in all over the world. It has been thought that microbes, especially iron-oxidizing microbes, are the key players for forming the iron mats. However, there was no direct evidence to this, due to cultivation difficulty of iron oxidizers. Recently, '*Mariprofundus ferrooxidans*' that belong to the Zeta-proteobacteria was successfully isolated. From this isolation, it has been proved that this microbe can oxidize ferrous iron as the electron donor, and can widely be observed in various deep-sea low-temperature hydrothermal fields. Therefore we have investigated how these microbes contributed to the formation of the iron mat using mineralogical and culture independent approaches.

We tried to clarify mineralogical properties of natural or lab-prepared iron oxides of iron-oxidizing microbes by using XAFS, SEM and EDX. Natural samples were collected at 3 sampling sites: iron mats from deep-sea hydrothermal fields in the Mariana Volcanic Arc, Mariana Trough and the Okinawa Trough. Lab-prepared iron-oxide synthesis was carried out using chemoautotrophic bacterium *Mariprofundus ferrooxydans* PV-1 (ATCC BA-1020) and was cultured by diffusion cell's method (Kikuchi et al., 2011, 2014). SEM observation showed similar morphology to all samples, which have distinctive plait-like structure, and at where iron oxides precipitate around distinctive materials. Although each natural iron-oxide sample was precipitated at different environments and with different dominant microbial species within the natural samples, XAFS showed identical spectrum. Regardless of medium employed in the cultivation, lab-prepared iron oxides also showed similar spectrum to natural samples. XANES fitting suggested that iron mats consist of ferrihydrite and iron-organic complex being the same as the lab-prepared iron oxides. These results strongly supported the iron-oxidizing chemolithoautotrophs had significant ecological roles in producing the iron mat. These mineralogical analyses may help to find biosignature in the deep-sea environments.

Keywords: iron-oxidizing bacteria, Biosignature, Mineralogical property, deep-sea, hydrothermal fields

## The trench biosphere observed from the transect water sampling for the Japan Trench

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We have discovered the presence of the trench biosphere that harbored distinct microbial populations comparing to those in the upper water masses in the Challenger Deep, Mariana Trench (Nunoura et al. in preparation). The deep locates under the oligotrophic ocean and is isolated from the other trenches while the Japan Trench locates under eutrophic ocean and in a series of long trenches in north Pacific. Therefore, the Japan Trench has one of the best environments to test the universality of the occurrence of trench biosphere. In this study, we conducted CTD casts in 8 stations across the Japan Trench in 2011 after the big earthquake and analyzed microbial structures for each sample in order to examine the occurrence of the trench biosphere.

Keywords: Japan Trench, nitrification

## SUP05 contribution for Carbon and Nitrogen cycles in semi-closed water mass

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In the deep sea hydrothermal plume, significantly elevated microbial biomass has been reported depending on chemolithoautotrophic activities by hydrothermal reduced chemicals. The potential energetic is sulfur, methane and hydrogen oxidation, and microbial production is up to date. The most important microbes in the plume is SUP05 phylotype (genus Thioglobes), which is known to have sulfur and H<sub>2</sub> oxidation pathway, RubisCO carbon assimilation pathway, and denitrification pathways. In this study, we compared the bicarbonate and inorganic nitrogen species with SUP05 cell densities in the hydrothermal plume of the TOTO caldera hydrothermal field with half-closed water mass system in the Southern Mariana Trough. The cell densities of SUP05 is strong negative correlation with bicarbonate and nitrate, however, the correlation slope indicated the nitrogen assimilation but not the nitrogen respiration (denitrification). Only the nitrogen assimilation occurred in the plume is also supported by the lack of denitrification genes in the plume sample with the metagenomic analysis.

Keywords: Chemolithoautotroph, SUP05, TOTO, metagenomics

## From who, where, how many and what to 'Earth science'

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Glancing at 50 years' history of aquatic microbial ecology since Wright and Hobbie proposed an uptake kinetics using radio-labeled glucose, I may pose issue(s) of consideration for microbial ecology as an earth science.

Keywords: <sup>14</sup>C-glucose uptake vs. <sup>3</sup>H-Thymidine uptake, Production vs. Respiration, sec vs. year

## Microbial potential and carbon cycle in deep aquifer of the accretionary prism of Southwest Japan

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The accretionary prism situated along the Pacific side of Southwest Japan forms thick sediments. The sediment contains deep aquifers that anaerobic groundwater is accumulated. In addition to the anaerobic groundwater, it has been reported that dissolved natural gases composed mainly of methane are present in the deep aquifers. The groundwater and natural gases are collected from deep wells (150-1500 m depth) which are drilled at the accretionary prism. In the past study conducted in a deep well situated Shimada, Shizuoka Prefecture, Japan, it has been shown that methane has been produced by subterranean microbial community in deep aquifer associated with accretionary prism. However, microbial and geochemical studies have not yet been performed at other areas of accretionary prism. In this study, we collected groundwater and natural gases from 14 deep wells of Shizuoka Prefecture, and we performed measurements of physical and chemical parameters, anaerobic cultivations of microbial communities and 16S rRNA gene analysis to understand microbial potential and carbon cycle in subterranean environments of the accretionary prism.

The temperature of groundwater samples ranged from 24.2 to 49.3 °C, and pH was weakly alkaline. Oxidation-reduction potential suggested -325 to -114 mV at all deep wells. Electric conductivity ranged widely from 92 to 2,110 mS m<sup>-1</sup> at each groundwater sample. NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and S<sup>2-</sup> in groundwater was below the detection limit. Dissolved organic carbon (DOC) ranged from <0.3 to 50 mg l<sup>-1</sup>. From componential analysis of the natural gases, methane was predominant gas component at many sites (>90%). On the other hand, we detected several natural gas samples contained a large amount of N<sub>2</sub> (20-50%). Stable carbon isotopic analysis of methane in the natural gases and dissolved inorganic carbon (DIC) in groundwater suggested that methane of biogenic origin are contained in the natural gases at a lot of sites.

Anaerobic incubations using groundwater amended with organic substrates revealed the high potential of H<sub>2</sub> and CO<sub>2</sub> generation by H<sub>2</sub>-producing fermentative bacteria. Furthermore, methane generation by syntrophic consortium of H<sub>2</sub>-producing fermentative bacteria and H<sub>2</sub>-using methanogen was also observed in 3-5 days after the start of incubation.

Bacterial 16S rRNA gene analysis indicated the dominance of H<sub>2</sub>-producing fermentative bacteria. The presence of denitrifying bacteria was also observed at the sites where N<sub>2</sub> is contained in the natural gas samples. In archaeal 16S rRNA gene analysis, H<sub>2</sub>-using methanogens dominant in the groundwater.

From these date, it was shown that carbon cycle that methane has been produced from organic matters which are contained in the sediments by syntrophic consortium of H<sub>2</sub>-producing fermentative bacteria and H<sub>2</sub>-using methanogens exist in wide area of the subterranean environments of the accretionary prism. In addition to methane production, the presence of denitrification using NO<sub>3</sub><sup>-</sup> or NO<sub>2</sub><sup>-</sup> and organic matter or methane was also suggested at a few site.

Keywords: accretionary prism, deep aquifer, methanogenesis, fermentation, syntrophic biodegradation, subsurface environment

## The global methane cycle revealed through geomicrobiological analysis

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Methane is one of the major end products of anaerobic microbial metabolism. Based on stable carbon and hydrogen isotopic compositions of methane, geochemical studies have systematically classified the origin of methane; 1) biological pathways consisting of carbon dioxide reduction coupled to molecular hydrogen oxidation and methyl-type fermentation, and 2) abiological pathways such as thermal degradation of organic matter and Fischer-Tropsch type reaction. In contrast, regarding methane consumption, recent advances in seafloor biosphere research have unveiled the complexity of processes involved in the transformation, migration and fate of methane. Particularly, it has been recognized that marine sediments with high methane flux harbor novel lineages of microorganisms, the physiological traits of which are largely unknown due to their resistance to cultivation. Recent advances in seafloor biosphere research indicate that microbes play much more important roles in methane production and consumption than previously assumed. Though these biogeochemical processes are not fully understood, future combined approach of geochemistry and geomicrobiology will shed light on the global methane cycle on Earth.

Keywords: seafloor biosphere, methane, methanogen, methanotroph

## Isotope systematics among H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O in fluid associated with serpentinization

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Serpentinite-hosted hydrothermal systems have attracted considerable attention as sites of abiotic organic synthesis and as habitats for the earliest microbial communities, because hydrothermal fluids derived from ultramafic rocks are characterized by high concentrations of H<sub>2</sub> and CH<sub>4</sub>. During water-rock reactions, Fe (II) in olivine of ultramafic rock is oxidized to Fe (III), which accompanies the reduction of water to yield H<sub>2</sub>. Methane and hydrocarbons are often observed in serpentinite-hosted hydrothermal systems and are thought to be produced from H<sub>2</sub> and CO<sub>2</sub> via Fischer-Tropsch-type (FTT) reactions. On the other hand, H<sub>2</sub> and CH<sub>4</sub> can be consumed and produced by microorganisms such as methanogens and methanotrophs around the hydrothermal systems. When we collect and analyze samples, those chemical compositions could have been altered due to microbial activities. Therefore, it is very difficult to clarify processes related to H<sub>2</sub> and CH<sub>4</sub> around the serpentinite-hosted hydrothermal systems.

Isotopic compositions are useful tool to discriminate origins and reaction pathways of chemical components. As representative controlling factors of isotopic compositions are temperature equilibrium, isotopic compositions of substrate, and isotopic fractionation, the dynamics of isotopic compositions are complicated in natural environments. Therefore, polyphasic aspects, such as hydrological, geological and microbiological interpretations, are needed. However, even complete hydrogen isotopic analysis of H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O from serpentinite-hosted systems and basic laboratory experiments has been reported in only a few studies. As the isotope systematics among H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O in fluid associated with serpentinization remain unexplored, I will present the review of some previous studies and results of explorations of hydrothermal systems at Mid Cayman Ridge during YK13-05 cruise.

Keywords: serpentinization, stable isotope, hydrogen, methane

## Acetate-oxidation activities in the deep subseafloor biosphere associated with coalbeds off the Shimokita Peninsula

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The IODP Expedition 337 was the first riser-drilling expedition dedicated to subseafloor microbiology using the drilling vessel Chikyu. During Expedition 337, we penetrated a 2466 m deep sedimentary sequence at Site C0020A with a series of coal layers at 2000 m below the seafloor (mbsf) off the Shimokita Peninsula, Japan. One of the primary scientific objectives of Expedition 337 was to understand ecological roles of subseafloor microbial activity in biogeochemical carbon cycles associated with the deeply buried coalbeds in the ocean. It has been hypothesized that immature coalbeds (i.e., lignite) release substantial dissolved organic compounds such as volatile fatty acids or hydrocarbons during the burial alternation process, which compounds may play important roles for supporting microbial population and activity in the deep sedimentary habitat. Alternatively, it is also conceivable that deep subseafloor microbial activities may contribute to the hydrocarbon reservoir system.

To examine those hypotheses, we measured methanogenic and acetate-oxidation activities by radiotracer incubation experiments using 2 cm<sup>3</sup> of the innermost sediment core samples that were supplemented with <sup>14</sup>C-labelled substrate ([2-<sup>14</sup>C]-acetate) immediately after core recovery. Activities of aceticlastic methanogenesis were observed in the sediment above the coalbed layers (>1990 mbsf), ranging from 0.2 to 4 pmol cm<sup>-3</sup> d<sup>-1</sup>. The highest activity was observed in a coalbed horizon at 1990 mbsf; however, no aceticlastic methanogenesis activities were observed below the 2 km-deep coalbeds. Activities of acetate oxidation to CO<sub>2</sub> were measured by <sup>14</sup>CO<sub>2</sub> production rate from [2-<sup>14</sup>C]-acetate. Interestingly, the acetate-oxidation activities were observed in sediments above the coalbeds, which values were generally higher than those of methanogenesis with the maximum value of 150 pmol cm<sup>-3</sup> d<sup>-1</sup> at 1800 mbsf. The rates gradually decreased with increasing depth from 1800 mbsf and reached below the detection limit in 2 km-deep coalbeds. The occurrence of relatively high acetate oxidation at around 1800 mbsf above the coalbeds indicates the presence of available electron acceptors (e.g., glauconitic iron oxides) in the deep sedimentary habitat.

## Temperature effect of sulfur isotope fractionation by sulfate reducers when used glucose as electron donor

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Sulfate reducing microbe (SRM) is responsible for over 50 % of organic carbon remineralization in marine sediments and thus plays a prominent role in sulfur cycle. Based on a large number of culture experiments of SRM, sulfur isotope fractionation by SRM changes depending on environmental factors including temperature, sulfate concentration and availability of electron donor. The isotope fractionation is recorded in sedimentary sulfates and sulfides. Hence, the sulfur isotopic fractionation is useful to reconstruct ancient environmental condition. However, the mechanism controlling the degree of the sulfur isotopic fractionation is still unclear. Particularly, we have to consider the physiology. Previous culture experiments of SRM indicated that the temperature effect varies with species of SRM. However, there is little temperature control experiments using various electron donor with same strain. We carried out temperature control experiments at 25 °C, 30 °C and 37 °C, by sulfate reducing bacteria DSM 642 using glucose as electron donor. Our results revealed growth rate of DSM 642 is fastest at 30 °C, when using glucose as electron donor. Growth rate is the fastest at 37 °C when using lactate as an electron donor. Sulfate reduction rate is thought to primary factor controlling isotope fractionation. In addition, growth rate and sulfate reduction rate have basically positive correlation. Accordingly, the shift of sulfur isotope fractionation by temperature must be changed when used glucose as electron donor. This result indicates that we should pay attention not only sulfate reduction pathway but also oxidation pathway of electron donor. We report temperature dependency of sulfur isotope fractionation by DSM 642 using glucose as electron donor at the first time, to elucidate the mechanism controlling the degree of the sulfur isotopic fractionation during microbial sulfate reduction.

Keywords: sulfur isotope, sulfate reducing bacteria

## A hot-alkaline DNA extraction method for deep seafloor communities

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Many of the DNA-based researches have greatly enhanced our understanding on stratified nature in seafloor microbial communities. An important prerequisite for DNA-based microbial community analysis is even and effective cell disruption for DNA extraction. With a commonly used DNA extraction kit, in average, roughly two-third of seafloor sediment microbial cells remain intact (i.e., the cells are not disrupted), indicating that microbial community analyses may be biased at the DNA extraction step, prior to subsequent molecular analyses. To address this issue, standardized a new DNA extraction method using alkaline treatment and heating by precisely monitoring microbial cell numbers in the treated samples. Upon treatment with 1 M NaOH at 98°C for 20 min, over 98% of microbial cells in seafloor sediment samples collected at different depths were disrupted. However, DNA integrity tests showed that such strong alkaline and heat treatment also cleaved DNA molecules into short fragments that could not be amplified by PCR. Subsequently, we optimized the alkaline and temperature conditions to minimize DNA fragmentation and retain high cell-disruption efficiency. The best conditions produced a cell disruption rate of 50-80% in seafloor sediment samples from various depths, and retained sufficient DNA integrity for amplification of the complete 16S rRNA gene (i.e., ~1,500 bp). The optimized method also yielded higher DNA concentrations in all tested samples compared with extractions using a conventional kit-based approach. Comparative molecular analysis using real-time PCR and pyrosequencing of bacterial and archaeal 16S rRNA genes showed that the new method produced an increase in archaeal DNA and its diversity, suggesting it provides better analytical coverage of seafloor microbial communities than conventional methods.

Keywords: Seafloor microbial community, DNA extraction, bias, archaea

## Effect of antimony on arsenite oxidation by soil microbial community

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Antimony (Sb) and arsenic (As) are naturally occurring toxic elements in the earth's crust, and both elements exist commonly in sympatric environment. The chemical properties and the mode of toxicity of those elements depend on their oxidation states. Although both oxidation states are toxic, trivalent is more toxic than pentavalent chemical form. The microbiological oxidation of As(III) can impact on the geochemical cycling of arsenic in the contaminated environment, and more than 30 phylogenetically diverse As(III)-oxidizing bacterial strains have been isolated. Although natural microbes are exposed to multiple contaminants in situ, the effect of co-contamination on microbial As(III)-oxidation activity is not well understood. To gain insight into the microbial roles in the biogeochemical cycles of As, we evaluated the effect of co-contamination of Sb and As on the microbial community and their As-oxidizing activity by using solid-phase culturing which was inoculated with antimony mine tailing soil (Ichinokawa, Ehime, Japan). As(III) oxidation rates increased exponentially and reached steady state at day-8 in which 0.15 mM As(III) was oxidized to As(V) in 22.9 hrs. The addition of antimonite tartrate (Sb[III]-tar, 0.15 mM) at day-9 inhibited arsenite oxidation, which was then reduced to 40% by day-15. Successional changes in bacterial community compositions were observed after Sb(III)-tar addition by 16S rDNA- and arsenite oxidase gene (aioA)-targeted analyses. Total of 69 As(III)-oxidizing strains were isolated from the solid samples obtained before and after the Sb(III)-tar addition, and the Sb(III)-tar tolerance of representative isolates were determined. Various As(III)-oxidizing strains exhibited different levels of Sb(III)-tar tolerance in growth response and As(III)-oxidation rates. These results indicated that the co-contamination of As and Sb affect the community composition and activity of As(III)-oxidizing microbial population reflecting the differences in cellular responses among strains to Sb toxicity.

Keywords: Heavy metal pollution, Arsenic, Antimony, Solid phase advective culturing, Soil bacterial community

## Bacterial community structure in different subsurface sediments of the southern Kanto Plain

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Ground source heat pump (GSHP) systems have become popular because of their efficiency in energy conservation and reduction of CO<sub>2</sub> emission. GSHP utilizes the groundwater or subsurface sediment, with an almost constant temperature during the year, as the heat source or sink. Although the temperature changes in subsurface would affect geological structure, groundwater quality, and subsurface microorganisms, very few studies have addressed temperature effects on subsurface biophysical processes. For evaluation of subsurface environmental effects and ensuring overall sustainability of GSHP use, it is essential to investigate how the temperature change may affect the subsurface microbial community structure. Before that, however, it is necessary to know the subsurface microbial community structure that has not yet been affected by temperature change. The purpose of this study was therefore to investigate initial (non-thermal-change-affected) bacterial community structure in deep boring core samples from three different sites in southern Kanto plain. The three sites were the university campuses of College of Humanity and Science, Nihon University (NU; Setagaya-ku, Tokyo), Saitama University (SU; Saitama-city) and Fuchu campus of Tokyo University of Agriculture and Technology (TAT; Fuchu-city, Tokyo). At all three sites, tests of GSHP systems and their environmental response are planned in the near future.

At each site, 10 to 12 sediment core samples were collected from different depths, and whole DNA was extracted from those core samples. PCR-amplified V2-V3 region of bacterial 16S rRNA gene was analyzed by pyrosequencing. The results showed that bacterial community structures of 0-30 m depth were distinctly different among the three boring sites. At the NU site, bacteria belonging to Actinobacteria and Firmicutes accounted for more than half of the whole bacteria population. On the other hand, Chloroflexi,  $\gamma$ -, and  $\delta$ -proteobacteria were predominant at the SU site, and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -proteobacteria were mainly detected at the TAT site. Especially, OTUs assigned to the classes Dehalococcoidetes and Anaerolineae (both belonging to phylum Chloroflexi) were predominant in a wide range of depths at the SU site, and they were particularly detected in former marine sediment. Below 30-m depth,  $\beta$ -, and  $\gamma$ -proteobacteria were predominant at all sites. The relative amounts of some taxonomic groups of bacteria were correlated with depth, pH, electric conductivity of pore water, and particle size distribution. Thus, the variety of bacterial community structure could be attributed to the differences of the depositional ages and environments and/or present subsurface environment at each site. The fundamental data on subsurface bacterial community structures in the southern Kanto Plain from this study will be a useful platform for evaluating the future GSHP-induced temperature change effects on the subsurface environments.

Keywords: subsurface microorganisms, ground source heat pump, next generation DNA sequencing, bacterial community structures

## TOWARDS THE NEXT GENERATION OF CARBONATE-BASED PROXIES

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Reconstructions of past climate and environments are largely based on stable isotopes and trace element concentrations measured on fossil foraminiferal calcite. Element and isotope composition of foraminiferal calcite roughly reflects seawater composition and physical conditions, which in turn, is related to paleoceanographic parameters. Additional biological controls on test composition biases such correlations and needs to be corrected for when aiming at precise and accurate reconstructions. The various physiological processes involved in foraminiferal biomineralization have, however, different impacts on different elements and isotopes. For instance transmembrane transport of Ca-ions has a large impact on Mg fractionation (and hence the Mg-temperature proxy), whereas it has very little effect on Na/Ca ratios (a novel proxy for salinity). Many foraminifera-based proxies are thus impacted by more than one physiological process, which can only be corrected for by 1) quantification of the impacts of these processes (ion pumping, photosynthesis, pH regulation, etc) on calcitic element and isotope composition and 2) combine high-resolution multi-element and isotope analysis to simultaneously correct for these impacts. Since trace metals and isotopes are affected by multiple parameters, combining analyses not only makes reconstructions more robust, but also fundamentally more accurate.

## The evolution of shell microstructure of protobranch bivalves

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Molluscs are the second largest taxa and most of them have the shell of calcium carbonate. Molluscan shells are composed of the complex structural units that are called shell microstructures. Molluscs demonstrate a great variety of microstructures which are similar in phylogenetically close taxa. Thus, investigations of shell microstructures can provide clues for systematic and phylogenetic analyses of molluscs, including fossil taxa. Additionally, these trends suggest the possibility that the shell microstructure had a crucial role in the evolution of Mollusca.

The Protobranchia is an ancestral group of the Bivalvia and comprise four superfamilies (Nuculoidea, Nuculanoidea, Manzanelloidea, and Solemyoidea). However, the systematics of protobranch bivalves has been also problematic, because their simple external shell morphology can provide an insufficient number of informative characters. Therefore, Comprehensive investigation of the shell microstructure and molecular phylogenetic study of protobranch bivalves are required for understanding molluscan evolutionary history. The purpose of this study is to reveal the relationship between the shell micro-structure of protobranch bivalves and molecular phylogeny, and to discuss the evolution of the shell microstructures and their significance as novel morphological characters.

As the result of molecular phylogenetic analysis, it is revealed that the species of protobranch bivalves formed a distinct clade with long branches expect for one exception. One species of Sareptidae were included in Nuculanoidean clade while Sareptidae is placed within Nuculoidea in earlier systematics. SEM observation revealed that each of four superfamilies has a distinct trend in the composition of shell microstructures. And the results of the molecular phylogenetic analysis and the observation of the shell microstructure were consistent with each other. This condition indicates the shell microstructures of the Resent protobranch bivalves show a phylogenetic constraint. Nevertheless, previous study shows this trend is imperfect in fossil taxa. Some fossil nuculoids have nacreous structures and some fossil nuculids possess homogeneous structures. The foliated aragonite that resembles nacreous structure is known as the most primitive shell microstructure. Ancestral nacreous structure was first originated in the Paleozoic protobranch bivalves prior to any other structures that are found in protobranchs of younger ages. Thus, the absence of the nacreous structure may represent the secondary condition in protobranchs. However, the loss of nacreous might be unreasonable, because nacreous structure is considered to be the strongest shell microstructure. In further studies, the evolution of the shell microstructure of protobranchs should be discussed in terms of the habitats and the production costs of the shells as well as protective functions of shells.

Keywords: shell microstructure, mollusca, bivalve, protobranch

## Tube mechanical properties and structural design of *Hydroides elegans* under multiple stressors

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Most marine calcifiers construct robust calcareous skeletons or shells through biomineralization to protect themselves from predatory attacks. Due to increased anthropogenic emission of CO<sub>2</sub> in recent years, reduced global ocean pH and decreased carbonate concentration in seawater are expected to impede the CaCO<sub>3</sub> accretion in shell formation and produce a mechanically brittle shell structure. In addition, the effect of elevated pCO<sub>2</sub> level can act synergistically with temperature and salinity changes in seawater, further affecting the calcification process adversely. To investigate the combined effects of multiple environmental stressors on calcifying marine organisms, we studied the effects of pH (8.1 and 7.8), salinity (34 and 27 ‰), and temperature (23 °C and 29 °C) on the mechanical properties of the tubes built by the tubeworm, *Hydroides elegans*. By employing Micro-CT scanning and micro-force testing, information on tube topography and mechanical properties were analyzed using finite element analysis (FEA). Markedly, despite the structural deterioration observed in reducing pH and salinity, the level of elevated temperature counteracts these effects and even strengthen the overall mechanical properties. This may suggest that warming conditions in the early subtropical summer seawater may rescue the tapeworms from decreasing pH and salinity in the near future.

Keywords: calcifiers, biomineralization, stressors, *Hydroides*, tubeworm

## The mechanical consequence of ocean acidification - the application of finite element analysis

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We studied the effects of low pH (near-future average pH 7.8) seawater on the structure and mechanical properties of the calcifying serpulid tubeworm, *Hydroides elegans*, compared to normal pH (current average pH 8.1).

We found that tubes produced at pH 7.8 altered tube ultrastructure, volume and density, and decreased the mean tube hardness and elasticity to a large extent by ~80% and ~70%, respectively. Specifically, mechanical properties of the outer and inner surfaces of the tube were curbed by pH 7.8, and the tube breaking force required to damage the tube was reduced by 64%.

Nano-indentation to spatially map the micromechanical properties of tubes built by the biofouling serpulid tubeworm, *Hydroides elegans*. The mechanical information was analyzed by computational model, finite element analysis (FEA). In order to study the details of strength properties of the shell, finite element analysis (FEA) was used to simulate the consequence of predatory attack in nature for both shells produced in the control and treatment seawater. The finite element analysis provided a reasonable answer to this phenomenon: altered mechanical properties shifted the stress development and distribution within the tubes and therefore resulting in mechanical weaker part of that were suffering from higher stress concentration.

Keywords: Hydroides, ultrastructure, tubeworm, calcifyer, mechanical properties

## Visualization approach on foraminiferal calcification under various pH

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Foraminifera, marine unicellular organism, have been thought as one of the major carbonate producer in ocean. Their calcareous tests are commonly utilized as paleo-environmental indicators in various studies of earth science because their tests have been archived as numerous fossil in sediment for long time and various environmental information are brought by population, morphology and geochemical fingerprints. The calcareous test itself is interested by many foraminifer scientists. The knowledge about the cytological process on carbonate precipitation has been described for couples of decade using by multi approaches. Foraminiferal regulations of calcium and carbonate ion uptake into calcareous tests from ambient seawater under different pH conditions are of great interest. Our previous studies showed the potential to understanding the biomineralization of foraminifera by the application of fluorescent indicators. Recently, we apply the method to show the spatial distributions of cytological calcium and pH in living cell at several pH conditions (7.5-8.1). Observed results show that foraminifera controls pH variation and concentration of calcium at even different environmental pH. These observations results will help to consider how the geochemical compositions arranging on the foraminiferal test, sensitivity of pH proxy of boron and others.

## Live confocal imaging of cytoplasmic structure and calcification processes in *Amphisorus kudakajimensis*

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Although complex processes of calcification processes have been reported in Foraminifera, details of the cellular events generating organic templates and causing calcification are still unknown. To better understand cellular mechanisms in foraminiferal calcification, it is important to observe the molecular dynamics in vivo (e.g., calcium ion, matrix proteins). Here we report confocal microscopic observations of cytoplasmic structures in a live cell of a *porcelaneous symbiotic foraminifer* *Amphisorus kudakajimensis* and discuss the application of calcium imaging combined with pharmacological manipulations to study intracellular calcium dynamics. In addition, we succeeded in observing the elevated pH (pH 9.0) in organic templates, and lowered pH (pH 6.0) around thread-like cells using a cell-impermeable fluorescent pH indicator (HPTS).

Keywords: calcification, calcium imaging, Live-cell imaging, confocal microscopy

## Internal pH distribution and post-metamorphic biomineralization in the tubeworm, *Hydroides elegans*

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The serpulid tubeworms produce a diverse tube structure through controlled calcification. Cellular environment associated with actively calcifying serpulid tubeworms at metamorphosis were studied using pH and calcium sensitive indicators. With a notable degree of compartmentation, the thoracic region between the collars showed a high pH value above 8.5 and elevated calcium ion levels. As suggested by SEM-EDX results, such region also demonstrated a higher Ca signal. To analyze the presence of crystalline CaCO<sub>3</sub>, the unpolished sample was characterized using SEM-EBSD at 20kV, this low voltage and non-destructive approach showed the direct formation of aragonite. Applying in situ lift-out technique at the calcified region, TEM specimen was prepared for structural analysis using selected area diffraction pattern. This study documents the cellular environment during the first calcification event in the serpulid tubeworm at the transition of metamorphosis and the subsequent aragonite formation.

Keywords: imaging, serpulid tubeworms, visualization, calcifyer, biomineralization

## Genomic Exploration of the Nautilus' Shell Matrix Hydrophilic Proteins: An Insight To Their Evolution in Mollusks

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The presence of a calcium-carbonate-based shell is a defining feature of most members of Mollusca. Thus, research on the genomic aspects of biomineralization of this group is interesting, since the resulting knowledge can be useful for understanding their evolutionary success. Interestingly, most members of cephalopods have secondarily lost their external mineralized shells. The nautiloids, however, is one of the two extant cephalopod groups still maintaining their true shells. Phylogenetically, the nautiloids had diverged from the ancestors of non-shelled, extant cephalopods (Neocoleoidea) in the mid-Paleozoic (Silurian/Devonian boundary,  $\pm 416$ MYA), older than the split between ammonoids and neocoleoids. This makes studies on nautiloid shell biomineral-proteins important and interesting, since insights from the nautiloids might shed light on how shell internalization and de-mineralization events evolved in cephalopods, while at the same time, might help to elucidate the evolution and identification of core components of mollusk shell biomineralization proteins, through comparisons with other molluscan biomineral-related protein data. In this talk, we are reporting our result of the genomic explorations to identify biomineralization-related proteins in the nautiloid *Nautilus pompilius*. To do so in our research, we first determined the total transcriptome sequences from the mantle tissue using pyrosequencing, while simultaneously did a total proteome analysis of the shell's hydrophilic proteins by orbital-trap mass-spectrometry. We then conducted a transcriptome-proteome comparative analysis in order to identify the hydrophilic components of shell biomineral-related proteins in the Nautilus, where we identified 51 distinct shell specific EST/proteins sequences. In the talk, we are also going to discuss how the findings provide an insight to the study of the evolution of mollusk shell biomineralization.

Keywords: Shell matrix protein, Nautilus, Transcriptome, Proteome, Biomineralization

## Using *Acropora digitifera* to bridge the gap between genome biology and geochemistry

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Coral's calcification mechanism has been receiving great attention in the fields of both geochemistry and biology. In geochemistry, high-resolution proxies using coral skeletal elements have been developed to reconstruct climate history (Gagan et al, 2012). In parallel, coral genomes have been sequenced progressively. However, trials that connect these two different fields of studies focusing on coral calcification have not been conducted yet. In this study, we focused on *Acropora digitifera* as the target species because enough genomic information is available (Shinzato, 2011) and its potential as geochemical proxies (Inoue, 2011). First, using ZoophyteBase, which has been recently developed as coral's proteome database (Dunlap et al, 2013), we investigated the genes that are potentially related to metabolism using inorganic minerals in seawater and analyzed their gene components and the correlations with seawater chemistry. Second, using next-generation sequencing, we are currently comparing *Acropora digitifera*'s gene expression between fast and slow calcification lineages of this species. In addition, coral skeletal elements of these materials have been analyzed by ICP-AES. In this presentation, we report the progress of these analyses focusing on calcification related genes and skeletal elements.

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Keywords: *Acropora digitifera*, Calcification, Gene, Skeletal elements

## Comprehensive identification of shell matrix proteins in brachiopods

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Brachiopods are marine invertebrates that appeared in the Cambrian, and they have two shells like bivalves composed of calcium carbonate or calcium phosphate. Shells contain organic matrix, which have important roles in the biomineralization processes. Recently, many shell matrix proteins in molluscs have been identified, and their roles in shell formation have been discussed. On the other hand, shell matrix proteins in brachiopods have not been identified, except for partial amino acid sequences of a chromoprotein, named ICP-1. In this study, we performed comprehensive identification of shell matrix proteins of the brachiopod *Laqueus rubellus* using proteomics combined with transcriptomics. As a result, we identified a total of 18 shell matrix proteins. BlastP search showed that these proteins have no homologues in skeletal proteins identified from other phylum, suggesting that brachiopod and mollusc shells are different in origin.

## Utility of nitrogen isotopic composition of amino acids in shell protein

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Stable isotopic composition of sedimentary organic nitrogen has been employed as a proxy to understand biogeochemical nitrogen cycles in marine and lacustrine environments. However, modification of the isotopic signals during early diagenesis (including heterotrophic assimilation/disassimilation, recycling, and reproduction) in water column and sediments always leads to much uncertainty on the interpretation of bulk isotope data. Recently, we found that a proteinogenic amino acid, phenylalanine, shows little change in the nitrogen isotopic composition during heterotrophic degradation even in long-length grazing food webs, whereas the other proteinogenic amino acid, glutamic acid, shows significant <sup>15</sup>N-enrichment at each step of food webs. Moreover, the isotopic signals of these amino acids in shell protein are always identical to those of biomass protein (e.g., muscle tissue) when the shell was produced. These results imply that the nitrogen isotopic composition of phenylalanine and glutamic acids from shell protein (e.g., in microfossils of foraminifera) captures (1) primary isotopic signals of organic nitrogen in the environment where the shell was produced and (2) trophic position of the shell-owner in ecosystems when the shell was produced.

In the presentation, we will show comparative data sets on the isotopic composition of amino acids between muscle and shell protein from various organisms, and discuss its applicability as a proxy to estimate the primary isotopic signals in environments and the trophic position of organisms of interest.

Keywords: amino acid, nitrogen isotope, food web

## Variation of North Atlantic nitrogen fixation in Caribbean coral skeletons

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Oceanic nitrogen fixation is important as new nitrogen in oligotrophic oceans and balances with denitrification in global nitrogen cycle controlling primary production. North Atlantic ocean is known to have higher nitrogen fixation rates, although the controlling factors have been debated by modern observations and sediment cores in geological time scales. Reef corals have been widely used as paleo-environmental proxy in oligotrophic oceans. Recent studies suggested that nitrogen isotopes of organic matter preserved in coral skeletons  $\delta^{15}\text{N}_{\text{coral}}$  have the potential to record coral nitrogen sources on decadal to millennia scale. In this study, we report recent 90-year records of nitrogen isotopes in *Diploria* sp. coral cores from Cayman Islands.  $\delta^{15}\text{N}_{\text{coral}}$  values were  $+1.9 \pm 2.6$  ( $\sigma$ ) ‰ (n=139), which suggested that the variation of  $\delta^{15}\text{N}_{\text{coral}}$  was controlled by nitrogen fixation ( $\sim 0$  ‰) in ambient seawater. The trend line of  $\delta^{15}\text{N}_{\text{coral}}$  increased  $\sim 4$  ‰ from 1920s to 2010s. This result suggests that nitrogen fixation rate in Caribbean Sea decreased during the past 90 years. Detrended  $\delta^{15}\text{N}_{\text{coral}}$  showed a negative correlation between Atlantic Multi-decadal Oscillation (AMO) index ( $R=-0.71$ ,  $P \ll 0.001$ ), which suggested that nitrogen fixation rate increased in higher SST condition leading an index for hurricane activity on multi-decadal scales. In this presentation, we discuss the relationship between nitrogen fixation and hurricane activity in global warming state.

Keywords: Coral skeletons, nitrogen isotopes, nitrogen fixation, Caribbean Sea, North Atlantic Ocean

## Fluorometric analysis of photosymbiosis: Toward quantitative validation of ecological proxy of planktic foraminifers

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Endosymbiosis of planktic foraminifers with photosynthetic algae (photosymbiosis) is established especially among species which dominate in warm, low-nutrient surface water. Here, photosymbiosis probably plays an important role for host foraminifers, and can be considered as an adaptive ecology to live in such oligotrophic oceans. Therefore, back in geologic time, photosymbiosis could have been involved with species adaptive radiation as well. In such viewpoint, stable isotopic change of foraminiferal test through ontogeny, attributed to change of symbiont photosynthetic effect, has been used as an indicator to detect fossil photosymbiosis. However, how host-symbiont association change through ontogeny, if any, is practically unknown and has never been quantified. Here, we offer new insights for photosymbiosis based on photosynthetic characteristics of symbionts, obtained by in vivo fluorometric analysis (Fast Repetition Rate Fluorometry, FRRF).

We cultured two symbiont-bearing species, *Globigerinoides sacculifer* and *Globigerinella siphonifera*, and conducted FRRF measurement on individual host-algal consortium during the culture period. FRRF can identify photosymbiosis of individual foraminifer instantly in a non-destructive manner, and gives us various photosynthetic characteristics of symbionts, i.e., maximum fluorescence yield ( $F_m$ , index of chlorophyll content), photochemical efficiency ( $F_v/F_m$ , index of potential photosynthetic activity), and effective absorption cross-section of photosystem II ( $\sigma_{PSII}$ , capability of the absorbed energy to promote a photochemical reaction).

Sequential FRRF analyses on single individuals revealed that  $F_m$  increases with growth, and then decrease drastically at the end of their life, which means that the algal biomass per individual foraminifer increases through ontogeny, but the symbionts are rapidly digested at the end.  $F_v/F_m$  and  $\sigma_{PSII}$  values were constant through ontogeny, though  $F_v/F_m$  drops in correspondence with the decrease of  $F_m$ . Compared between the two species, average values of both  $F_v/F_m$  and  $\sigma_{PSII}$  showed statistically significant differences.  $F_v/F_m$  was significantly higher in *Gs. sacculifer*, which means that symbionts are more actively photosynthesizing in *Gs. sacculifer*. Because  $F_v/F_m$  is mainly depends on nutrient availability, it is a direct evidence of nutrient (metabolite) flow from host to symbionts. On the other hand,  $\sigma_{PSII}$  was higher in *Gn. siphonifera*, indicating that this species can utilize low light energy more efficiently, i.e., more " low-light-adapted " than *Gs. sacculifer*. Actually, it is consistent with inferred habitat preference of *Gn. siphonifera*, which is relatively deeper than *Gs. sacculifer*.

These FRRF results provide us information of foraminiferal photosymbiosis both quantitatively and qualitatively. When the information is combined with test geochemistry mentioned above, it will presumably enable us to quantify the photosynthetic activity from foraminiferal tests. Then, it can be applied to fossil specimens as a validated ecological proxy of photosymbiosis.

Keywords: planktic foraminifers, photosymbiosis, Fast Repetition Rate Fluorometry

## Skeletal isotope compositions of *Acropora* coral primary polyps experimentally cultured at different temperatures

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We investigated temperature and growth-rate dependency of skeletal oxygen and carbon isotopes in primary polyps of *Acropora digitifera* (Scleractinia: Acroporidae) by culturing them at 20, 23, 27, or 31 °C. We cultured primary polyps of *A. digitifera* at Sesoko Station, University of the Ryukyus, Motobu, Okinawa Prefecture, Japan for 10 days. From the results of the polyp weight and polyp area, calcification was most rapid at 27 and 31 °C. The  $\delta^{18}\text{O}$  — temperature relationship ( $-0.18\text{‰}/\text{°C}$ ) is consistent with reported ranges for *Porites*, indicating that juvenile *Acropora* polyps can be used for paleotemperature reconstruction. We found a gap between curves for the experimental polyps and the equilibrium curves for inorganic aragonite of about 3.0 ‰ for  $\delta^{18}\text{O}$  and 8.0 ‰ for  $\delta^{13}\text{C}$ , with the primary polyp values being lower than the equilibrium values of inorganic aragonite. The kinetic isotope effect was evident in the polyps cultured at low temperature but disappeared at high temperatures, despite relatively low light levels. The estimated upper calcification flux limit for a kinetic isotope effect ( $\sim 0.4 - 0.7\text{ g CaCO}_3/\text{cm}^2\cdot\text{y}$ ) was similar to that of *Porites* colonies with a linear extension rate of  $<5\text{ mm/y}$ , suggesting that the calcification flux may be used as a measure of kinetic isotope effect dominance in different genera at different growth stages.

Keywords: coral, temperature, stable isotopes, polyp, kinetic effect

## Corals at marine volcano of Satsuma iwo-jima: Implication for a new proxy of hydrothermal events and biological adaptati

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Coral cores from massive corals could record marine environmental and ecological changes in their annual bands with monthly temporal resolution in the present and/or the past. We discovered large massive Porites corals living at active volcanic island of Satsuma Io-Jima, located 50 km south from Kyushu area, southern part of Japan. Satsuma Io-Jima provides a unique opportunity to observe marine organism living under extreme environments of volcanic gases emission and different types of hydrothermal activities from sea flower. We collected eleven coral cores from four different conditions around the island to test if corals could record volcanic and hydrothermal activities and how corals could survive in extreme environments such as very low pH condition with CO<sub>2</sub> emission. Coral annual bands recorded in x-ray images revealed that these corals have been survived at least during last a few hundreds years. Coral extension rate for the site near hydrothermal vent was significantly small (1-2mm/year) relative to that for general condition of Porites corals (ca. 10-20 mm/year), suggesting that coral growth was influenced by hydrothermal activity. We will demonstrate our preliminary results of geochemical approaches of  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , Sr/Ca, Mg/Ca, Ba/Ca, and F/Ca in coral skeletons and in surrounding seawater and discuss the possibility for reconstructing the past hydrothermal events and relationship between marine ecosystem and extreme environments at volcanic activity as the analogues for coral adaptation to future ocean acidification.

Keywords: Coral geochemistry, hydrothermal activity, coral adaptation, ocean acidification

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BPT02-16

Room:421

Time:May 1 14:45-15:00

## Sediment ecosystems dynamics on proxies development of foraminifera

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<sup>1</sup>Japan Agency for Marine-Earth Science and Technology

I would like to discuss how sediment ecosystems dynamics give affection to foraminiferal environmental proxies developments.

Keywords: Sediment ecosystems, dynamics, deep-sea foraminifera, environmental proxies

## Benthic Foraminifera from the deep-water Niger delta (Gulf of Guinea): Assessing activity of hydrate pockmark

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We present an ecological study of foraminifera from 4 deep-sea stations sampled in a pockmark field from the deep-water Niger delta (Gulf of Guinea, Equatorial Atlantic Ocean). All stations are located very close to each other (less than 1.2 km distance). Both sites GMMC-01 and GMMC-02 settle in an active pockmark where methane seepages were recorded by ROV observations. A third station (GMMC-03) is located in a topographic depression which is interpreted as a collapsed pockmark where no gas seepage takes place. The site GMMC-04 is a reference station, without past or present seepages. The main objective of this study is to define whether fossilizing benthic foraminifera are reliable and relevant proxies to detect gas emission in relation to hydrocarbon resources. We focus on living (stained) and dead individuals from present environments, and combine our observations with an outstanding analysis of stable isotopes ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) in tests of living and dead foraminifera. Our observations show that degraded organic matter with low bio-availability is present at all stations with a preferential burial of organic compounds in topographic depression (GMMC-03 station). Mudclast breccias cemented by authigenic carbonates (mainly aragonite) are recorded at both station of active pockmark (GMMC-01 and -02). There, prokaryotic consortia involved in both sulphur and methane cycles underline that both sulphide production and methane oxidation take place in the sediment close to sediment-water interface. Compared to the reference site GMMC-04, living foraminifera recorded at active and inactive pockmark show only minor changes in terms of diversity, standing stocks and faunal composition. However, the  $\delta^{13}\text{C}$  signal of some living and dead (but well-preserved) foraminiferal species (*Ceratobulimina contraria*, *Melonis barleeanus*, *Uvigerina peregrina*) is moderately depleted in active pockmark compared to both other stations. This depletion may be related to (1) a discrete geochemical imprint of anaerobic methane oxidation in upper sediments and (2) a potential effect of prokaryotic  $^{13}\text{C}$ -depleted biomass as a potential food source for benthic foraminifera. Overgrowth of authigenic carbonate on badly preserved foraminifera generates an important shift to lower  $\delta^{13}\text{C}$  values. Whereas living faunas reflect "snapshot" environmental conditions at the sampling period (November 2011) when seepages were likely discrete, dead faunas (modern thanatoconosis) carry a reliable message integrating temporal variability of gas emission. They reveal major faunal differences that are quite reliable to detect gas hydrate seepages in different pockmark stages with some key-species (i.e., *Bulimina marginata*, *Bolivina albatrossi*) underlining periods of enhanced methane emission and pockmark collapsing.

## Potentials and challenges on the use of environmental DNA to reconstruct deep-sea ecosystem and environmental changes.

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Deep sea is one of the most difficult to access environment, and consequently one of the most poorly known. However, deep-sea sediments and the organisms inhabiting this environment play a crucial role in the oceans geochemical cycles. Benthic communities are often well adapted to their local environment and therefore can reflect accurately the present conditions but also can provide insights into the past history of environmental changes. Unfortunately, except for a few specific taxa, most knowledge on deep-sea biodiversity is still missing. Deep-sea fauna is very patchy and rarity of most taxa adds to the sampling difficulty using traditional methods. Environmental DNA (eDNA) presents the advantage not to rely only on living organisms present in the sample. The presence of a species in an environment can also be detected using trace DNA left by the organism in the sediments (fragment of dead organisms, fecal pellets, etc). Recent development of DNA sequencing technologies led to promising results in the large-scale exploration of biodiversity from deep-sea environments based on eDNA using environmental DNA.

Here we will examine the use of environmental DNA as a proxy to reconstruct deep-sea communities and estimate environmental conditions in the deep-sea ecosystem. We will present data obtained from deep-sea (500-9000 m) around Japan as well as from worldwide deep-sea oceans to explore the potential use of eDNA as a proxy at various geographical and historical scales and levels of resolution. The data obtained from Iheya North vent field in the Okinawa Trough allowed us to compare the signal of eDNA along extreme environmental gradients at a very restricted geographical scale, while worldwide deep-sea eDNA survey provided us with information of on the global deep-sea environment history and colonisation. Potential of eDNA obtained from sediments to obtain information on water column processes such as plankton blooms will also be discussed.

Keywords: Deep Sea, Environmental DNA, Biodiversity, Sediment, Hydrothermal vent

## Long term monitoring of oxygen distributions at sea floor, Sagami bay, Japan.

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<sup>1</sup>JAMSTEC

Oxygen (O<sub>2</sub>) distributions at the sediment water interface (SWI) are fluctuated by physical, chemical and biological interactions. Especially, bioturbation and bioirrigation at SWI enhance O<sub>2</sub> supply into the sediment, and such benthic activities play significant role on maintaining oxic environment at sediment surface. However, studies of these interactions in deep sea SWI have been limited due to technical limitations for the instrument developments and the operations. In order to investigate the SWI, we constructed a planar O<sub>2</sub> optode system to visualize O<sub>2</sub> distributions across SWI. This system was optimized for low O<sub>2</sub> concentrations, which value was equivalent to the typical O<sub>2</sub> minimum zone, ~50 μM. Using with a platform (so-called lander) to mount the planar O<sub>2</sub> optode, the system was set on the sea floor. On 21/Jan/2008, the deployment for the measurement was stated at Sagami bay, 1170m in water depth by extension of the power cable from Hatsushima deep-sea observatory. Until 31/Jan/2008, the two dimensional O<sub>2</sub> profiles were obtained at 1 hour interval. Throughout the deployment, 245 O<sub>2</sub> profile images and the corresponding grayscale images were obtained. Throughout the analysis of the images, we found the following aspects and phenomena: (1) O<sub>2</sub> penetration depth ranged 5~8mm. (2) O<sub>2</sub> irrigations sporadically enhanced the O<sub>2</sub> penetration depth to ~10mm. (3) O<sub>2</sub> concentrations in the sediment were fluctuated by time. (4) Microtopography and hydrodynamics affected to the O<sub>2</sub> concentrations on the sediment surface. (5) Meiobenthic activities suggesting anoxic metabolism were found below O<sub>2</sub> penetration depth. In the presentation, we present these characteristics with the O<sub>2</sub> images obtained from the *in situ* measurement.

Keywords: sediment-water interface, oxygen, optode, meiobenthos

## New evidence for halite co-precipitation during coral calcification

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In the last JpGU Meeting, we reported halite grains in coral skeleton through the observation of massive coral skeleton of *Porites lobata* by Analysis Transmission Electron Microscope (ATEM). Each halite grain typically shows a square shape and its grain size is around 80 nm. The spatial distribution of halite grains is inhomogeneous and seems to be independent on the arrangement of growth lines.

We observed new evidence that the halite grains in coral skeleton could precipitate during coral calcification. The electron diffraction patterns from some selected areas including both an aragonite and a halite grain show that there are special crystallographic orientation relationships between them. In consideration of misfit ratios between some selective bond lengths of halite and those of aragonite, crystallographic orientations of halite and aragonite seem to be a kind of hetero-epitaxial relationship.

This is the first observation for a primary precipitated mineral phase other than aragonite in coral skeletons. The halite phase in coral skeleton will provide a new perception for understanding the process of coral calcification.

Keywords: reef-building coral, calcification, biomineral, aragonite

## Ocean acidification in the tropical Northwest Pacific since the mid-20th century reconstructed from coral boron isotope

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<sup>1</sup>University of the Ryukyus, Japan, <sup>2</sup>National Cheng Kung University, Taiwan, <sup>3</sup>Tohoku University, Japan

Ocean acidification has been accelerating as a result of absorption of increasing anthropogenic CO<sub>2</sub> in the atmosphere emitted by fossil-fuel combustion and land-use practices since the Industrial Revolution, which can be resulting in decreased surface ocean pH and posing a critical threat to marine ecosystems (e.g., Sabine et al., 2004; Orr et al., 2005). By the end of the 21st century, predictions based on different scenarios indicate that ocean pH will decrease by 0.3-0.4 pH units. Only a few long-term continuous observations of sea surface pH have been derived from Station ALOHA off the Hawaiian Islands in the North Pacific, near the Bermuda Islands, and near the Canary Islands in the North Atlantic. A decreasing pH trend in the western North Pacific surface waters for 1983-2007 was estimated from the observational data of oceanic CO<sub>2</sub> partial pressure and related properties (Midorikawa et al., 2010). To elucidate the natural variability of ocean pH and assess the actual trend in ocean acidification more accurately, we must go further back in time. For these reasons, we rely on paleo-pH archives or other related parameters.

Massive corals, an informative archive of past ocean environments, precipitate annually banded calcium carbonate skeletons at a relatively rapid rate (about 1 cm per year), allowing for accurate chronological control and high-resolution sampling. Because of pH-dependent isotopic fractionation between the two dominant boron species in seawater, boron-isotopic systematics in marine carbonates provide a potential proxy for ocean pH in the past (e.g., Hemming and Hanson, 1992). Nevertheless, only two previous investigations provided boron-isotope time series from long-lived corals from the Great Barrier Reef in the South Pacific for the last 300 years. Unlike seawater temperature and salinity records (Asami et al., 2005; Felis et al., 2009), no coral-based reconstruction of long-term pH variation in the North Pacific has been reported.

Here, we generated an annually resolved 60-year-long (1940-1999 A.D.) record of seawater pH from boron isotope composition in a *Porites* coral collected in Guam Island, located in the Western Pacific Warm Pool which contains the highest annual sea surface waters and serves as a heat engine for the earth climate. The first long-term continuous boron isotope-pH proxy record in the North Pacific from the coral provides evidence of a slight ocean acidification trend (equivalent to 0.05-0.08 pH units for surface water) since the mid-20th century, although the critical factors that affect interannual variability remain unknown (Shinjo et al., 2013). From this perspective, the results of this study will provide improved constraints on global atmosphere-ocean interaction models and understanding of the future coral reef ecosystems.

Keywords: coral skeleton, boron isotope composition, pH, ocean acidification, North Pacific

## 15N/14N mapping of the isotope labeling cultured foraminifera using ultra thin section

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<sup>1</sup>JAMSTEC, <sup>2</sup>AORI, University of Tokyo, <sup>3</sup>Marine Works Japan

Shallow water benthic foraminifera, *Ammonia beccarii*, survive under anoxic conditions in conjunction with possible endobionts. Based on the amino acid analysis, those endobionts are expected to utilize nitrate pool in the foraminifera. However, nitrogen cycles in the foraminiferal cell and endobionts are still unclear. Here, we obtained two dimensional-nitrogen isotopic compositions of *A. beccarii* which had been incubated under oxic and anoxic conditions with <sup>15</sup>N-labeled nitrate. After observing with transmission electron microscope to confirm cellular ultrastructure and endobiont distribution, same ultra thin section was examined for nitrogen isotopic composition analysis using secondary ion mass spectrometer. Nitrogen isotopic compositions were measured with spatial resolution better than 400 nm. <sup>15</sup>N-enriched parts were found in certain structures in the cell, but not in the endobionts in this experiment.

Keywords: Benthic foraminifera, nitrate respiration, symbiotic microbe, NanoSIMS

## Snowball Earth and GCM simulation

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Numerical simulation of snowball Earth, using out-of-date supercomputer program has been performed recently in USA, France and Germany. It seems to be difficult to reconstruct Snowball state by their simulation, while freezing more than 55% of ocean. If continents are gathered along the equatorial region such as Rodinia in the case of Sturtian and Marinoan Snowball Earth in Neoproterozoic, total surface irradiance (TSI) seems plausible to be 95% of present day and CO<sub>2</sub> level as same as today. However, if the atmospheric CO<sub>2</sub> is 2-6 times more than today, Snowball state cannot appear (Voigt et al., 2011). More realistic CO<sub>2</sub> concentration of Neoproterozoic Earth was 20-50 times more than today. In addition, the temperature fluctuation of Snowball Earth period, from Sturtian to Marinoan, was -40 °C to +40 °C and vice versa within a short period <10 m.y. which seem to be impossible because input and output of CO<sub>2</sub> by plate tectonics usually takes time more than several hundreds of millions years.

GCM simulation exaggerates positive feedback of CO<sub>2</sub> too much. It is time to remodel GCM, considering the amount of clouds and its effect.

## Glaciation carbon cycle in Neopaleozoic and Phanerozoic by numerical carbon cycle box model to fix carbon isotope ratio

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In Ediacaran period, some environmental changes are proposed (e.g. Oxidation, nutrient and carbon cycle) before the Cambrian explosion and macroscopic multicellular metazoan first appeared and their sizes became drastically large. It suggests that carbon cycle in ocean changes in Ediacaran period. Therefore, we assumed box model that there were two carbon reservoirs in Ocean and fluxes are taken as the first order reaction of each reservoir (Rothman et al., 2003; Ishikawa et al., 2012). Thus, we could estimate both  $\delta 1$  and  $\delta 2$  by changes of parameters to trace analyzed  $\delta 13C_{carb}$  and  $\delta 13C_{org}$  curves from drilling core samples in Three Gorges through the Ediacaran to the early Cambrian (Tahata et al., 2012; Kikumoto et al., 2013; Ishikawa et al., 2012). The  $\delta 13C_{carb}$  in Three Gorges shows negative excursions in Gaskiers glaciation (ca. 580 Ma), Shuram excursion (ca. 570-550 Ma) and Precambrian/Cambrian boundary (ca. 542 Ma). On the other hand, the  $\delta 13C_{org}$  in Three Gorges show constant ca. -30 per mill in early Ediacaran and correlation to  $\delta 13C_{carb}$  after Shuram excursion.

The parameter sets suggested carbon cycle changes in Ediacaran period. This Reconstructed Three Gorges carbon cycle quantitatively estimated carbon cycle changes in these periods. The results indicate the rate of remineralization need to increase before the Shuram excursion and the rate of organic carbon burial increase to ca. 100 times in the late stage of Shuram excursion. The increase of remineralization might indicate step-by-step changes of dominant metabolism from anaerobic respiration to aerobic respiration. In addition, the change of organic carbon burial is possibly consistent with the first appearance of mobile metazoan and zooplankton.

The parameters in early Ediacaran apply to carbon cycle in Marinoan glaciation before Ediacaran period. On the other hand, parameters in modern Ocean apply to carbon cycle in P-T boundary. It has possibility that there is glaciation in P-T boundary. The DOC reservoir size differed in Marinoan and P-T boundary. The different DOC reservoir size cause different carbon isotope changes in Marinoan glaciation and P-T boundary.

Keywords: Glaciation, Carbon cycle, Ediacaran, Marinoan, Phanerozoic

## Evidence for meteoric diagenesis during Gaskiers glaciation recorded in the Ediacaran carbonate in South China

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<sup>1</sup>Kyushu University

Carbon isotope ratios fluctuate globally in association with environmental changes in atmosphere and ocean system. The major carbon isotopic excursions happened in Earth history would be linked to biological evolutions and extinctions and these causes have been investigated actively (e.g. Grotzinger et al., 2011). The Ediacaran period when multicellular animals dramatically evolved also have two major excursions reflected from the Gaskiers glaciation (Sawaki et al., 2010) and the Shuram event (Fike et al., 2006). The Ediacaran Yangtze block in South China is unmetamorphosed sedimentary rocks, and high-resolution carbonate carbon isotopic data have been extensively reported from this block (e.g. Jiang et al., 2011). Although these data could have reflected characteristic oceanic structure and influenced by oceanic oxidation in Ediacaran, those causes have been not fully understood. This study investigated the Yangjiaping section that records large fluctuation of bulk carbonate carbon isotope (e.g. Kunimitsu et al., 2011) and analyzed the cause of fluctuation by measuring the bulk strontium isotope ratios and the carbon-oxygen isotopes of cement components.

Yangjiaping section is about 470 m thick and divided into the Nantuo Formation, the Doushantuo Formation and the Dengying Formation in ascending order. The Nantuo Formation is extensively distributed as post-Marinoan diamictite in the Ediacaran Yangtze platform. The Doushantuo Formation consists of carbonate, black shale, chert and phosphate and the Dengying Formation consists of carbonate and chert. Kunimitsu et al. (2011) subdivided the Doushantuo Formation into Unit 1, Unit 2 and Unit 3 in ascending order, based on the trends of carbonate carbon isotope. The large fluctuation of carbon isotope occurs in Unit 3. Coarse-grained carbonate in upper Unit 2, Unit 3, and the Dengying Formation are available for analyzing isotopic composition of the cement components. Unit 2, lower part of Unit 3 and the Dengying Formation exhibit only minor difference between the bulk and the cement parts in carbon and oxygen isotopes. While, middle to upper parts of Unit 3 record significantly lower isotopic composition of the cements, which are lower than the bulk values by ~25 permil for carbon and by ~7 permil for oxygen. Additionally, the strontium isotopic ratios in Yangjiaping section ranging from 0.7079 to 0.7105 indicate an increasing trend from Unit 3 to upward.

Extremely low carbon isotope of the cement parts is responsible for the large fluctuation of the bulk values in Unit 3. It was formed by secondary addition of cement in meteoric diagenetic environments. Upper part of Unit 2 and Unit 3 consist of very shallow water lithofacies implying that the platform was easily exposed during sea level fall. Oxygen-rich meteoric diagenetic water induced remineralization of organic matter that occurred in pore spaces, and formed low carbon isotope of the diagenetic water. Additionally, increase of strontium isotope in Unit 3 reflected an enhanced continental fluxes that could be attributed to the promotion of continental weathering at the Gaskiers glaciation (ca. 580 Ma). The line of evidence suggests that very shallow part of the Yangtze platform was exposed above sea level during the Gaskiers glaciation.

Keywords: South China, Ediacaran, meteoric diagenesis, the Gaskiers glaciation, carbon isotope

## Nitrogen isotope chemostratigraphy of the Early Cambrian platform sequence at Three Gorges, South China

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The earth is only the planet where higher forms of life exist. The appearance and evolution of metazoans are the most important issue of the evolution of the earth and life, but the causes are still obscure. We made multi-isotope and elemental chemostratigraphies of drill core samples from the Ediacaran to Cambrian in South China. The results show that secular changes of nutrients influenced the evolution of the metazoan. We focused nitrogen that is one of the most important nutrients in bioessential elements, and reconstructed the temporal variation of the oceanic nitrate contents in the early Cambrian. Preservation of continuous and fossiliferous strata from the Ediacaran to the Cambrian, South China provides reconstruction of secular change of compositions of seawater through the time.

Kikumoto et al.(2014) analyzed the nitrogen isotope ratios of the organic nitrogen. The results show that the nitrogen isotope ratios were high from early to middle Ediacaran, and decreased from middle Ediacaran to earliest Cambrian and then became high. They interpreted the change in the nitrogen isotope as secular change of nitrate contents of seawater through the time. And Shimura et al.(2014) showed phosphorus contents in carbonate rocks and minerals from the Ediacaran to the Cambrian, and estimated secular change of phosphorus contents of seawater through the time. As a result, they interpreted that the seawater was depleted in nitrate contents from the early to the middle Ediacaran due to high phosphorus contents. From the middle Ediacaran to the earliest Cambrian, the seawater had higher nitrate contents because of decrease of phosphorus contents possibly due to oxidation of seawater and then lower nitrate contents after the early Middle Cambrian.

The hypothesis is very attractive, but many problems remain, especially in the Cambrian samples. One is whether the change in the nitrogen isotope values is controlled by lithological change. The second is which the change was transient or abrupt because the previous work showed no nitrogen isotope variation between them. Correlation of the nitrogen isotope values with other proxies was unclear, too. This work presents the nitrogen isotope ratios of organic nitrogen in black shales and carbonate rocks of drill core samples from the Shuijintuo and Shipai formations. The nitrogen isotope ratios gradually increase from +2 to -2 ‰ in the Shuijintuo Formation, whereas they are fluctuated from ca. +1 to +3 ‰ in the Shipai Formation. In addition, the variation of the nitrogen isotope ratios is not related with difference of lithology: carbonate rocks and black shales, respectively. Although low nitrogen isotope anomalies are found in samples with low organic nitrogen contents, no clear correlation between the total organic nitrogen contents and nitrogen isotope ratios is observed. The results indicate that the variation in the nitrogen isotope values is not artificial due to lithological change and secondary alteration but it was caused by environmental change through the Early Cambrian. The increase of the nitrogen isotope ratios was gradual, and was found in the black shales at the upper part of the Shuijintuo Formation, indicating that the change was transient. There is no correlation between the nitrogen and carbon isotope values of organic matter through the time.

The increase of the nitrogen isotope ratios indicates that the nitrate content of the surface seawater decreased. In other words, it shows that the nitrate-rich environment was completed in the early Cambrian and that nitrate started to be limited with increasing primary production and denitrification activity became significant. It shows that the modern-style marine nitrogen cycle was established in the early Cambrian. Higher primary productivity led to increase of the oxygen content of the atmosphere and ocean, promoting the Cambrian explosion.

## Dendroid multicellular thallophytes preserved in a Neoproterozoic black phosphorite in southern China

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Both metaphytes and metazoans are reported from the well-preserved multicellular assemblage in the Neoproterozoic Doushantuo phosphorite in Weng'an of the Guizhou province, southern China. Here, a new form of dendroid multicellular thallophytes is documented. The new thallus is slightly heteromorphic. Several lateral branches extend from upper portion of the main axis, bearing terminal vegetative vesicles, carpogonial vesicles, monosporangium-like discoidal vesicles and urn-shaped pseudoparenchymatous structures. The vegetative vesicle gives rise to a club-shaped pseudoparenchymatous structure, characterised by the medulla?cortex thallus differentiation, which may represent the early stage of the thallus. An oogamous conceptacle arising from one carpogonial vesicle is a highly specialised goblet-shaped conceptacle. The discovery and identification of these new dendroid multicellular thallophytes not only document the first fossil-histological evidence for the heteromorphism of Precambrian organisms but also provide a potential insight for our enhanced understanding of the life cycle of the Precambrian red algae.

Keywords: Neoproterozoic, Doushantuo, multicellular thallophytes, dendroid, heteromorphic

## Marine biomass changes after the Neoproterozoic Marinoan Glaciation in Australia

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The late Neoproterozoic Marinoan glaciation (ca. 635 Ma) was one of the most severe ice ages in the Earth history. It is thought that the glaciation affected the biosphere and caused some succeeding evolutionary events, such as the occurrence of the Lantian biota, the first known macroscopic multicellular eukaryotes (Yuan et al., 2011, 2013). We analyzed sedimentary organic molecules from post-Marinoan deposits in three Australian cores and a section: the Wallara-1 drillhole in the Amadeus Basin, the GILES-1 drillhole in the Officer Basin, the SCYW79-1A drillhole in the Adelaide Geosyncline, and the Moonlight Valley type section in the Kimberley region.

The analysis identified more than 10 types of sedimentary organic molecule, and some of these were used as indicators of biomass for this time. The trends and correlations among the indicators through the researched formations revealed that sum of pristane and phytane (biomass of photosynthetic organisms), 2- $\alpha$ -methylhopane (biomarker of cyanobacteria), aryl isoprenoids (photosynthetic organisms and/or green sulfur bacteria), and Cholestane (biomarker of eukaryotes) relative to total organic carbon (TOC) had a positive peak(s) in the lowermost Ediacaran System, which represents an increase in biomass of photosynthetic organisms and eukaryotes immediately after the retreat of the Marinoan glacier, probably caused by an increased nutrient flux to the sea. Except for aryl isoprenoids, those indicators relative to TOC increased through the upper part of the lowermost Ediacaran formations, which may correspond to a recovery and/or evolution of eukaryotes after the Marinoan glaciation.

Yuan, X., Chen Z., Xiao, S., Wan, B., Guan, C., Wang, W., Zhou, C. & Hua, H. (2013) The Lantian biota: A new window onto the origin and early evolution of multicellular organisms. *Chinese Science Bulletin* 58, 701-707.

Yuan, X., Chen, Z., Xiao, S., Zhou, C. & Hua, H. (2011) An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature Letter* 470, 390-393.

Keywords: Organic Geochemistry, Neoproterozoic, Ediacara, Marinoan Glaciation

## Oceanic oxidation mechanisms spanning the Snowball Earth and early animal diversification

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The late Neoproterozoic (780 million years ago (Ma)) to early Cambrian (520 Ma) interval witnessed the rise and evolution of early animals. Oceanic oxidation is believed to be crucial in driving the early animal evolution. However, the oxygenation mechanism in seas during this critical period remains unknown. Here we found (i) oceanic anoxia before and during the Marinoan global glaciation (MGG) (660-635 Ma), (ii) surface-water reoxidation immediately after the MGG (635 Ma), (iii) intermediate-water oxidation in the mid-Ediacaran (600 Ma), (iv) deep-water oxidation in late Ediacaran (580 Ma), (v) oceanic anoxia at the end of the Ediacaran (541 Ma), and (vi) reoxidation in the early Cambrian (535 Ma). Thus, a stepwise marine oxygenation took place from shallow to deep water through the Ediacaran epoch, and every major changes in oxygen levels coincided with an important revolutions of marine life, suggesting a coevolution of ocean chemistry and early animals occurred during this period.

Keywords: Ediacaran, Cryogenian, Neoproterozoic, oxygen, biomarkers

## Geochemical identification of projectile from the Upper Triassic ejecta deposits in Japan

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Our previous studies have revealed that the Sakahogi section in central Japan contains an impact ejecta layer in the Late Triassic, which was derived from an extraterrestrial impact event. This ejecta layer is characterized by platinum group element (PGE) positive anomalies and Os isotope negative excursion together with enrichments in Ni and Cr, and abundant occurrences of Ni-rich magnetite grains and microspherules. PGE anomalies in the Late Triassic sediments were also discovered from deep-sea claystone layers at three bedded chert sections in southwest Japan as follows: (i) Unuma section in the Inuyama area, Mino Belt, (ii) Hisuikyo section in the Kamiaso area, Mino Belt, and (iii) Enoura section in the Tsukumi area, Chichibu Belt. Combined PGE and various isotope data from these ejecta layers are insightful so as to identify the meteoritic material which has caused the Late Triassic impact event. Here we report the PGE element ratios, and Cr and Os isotope compositions of these ejecta layers to understand the projectile component.

The Ru/Ir and Pt/Ir ratios of all the claystone samples from the study sites are plotted along the mixing line between chondrites and upper continental crust. Although a chondrite cannot be distinguished from iron meteorites by using PGE/Ir ratios, the claystone layers show Cr/Ir ratios between  $10^4$  to  $10^5$ , indicating that the claystone layers are clearly contaminated by chondritic material. The Os isotope compositions ( $^{187}\text{Os}/^{188}\text{Os}$  ratios) in the claystone have a narrow range from 0.126 to 0.128 and these values are well similar to those of chondrites. The Cr isotope data are useful to identify the extraterrestrial components in the ejecta deposits because meteorites of different classes have a distinct  $^{54}\text{Cr}$  isotope anomaly. The presence of positive  $\epsilon^{54}\text{Cr}$  anomaly in all claystone samples strongly suggests that a carbonaceous chondrite-like material was involved in the studied ejecta layers. Consequently, these geochemical lines of evidence indicate that the Upper Triassic ejecta layers in the Japanese accretionary complexes have been most likely derived from a carbonaceous chondrite.

Keywords: impact event, platinum group element, osmium isotope, chromium isotope

## Stratigraphic Sequence in the Axim-Princess Town section of the coastal Paleoproterozoic Greenstone Belt in the Birimian

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The coastal Axim-Princess Town sequence of the Paleoproterozoic Birimian Greenstone Belt contains very thick volcanoclastic and organic rich sedimentary rocks. Recent work in this area has revealed more than 5 km wide excellently preserved and continuously outcropping rocks which generally exhibit isoclinal fold with west vergence and east-ward younging lithologies of over 1000m total thickness.. Stratigraphically, the lower portion contains thick vesicular volcanoclastic rocks probably of sub-aerial origin. The middle portion is made up of well laminated alternation of volcanoclastics and black shale but the upper portion is dominated by well laminated black shale sequence. This fining upward sequence is likely indicative of shallow to deep sea depositional conditions of the rocks. Though preliminary evidence gathered suggests an oceanic island arc in shallow to deep ocean setting for the rocks, highly negative  $\delta^{13}C$  values ranging from -43 ‰ to -37 ‰ obtained from the black shale further suggests deep ocean anoxic conditions prevailed during deposition of the rocks, presumably with carbon derived from organic matter via cyanobacteria.

Keywords: Paleoproterozoic, Berimian Greenstone belt, island arc ocean floor environment

## Geochemistry of the Nsuta Mn deposit in Ghana: Implications for the Paleoproterozoic ocean redox state

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Oxygenation of the atmosphere and oceans may have influenced the ocean chemistry and diversified contemporaneous life. A number of large manganese (Mn) deposits are distributed in the Paleoproterozoic sedimentary successions that were formed during the great oxidation event (GOE) around 2.4-2.2 Ga (Maynard, 2010 *Econ. Geol.*). Due to the high redox potential of Mn, occurrences of Mn deposits have been regarded as important evidence for a highly oxidized environment during the Paleoproterozoic (Kirschvink et al., 2000 *PNAS*). Furthermore, because Mn oxides are efficient scavengers of various elements, including bio-essential elements such as Mo, formation of large Mn deposits may have affected the seawater chemical composition and ecology during the Paleoproterozoic. However, due to lack of detailed geochemical records constraining the genesis of each Mn deposit, the relationships among the formation of Mn deposits, the evolution of atmospheric and ocean chemistry, and the diversification of early life are still ambiguous.

In this study, we report the Re-Os isotope compositions, rare earth element (REE) compositions, and abundance of manganophile elements in the Mn carbonate ore and host clastic sedimentary rock samples collected from the Nsuta Mn deposit of the Birimian Supergroup, Ghana. The Nsuta deposit is one of the largest Paleoproterozoic Mn deposits, although its genesis remains controversial (Melcher et al., 1995 *Mineral. Mag.*; Mucke et al., 1999 *Miner. Deposita*). The composite Re-Os isochron age (2149 ± 130 Ma) of the Mn carbonate and sedimentary rock samples is consistent with the depositional age of the sedimentary rocks (?2.19 Ga) obtained from U-Pb zircon age of the volcanic rocks (Hirdes and Davis, 1998 *J. Afr. Earth Sci.*), suggesting that the timing of Mn ore deposition was almost equivalent to the host rock sedimentation. The PAAS-normalized REE patterns show positive Eu anomaly in all samples and a positive Ce anomaly only in the Mn carbonate ore. These REE patterns suggest possible contribution of Eu-enriched fluids derived from hydrothermal activity and Ce enrichment due to the oxidation of Ce(III) by Mn(IV) during ore formation. Among the manganophile elements, only Mo is enriched in the Mn carbonate ore compared to the host sedimentary rocks. The profile of manganophile elements is similar to that of modern hydrothermal Mn oxide (Kuhn et al., 2003 *Chem. Geol.*), although the Mo/Mn ratio is much lower. These geochemical lines of evidence provide the following plausible genetic model for the Nsuta deposit: (1) Mn(II) was derived from hydrothermal fluids, (2) Mn(II) was oxidized to Mn(IV) oxide by the oxygenated seawater, (3) the precipitation of Mn oxide is almost concurrent with the deposition of the host sedimentary rocks, (4) Mn oxide was diagenetically transformed to Mn carbonate ore by the reaction with organic matter.

The geochemical features of the Nsuta deposits suggest that, as in the present oxic oceans, Mn oxide was a potential sink for several trace elements in the Paleoproterozoic oceans. The low Mo/Mn ratio in the Mn carbonate ore may reflect the large difference between the chemical compositions of Paleoproterozoic and present seawater. As the Paleoproterozoic black shales also tend to show low Mo abundance (Scott et al., 2008 *Nature*), the observed low Mo/Mn in the Mn carbonate ore suggests low Mo inventory in the Paleoproterozoic seawater. In the presentation, we will also discuss the oceanic redox condition responsible for the low Mo inventory during the Paleoproterozoic.

Keywords: Paleoproterozoic, Great Oxidation Event, Mn ore, Re-Os isotope, manganophile elements, Birimian Supergroup

## Geochemical study on the variation and stability of atmospheric oxygen in Paleoproterozoic

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Atmospheric oxygen level is considered to have dramatically increased during the early Paleoproterozoic (i.e., 2.4-2.2 Ga). Severe glaciations occurred at least three times in this same interval. The rises of atmospheric oxygen have been indicated just after the second (Bruce) and third (Gowganda) glaciations (Sekine et al., 2011 EPSL, 2011 nature comm.). However, the atmospheric oxygen level between the two glaciations remains unclear.

In this study, we investigated the evolution of redox conditions of the atmosphere and oceans between the second and third Paleoproterozoic glaciations, by analysing redox sensitive elements, such as osmium (Os), rhenium (Re), and molybdenum (Mo), and stable isotope analyses of organic carbon and sulfur for the sedimentary rocks from the Huronian Supergroup, Ontario, Canada. We found no enrichment of redox sensitive elements in these rocks. The Re-Os data yields an isochron age of 3089 +/- 98 Ma, which is significantly older than the depositional age of the Huronian Supergroup (~2.45-2.2 Ga; Young et al., 2001 Sediment. Geol.). The obtained Re-Os isochron age indicates that Os and Re in the sediments were mainly supplied as detrital components originally formed at ~3.1 Ga without any significant disturbance of Re-Os system during chemical weathering and sediment transport. This, in turn, implies that Os and Re were highly depleted in the seawater at the time of deposition, suggesting that oxidative weathering did not occur in the time interval between the second and third Paleoproterozoic glaciations. This conclusion is supported by the little variation of  $\delta^{34}\text{S}$  and low abundance of other redox sensitive elements in the sediments.

Together with the geochemical data from the previous studies, we suggest that atmospheric oxygen level increased shortly after the second Paleoproterozoic glaciation, but then, returned to low levels. In the aftermath of the third glaciation, a shift to an oxidizing atmosphere would have occurred.

## Reconstruction of 3.2Ga sea floor environment: Carbon and sulfur isotopic ratios of DXCL drill cores.

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In the Pilbara Coastal Greenstone Terrane in Western Australia, the Dixon Island and Cleaverville formations of 3.2-3.1 Ga is exposed. DXCL Drilling Project was performed in 2007 and 2011 for the purpose of the high-resolution reconstruction of the change of past sedimentary environment in this area, and four core samples (DX, CL1, CL2, and CL3) were acquired. Through these cores except for CL3, previous study revealed carbon isotopic ratio ( $=\delta^{13}\text{C}$ ) with about -30 ‰ and sulfur isotopic ratio ( $=\delta^{34}\text{S}$ ) of black shale from DX core obtained by combustion method with wide range of fluctuation and had very high values ( $\delta^{34}\text{S}=-10.1\sim+26.8$  ‰,  $n=93$ : Sakamoto, MS2010; Kobayashi, MS2013). This is dissimilar to the previously reported sulfur isotopic ratio of sedimentary sulfides of the early Archean ( $\delta^{34}\text{S}=-16.8\sim+8.7$  ‰,  $n=351$ : Strauss, 2003).

In this study, we evaluated the change of carbon and sulfur isotopic ratio through whole DXCL cores. Moreover, in order to clarify the cause of positive shift and dispersion, we performed in situ analysis with NanoSIMS focusing minute spherical pyrites observed in the DX core.

Three cores (CL2: 44.4m, CL1: 66.1m, CL3: 200m to the top) were collected from the Cleaverville Formation which consists of lower Black Shale Member and upper Banded Iron Formation Member. DX core (100.40m) of the upper part of Dixon Island Formation is composed of black shale, gray chert, and alternated pyrite layers. Especially, the DX core contains the layer of tens-hundreds micrometer euhedral pyrites and the layer of the minute spherical pyrites (about 10  $\mu\text{m}$  in diameter) which are fulfilled with silica. We considered that the minute spherical pyrites formed at early stage of sedimentation from their morphology and occurrence.

We did whole-rock analysis of sulfur isotope by NA 1500NCS (EA) manufactured by FISONs and DELTA plus XL (IRMS) manufactured by Thermo Finnigan. The instruments are equipped in Organic Geochem. & Cosmochem. Lab., Kyushu University. In situ analysis of sulfur isotope was performed using NanoSIMS50 manufactured by CAMECA at Atmosphere and Ocean Research Institute, Tokyo University. Carbon isotope analysis was performed using Delta Plus Advantage (EA/IRMS) manufactured by Thermo Finnigan at the Center for Advanced Marine Core Research, Kochi University.

As a result, minute spherical pyrites were revealed to have 5~10 ‰ isotopic fractionation on the inside, showing distribution that area of high value is in ring-shape on the inside and area of low value is in the outer side and the central part of the crystal. Besides, CL3 core ( $n=27$ ) showed  $\delta^{34}\text{S}=+1.33\sim+21.52$  ‰,  $\delta^{13}\text{C}_{org}=-30.79\sim-28.57$  ‰,  $C_{org}=0.09\sim1.65\text{wt}\%$ .

In this analysis, most of carbon isotopic data had value between -30 to -28 ‰ in about 400m forming the Dixon island to Cleaverville formations. The carbon isotope result indicates that the same kind of carbonaceous material was deposited on the seafloor and the value corresponds with photosynthetic bacteria like cyanobacteria origin. Besides, pyrites formed in the anoxic marine sediment rich in organic matter. Particularly, closed system to sulfate was formed and Rayleigh fractionation was promoted by sulfate reducing bacteria. As a result, the feedback occurred and pyrites isotopically heavier than contemporary seawater sulfate (+2 ‰: Ohmoto, 1992) formed on the inside of pyrite shell. Although generally, in case sulfate reducing bacteria is concerned, sulfur isotopic ratio of sulfides has negative value, but +20 ‰ or more is observed in these sequence. It is possible that sedimentary sulfides in that time were in a condition that they had high sulfur isotopic ratio.

Keywords: Archean, carbon isotopic ratio, sulfur isotopic ratio, pyrite, SIMS, sulfate reducing bacteria

## S-MIF geochemistry of the Early Archean in the Onverwacht Suite, South Africa

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The recent study of sulfur mass independent fractionation (S-MIF) in the Archean sedimentary rocks represented that multiple sulfur isotope ratios ( $^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$ ) could be useful new tracer for Archean sulfur cycles. Farquhar et al. (2000) first discovered that Archean sedimentary rocks before 2.4 Ga have  $\Delta^{33}\text{S}$  anomaly, whereas no such anomaly was found in younger samples. This contrast implies the rise of atmospheric oxygen content that fundamentally changed atmospheric sulfur cycle. The hypothesis are based on the studies from Western Australia and South Africa (Kaufman et al., 2007; Ono et al., 2009; Zerckle et al., 2013). High-resolution stratigraphic studies provide a detailed view into the late Archean marine sulfur cycle, which can help our understanding of both atmospheric and biological processes. In the early Archean, S-MIF data are almost from hydrothermal sulfate and sulfide. For comparing early and late Archean data precisely, it is necessary to investigate stratigraphical and petrological distributions and variations of the multiple sulfur isotopes. We have studied Early Archean sedimentary sulfides which are well preserved in the Barberton Greenstone Belt, South Africa. Sulfur isotope analysis of extracted sulfide of sedimentary rocks from Barberton Greenstone Belt, show a clear MIF ( $>1\text{‰}$ ) and  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ ,  $\Delta^{33}\text{S}-\Delta^{36}\text{S}$  correlation. The Noisy Complex which consists of fluvial sediments and diamictite show negative  $\delta^{34}\text{S}-\Delta^{33}\text{S}$  correlation, and  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope of -0.72. On the other hand, the Kromberg Formation which consists of deep marine sediments show positive  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ , and scattered  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope.  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ ,  $\Delta^{33}\text{S}-\Delta^{36}\text{S}$  relation from each stratigraphic level shows somewhat different trend, possibly reflecting local environment and/or bacterial sulfate reduction activity.

Keywords: South Africa, Sulfur, MIF

## Atmospheric oxygen in the Earth's 4.6-billion-year history

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The oxygen content of the Earth's surface environment is regarded to have increased in two steps; the Great Oxidation Event (ca. 2.4 Ga) around the Archean-Proterozoic boundary and the Neoproterozoic Oxygenation Event (ca. 800-550 Ma). These two events are supported by geochemical or paleobiological evidences; however, the estimation of the oxygenation level of the surface environment through time still have many problems to solve. We will review and discuss the previous researches for the better quantitative estimation of the atmospheric oxygen content in the Earth's 4.6-billion-year history.

## Convective stirring versus compositional stratification in the early mantle of terrestrial planets of various sizes

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<sup>1</sup>University of Tokyo at Komaba

Systematic numerical studies of magmatism in the convecting mantle of terrestrial planets suggest that how the compositional differentiation by magmatism in the earliest mantle affects its subsequent history depends on the size of the planets. In large planets like the Earth and Venus, the global scale magmatism induced by the high initial temperature of the mantle does not differentiate the mantle so much because of a strong positive feedback that arises between magmatism and mantle convection: Ascending flow of mantle convection induces decompression melting, but the buoyancy of the melts further enhances the ascending flow itself. This ascending flow enhanced by melt buoyancy strongly stirs the mantle and suppresses prominent compositionally stratified structure to develop in the early mantle. In Mars, the positive feedback still works, but the convection does not stir the mantle so strongly and the initial global scale magmatism makes the mantle compositionally stratified; the subsequent mantle evolution occurs as a convective relaxation of the compositionally stratified structure. In the moon and Mercury, the positive feedback itself does not work, and the convective current is mild even in the earliest stage of the history of the mantle. In the moon where the heat flux from the core is negligible and the gravity is small in deep mantle, in particular, a compositionally stratified structure formed in early mantle survives the subsequent stirring by such a mild convective flow.

Keywords: planetary size, magmatism, mantle convection, compositional stratification

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BPT23-16

Room:411

Time:April 30 14:30-14:45

## Lunar and Planetary Cratering Records: Evidences for and against the Cataclysmic Late Heavy Bombardment

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In this talk, I will discuss about the cataclysmic late heavy bombardment hypothesis based on the findings from studies of lunar and planetary cratering records.

Keywords: Late Heavy Bombardment, Crater, Moon

## Timing of late veneer on Earth: a siderophile element perspective

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The short-lived  $^{182}\text{Hf}$ - $^{182}\text{W}$  decay system (half life is ca. 9 Myr) has long been recognised as a powerful tracer for accretionary and differentiation processes on the early Earth. Recent advances in analytical technique made it possible to conduct high-precision ( $\pm 5$  ppm or better) W isotope ratio measurements and have allowed exploitation of  $^{182}\text{W}/^{184}\text{W}$  variations (expressed in the conventional  $\epsilon^{182}\text{W}$  notation) in a wide variety of geological samples. To date, the presence of  $\epsilon^{182}\text{W}$  anomalies have been documented for the 3.8 Ga Isua supracrustal belt in West Greenland, the 2.8 Ga Kostomuksha komatiites, the  $\geq 3.8$  Ga Nuvvuagittuq greenstone belt in Northeastern Canada and the 4.03 Ga Acasta gneiss complex in Northwestern Canada, all of which exhibit similar positive  $\epsilon^{182}\text{W}$  anomalies up to 15 ppm relative to modern terrestrial samples ( $\epsilon^{182}\text{W} \simeq 0$ ). These  $^{182}\text{W}$  enrichments have been interpreted to represent the composition of anciently isolated domains in Earth's mantle that escaped addition of the chondritic late veneer ( $\epsilon^{182}\text{W} \simeq -2$ ). This hypothesis is apparently consistent with the idea that  $\sim 0.5\%$  of the Earth's mantle was added after the cessation of core formation, required to account for the overabundance of highly siderophile elements (HSEs) in modern mantle. In order to test this hypothesis, we produced the HSE concentration data for basaltic amphibolites in the 4.03 Ga Acasta gneiss complex, meta-komatiites and meta-dunites in the  $\geq 3.8$  Ga Saglek-Hebron segment in Northern Labrador, Canada with the motivation in the search for the pre-late veneer mantle almost devoid of HSEs. The results demonstrated that the relative and absolute HSE abundances in all these rocks are akin to their late Archean to modern equivalents, indicating the delivery of late-accreted materials prior to 3.8-4.0 Ga at the period of late heavy bombardment on the Earth-Moon system. Considering the results of other studies demonstrating high-HSE contents of the mantle sources for the 3.8 Ga Isua rocks and the 2.8 Ga Kostomuksha komatiites, we can now conclude that  $^{182}\text{W}$  enrichments are largely decoupled from HSE depletions, inconsistent with the pre-late veneer hypothesis. Further studies are necessary focusing on the siderophile element behaviors in Eoarchean rocks to advance in the knowledge of late accretion on Hadean mantle and the source of  $^{182}\text{W}$  enrichments.

Keywords: siderophile element, late veneer, Archean, mantle

## Destruction and melting of Hadean continent by Late Heavy Bombardment

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There are no rocks, which were made in Hadean Earth. In recent years, however, sedimentary rocks including zircons made in Hadean indicated the existence of some continental crusts in Hadean. So, how were the continental crusts to disappear? One hypothesis to solve this problem is destruction and/or melting of the crusts by the Late Heavy Bombardment (LHB), a concentration of impacts in last phase of Hadean. However, there are few quantitative studies so far.

We developed the expressions to deduce the effects of LHB to the Hadean crusts, and showed that the concentration of impacts could not destruct/melt the whole Hadean crust. We assumed the impact flux of based on the following three models: "Cataclysm" model, "Soft-Cataclysm" model, and "Standard" model.

First, we estimated the scale of LHB through the main asteroid belt's size-frequency distribution by the basins on the moon (Cataclysm model), results of numerical simulations (Soft-Cataclysm model), and cratering rates of the moon (Standard model). We approximated the main asteroid belt's size-frequency distribution estimated by observations as a power-law scaling, and gave some power indexes as a parameter. This parameter can change the effects of LHB widely. Then we estimated the sum of volume and area of craters made by LHB using the scaling law of cratering.

The result is that the LHB in any models had a chance to melt roughly same volume of the Hadean crusts, but could not cover the whole surface of the Earth by the craters. As the Hadean crusts are considered to be dotted on the surface, it would be impossible to melt the all dotted crusts by impacts. In conclusion, the Late Heavy Bombardment could not destruct/melt the whole Hadean crusts.

Keywords: Late Heavy Bombardment, Hadean, continental crust, asteroid, crater, impact

## The first recovery of impact-shocked zircons from the Jack Hills metasedimentary rocks, Western Australia

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The first 500 million years of the Earth history remain poorly understood because terrestrial rock records during Hadean era (>4.0Ga) are scarcely preserved, probably due to surface and/or tectonic erosion and intense meteorite bombardment. The Late Heavy Bombardment (LHB) is the period from ca. 3.85-3.95, an intense flux of asteroidal bodies into inner solar system originally proposed to have impacted the Moon. To date, the oldest impact structure on the Earth is the 2.02 Ga Vredefort Dome, South Africa, and another oldest evidence of bolide impact is 3.47-3.24 Ga spherule layers in the Barberton Greenstone Belt, South Africa (e.g. Lowe et al., 2003). The impact chronology from these spherule layers suggest that the impactor flux was significantly higher 3.5 Ga than today (Jhonson & Melosh, 2012).

Geological conditions during Hadean era can be deduced from detrital zircon grains as old as 4.4 Ga preserved in metasedimentary rocks at Jack Hills in the Narryer Gneiss Complex, Western Australia (e.g. Compston & Pidgeon, 1986; Wild et al., 2001). Jack Hills metaconglomerates deposited in ca. 3 Ga contain detrital zircons with ages continuously spanning from 3.0 to 4.4 Ga. Previous investigations of these grains have suggested the existence of a thermal excursion during LHB era (Abbott et al., 2012; Bell and Harrison, 2013), but temperature approach of detrital zircons do not restrict impact-related heating.

Here, we first report zircons with shock-induced textures, such as granular (polycrystalline) texture, from the Jack Hills metaconglomerate. Granular-textured zircons have been frequently reported from impact ejecta layers and craters, such as K-Pg boundary, the Chicxulub crater (e.g. Bohor et al., 1993; Krogh et al., 1993) and also from shock experiments (Witmann et al., 2006). Polycrystalline zircon grains recovered from the Jack Hills metaconglomerates represents several micro-meter sized crystallites of zircon in a glassy ZrSiO<sub>4</sub> matrix that may resulted from shock-induced amorphization and subsequent recrystallization (Witmann et al., 2006). Several grains show the granular texture with abundant micro-vesicles and tiny ThSiO<sub>4</sub>, suggesting incipient melting and vaporization. The first recovery of shock-induced zircons from the Jack Hills metaconglomerate would provide significant clues on the early Earth environment and on constructions/destructions of Earth early crust.

Keywords: early Archean, Hadean, Jack Hills, zircon, shock metamorphism

## Trace element variety of mafic rocks in the Acasta Gneiss Complex

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The Hadean from birth of the Earth to 4.03 Ga is the earliest period of the history of the earth, and defined by no preservation of rock records in the earth. Eoarchean crustal records are also rare, so that the details of early Earth are not revealed yet.

Acasta Gneiss Complex (AGC), located in the western part of the Slave Province, Canada, is one of the Early Archean terranes, and mainly consists of 3.6-4.0 Ga felsic and layered gneiss suites and mafic rocks. Minor mafic rocks are distributed all over the AGC and occur as rounded to elliptical enclaves and inclusions in the felsic and layered gneisses. These field occurrence of the mafic rocks suggest that they were formed before the formation of granitoid precursor of felsic gneisses and have potential to demonstrate the Early Archean mantle evolution. However, the AGC is subjected to numerous metamorphic and alteration events. The Acasta mafic rocks mainly consist of amphibolites with hornblende, plagioclase and quartz, suggesting that they underwent at least amphibolite facies metamorphism. No relict igneous minerals are preserved. At some localities, hornblendites with over 90 % modal abundance of hornblende occur as restites of anatexis. This study constrain the Early Archean mantle characteristics from the least altered samples, which selected based on the effects of alteration process by methods of whole rock major and trace element compositions.

The compositions of the amphibolites range from basalt to basaltic andesite ( $\text{SiO}_2=48-57$  wt. %,  $\text{MgO}=2.1-9.8$  wt. %) and negative correlations can be seen between  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  contents and  $\text{Na}_2\text{O}$  and  $\text{MgO}$  contents respectively. The hornblendites have higher  $\text{MgO}$  and lower  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  contents than amphibolites, supporting the geological evidence that the hornblendites were derived from residue of anatexis. Amphibolites are divided into three groups based on their major elements and primitive mantle (PM)-normalized trace element patterns: Low-Al, Intermediate-Al and High-Al amphibolite respectively.

The Low-Al amphibolites are plotted between the Intermediate-Al amphibolites and hornblendites on the  $\text{Al}_2\text{O}_3$  vs  $\text{MgO}$  diagram. They have relatively higher LREE contents than the Intermediate-Al amphibolites. They display negative Zr and Ti anomalies on the PM-normalized trace element patterns. Those characteristics are similar to those of hornblendites. On the other hand, PM-normalized trace element patterns of the High-Al amphibolites are highly scattered. The geochemical characteristics of the amphibolites suggest that the Low-Al amphibolites were formed as a residue with incomplete melt loss due to the partial melting of the Intermediate-Al amphibolites, whereas the High-Al amphibolites as the melts addition. The geological and geochemical evidence indicates that the compositions of almost mafic rocks at the AGC were affected by secondary partial melting, but some mafic rocks, the Intermediate-Al amphibolites, possibly preserve their primary characteristics.

Except for Nb, the Intermediate-Al amphibolites have flat PM-normalized trace element patterns. Their negative Nb anomalies suggest that they were generated at the subduction setting, implying slab-dehydration process already occur in the Early Archean. Mantle evolution through geologic time is an alternative candidate for the Nb negative anomaly.

Keywords: Archean, mafic, mantle

## Growth curve of continental crust on the surface of the Earth

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The growth curve of continental crust through the Earth's history has been estimated by many methods, which include geologic-geophysical-, and geochemistry-based. Many studies through geophysical and geochemical modeling indicate that there was rapid formation of continental crust during the early part of the history of the Earth. The geological record shows, however, that less than 20% of continental crust before 2.6 Ga remains and an absence Hadean geological body. The difference between the formation of continental crust, indicated by modeling to be more extensive than what is observed in the geological record has been thought to be effect of crustal recycling or subduction of crustal material into the mantle. Recently, the importance of arc subduction (Yamamoto et al., 2009) and large scale subduction erosion around circum-Pacific active subduction zones has been revealed through geologic investigation of the Japanese islands (Isozaki et al., 2010; Suzuki et al., 2010). The crustal material subducts into the mantle transition zone and forms a second continent (Kawai et al., 2009; 2013). It is the aim of this study to delineate the growth history of continental crust which takes into account the subduction of continental crustal material into the mantle global scale.

River sand zircon method is one of the most powerful methods to determine the age frequency distribution of the continental crust (Rino et al., 2004; 2008). In this study, the global unconformities are regarded to be past continental margins, with river sand in clastic rocks occurring above them. The age frequency distributions of detrital zircons at given global unconformities with ages of 2.6, 1.0 and 0.6 Ga were determined in this study. This included analyzing detrital zircons separated from sedimentary rocks which occur above global unconformities with surfaces covering the Pilbara, Kaapvaal, Zimbabwe and Wyoming cratons, with U-Pb ages determined through the LA-ICP-MS at Hirata Laboratory in Kyoto University. In addition, in order to make this more of a global study, published data was also used to determine the age frequency distribution of continental crust at 2.6, 1.0 and 0.6 Ga.

The growth history of continental crust is discussed by showing the compilations of age frequency distribution of detrital zircons at 2.6, 1.0, 0.6 Ga (this study) and at present (Rino et al., 2008). The shape of these curves indicates that there was rapid formation of continental crust with large scale subduction of crustal materials into the mantle during a time range of 4.5 to 2.6 Ga, and that during 1.0 Ga to present, continental crust on the Earth's surface has been declining due to subduction erosion being more dominant than crustal formation. In addition, the growth history of continental crust was estimated in this study by using the evolution of oceanic Sr isotope ratio recorded in carbonate rocks (Shields and Veizer, 2002). In this study, the Sr flux estimated from the carbonates is assumed to be proportional to the volume of the continents.

Based on these works, a model of growth history of the continental crust is proposed here. From the Hadean through the Archean to the early part of the Proterozoic, there was rapid formation of granitic crust as most oceanic island arcs were subducted into the mantle with only a limited number of them colliding and contributing to the growth of continental crust of the surface of the Earth. At 2.6 Ga, the amount of continental crust was 75% of that at present. Subsequently, magmatism at subduction zones was superior to subduction erosion with about 150% continental crust at 1.0 Ga compared to that at present. Since about 1.0 Ga, the continental crust has been reducing in volume due to subduction erosion being superior to growth at subductions zones.

Keywords: U-Pb age, detrital zircon, global unconformity, growth of continental crust

## Geological and geochemical studies about the Eoarchaean-aged Banded Iron Formations in Nain Province, Northern Labrador.

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Banded iron formations (BIFs) are chemical sediments, deposited in seawater before the Paleoproterozoic, and are often utilized as proxies for chemical compositions of seawater. However, the scarcity of >3.6 Ga supracrustal rocks including BIFs hampers the use of BIFs for estimate of the seawater composition, especially bioessential elements, in the early earth. Recently, Konhauser et al. (2009) showed secular change of Ni/Fe ratios of BIFs through geologic time, and suggested that the Archean seawater was enriched in dissolved Ni, suitable for methanogenic bacteria. But, their data show quite large variations in Ni/Fe ratios at the same ages from the modern value to about ten times value. Therefore, more comprehensive investigation of the BIFs through geological time is necessary to estimate secular change of chemical composition of seawater. For the purpose, we performed comprehensive investigations of geology, geochronology, stratigraphy and geochemistry of the oldest supracrustal rocks, in >3.96 Ga Nulliak Supracrustal rocks in the Nain Province, Northern Labrador, Canada (Shimojo et al., 2013).

Based on the lithostratigraphy and accompanied rocks, we classified into two types of BIFs: BIFs interlayered with metabasite in the Nulliak Island and BIFs accompanied with carbonate and/or chert layers, respectively. The former are Algoma-type BIFs, which was deposited in deep-sea near basaltic volcanism. The latter are uncommon in the Early Archaean, which are possibly formed in shallow-water environment.

Their PAAS-normalized REE+Y patterns display positive La, Eu and Y anomalies, suggesting that they were deposited in a mixing zone of seawater and hydrothermal water. In addition, transitional element contents such as Ni and Zn (>50 ppm) are high, similar to other Archean BIFs (Konhauser et al., 2009, Mloszewska et al., 2012). But, HFSE (e.g. 1~20 ppm in Zr contents) and Al<sub>2</sub>O<sub>3</sub> (0.5~2 wt%) contents are variable, and positively correlated with REE+Y and the transitional element contents, suggesting that the variation in the REE+Y contents is due to detrital inputs so that samples with low Zr and Al<sub>2</sub>O<sub>3</sub> contents preserve the detritus-free compositions. The samples with low detritus inputs show a negative correlation between Eu/Eu\* and REE and Y/Fe ratios, and between Eu/Eu\* and LREE/REE and Y ratios, respectively. The similar correlations are reported for iron-rich suspended particulates collected from the TAG hydrothermal field (German et al., 1990). Therefore, the REE+Y variations can be explained by continuous scavenging processes by iron-oxyhydroxide particles. Moreover, no Ce/Ce\* anomaly is consistent with anoxic seawater in the Early Archaean.

In addition, transition metals (Ni, Zn, Co)/Fe ratios correlate negatively with Eu/Eu\*. The correlations were also shown in BIFs in the Isua Supracrustal Belts and the Nuvvuagittuq Supracrustal Belts (Bolhar et al., 2004; Mloszewska et al., 2012), suggesting that their variations are due to same scavenging processes by iron-oxyhydroxide particles as REE+Y. Namely, the transition metals/Fe ratios of BIFs don't provide direct estimate of those concentrations of seawater. We normalize their transitional metals by rare earth elements (e.g. Sm), which are adsorbed on iron-oxyhydroxide similar to the transition metals. Sm-normalised transitional metals contents of the Archaean BIFs are higher than those of Proterozoic BIFs, suggesting that the Archaean seawater was enriched in transitional metals such as Ni and Zn, which are essential for protein synthesis of the early life.

**Reference** : Konhauser et al., 2009. *Nature* 458, 750-754. ; Shimojo et al., 2013. *Goldschmidt 2013*, Florence, Italy.; German et al., 1990. *Nature* 345, 516-518. ; Bolhar et al., 2004. *EPSL* 222, 43-60. ; Mloszewska et al., 2012. *EPSL* 317-318, 331-342.

Keywords: Eoarchaean, bioessential elements, Banded Iron Formations

## In-situ iron isotope analysis of pyrite in ca. 3.8 Ga metasediments from Isua supracrustal belt, Greenland

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The timing of emergence of life still remains one of the unresolved questions in the early Earth. Early life could be identified and characterized by its metabolic processes, which must be deposited and preserved in the old rocks. The oldest (ca. 3.8Ga) sedimentary rocks on Earth occur in the Isua supracrustal belt (ISB), southern West Greenland. These rocks have been subjected to until amphibolite facies metamorphism (Nutman, 1986; Hayashi et al., 2000). Despite the contribution of the intense thermal metamorphism, carbon isotope compositions from the Isua metasediments suggested the evidence for biological carbon fixation. Microbial dissimilatory iron reduction (DIR) is also considered to be one of the earliest metabolisms on Earth.  $\sigma^{56}\text{Fe}$  value of  $\text{Fe}^{2+}_{aq}$  generated by DIR is expected to have lower value, whereas negative  $\sigma^{56}\text{Fe}$  values lower than -1 ‰ are not found in the sedimentary record prior to 2.9Ga. Here, we report the *in-situ* iron isotope analysis of pyrite in sedimentary rocks from the ISB, using femtosecond laser ablation multi-collector ICP-MS technique (fs-LA-MC-ICP-MS). We obtained a large variation of iron isotope data from -2.41 to +2.35 ‰ in  $\sigma^{56}\text{Fe}$  values, from 212 points of pyrite grains in 15 rock specimens, including metachert, muddy metachert, BIF, carbonate rock and conglomerate. The distribution of  $\sigma^{56}\text{Fe}$  values varies depending on the lithologies and depth gradient, whereas no correlation could be found between  $\sigma^{56}\text{Fe}$  values and the metamorphic zone.

Low  $\sigma^{13}\text{C}$  values of graphite in ISB muddy metachert suggested the existence of biological carbon fixation (e.g., Schidlowski et al., 1979).  $\sigma^{56}\text{Fe}$  values of pyrite grains from the shallow water samples show lower  $\sigma^{56}\text{Fe}$  values, which suggested the occurrence of microbial DIR in the Early Archean.

Keywords: Early archean, Isua supracrustal belt (ISB), iron isotope ratio, pyrite, microbial dissimilatory iron reduction (DIR)

## The origin of carbonaceous material in the Early Archean Nain Complex, northern Labrador, Canada

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Presence of early life in the Early Archean is still controversial, and it is a key issue to find evidence for early life from the Early Archean rocks. Carbon isotope ratio ( $\delta^{13}\text{C}_{org}$ ) of carbonaceous matter (CM) is widely used as an indicator of existence of life (Schidlowski, 2001). CM in the 3.80 Ga metasediments of the Isua Supracrustal Belt (ISB), southern West Greenland has low  $\delta^{13}\text{C}$  values, interpreted as evidence for organism in the Early Archean (Rosing, 1999). Recently, Ohtomo et al (2013) showed the nano-scale microstructure of the CM, evident for originating from organisms. In contrast, it is presumed that CM in the Nuvvuagittuq Supracrustal Belt (~3.75Ga) has a secondary metamorphic origin because the crystallization temperature (~380 °C) of the CM estimated from LA-Raman spectrums is much lower than than metamorphic temperature (~640 °C) (Papineau et al., 2011). Moreover, a putative banded iron formation in the Akilia Island (~3.83 Ga) including apatites with carbonaceous inclusions with the low  $\delta^{13}\text{C}$  provides another evidence for the life, but the precursor is still controversial (Fedo and Whitehouse, 2002). Thus, there is no obvious evidence for presence of life in the Early Archean except for that from ISB.

Shimojo et al. (2013) showed that >3.96Ga metasediments exist in the Nain Complex, northern Labrador, Canada. The Nain Complex is ca. 100 million years older than the Akilia association, which has the oldest supracrustal rocks in the world. The purpose of this research is to reveal the origin of the CM in the sedimentary rocks in the Nain Complex.

We selected pelitic gneisses (n=70), conglomerates (n=14), carbonate rocks (n=39), cherts (n=30), chert nodules in carbonate rocks (n=3) and amphibolites (n=5) from over 2000 samples over the Nain Complex based on the metamorphic grade, geography, their field occurrence and degree of alteration. Among the metasedimentary rocks (n=156), 54 specimens including pelitic gneisses (n=21), conglomerates (n=4), carbonate rocks (n=26) and chert nodules in carbonate rocks (n=3) contain CM. Seven CM-bearing rock samples were selected for  $\delta^{13}\text{C}_{org}$  analysis: pelitic gneisses (n=4), conglomerates (n=1), carbonate rocks (n=1) and chert nodules (n=1), and 3 carbonate rock samples for  $\delta^{13}\text{C}_{carb}$  analysis, respectively.

Metamorphic grade was estimated for mineral paragenesis and garnet-biotite thermometry. Among the seven CM-bearing rock samples, the six samples were metamorphosed under up to the amphibolite facies condition, and a sample under the lower granulite facies condition, respectively. The metamorphic temperatures are consistent with the estimated crystallization temperature of the CM calculated by Raman spectral parameters.

$\delta^{13}\text{C}_{carb}$  values range from -3.75 to -2.63 ‰. Because it is well known that secondary alteration and metamorphism decrease a  $\delta^{13}\text{C}_{carb}$  value (Schidlowski et al., 1979), a primary  $\delta^{13}\text{C}_{carb}$  value was estimated to be higher than -2.63 ‰. As a result, the  $\delta^{13}\text{C}_{carb}$  value of marine bicarbonate was at least -2.63 ‰ in the Early Archean.

$\delta^{13}\text{C}_{org}$  values of pelitic gneisses range from -28.86 to -14.07 ‰. The  $\delta^{13}\text{C}_{org}$  values of conglomerate, carbonate rock and chert nodule are -17.52, -5.72 and -10.60 ‰, respectively. Metamorphism, generally speaking, increases a  $\delta^{13}\text{C}_{org}$  value of CM due to partial thermal decomposition, especially methane degassing, suggesting that the variation in the  $\delta^{13}\text{C}_{org}$  values is due to secondary thermal decomposition. The correlation of the  $\delta^{13}\text{C}_{org}$  values with distribution of organic matter under microscopic observation also supports the partial decomposition and consequent increase of the  $\delta^{13}\text{C}_{carb}$  values. As a result, the lowest  $\delta^{13}\text{C}_{org}$  value is a maximum estimate of the  $\delta^{13}\text{C}_{org}$  value.

The minimum fractionation between the  $\delta^{13}\text{C}_{org}$  and  $\delta^{13}\text{C}_{carb}$  reaches 25 ‰, indicating biologic origin for the CM. This work presents the organism has already existed ca. 3.96 Ga.

Keywords: CM, Labrador, early life, carbon isotopic ratio

## Sr-Nd-Pb isotopic compositions of hot spring water in the Toyoha Mine, Hokkaido Japan: Implications for the origin of hy

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Chemistry and dynamics of slab-derived fluids in subduction zones have been rigorously studied by high pressure experiments, geochemical and hydrological modellings, and geophysical observations [1-5]. Surface manifestation of deep slab-derived fluids are now suggested by geochemistry, such as slab fluid-like chemical affinities found in volcanic rocks [6,7] and in hot spring waters [8]. In this study, we aim to examine the presence (or absence) of slab derived fluid signatures in hot spring water related with the Toyoha Mine ore deposits in Hokkaido, one of the largest hydrothermal vein-type deposits in Japan. We applied Sr-Nd-Pb isotope analyses of the hot spring water and compared the results to those from the volcanic rocks and the ore minerals from the Toyoha Mine.

For this purpose, we have examined a ferric co-precipitation pre-concentration method for the hot spring water from the Toyoha Mine. This was necessary because the abundances of Nd and Pb were very low, less than several ppb for Nd, in particular. The method has previously been applied to brines with high chlorine concentration at Arima hot spring [9], and the method worked well with the Toyoha hot spring water. The concentrated sample has been analyzed by Q-ICP-MS and MS-ICP-MS for both element abundances and Sr-Nd-Pb isotopic compositions. We examined origin of the hot spring water by using Sr-Nd-Pb isotope systematics in comparison with the data from the ore deposit, volcanic rocks related with the ore deposition, and the basement rocks of the Toyoha Mine. A recent study has shown that Sr-Nd-Pb isotopic ratios of sulfide ores in the Toyoha Mine exhibit a high contribution of slab-derived fluid from the Pacific Plate slab [10]. Our preliminary results on the hot spring water suggest that the water may also preserve the slab-fluid signatures and/or may also be affected by the chemical components in the basement rocks.

[1] Schmidt and Poli, 1998, EPSL [2] Hacker et al., 2003, JGR [3] Iwamori, 1998, EPSL [4] Arcay et al., 2005, PEPI [5] Cagnioncle et al., 2007, JGR [6] Pearce et al., 2005, G3 [7] Nakamura et al., 2008, NGeo [8] Kusuda et al., in revision [9] Nakamura et al., submitted [10] Hieda, 2013, Master Thesis, Univ. of Tokyo

Keywords: hot spring, isotope, Toyoha, mine, ore

## The contribution of slab-fluids to the formation of hydrothermal vein-type deposits

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It has been recently pointed out that "geofluids" released from the subducting plates are involved in various products in subduction zones, such as arc magmas, deep-seated hot springs and hydrothermal vein-type deposits. Systematic investigations of these various materials are needed for identifying the geochemical characteristics of the geofluids. Nakamura et al. (2008) revealed the heavy isotopic compositions of slab-fluids derived from two subducted plates (the Pacific plate and the Philippine Sea plate) which contribute largely to the genesis of arc magmas in Central Japan.

In this study, we focus on the hydrothermal vein-type deposits in Japan. It has been previously considered that hydrothermal fluids that form sulphide mineral (pyrite, chalcopyrite, sphalerite, galena etc.) deposits were originated from magmatic and/or meteoric waters [2]. However, we reported that Pb isotopic compositions of the sulphide ore samples were plotted between Philippine Sea plate (PHS)-fluid and Pacific plate (PAC)-fluid, suggesting that ore fluids responsible for the hydrothermal deposits are directly derived from deep slab-fluids. Here we report multi-isotopic compositions (Pb-Nd-He) of sulphide ores, associated volcanic rocks, and the surrounding country rocks from the Toyoha polymetallic (Zn-Pb-Ag-Cu-Sn-In) vein-type deposit (one of the largest hydrothermal vein-type deposits in Japan) in order to understand the relationship between slab-fluid and formation of vein-type deposit in more detail.

**Results and Discussion:** We collected twenty-six sulphide ore samples, and fifteen associated volcanic and country rocks from the Toyoha Mine. The  $^{206}\text{Pb}/^{204}\text{Pb}$  values of sulfide ore samples are significantly larger than those of the Muine volcanic rocks which have been long thought to be genetically related to the formation of Toyoha deposit. In addition, the  $^3\text{He}/^4\text{He}$  values of Toyoha galena samples range between 5 and 6 times the atmospheric ratio, implying the significant contribution of the mantle component, and strongly suggest that there is a contribution from deep-derived fluid to the Toyoha ore fluid. The correlation between  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  shows that the relative contribution of PAC fluid component in the Toyoha ores is significantly higher than that involved in the Muine volcanic rocks. It can be estimated that more than ~80% of Pb of the Toyoha ore deposit is derived from slab-fluids. Based on the present measurements and mass balance calculations, it is very likely that the slab-fluids supplied the major part of Pb and other metals concentrated in the Toyoha district.

**Keywords:** Pb isotopic composition, hydrothermal deposit, slab-fluid

## The Archean hydrothermal alteration: Significance of silicification for seawater composition and biological evolution

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The earth is the active planet, where higher forms of life live. Presence of liquid water on surface of planet is necessary to organisms: thus a planet with the liquid water is called a habitable planet. But, enrichment in bioessential elements is also important because they are demanded for their activity. In addition, it is required that they are continuously supplied to biosphere through the elemental cycle. Especially, phosphate is one of the most important nutrients because the DNA and RNA contain large amounts of phosphate contents. Nickel is a bioessential element for methanogen, which was more active in early Earth. However, phosphorus, iron, and nickel are highly depleted in modern seawater because oxic modern seawater causes precipitation of iron oxyhydroxide, which effectively remove the phosphorus and nickel through their adsorption on iron precipitates. The evolution of seawater composition through geologic time accounts for the apparent paradox, namely ancient seawater was enriched in the phosphorus and nickel contents (Planavsky et al., 2010; Konhauser et al., 2009). But, the mechanism of high phosphorus and nickel contents in seawater is still ambiguous. This work presents silicification plays important roles not only on the supply of the phosphorus and nickel into seawater but also on preventing adsorption of the elements on iron hydroxide.

Comparison between major element compositions of modern altered and non-altered MORB (Alt & Honnorez, 1984) indicates present-day hydrothermal alteration increased phosphorus contents relative to titanium contents in the altered basalts because altered MORBs commonly contain over four times higher phosphorus contents than the fresh equivalents (e.g. Alt & Honnorez, 1984, CMP). Therefore, the hydrothermal fluid has relatively low phosphorus content. On the other hand, comparison between Archean altered and non-altered MORB indicates the Archean altered basalts contain relatively lower phosphorus contents than the fresh equivalents (Komiya et al., 2002, IGR, Nakamura & Kato, 2004, GCA). The different behavior of phosphate during the hydrothermal alteration of basalts suggests higher phosphate contents in the Archean hydrothermal fluids. In addition, silicified basalts in the Archean greenstone belts are completely depleted in phosphorus, indicating much amounts of phosphorus were supplied into seawater. Comparison between nickel contents of altered and non-altered basalts and peridotitic komatiites indicates the altered rocks are more enriched in nickel under the moderate hydrothermal alteration condition, contrast to previous hypothesis (Konhauser et al., 2009). However, silicified basalt and peridotitic komatiite are completely depleted in sodium, phosphorus and nickel except for potassium, indicating silicification effectively supplied nickel and others to ocean. It is considered that formation of banded iron formation caused effective removal of nickel and phosphorus from seawater. Especially, recent study of their rare earth element patterns, namely Y/Ho and Sm/Yb ratios, indicate iron oxyhydroxide were precipitated much more from seawater in the Early Archean, suggesting phosphorus and nickel were more efficiently removed from seawater. Higher silica content of seawater in the early Earth accounts for the apparent paradox. The high silica content of ancient seawater had a significant role of the preventing adsorption of phosphorus and nickel on iron oxyhydroxide as well as supplying more phosphorus and nickel to seawater at the hydrothermal alteration.

We propose that high silica contents of ancient seawater resulted in high phosphorus and nickel contents of seawater in the early Earth.

Keywords: Silicification, Early Earth, Paleo-seawater, Nutrient and biological evolution, Basalt and komatiite

## Potential nitrogen fixation by hyperthermophilic methanogens on the early Earth

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Hyperthermophilic hydrogenotrophic methanogens are considered to represent one of the most important classes of primary producers in hydrogen (H<sub>2</sub>)-abundant hydrothermal environments throughout the history of Earth. Despite extensive studies of methanogenesis, comprehensive research on nutrient anabolism in hyperthermophilic methanogens is limited. We first investigated the physiological properties and isotopic characteristics of experimental cultures of hyperthermophilic methanogens during the fixation of dinitrogen (N<sub>2</sub>), an abundant but less-bioavailable compound in hydrothermal fluids. We found that these hyperthermophilic methanogens actively assimilated N<sub>2</sub> via molybdenum (Mo)-iron (Fe) nitrogenase under broad ranges of Mo and Fe concentrations relevant to present and past oceanic and hydrothermal environments. Furthermore, the methanogens produced more <sup>15</sup>N-depleted biomass than that previously reported for diazotrophic photosynthetic prokaryotes. These results indicate that diazotrophic methanogens can be broadly distributed in seafloor and subseafloor hydrothermal environments, where the availability of the transition metals is variable and organic carbon and nitrogen compounds and ammonium are extremely scarce. The possible emergence and function of diazotrophy coupled with methanogenesis 3.5 billion years before the present may be inferred from the nitrogen and carbon isotopic records of kerogen and fluid inclusions from hydrothermal deposits.

## Reconstruction of tectonic history of the Cleaverville area in Coastal Pilbara Terrane, western Australia

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The Dixon Island - Cleaverville formations of the Coastal Pilbara Terrane, Western Australia, is one of the most complete sections of a volcano-hydrothermal sequence of the immature island arc (Kiyokawa & Taira, 1998). These formations composed of the Dixon Island (DX) Formation, Dixon pillow basalt and the Cleaverville (CL) Formation. The CL Formation is unconformably overlain by the Lizard Hills Formation. The Lizard Hills Formation was formed in syncline basin (66 Hill Member) during collisional D1 deformation and pull-apart basin (44 Hill Member) during sinistral slip D2 deformation (Kiyokawa et al., 2002).

In this study, depositional ages of the CL Formation and the Lizard Hills Formation (44 Hill Member and 66 Hill Member) were examined by the analysis of U-Pb zircon dating. Zircons were measured using SHRIMP2 at National Institute of Polar Research. Metamorphic age of the DX Formation was obtained by the whole-rock <sup>87</sup>Rb-<sup>86</sup>Sr isochron using TIMS (Thermo TRITON and MAT253) at the Pheasant Memorial Laboratory, Institute for the Study of the Earth's Interior at Misasa.

As a result, U-Pb zircon age of felsic tuff in the CL Formation is 3108(+14/-7) Ma. Detrital zircon ages of the 44 Hill Member showed main peaks at 3280-3200Ma and 3030-3020Ma. Detrital zircon ages of the 66 Hill Member also showed peaks at 3300-3200Ma, 3100-3050Ma, and minor group of 3700Ma. The Rb-Sr data define clear correlation line in the <sup>87</sup>Rb-<sup>87</sup>Sr evolution diagram which corresponds to an age of 2210±60 Ma.

In conclusion, sedimentation age of the DX formation is 3195±12Ma (Kiyokawa et al., 2002) and the CL Formation is 3108(+14/-7) Ma. The average of sedimentation rate in DX-CL formations is 2~3mm/ky as total thickness between these ages is 250m. After the sedimentation of the CL Formation, syncline basin (the Sixty-Six Hill Member) was formed by D1 during 3088~3020 Ma. D2 faulting with pull-apart basin (44 Hill Member) was formed after the quartz porphyry (3020Ma) and the massive tonalite became to expose on land surface. The Rb-Sr age in the DX Formation as 2210±60 Ma corresponds to the timing of Ophiolite orogeny (2145~2215Ma) in the southern margin of the Pilbara Craton (Rasmussen & Sheppard, 2005). The DX-CL formations probably had been affected by wide scale metamorphism at this timing.

## Lu-Hf isotope systematics of 3.45Ga Barberton basalts : implications for early mantle evolution

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Lu-Hf isotope systematics of Archean rocks can provide valuable insights into early crust-mantle evolution. In particular, those of Archean mafic rocks allow us to constrain the degree of early mantle depletion. Furthermore, a combination of Lu-Hf and Sm-Nd isotope systematics provides constraints on the physical condition of the mantle differentiation. Recent studies have indicated that 3.8 Ga mafic rocks from Isua have highly positive  $\epsilon_{\text{Hf}}$  with nearly chondritic  $\epsilon_{\text{Nd}}$ , suggesting that the source mantle had differentiated under a lower mantle condition. This may reflect that the differentiation of the Earth's deep mantle occurred much earlier than 3.8 Ga, possibly during the solidification of a magma ocean. In this study, we report new <sup>176</sup>Lu-<sup>176</sup>Hf data for 3.45 Ga basalts in the Kromberg Complex of the Barberton Greenstone Belt, South Africa. The data for all analyzed samples define an isochron age of  $2801 \pm 690$  Ma (MSWD=49,  $2\sigma$ , N=8), whereas those for relatively pristine samples yield an age of  $3890 \pm 1100$  Ma (MSWD=9.6,  $2\sigma$ , N=4). The latter age is consistent with the formation age. We obtained the average  $\epsilon_{\text{Hf}}$  value at 3.45 Ga of  $2.63 \pm 0.33$  ( $2\sigma$ ) for the pristine samples. This indicates that the source mantle of the basalts had been depleted in incompatible elements by 3.5 Ga, but the extent of the depletion was not as strong as that of the source mantle of 3.8 Ga Isua mafic rocks. Furthermore, we found that there is no resolvable Hf isotopic difference between Barberton basalts and komatiites. This observation suggests that Barberton komatiites and basalts share the source mantle, and their formation mechanisms resulted in their petrologic difference. By combining our results with previously reported Sm-Nd isotopic data, we propose that the source mantle of the Barberton experienced early differentiation under high pressure conditions possibly during magma ocean solidification, and subsequently the differentiated mantle had been re-homogenized by mantle mixing.

Keywords: Mantle Evolution, Basalts, Barberton, Lu-Hf, Archean, Isotopic Analysis

## Major element composition and forming condotion of the hidden reservoir

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Solidification of the magma-ocean and subsequent mantle-crust differentiation could have significant influence on the evolution of the solid Earth and hydrosphere, but its detail is still unclear. Previous studies have suggested that the difference in  $^{142}\text{Nd}/^{144}\text{Nd}$  between chondrites and bulk silicate Earth (BSE) resulted from the formation of an incompatible element-rich reservoir that had formed in the early Earth and then got hidden into the Earth's interior or lost outside the Earth. Although various models for the composition and the origin of such a "hidden reservoir" have been proposed, they have not focused on the major element composition of the hidden reservoir. However, the major element composition is crucial to know the density of the hidden reservoir and to examine whether the hidden reservoir rose to form the proto-crust or sunk in the early mantle. In order to determine the major element composition of the hidden reservoir, we estimated the melting condition for the formation of the hidden reservoir with constraints of  $^{142}\text{Nd}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  systematics in the ancient and modern mantle.

This study assumed that the hidden reservoir had formed at pressures less than 10 GPa, on the basis of previous studies that estimated the initial depth of melt segregation to be at this pressure range in the solidifying magma ocean. Then we calculated the Sm/Nd ratio that is conformable to the difference in  $^{142}\text{Nd}/^{144}\text{Nd}$  between chondrites and BSE, and estimated the melt fraction that satisfies this Sm/Nd ratio. From this calculation, the melt fraction was estimated to be <5.2% at 1 GPa, <3.2% at 3 GPa and <1.4% at 7 GPa. From these calculated melt fractions and previous experimental data, we estimated that the major element compositions of the hidden reservoir were incompatible element-rich tholeiite, picrite, and komatiite, respectively.

Ancient hotter mantle should have melted at higher pressure, but on the other hand, the melt fraction was estimated to be small. In order to satisfy the small melt fraction at deep melting, the lithosphere must be thick, as suggested by Korenaga (2009) who showed the possibility of thick lithosphere in the hotter mantle. From these results, a likely composition of the hidden reservoir is incompatible element-rich picrite-komatiite.

Solomatov and Stevenson(1993),*Journal of Geophysical Research*, **98**, 5407-5418

Korenaga(2009), *Geophysical Journal International*, **179**, 154-170

Keywords: hidden reservoir, proto-crust,  $^{142}\text{Nd}/^{144}\text{Nd}$

## Differentiation and material recycling of Archaean mantle estimated from North pole basalt, Western Australia

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Mid-ocean ridges and hotspots are the prominent surface manifestations of mantle upwelling with different mechanisms. In these domains, two types of basalts, i.e., mid-oceanic basalt (MORB) and oceanic island basalt (OIB) occur. Recent statistical analysis on the global data set of the Sr-Nd-Pb isotopic compositions demonstrates that modern MORB and OIB are clearly separated: MORB is derived from a mantle source that has undergone long-term depletion in a "melt component", while OIB is derived from a mantle source with long-term enrichment in the melt component through the recycling of subducted plate material (Iwamori and Albarede, 2008; Iwamori et al., 2010). Therefore, when plate recycling started to develop the geochemical domains is of great importance to understand the material differentiation and evolution of the Earth.

In this study, we present new trace element and Sr,-Nd isotope composition of Archaean MORB and OIB, in order to discuss the differentiation of the mantle at that period and compositional evolution of the mantle for a longer period of the Earth's history. The basaltic rocks of ca. 3.5 Ga from North Pole in northwestern Australia have been analyzed, which include have been classified as MORB and OIB by their geological occurrence and stratigraphy in by Komiya et al. (2002). The rocks have undergone greenschist to amphibolite facies transition metamorphism (Komiya et al., 2002). The original rock compositions may have been modified by metamorphism. In order to examine potential metamorphic modification of the bulk rock composition, so we have measured composition of igneous clinopyroxene which shows original igneous texture, in addition to bulk composition, with special reference to equilibrium/disequilibrium partitioning of trace elements between clinopyroxene and the bulk rock to estimate the effect of metamorphism using partition coefficient.

The composition of North Pole MORB (NP MORB) and OIB (NP OIB) show slightly different trace element patterns. Some spikes in alkaline elements and alkaline earth metal elements and variability of the initial Sr isotopic compositions may result from metamorphic modification. The initial Nd isotopic compositions of NP MORB and NP OIB are similar to each other. However, most of the samples have  $\epsilon_{Nd} < 0$ , which is not typically expected for a mantle-derived basalt. characteristic is typical for felsic rocks. The apparent elemental partitioning between partition coefficient of clinopyroxene and the estimated 'melt', as well as a relatively clear correlation between Sm/Nd and Nd isotopic ratio, suggests that metamorphism has also disturbed Nd isotopic compositions even for clinopyroxene which preserves igneous texture, resulting in  $\epsilon_{Nd} < 0$  of the bulk rocks. The isochron may show the metamorphic age of ca. 3.1 Ga. These approaches, therefore, may provide a quantitative measure for metamorphic geochemical modification of us, we need to gain the original composition from Archaean rocks, and will be useful, or even compulsory to discuss the true mantle signatures. to discuss the differentiation of mantle.

Keywords: Archaean, North Pole, basalt, mantle, isotope, differentiation

## Development of the African continent constrained from U-Pb chronology of detrital monazite

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Monazite, a light rare earth element phosphate, occurs as an accessory mineral in peraluminous felsic rocks and metamorphic rocks from subgreenschist- to granulite-facies. Because monazite has high U and Th and low common Pb contents, it is suitable for precise U-Pb chronology. In addition, monazite is moderately resistant to chemical and mechanical weathering, detrital monazites are well preserved and potentially record the timing and nature of peraluminous igneous activities and a wide range of metamorphic events in their provenance area. Consequently, detrital monazites from large rivers can provide valuable insights into orogenic events in the drainage basins on a continental scale (Hietpas et al., 2013). In this study, we have determined U-Pb ages of ca. 100 detrital monazite grains from the Nile and Niger Rivers, which give chronological information on orogenic events in the African continent with a high time resolution.

The African continent comprises several Archean-Paleoproterozoic cratons, which are rimmed by orogenic belts. A significant part of igneous and metamorphic basement rocks are covered by sediments and therefore inaccessible to in situ sampling at present. Considering that detrital monazites sampled from river sands would partly be derived from the currently inaccessible basement rocks over an extensive area, U-Pb dating of detrital monazite from large rivers can provide chronological information of the basement rocks complementary to studies of the exposed geology. The samples used in this study were collected at the river mouths of the Nile and Niger Rivers. The sand samples used in this study were previously used for zircon U-Pb dating and Hf isotopic studies by Iizuka et al. (2013). Monazite grains were newly concentrated from the river sand samples using the conventional magnetic and heavy liquid separation techniques. Monazites were randomly hand-picked from the aliquots of monazite concentrates and mounted in an epoxy mount. Before analysis, each grain was imaged by BSE using FE-SEM to check elemental zonation and the presence of inclusions. Monazite U-Pb isotopic dates were measured using 200nm-FsLA-ICP-MS. Reference monazite 44069 (U-Pb age 425 Ma) is used to correct for instrumental Pb/U fractionation.

The monazite grains from the Nile River gave U-Pb ages between 560 and 2100 Ma with a dominant population at 580-800 Ma. Furthermore, the U-Pb age population indicates a sharp peak at 600 Ma. The age peak at 600 Ma of Nile River suggests metamorphic and/or felsic igneous events occurred at that time in the drainage basin, probably related to the collision of the East and West Gondwana continents.

The monazite age population of Niger River is dominated by Neoproterozoic ages with the most prominent peak at 580 Ma and peaks at 625 and 645 Ma. The peaks shown in the Niger River monazite (580 Ma and 620-630 Ma) correspond with the timing of previously known orogenic events in Northwest Africa. A peak at 620-630Ma is consistent with a metamorphic event at ca.  $625 \pm 29$  Ma, likely related to the collision of the West Africa Craton and West Gondwana continent (Agbossoumonde et al., 2007). The other peak at 590-600Ma is consistent with a ca.  $576 \pm 4$  Ma post-collisional igneous event at the Pan-African Belt in Cameroon (Kuekam et al., 2013).

The age difference in the most prominent peaks of Nile and Niger monazites suggests that the timing of orogenic event in Northwest Africa was prior to that of in East Africa by ca. 10 Ma.

The accumulated monazite age distribution shows populations at 580-590 Ma, 630-640 Ma and 710-720 Ma, corresponding with the timing of Snowball Earth glaciation events. The chronological correspondence can be interpreted that the multiple Pan-African orogenic events during the Gondwana supercontinent assembly enhanced the rates of erosion and weathering via supermountain building that in turn decrease atmospheric carbon dioxide concentration resulted in glaciation.

Keywords: monazite, U-Pb age, LA-ICP-MS, Pan-African

## Significance of serpentinization of lower crust in deep-sea hydrothermal biosphere

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Hydrothermal activity in the Archean-Ridge system has been considered to play a major role to maintain the oldest biosphere in early Earth. In the present ridge-system, hydrogen production in the serpentinized peridotite layer, is considered as major energy source. However, low temperature hydrothermal zone in the lower crust layer in the ridge has been recognized as hydrogen producing zone. Thickness of oceanic crust is less than 10 km in the present Earth. However, the thickness of Archean oceanic crust has been estimated as 50 km. That is, hydration process of oceanic crust in the Archean-ridge is significantly important. Hydration rate of the peridotite layer in the Archean ridge is less extensive than Phanerozoic because thicker oceanic crust prevents hydration in the peridotite layer. Lower crustal rocks of accreted oceanic plateau is one of the best sample to describe hydration process due to deep-sea-hydrothermal alteration because it is easy to observe huge outcrops and collect samples systematically in whole section. We have collected gabbroic rocks from Mikabu high P/T rocks in Toba area and from Ootoyo area, Japan because there are large scale trench cliffs in the mine. Serpentinization of olivine gabbro and troctolite and hydrogen production rate will be shown in the present poster.

Keywords: the oldest biosphere in early Earth, serpentinization, gabbroic rocks

## Production mechanism for hydrocarbons in serpentinite-hosted hydrothermal systems: Hakuba Happo hot spring

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Serpentinite-hosted hydrothermal systems have been considered to be important environment for birth or evolution of earlier life. Serpentinite is a rock that results from the geological processes of hydration and metamorphic transformation of ultramafic rock from the Earth's mantle. Although ultramafic rocks are rarely exposed at the surface of the Earth today, they were likely to be an abundant component of the early crust owing to the higher potential temperatures compared to the present-day mantle [Komiya et al., 2004]. The presence of hydrocarbons has been reported in serpentinite-hosted systems at not only seafloor but also continental settings [e.g., Charlou et al., 2002; Proskurowski et al., 2008; Etiope et al., 2011; Szponar et al., 2013]. However, production mechanisms of the hydrocarbons in serpentinite-hosted hydrothermal systems so far has not been satisfactorily understood. In this study, we conducted chemical and isotopic analyses of hydrocarbons from a continental serpentinite-hosted hydrothermal system; Hakuba Happo hot spring in central Japan. Hakuba Happo hot spring is situated in the ultramafic rock body and is a site where serpentinitization processes are likely to be ongoing at low-temperature of 50-60 [Suda et al., 2014]. The water at Hakuba Happo is strong alkaline (pH >10.5) and rich in H<sub>2</sub> and CH<sub>4</sub>. Gas and water samples were obtained directly from two drilling wells in November 2013. Water temperature, pH, dissolved oxygen level (DO), oxidation-reduction potential (ORP) and salinity were measured at the sampling points using portable sensors. The water temperatures and chemistries were almost exactly the same as that at previous investigations conducted in 2010 and 2011. The hydrocarbon constituents of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iso-C<sub>4</sub>H<sub>10</sub> and normal-C<sub>4</sub>H<sub>10</sub> were detected from gas samples of Hakuba Happo hot spring. We report the isotopic analyses of hydrocarbons and discuss the process of hydrocarbons generation in serpentinite-hosted hydrothermal systems.

Keywords: serpentinite-hosted hydrothermal system, hydrocarbon, isotopic analyses, abiotic synthesis

## Geology and biology of the Shinkai Seep Field in the Southern Mariana Forearc

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The Shinkai Seep Field (SSF), located in the inner trench slope of the southern Mariana Trench, ~80 km northeast of the Challenger Deep, is a serpentinite-hosted ecosystem mainly consisted of vesicomid clams. Although vesicomid clams are among the dominant invertebrates of chemosynthesis-based communities found principally at methane cold seeps derived from sediment diagenesis (such as at the Japan Trench, Nakai Trough, and Sagami Trough) and high-temperature hydrothermal vents (such as at the Galapagos Rift and Okinawa Trough), there have been no live examples from a serpentinite-hosted hydrothermal system including serpentinite mud volcanoes.

The SSF was serendipitously discovered by a Shinkai 6500 dive to map the mantle peridotite in the southern Mariana forearc, during YK10-12 cruise of R/V Yokosuka in September 2010. Although the dive was successful in collecting mantle peridotites and vesicomid clams, no water and sediments were collected. TN273 cruise of R/V Thomas G. Thompson in January 2012 performed Deep-towed IMI-30 sonar backscatter imaging. The result indicates that the SSF is associated with a small, low backscatter feature that may be a small mound. Such low backscatter features can be widespread in the mapped area.

In order to understand the SSF, YK13-08 cruise had the following objectives:

- (1) Finding and locating active fluid venting in the SSF. If successful, sampling the vent fluid and associated sediment for chemical and microbiological study.
- (2) Finding seep fields other than the SSF in the southern Mariana forearc, using the low backscatter feature on IMI-30 image as a guide.
- (3) Comprehensive understanding of the geology of the SSF. It is important to understand the geological background of the SSF including tectonic development of the southern Mariana forearc.

During YK13-08 cruise, Shinkai dives 1362, 1365 and 1366 successfully revisited the SSF, obtaining core samples for investigation of faunal composition, microbial and geochemical analyses in sediments, Niskin and pressure-tight water samples for geochemical analyses, and discovering chimneys. Shinkai dives 1363 and 1364 investigated the landward slope of the southern Mariana Trench ~7 km west of the SSF, revealing that the mapped slope is entirely consisted of serpentinitized harzburgites. New seep fields were not discovered during the cruise, indicating that not all low backscatter features on IMI-30 image correspond to seep fields. In this talk, we will show the preliminary results of YK13-08 cruise and discuss the geology and biology of the SSF.

Keywords: chemosynthetic community, serpentinite, Shinkai Seep Field

## Deep-sea hydrothermal vent fauna on the Central Indian Ridge

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In deep-sea hydrothermal vent fields, faunal distribution is associated with the geochemical environments generated by hydrothermal vent activity. Hydrothermal vent fields on the Central Indian Ridge (CIR) are associated with vent fauna which is a mixture of Atlantic and Pacific and are discretely distributed along the ridge axis of more than 1000 km apart. In this presentation, faunal distribution in hydrothermal vent fields on the CIR is summarized at the intra- and inter-field levels. The species composition of the vent fauna in the four vent fields hitherto known is reviewed and updated, and faunal resemblance among the four vent fields of the CIR appears to reflect the number of species recorded, indicating that faunal surveys are not sufficient in describing the total vent fauna on the CIR. All the genetic studies of the CIR vent fauna have indicated a high genetic connectivity among the local populations, despite the many potential dispersal barriers existing between the vent fields. On the basis of the spatial distribution of vent species in a vent field, typical vent fields on the CIR were classified into six zones, of which the central two zones are often covered by *Rimicaris* swarms in the Kairei and Edmond fields. The close relationship between vent fauna from the CIR and the western Pacific, compared to those from other regions, is highlighted. Knowledge of the Indian Ocean vent fauna is limited, and further quantitative information on the biodiversity of vent fauna will provide clues to the formation of biogeographical regions and the dispersal of vent fauna among deep-sea hydrothermal vent fields.

Keywords: chemosynthetic biological community, biogeography, faunal similarity

## A trial on evaluating hydrothermal system evolution using geochronological dating and biological diversity analyses

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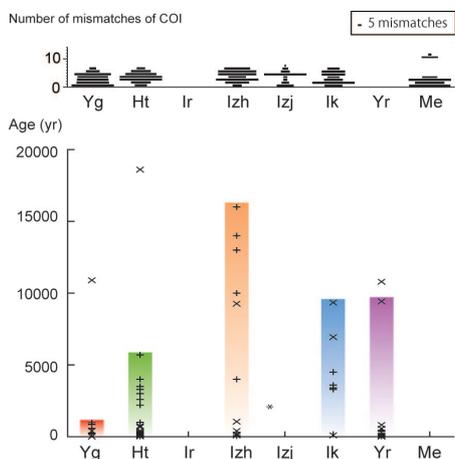
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To elucidate the evolution of hydrothermal activities, we conducted an interdisciplinary study including geochemistry and biology to develop a method of obtaining reliable age information. Because there was a small amount of constraint on the lifetime of activity at hydrothermal sites, this study is one of the principal goals of the TAIGA-project, "Trans-crustal Advection and In-situ biogeochemical processes of Global sub-seafloor Aquifer" funded by a Grant-in-Aid for Scientific Research on Innovative Areas. As geochemical dating techniques, two methods applicable for hydrothermal ore minerals were developed and improved to fill the gap of the time-ranges in the conventional dating methods: electron spin resonance method and uranium-thorium disequilibrium method. Cross checks between the two methods generally showed good agreement for the range of hundreds to thousands of years. Except for the extreme values for each hydrothermal site, geochemical ages exceed 9ka for the southern Mariana Trough and for 16ka for the Okinawa Trough, respectively. As biological analysis, the biodiversity among faunal communities in the targeted areas was analyzed at the species and DNA levels. In the southern Mariana Trough, *Alviniconcha* gastropods and *Neoverruca* barnacles clearly show the greater genetic diversity with greater distances from the ridge axis, which fairly corresponds to the geochemical ages for ore minerals. In the Okinawa Trough, *Bathymacrea* limpet showed greater genetic diversity at the Hakurei site in the Izena Hole where the ore minerals show oldest ages among the studied sites (Fig.).

Species and genetic diversity of the local fauna were not always correlated to geochemical dating, either in the southern Mariana Trough region or in the Okinawa Trough region. Although the results are not simple, comparison of age information obtained from analyses of these two disciplines potentially provides important constraints for discussion of the history and evolution of hydrothermal activities.

Figure caption (upper): Genetic divergence of COI gene indicated as mismatches in base sequences of *Bathymacrea secunda* limpet of the Okinawa Trough. Scale bars are shown as five mismatches of partial COI sequences. (lower) Geochemical age range determined from the sulfide and sulfate deposits in Okinawa Trough. Active sites are shown from approximately SW to NE. The left-hand side is the southwestern end. Colored bars represent reliable age ranges for respective sites. The localities are denoted as follows: Yg, Daiyon-Yonaguni Knoll; Ht, Hatoma Knoll; Ir, Irabu Knoll; Izh, Hakurei-site in Izena Hole; Izj, JADE-site in Izena Hole; Ik, Iheya North Knoll; Yr, Yoron Hole; Me, Minami-Ensei Knoll.

Keywords: geochronology, biodiversity, TAIGA-project, ESR, U-Th disequilibrium, mitochondrial mismatch analysis



## Chemosynthesis-based ecosystem discovered on a Cretaceous sea turtles from Japan

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One of the basic types of chemosynthetic ecosystems is known to develop on vertebrate carcasses. Within the framework of efforts to trace the evolution of chemosynthetic animals thriving in the modern vents and seeps, it has been hypothesized that these chemosynthetic animals adapted to the vent and seep environments via the transient environment formed by the decomposition of bones of vertebrate animals (e.g. Distel et al., 2000). Thus a study of the geological record of chemosynthetic ecosystems on vertebrate carcasses became of increasing importance in understanding the evolution of chemosynthetic animals. However, such studies were not fully assessed so far. Kaim et al. (2008) reported the existence of chemosynthetic ecosystems on plesiosaurid carcasses, marine reptiles which flourished in the Cretaceous oceans. However, we still were uncertain whether any other marine reptile carcasses could support chemosynthetic ecosystems. Here we document the first chemosynthetic community found on carcasses of the Cretaceous sea turtles.

The fossil sea turtle (*Mesodermochelys* sp.) has been collected from the Upper Cretaceous Campanian deposits cropping out along the Nio River, Nakagawa Town, Hokkaido. Sediments surrounding the turtle yielded provannid gastropods and thyasirid bivalves, both known to be members of chemosynthetic communities. Those chemosynthetic molluscan fossils have also been found in Cretaceous hydrocarbon seeps and on plesiosaurid carcasses (Kaim et al., 2008; 2009; Kiel et al., 2008).

This finding indicates that the chemosynthetic communities were supported not only by plesiosaurid carcasses but also by decomposing sea turtles. The sea turtles are a rare example of Cretaceous marine reptiles surviving the Cretaceous/Paleocene extinction event. Thus, it is reasonable to assume that sea turtle carcasses could continuously support chemosynthetic ecosystems linking the Mesozoic reptile fall communities with Cenozoic and modern whale fall communities, the latter occurring in the fossil record not earlier than Eocene.

## A chemosynthetic community on plesiosaurid carcass: with focus on distributions of microbes and invertebrate fossils

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Chemosynthesis - based communities are known to have been established not only in hydrocarbon seeps and/or hydrothermal vents but also on Cretaceous plesiosaurid carcasses (Kaim et al., 2008a). However, no detailed reconstruction of chemosynthetic ecosystems on plesiosaurid carcasses has yet been undertaken. To reconstruct the detailed development of ecosystems, we examined distribution patterns of chemosynthetic molluscs and micro- and macroborings around/on a plesiosaurid carcass. The examined carcass derived from a Cretaceous marine deposit distributed in Haboro Town, Hokkaido, and thought to have perhaps supported chemosynthetic ecosystems (Kaim et al. 2008a).

We observed the surface and a cross section of the plesiosaurid specimen. Chemosynthetic gastropods (Abyssochrysoidea) were densely distributed around the plesiosaurid bones (especially on the upper side). Several types of borings (e.g. micron-sized filamentous microborings and rounded boring holes with apertures) could be found on the plesiosaurid bones. On the basis of their genera shapes and juxtaposition to pyrites, we hypothesize that the filamentous borings might have been formed by sulfur-oxidizing bacteria. The rounded boring holes with apertures within the bones are similar to modern borings made by *Osedax*.

The borings were distributed on the upper side of the bones relative to the lower side, resembling the distribution pattern of chemosynthetic gastropods. Most Recent abyssochrysoid gastropods are known to graze bacterial mats. The coherent distribution patterns of abyssochrysoid gastropods and microborings on the plesiosaurid bones indicate that the gastropods grazed bacterial mats even in the Cretaceous age. In addition, bone-eating animals also accumulated on the upper side of the bones. These distribution patterns might be influenced by the difference in exposure duration times of the upper and lower bone surfaces (upper side exposed on sea floor for a longer time than the lower side due to continuous sedimentation).

Keywords: Reptile fall, Plesiosauridae, distribution patterns, borings, chemosynthetic molluscs

## Paleoecology of the Upper Cretaceous echinoderms from cold seep carbonates in South Dakota, USA

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Echinoderms were thought to be rare in a cold seep environment and had not been considered as a member of the chemosynthetic community until recent years, whereas the chemosynthesis community consists of a variety of other taxa. In the last 10 years, some species of echinoderms have been reported as a member of the modern chemosynthetic community, and some fossil echinoderms have also been found from or near carbonate mounds associated with cold seep. However the taxonomic and paleoecologic studies about these echinoderms have not been sufficiently done, and the ecologic relationship between these echinoderms and cold seeps has been also unsolved. The purposes of this study is to discuss paleoecology and process of adaptive evolution of echinoderms associated with a cold seep environment found from the Upper Campanian Pierre Shale in South Dakota, by field surveys, taxonomic of and morphological observation of fossil echinoderms. Chemical analyses of fossil echinoderm skeletons were also conducted, including element analysis for estimating the degree of diagenesis, and stable carbon isotopes analysis for clarifying the degree of relation between the echinoderms and the seep hydrocarbon.

As a result of field surveys, it is proved that the diversity of fossil species from carbonate mounds associated with cold seeps is different among mounds, even between adjacent mounds. Such a difference of species diversity is considered to reflect the difference of environments during the time when the carbonates were formed. It is presumed that the carbonate mounds with high diversity were exposed on the sea floor for a long time and provided a suitable environment for epifauna such as many echinoderms. Fossil crinoid from seep carbonates has low values of  $\delta^{13}\text{C}$  (-20 ‰ or less). These values are considerably lower than modern crinoids which inhabit non-seep environments, and are also lower than the values of other fossil echinoderms from seep carbonates of the Pierre Shale. The crinoid from seep carbonates also has very strange, characteristic morphology, not seen in other stalked crinoids. Considering these chemical and morphological data, the crinoid from seep carbonates had probably adapted to the environments of cold seeps. On the other hand, echinoids from cold seeps do not have low values of  $\delta^{13}\text{C}$ , and morphologically they are not significantly different from those found from non-seep environments. Therefore, it is considered that the echinoids from seep carbonates are not regarded as a true member of chemosynthetic community, but they came into cold seeps to benefit irregular, hard substrate to live on, or to obtain ample food sources from this cold seep environment.

The degrees of adaptation to cold seeps are therefore different among echinoderm species.

Keywords: cold seep, echinoderms, paleoecology, chemosynthetic community

## Molecular phylogenetic evidence for host switching in chemoautotrophic symbionts of deep-sea *Calyptogena* clams

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*Calyptogena* clams are living in deep-sea chemosynthetic habitats and globally distributed in seeps and hydrothermal vents. They are nutritionally dependent on chemoautotrophic sulfur oxidizing bacteria, which are harbored within their gill epithelial cells. The *Calyptogena* symbionts are thought to be vertically transmitted via clam's egg to the next generation. Both host and symbiont are thought to coevolve, because topologies of the phylogenetic trees of them form a mirror image. However, their phylogenetic trees have not been robust enough for analyzing their coevolutional relationship, because of using partial gene sequences of host (mitochondrial *cox1* and *rrnL* genes) and symbiont (16S rRNA gene). The possibility of lateral acquisition of the symbiont has been reported in some *Calyptogena* lineages. To improve the phylogenetic trees of *Calyptogena* clams and of symbiont, we sequenced the mitochondrial genomes of *Calyptogena* clams, and several their symbiont genes, and analyzed the phylogenetic trees by using the concatenated sequences.

Mitochondrial genomes of *C. phaseoliformis*, *C. okutanii* and *C. fossajaponica* were sequenced. Based on these mitochondrial genome sequences, primer sets for PCR of mitochondrial genes of other *Calyptogena* clams were designed. Using them, 11 mitochondrial genes (*cox1*, *cox2*, *cox3*, *nad1*, *nad3*, *nad4*, *nad5*, *cytb*, *atp6*, *atp8* and *rrnL*) of other 8 *Calyptogena* species (*C. fausta*, *C. kawamurai*, *C. kilmeri*, *C. laubieri*, *C. nautilei*, *C. pacifica*, *C. soyoae*, *C. stearnsii*) were amplified by PCR and sequenced. Eight genes (16S rRNA, 23S rRNA, *uvrA*, *uvrD*, *mfD*, *groEL*, *groES* and *gyrB*) of symbionts of these *Calyptogena* clams were also sequenced. Phylogenetic trees of clams and symbionts were constructed by maximum likelihood and bayesian analysis based on concatenated 11 mitochondrial and 8 symbionts genes, respectively.

The reliabilities of phylogenetic trees of the hosts and their symbionts were significantly improved by using the concatenated genes sequences (Fig.1). Bootstrap values and posterior probabilities of internal nodes were better supported than those of the previous phylogenetic trees using partial gene sequences. Topological congruence of host and symbiont that was supported by bootstrap value (100%) and posterior probabilities (1.0), was shown in *C. okutanii*, *C. soyoae*, *C. kilmeri*, *C. pacifica* and *C. fausta*. These results suggested that these symbionts were cospeciated with their host clams (green boxes in Fig.1). Although the topologies of host and symbiont were congruent with *C. fossajaponica* and *C. phaseoliformis*, there were the low bootstrap values and low posterior probabilities in the host clade.

Topological incongruence between host and symbiont trees was shown in *C. kawamurai* - *C. laubieri* clade and *C. nautilei* - *C. stearnsii* clades (Fig.1) Congruence of topologies was rejected by approximately unbiased test using sitewise log-likelihoods (red branches in Fig.1). This result suggested that these symbionts have not cospeciated with their host clams. Host switching of the symbionts in the clades of *C. kawamurai* - *C. laubieri* and *C. nautilei* - *C. stearnsii* were examined by coevolution software, which compared the topologies of host and symbiont. Host switching is the event that symbiont is transferred from a host to a new host in a different lineage during speciation. The host switching of symbiont between *C. kawamurai* and *C. laubieri* was suggested by this software. Moreover, both clams are living in different depths of the same area (blue box on Fig.1). However, this software did not suggest the host switching of symbionts between *C. nautilei* and *C. stearnsii*. They are living in different areas. In this study, we show the phylogenetic relationships of cospeciation and non-cospeciation species with the symbionts among examined 11 *Calyptogena* species. It was suggested that topological incongruence of host and symbiont trees in clade of *C. kawamurai* - *C. laubieri* may be due to the host switching

Keywords: symbiosis, deep-sea *Calyptogena* clams, coevolution, host switching

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Time:April 29 11:00-11:15

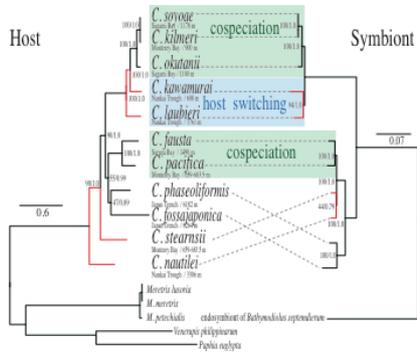


Fig1. cospeciation and host swithing on *Calyptogenia* clam and symbiont trees.  
 Numbers in the nodes correspond to maximum likelihood bootstrap values and posterior probabilities.  
 Reg branches correspond to topological congruence rejected by approximately unbiased test using  
 sitewise log-likelihoods.

## Two forms of *Calyptogena (Ectenagena) nautilei* recognized in shell morphologies

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*Calyptogena (Ectenagena) nautilei* was originally described by Okutani and Métivier (1986) from the cold seep sites in the Tenryu Canyon at the Nankai Trough based on six living specimens. After that, this species has been reported from the continental slope off Kumano, the Daiichi-Minami-Muroto Knoll, Zenisu Ridge, and Shionomisaki Canyon in the Nankai Trough (Fujikura et al., 2000; Okutani et al., 2002; Kojima et al., 2004; Anma et al., 2010). Okutani et al. (2002) examined the species from the Tenryu Canyon, the continental slope off Kumano, and the Daiichi-Minami-Muroto Knoll, and described that the species had a great variety in the shell outline. We observed the shell morphologies and structures of *C. (E.) nautilei* from some localities above including the type materials, and concluded that this species can be divided into two forms (form 1 and 2) by the shell morphologies and the shell structure.

We examined three type specimens from the Tenryu Canyon (Nautile Dive KD-3 and KD-5: Holotype, MNHN 26983, Paratype, MNHN 26984, Paratype, MNHN 26985), four specimens from the continental slope off Kumano (Shinkai 6500 Dive 615), five specimens from the Shionomisaki Canyon (Shinkai 6500 Dive 889, 890, and 891), and eight specimens from the Daiichi-Minami-Muroto Knoll (KAIKO Dive 189, 192, and 193). All specimens were observed with an optical microscope and bare eyes, and two specimens from the Shionomisaki Canyon were observed with a scanning electron microscope in the shell surfaces and cross sections.

The specimens from the Tenryu Canyon are assigned to form 1, and the other specimens are assigned to form 2. Two forms are most easily distinguished in the shell inner surface characters. That is, form 1 has smooth inner surface whereas form 2 is ornamented nearly overall the surface in hole-like structures that consist of about 61-548  $\mu\text{m}$  in diameter. In addition to the inner surface ornamentation, form 1 is distinguished from the form 2 in having a subumbonal pit in the hinge plate of both valves, anterior ramus of right subumbonal cardinal tooth, and pallial sinus.

Keywords: Vesicomidae, *Calyptogena (Ectenagena) nautilei*, Shell morphology, Hole-like structure

## Archives of long-term deep seafloor videos at chemo-synthetic biological community off Hatsushima Island in Sagami Bay

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More than 20 years of multidisciplinary long-term observation, including visual observation, has been carried out with a cabled observatory on deep seafloor at a depth of 1175 m off Hatsushima Island in Sagami Bay since the first deployment in 1993, experiencing entire replacement for upgrade in 2000. The observatory was installed at a cold seepage site where large chemo-synthetic biological communities mainly consisted of vesicomid clams exist. The observatory is composed of several kinds of sensors, including video cameras, a hydrophone, CTD sensor and seismometer in order to observe biological phenomena visually and also to investigate environmental fluctuation on deep seafloor.

All those data obtained with the underwater unit are transmitted through a submarine cable to the shore station in Hatsushima Island. The video signal was recorded on S-VHS videotape before the replacement of the observatory in 2000 and mainly on DVCAM videotape after the replacement, both with acoustic signal obtained with a hydrophone on soundtrack as audible sound. The shore station is usually uninhabited, and daily visual monitoring of seafloor, 30 minutes a day before the replacement and 26 minutes a day after the replacement, has been performed automatically. The videotape has been replaced once a week on the day when manual observation is performed usually for 6 hours. As for lighting, six halogen lights were attached at first and two of them were turned on simultaneously by turn for usual observation considering lifetimes. However, most of those lights were broken by 2008 and since then an LED light is used which is darker but has longer lifetime than the halogen lights, resulting narrow view.

Although visual observation has been performed about ten hours a week, more than 20 year observation produced thousands of videotapes. Archiving those videotapes becomes important because they degrade over time and the devices to replay them are going out of production and the opportunities to utilize them are being lost.

Meanwhile, vocalizations of sperm whales were found in the acoustic signal recorded on the soundtrack of the videotapes and, in order to utilize them as one of the *in situ* data for the remote species identification, archiving the videotapes started under one of the research project in Core Researches for Evolutional Science and Technology (CREST) founded by Japan Science and Technology Agency (JST) since December 2011. At the end of the fiscal year 2013, more than half of those videotapes will be archived. Although the main target of the CREST project is acoustic data, video signals on the videotapes are converted to MPEG-2 files for S-VHS tapes and both AVI and MPEG-2 files for DVCAM tapes before extracting acoustic data.

In those video images, not only the long term change of the clam colony but also some episodic events, such as spawning of the clams, sudden increase of snails and other unidentified events have been recognized, which would be invaluable data for the investigation of chemo-synthetic ecosystems. Those archived video images will be able to supply researchers outside the project in near future. However, there still exists a problem that the number of hard disks in which the video images are stored is very large even though it is less than a thousand.

Keywords: off Hatsushima Island in Sagami Bay, long-term visual observation, archives of videos

## Paleoecology of Neogene vesicomyids from Niigata, Japan and their adaptations to geochemical environments of cold seeps

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Living vesicomyid bivalves are known to adapt to different hydrogen sulfide concentration and various habitats such as methane seeps, hydrothermal vents, whale falls, and petroleum seeps depending on species. Fossil vesicomyids are reported especially from Neogene seeps worldwide, but their adaptations to the geochemical environments of ancient seeps, which can help to understand the diversity and evolution of them, remain unrevealed. This study examined the paleoecology of fossil vesicomyids and geochemical environments of seeps to which they adapted by investigating their modes of fossil occurrence and geochemistry and petrography of seep carbonates from the two Neogene seep localities in Niigata Prefecture.

The lower Pliocene part of the Kurokura Formation mainly consists of gray to dark gray siltstones which deposited in upper bathyal depth. At the riverside cliff of Echido River at Matsunoyama-Matsuguchi, Tokamachi City, pebble-sized carbonate concretions are contained in 60 cm-thick massive gray siltstone. Fossil vesicomyids, *Archivesica kannoi*, are contained in the concretions some of which are gradually bounded by surrounding siltstone. A large individual (ca. 90 mm length) and surrounding small individuals (ca. 20 mm in the mean length) of *A. kannoi* are contained in the same concretions with various other bivalves, gastropods, and scaphopods which are not unusual to the modern cold-seep communities. Lucinid bivalves are contained in surrounding siltstone and burrows filled with carbonates are also observed in the siltstone. Concretions are mainly composed of micritic Mg-calcite, containing abundant pyrite crystals, and stable carbon isotopic compositions of them are very low values (-43.3 to -27.1 ‰ vs. PDB), showing their derivation from methane, whether they contain fossils or not. Only fossil-bearing concretions contain clast-like carbonates (ca. 5 mm in diameter) which are triangular or oval-shaped in cross section and composed of many fine dolomite crystals surrounded by Mg-calcite matrices in thin section. Dolomite formation is related to the removal of dissolved sulfate by sulfate reduction, thus it may suggest active produce of hydrogen sulfide. It can be concluded that *A. kannoi* was adapted to the habitat where hydrogen sulfide concentration was relatively higher due to more active sulfate reduction than surroundings, or pumping activity of *A. kannoi* supplying sulfate was active enough to promote active sulfate reduction.

The upper Miocene Nodani Formation consists of alternation of gray sandstone and dark gray siltstone which deposited in upper bathyal depth as submarine fan turbidites. At the river cliff of Nakanomata River at Nakanomata, Joetsu City, pebble-sized carbonate concretions are contained in dark gray siltstone just below gray, oily sandstone. Fossil vesicomyids, *Calyptogena pacifica*, are contained in these concretions or surrounding siltstone. Some of them are preserved in life position. Fossils and concretions are contained in a narrow range of 30 cm wide and 5 cm thick, and pipe-shaped carbonate concretions are contained parallel to bedding in siltstone 50 cm below. These concretions are mainly composed of micritic calcite and carbon isotopic values of them are moderately low (-21.7 to -13.2 ‰), suggesting their derivation from crude oil. In thin section, the fossil-bearing concretion contains many micritic peloids. Central void space of pipe-shaped concretion is fringed with bladed calcite which also shows low carbon isotopic value (-22.6 ‰), suggesting that these pipes acted as conduits of seepage. *C. pacifica* lives in the Recent methane seeps, but it is suggested that this species was also adapted to narrow-ranged, local petroleum seep in the Miocene.

Keywords: vesicomyids, Neogene, sulfide concentration, petroleum seep

## Recent trials of laboratory culture with chemosynthetic organisms

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

Chemosynthetic ecosystem is dominated by the organisms what has symbiotic bacteria in their body. Deep-sea bivalve *Bathymodiolus septemdiarum* have been hosting some sulfur oxidizing bacteria in their gills. The bacteria have ability to synthesize such organic compounds as sugars from inorganic carbon source with hydrogen sulfide (H<sub>2</sub>S). Many questions have been still remaining about the emergence and maintenance mechanisms of such symbiotic relationship between host animal and bacteria. Even though the development of laboratory culture techniques of such chemosynthetic bivalves are very useful approach to understand the detailed ecology and for further experiments, the technique is not developed very well. Our research group try to set chemostat water bath up with hydrogen sulfide to keep *B. septemdiarum* as healthy condition. We try to use the culture system to evaluate the bivalves can keep their symbiotic bacteria to make much longer life time in laboratory. The activity of symbiotic bacteria has been tested by the uptake ability of <sup>13</sup>C labeled inorganic carbon into their body.

Individuals of *B. septemdiarum* are captured during dive series of ROV Hyper-dolphin system of two cruises of R/V Natsushima operated by Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in April of 2012 and in March of 2013. The samples are collected around Myojin-Sho submarine volcano on the Izu-Ogasawara Ridge. Collected samples were kept under 4 °C water tank in an on-board low-temperature room till the end of cruise. Then, the individuals are immediately transfer to on-land laboratory water tank after cruise to avoid the unfavorable environment. The water tank has been designed as chemostat system with H<sub>2</sub>S supply to maintain symbiotic bacteria of deep-sea chemosynthetic animals. The individuals are cultured in this system for three months and fourteen months respectively. Here, previous study shows the symbiotic bacteria disappeared within three months without H<sub>2</sub>S source. Therefore, we prefer to confirm the bacteria have been hopefully maintained more than three months in our chemostat system or not. For this purpose, carbon isotope labeling experiments were carried out to clarify the existence of symbiotic bacterial activity. The carbon isotope will be taken into organic matter of *B. septemdiarum* if the symbionts are active after laboratory culture. We have compared the carbon isotopic uptake between under H<sub>2</sub>S positive and under H<sub>2</sub>S negative (control) conditions, respectively. Meantime, dissolved oxygen (DO) of each cultivation was monitored to check health and activity of individual bivalves. The results show the labeled <sup>13</sup>C signals were detected on the organic matters of both gills and foot especially under H<sub>2</sub>S positive condition. Surprisingly, the activity was much positive even the individuals were kept for fourteen months in the chemostat system.

Keywords: laboratory culture, chemosynthetic organisms, *Bathymodiolus septemdiarum*

## Distribution and internal structure of the nodules occurring in the Shimanto sedimentary rocks, Muroto Peninsula, Shikoku

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Nodules have often been discovered on the deep-sea floor. The mechanism of their formation however is not yet clear. Nodules found in the outcrops of the Tertiary Shimanto belt in Muroto Peninsula are found as concretions that can easily be separated from the host rock. Those nodules very likely record the formation process at the deep-sea floor, and also the accretional process thereafter. This study aims to show the origin of the nodules through the spatial distribution, the occurrence, the shape, and the internal structure of the nodules sampled in Muroto Peninsula.

Spatial distribution of carbonate nodules were investigated along the coastline of Muroto Peninsula. Nodules were found in almost every outcrop, the abundance, however, varied from one locality to another. Outcrops with abundant nodules had more than 50 nodules within the area of 100 m<sup>2</sup>. Six localities were discovered with abundant nodules. Four of them were mudstone outcrops, and two the alternation of sandstone and mudstone. Most nodules occurred in the mudstone layers within the alternation of sandstone and mudstone. It is indicated that the distribution of nodules as are mainly controlled by lithology. The localities were scattered along the coastline of Muroto Peninsula. Comparing the distribution with the temperature estimated using vitrinite reflectance by Laughland and Underwood (1993), the distribution of nodules was not correlated with the thermal structure of the Shimanto Belt.

The length of the long axis of the nodules were 12-250 mm and the length of the minor axis were 10-180 mm, most of them with aspect ratios of 1.3 to 1.4. The aspect ratio is the ratio of the long axis diameter to the short axis diameter of an ellipse. At one outcrop, all nodules with the short axis diameter of 40mm or less were long in shape, with the aspect ratios 3 or larger. This can be explained if the nodules were originally equivalent in size and were deformed during the accretional process. The locality is where high vitrinite reflectance has been reported (Laughland and Underwood, 1993).

Surface of section of 18 nodules were examined. Dark colored matrix, which was similar to the country mudstone, composed most of the interior of the nodules. One of the nodules had small whitish core near the center. The size of the core was approximately 4 mm in length with irregular shape. Triangular or quadrangular pyrite grains, with the length of the sides approximately 50-450  $\mu$ m, are often found scattered within the nodules. The shape of the pyrite grains indicated chemical origin. Heterogeneity was observed in the matrix: darker and lighter colored bands with 1 to 2 mm width were observed. The chemical mapping image of the matrix obtained using EDS showed that different colored bands contained different mineral assemblage. One band was mainly composed by quartz and calcite, the other was presumably rich in clay minerals.

In conclusion, nodules were formed mainly in the mudstone layer in Shimanto Belt of Muroto peninsula, indicating that the nodules were originally formed near the surface of the mud of the quiet deep-sea floor. One of the nodules had small whitish core near the center, indicating the origin of the nodules being trace fossils produced by probable annelid worm. Observation of the internal structure indicated that the activity of the habitant of the trace likely accelerated the concretion of the mud in the vicinity.

### References

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Keywords: nodule, Shimanto belt, mudstone layer, pyrite, trace fossil

## New localities of fossil cold-seep assemblages from the Pleistocene Otsuka Formation of the Nakatsu Group, central Japan

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We report two new localities of fossil cold-seep assemblages from the Pleistocene Otsuka Formation, Nakatsu Group, exposed along the northeastern bank of the Sagami River, Sagami City, central Japan. The Otsuka Formation is composed mostly of massive mudstones in which pumice-rich lapilli tuff beds (several cm to several dozen cm in thickness) and thin sandstone beds are intercalated.

Our new localities (Locs. 1 and 2) occur lucinid fossils in the massive mudstones associated sporadically with the authigenic carbonate concretions (several cm to several dozen cm in size). In Loc.1, scoria and pumice grains (0.5 to 2 mm in size) are scattered and lenticular fine grained sandstone, 7 cm in maximum thickness, is intercalated. The 17 large bivalve fossils, mostly articulated lucinids, occur sporadically in 0.4 m in height and 1 m in width of the outcrop. Most of the fossils are entirely dissolved in this locality. The commissure planes of articulated bivalves are arranged perpendicular to the bedding plane, with their umbos oriented upward. In Loc.2, scoria and pumice grains (0.5 to 2 mm in size), and granule-size pumice grains are scattered. The 42 articulated and disarticulated bivalve fossils, mostly lucinids, occur sporadically in 2 m in height and 1.2 m in width of the outcrop. Most of the fossils are entirely dissolved as well as in Loc.1. The articulated and disarticulated bivalve fossils are counted, respectively, 27 and 15 in numbers. The commissure planes of many articulated bivalve fossils are arranged perpendicular to the bedding plane, with their umbos oriented upward, whereas the commissure planes of disarticulated shells are arranged parallel to the bedding plane with convex-down (8 in number) and convex-up (4 in number) in positions.

Lucinids are known to live in their umbos oriented upward to the sediment (Stanley, 1970 ; Kondo, 1990 and Kanno, 1993). So that, the many articulated lucinid fossils reported herein are interpreted to be preserved in their life positions.

Keywords: Nakatsu Group, fossil cold-seep assemblage, Pleistocene

## Cretaceous chemosynthetic communities in Japan

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The earliest occurrences of many molluscan genera, which are living in modern chemosynthetic ecosystem, were in the late Mesozoic. In addition, the oldest occurrences of chemosynthetic communities on decomposed vertebrate bones and sunken-drifted wood were in Cretaceous. Japanese Islands are located at junction of several continental and oceanic plates since hundreds of millions of years ago and provide many important material to establish evolutionary history of modern-type chemosynthetic ecosystems. Here I review Cretaceous chemosynthetic ecosystems with special focus on Japanese material.

Keywords: chemosynthetic community, whale bone, sunken wood, hydrocarbon seep, hydrothermal vent, cold seep

## Rapid change of atmosphere in the Hadean Earth: Beyond Habitable Trinity on a tightrope

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Surface environment of Hadean Earth is a key to bear life on the Earth or not. All of previous works assumed that high PCO<sub>2</sub> has been decreased to a few bars in the first a few hundreds millions of years (e.g., Zhanle et al., 2011). However, this process is not easy because of material and process barriers as shown below. Four barriers are present.

First, the ultra-acidic pH (<0.1) of 4.4Ga ocean prevented the precipitation of carbonates at mid-oceanic ridge or its pseudo-system through water-rock interaction after the birth of primordial ocean. To overcome this barrier, primordial (anorthosite + KREEP) continents must have been above sea-level to increase pH rapidly through hydrological process.

Second, major cap rocks on the Hadean oceanic crust must have been komatiite with minor basaltic rocks to precipitate carbonates through water-rock interaction and transport them into mantle through subduction at higher than the intermediate P/T geotherm on the Benioff plane. If not, carbonate minerals are all decarbonated at shallower depths than the Moho plane. Komatiite production depends on mantle potential temperature which must have been rapidly decreased to yield only Fe-enriched MORB by 3.8Ga.

Third, the primordial continents composed of anorthosite with subordinate amounts of KREEP basalts must have been annihilated until 4.0Ga to alter pH to be possible to precipitate carbonates by hydrothermal process. The value of PCO<sub>2</sub> must have been decreased down to a few bars from 35 bars at TSI (total surface irradiance) = 75% under the restricted time limit. If failed, the Earth must have been Venus state which is impossible to bear life on the planet.

Fourth is the role of tectonic erosion to destroy and transport the primordial continent of anorthosite into deep mantle by subduction. Anorthosite + KREEP was the mother's milk grow life on the Earth, but disappeared by 4.0Ga or even earlier, but alternatively granites were formed and accumulated on the Earth to supply nutrients for life. This is time-dependent process to increase new continents.

Fifth is the water content 3-5km thick, if the value was over, no way to bear life nor evolution afterwards.

After all, the Hadean Earth has passed the really naive tightrope processes to bear life. If any of above five conditions was lost, life has not been appeared.

## Global paleogeography and life evolution: 3. Paleozoic

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In modern oceans, there is no remaining information about past oceans older than 200Ma. For reconstructing paleo-plate motions with respect to collision-amalgamation of continents, on-land geology, in particular, orogenic belts that cemented older continents provide a sole source of information.

The onset of the Paleozoic is marked by the Gondwana semi-supercontinent formation at 540Ma around the South Pole. During the Paleozoic, Gondwana broken up, whereas Laurentia aggregated to form a real supercontinent by 430 Ma. Immediately after that, Gondwana began to be rifted, and its fragments and other blocks such as Baltica, Kazakhstan, Siberia, N China, South China, Indochina, and smaller pieces of Cimmeria, were dispersed; most of these were eventually amalgamated to form the northern half of Pangea, i.e., Laurasia.

The mode of mantle dynamics was represented by the high MORB production rate during 540-350Ma, almost the same as that in the Cretaceous, but it dropped after 350 Ma, probably by the activation of Pacific superplume. According to such continental assembly/ disassembly, sea-level changed remarkably as represented by the glaciation/deglaciation; the major Gondwana glaciations during the Carboniferous-Permian with 3 more minor episodes; the Paleozoic-Mesozoic transition interval might be close to the snowball Earth condition with extremely cold climate. The continent dispersion/amalgamation likely drove the development of remarkable floristic provincialism, e.g., Gondwana, North America, and Angara, that particularly reflected the formation of Laurentia. Not only the post-Ordovician land trees, this also controlled the diversification pattern of soil bacteria, moss, and land animals. Biodiversity changes including mass extinctions occurred in accordance with the secular change in seawater Sr isotope ratio; extremely high in the Cambrian with high bio-diversification, and the minimum at the G-L boundary (Permian) with onset of the greatest mass extinction.

Keywords: paleogeography, Paleozoic, supercontinent, Gondwana, Pangea, evolution

## Neodymium isotopic signature for deep/intermediate water formation in the late Cretaceous northwestern Pacific

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The Cretaceous is known to be one of the archetypal greenhouse periods, and intensively studied for evaluating the climate sensitively in the high pCO<sub>2</sub> region. The meridional sea surface temperature distribution, secular changes in sea surface and deep water temperatures have also been discussed globally. In addition to the thermal structure, analyses of ocean circulations on the basis of neodymium isotope signatures become more popular especially in the Atlantic Ocean. On the other hand, the ocean circulation in the Pacific Ocean is still uncertain, because of fundamental lack of deep sea sediments in the Pacific. In this study, instead of deep sea sediments, fore arc basin sediments have been utilized for discussing the ocean circulation in the late Cretaceous (late Turonian through early Campanian) northwestern Pacific.

Neodymium isotopic signatures in fish remains obtained from clayey sediments in the Yezo Group show highly radiogenic values of  $-1$  to  $-2$   $\epsilon$ -unit. These values are significantly higher than those in the Atlantic and the equatorial Pacific. This result indicates the presence of highly radiogenic intermediate/deep water formation in the northwestern Pacific, because it is expected that the radiogenic neodymium has been delivered from volcanic arcs in the northwestern Pacific. This results is also supported by climate models showing the potential deep water formation in the late Cretaceous northwestern Pacific.

Keywords: Cretaceous, Ocean circulation, Neodymium isotopes, North Pacific, Deep water, Intermediate Water

## Campanian-Maastrichtian clay-rich sequences along North Pacific Margin: Early Cooling History of Cretaceous Greenhouse

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Cretaceous shelf and fore-arc basin sandstone and mudstone are preserved in the coastal regions of Japan, Far East Russia, and the Pacific coast of Canada and USA. Several of these sequences have been variously assessed in terms of their biostratigraphy and chemostratigraphy, and correlated to the Aptian through Maastrichtian. In addition to macro- and microfossil biostratigraphy, carbon isotope ( $\delta^{13}\text{C}$ ) stratigraphy has also identified some important event horizons within these successions, such as OAE2. Owing to the clay-rich nature of the strata, parts of the sequences yield excellently preserved calcareous fossils available for oxygen isotope thermometry (Moriya et al., 2003).

This study examines the Campanian-Maastrichtian interval. Its chronostratigraphy, including detailed  $\delta^{13}\text{C}$  stratigraphy, has been summarized recently (Voigt et al., 2012) and it records the initial phase of global cooling of the Cretaceous greenhouse Earth (Moriya, 2011; Friedrich et al., 2012). As the northern paleo-Pacific Ocean had a large heat capacity, its paleoceanography should provide insights for understanding the subsequent environmental transition from greenhouse to ice house Earth.

The Yezo Group and its equivalent in Hokkaido (Japan) and Sakhalin (Russian Far East), as well as the Nanaimo Group of the Canadian Pacific coast (British Columbia), are examined in this study. From the Yezo Group, a clear negative  $\delta^{13}\text{C}$  excursion as large as 1.4‰ has been identified. On Sakhalin, its Campanian-Maastrichtian boundary age is constrained by local bio- and magnetostratigraphy, and the excursion is thus identified as the Campanian Maastrichtian Boundary Event (CMBE), associated with some subevents.

Carbon isotopic event, CMBE, suggested from magneto- and biostratigraphy (Haggart et al., 2011; Ward et al., 2012) of the Nanaimo Group near the top of the Northumberland Formation is well observed at the expected mudstone-dominated interval of the formation with negative 1.5‰ excursion. These progresses of stratigraphic correlational potential enable us to correlate CMBE interval between NW and NE Pacific with higher resolution.

Friedrich, et al., 2012, *Geology*, 40, 107-110; Haggart et al., 2011, *Can. Paleont. Conf., Field Trip Guidebook No. 16*, 31-62; Hasegawa et al., 2003, *Palaeo-3*, 189, 97-115; Moriya, 2011, *Paleont. Res*, 15, 77-88; Moriya et al., 2003, *Geology*, 31, 167-170; Voigt et al., 2012, *Newsl. Str.*, 45, 25-53; Ward et al., 2012, *GSA Bull.*, 124, 957-974.

Keywords: Cretaceous, Greenhouse, Cooling, Campanian, Maastrichtian

## Composite trace fossils: *Phymatoderma* reburrowed by *Chondrites*/*Phycosiphon* and its paleoecological implications

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Composite *Phymatoderma* specimens from the Pliocene deep-sea Shiramazu Formation in Japan, particularly those reburrowed by *Chondrites* and *Phycosiphon*, were analyzed to reveal the differences caused by the activities of these trace-makers. *Phymatoderma* reburrowed by *Phycosiphon* is significantly larger than non-reburrowed *Phymatoderma*, whereas *Phymatoderma* reburrowed by *Chondrites* shows no significant difference in burrow diameter compared with non-reburrowed *Phymatoderma*. The recognized size selectivity (i.e., preference for larger burrows) by the *Phycosiphon* trace-makers can be explained by considering the different feeding strategies of these two ichnogenera; namely deposit-feeding *Phycosiphon*-makers, which must have processed a significant mass of sediment to obtain sufficient organic matter, whereas chemosymbiotic *Chondrites*-producers, which did not require a lot of sediment to obtain nutrients. In order to test these interpretations, records of the Phanerozoic trace fossils reburrowed by *Chondrites*/*Phycosiphon* were compiled. Consequently, the *Phycosiphon* -preference toward relatively larger burrows was recognized, which supports the results of this study. The compilation also indicates that the burrow size has become a limiting factor for the *Phycosiphon*-producers that tried to rework the sediments within previous subsurface burrows, at least for 80 million years.

## The influences of durations of geologic time units on diversity assessments

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The study on global diversity change has been at the center of paleontological studies during the past quarter-century. It is well known that the diversity estimates are readily biased by unevenness of sampling density and there have been many debates on how to remove sampling overprints. In addition, taxonomic richness in a given chronological interval can be also biased by variation in time interval duration because the piled up diversity becomes much greater as the interval gets longer. However, there is no simple solution for this problem because the rate of taxonomic turnover is not uniform through time; that's why we can define discrete chronostratigraphic units with various durations. In addition, actual data registered in the Paleobiology Database indicate less correlation between sampled-in-bin taxonomic richness and time interval duration.

In the present study, the following simple computer simulations were performed to understand biases on diversity estimates derived from variation in time interval duration of chronologic units. A total of one million hypothetical taxa originated and went extinct at each time step (= 0.1 Ma) during the Phanerozoic at a given rate. In the present simulations, most (80%) of the turnovers were set to be concentrated at the boundary between intervals. The following different conditions were adopted for the turnover rates and sampling probability per time step within the interval; 1) fixed independent of the interval duration or 2) inversely proportional to the interval duration. The sampled-in-bin richness was counted for each age in each simulation.

As a result of the above simulation, a positive correlation between piled up diversity and time interval duration was generated when sampling probability was fixed through time. This result seems a natural consequence because the number of sampling for each bin depends on the duration of the time interval and the sample-size effect was not removed in the present analysis. The correlation was particularly remarkable when the mean turnover rate was high and/or probability of sampling was low. However, such a correlation was found also in some cases even when the sampling probability per time step was inversely proportional to the interval duration. In the latter case, the correlation was significant when the sampling probability was moderate.

Keywords: paleobiodiversity, time interval duration

## Upper Oligocene to Lower Miocene radiolarian biostratigraphy in the Northwest Pacific

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Ocean Drilling Program Leg 145 Hole 884B core provides the most continuous Neogene sequence of pelagic sediments in the northwest Pacific. We examined radiolarians from the Upper Miocene to Lower Miocene sediment of the core to establish subdivided radiolarian biozones.

The Upper Oligocene sequence can be divided into three zones, *Actinomma* sp. A, *Hexacantium* sp. B and *Cyrtolagena laguncula* Zones, in ascending order. The Lower Miocene sequence can be divided into four zones, *Botryopyle* sp. B, *Pentactinosphaera hokurikuensis*, *Stichocorys subligata* and *Dendrospyrus sakaii* Zones, in ascending order. Each of *Botryopyle* sp. B Zone and *P. hokurikuensis* Zone has been subdivided into subzones a, b and c.

Some episodes of significant faunal changes of radiolarians are identified within the studied interval. They seem not to reflect global cooling events but to reflect some regional events.

Keywords: Radiolaria, biozone, Site 884, North Pacific

## Available or unavailable? : nomenclatural examination of the Cretaceous ammonite genus *Polyptychoceras*

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It goes without saying that scientific names are useful for representing kinds of organisms. However, using names properly in accordance with the rules of nomenclature is not necessarily easy and a confusion of names could damage the objectivity of researches.

*Polyptychoceras* Yabe, 1927 from the Upper Cretaceous is a genus of heteromorph ammonites, which is characterized by paper clip-like shell morphology. It has been pointed out that this genus needs re-examination of species-level classification whereas occurrences of 12 species have been reported from Japan since *P. pseudogaultinum* (Yokoyama, 1890) was described. However, there are still many unclear points in the species names of this genus proposed until today. For example, *P. yubarensense* has been attributed to Yabe, 1927 in many literatures probably because Yabe (1927) first proposed this name. In fact, Yabe (1927) is not the original description of this species by reason that the literature only listed the name of this species and gave no biological description (the *Code's* Article 12.1).

In the present study, we examined the nomenclature of these 12 species on the basis of the currently used *International Code of Zoological Nomenclature Fourth Edition* (International Commission on Zoological Nomenclature, 1999). As a result, nomenclatural availability, authors, dates of publication, and original descriptions were revealed. These results will ensure the objectivity of relevant studies and will contribute to future taxonomic works.

For your information, this abstract is not issued for the purposes of zoological nomenclature (Disclaimer based on Art. 8.2).

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Keywords: *Polyptychoceras*, heteromorph ammonite, scientific names, International Code of Zoological Nomenclature, Cretaceous

## Assessment of local diversity in Cretaceous ammonoids from the Yezo Group using individual taxonomic abundance

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Exploring global diversity change across the Phanerozoic has been an important part of paleontology in the past quarter-century. It is widely known that the diversity estimates are seriously biased by variation in the volume of paleontological data and there have been many debates on how to remove the sampling intensity biases. The taxonomic richness has been standardized by sampling proxies such as collection-based occurrences and the amount of rock records. On the other hand, use of the number of individuals observed in each taxon is limited to the studies on sample level diversity at the outcrops because those data are not available at the global level. An intermediate approach between at the global and sample levels is commonly found in the tabulation of number of species for a particular taxonomic group through a restricted geologic time interval at the local level. However, such a local database compiled in a traditional manner does not record any information on abundance of each species in most cases.

Here, we studied chronological change in species diversity of Cretaceous ammonoids from the Yezo Group exposed in central Hokkaido, Japan, using the diversity indices that take into account the abundance of each species. This study was based on the fossil collections collected from Soya, Nakagawa, Haboro, Kotambetsu, Obira, Mikasa, Oyubari or Hobetsu areas and stored at Shizuoka University, National Museum of Nature and Science, Tokyo, Nakagawa Museum of Natural History, Mikasa City Museum and Hobetsu Museum. The number of individuals was counted for each species for each stratigraphic unit from the Cenomanian to Maastrichtian. A total of 9,834 individuals of 266 species was identified and counted.

The patterns of diversity change estimated in the present analysis were considerably different among collections even when the same diversity index was adopted. A plausible reason of this discrepancy is the difference in relative species abundance observed among collections. The only exception is the Shannon-Weiner function which exhibited a consistent pattern of diversity change independent of which collection was utilized. This result suggests that the Shannon-Weiner function is the most robust against variation in relative species abundance. The diversity estimates based on species richness tended to be correlated with the proportion of the rare species to the total number of species. This result suggests that these diversity estimates are readily distorted by the impact of rare species.

Keywords: paleobiodiversity, Cretaceous, ammonoids, Yezo Group, individual taxonomic abundance

## Estimation of the environmental temperatures at the early evolutionary periods by resurrection of ancient proteins

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To understand the origin and history of terrestrial life, it is important to clarify the environment where early life evolved. Geological records on the early evolution of terrestrial life are quite limited. Therefore, it is not easy to assume the ancient environment where our extinct ancestors had lived.

The 16S/18S rRNA based-tree of life by Woese et al. (1990, PNAS, 87: 4576-4579) has been treated as the "standard" tree of terrestrial life, although there are many objections. In this tree, all extant terrestrial organisms have common ancestor (the last common universal ancestor: LUCA or Commonote), and are classified into three domains, Bacteria, Archaea, and Eukarya. If all extant terrestrial life has the Commonote, its nature is the next question. In particular, the growing temperature of Commonote (or LUCA) has been interested and discussed. Pace (1991, Cell, 65: 531-533) proposed that the LUCA (or Commonote) was thermophilic. However, there are many objections. However, the discussion on this issue has been done mostly based on the predicted growth temperature estimated from the GC contents and amino acid frequencies of LUCA's genes and proteins inferred with molecular phylogenetic analyses, so that they are not proven by the experimental data (e.g. Galtier et al. (1999, Science, 283:220-221)). Recently, as one of powerful tools to evaluate the characteristics of extinct organisms, it has become to be used that experimental resurrection of ancient proteins based on the estimation of ancient amino acid sequences being possessed by ancient organisms estimated from the molecular phylogenetic analysis (e.g. Gaucher et al. (2003, Nature, 425: 285-288)).

To evaluate the growth temperature of ancient organisms, we resurrected amino acid sequences of nucleoside diphosphate kinases (NDKs) of the last archaeal common ancestor (LACA) and the last bacterial common ancestor (LBCA) with the maximum likelihood method for tree reconstruction by using NDK amino acid sequences of extant archaea and bacteria. The ancestor NDKs with resurrected amino acid sequences were expressed in *Escherichia coli* cells, purified, and then temperature-dependence of their denaturation was measured. The  $T_m$  of denaturation of resurrected NDKs of LACA and LBCA were higher than 100 °C. Since there is strong correlation between the  $T_m$  of NDKs and optimal growth temperature of their host organisms, both LACA and LBCA are suggested to be hyperthermophiles. Errors of estimation of ancestral sequences and different tree topologies used for resurrection of sequences did not affect seriously on the thermal stabilities of resurrected NDKs of LACA and LBCA. We also estimated the possible NDK sequences carried by the Commonote based on the sequences of resurrected NDKs of LACA and LBCA. The  $T_m$  of the most thermally unstable Commonote's NDK we resurrected was 90 °C (Akanuma et al. 2013, PNAS, 110: 11067-11072). This suggests that the Commonote was thermophilic organism.

Keywords: Commonote, resurrection of proteins, nucleotide diphosphate kinase, thermophiles

## Evolution of the Earth's environment: A view from sedimentary alkyl porphyrins

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Alkyl porphyrins are derivatives of chlorophylls that are formed in the surface of the Earth by photosynthesizers. Structural changes associated with the diagenetic processes have been intensively studied during the last half a century. Now we know that some alkyl porphyrins are derived only from specific chlorophylls that are originated from a specific type of photosynthesizers. Together with carbon and nitrogen isotopic compositions, such structural information provides a profound insight on the critical evaluation of the surface water environment in the geological past. In this presentation, I will review the diagenetic alteration of chlorophyll structures and review the current evidence.

Keywords: Porphyrins, Sediment, Earth's surface environment

## The close correlation between environmental change and evolution of metazoans: Genome duplication and rapid adaptation

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The Neoproterozoic to Cambrian is one of the most exciting periods when Metazoa first appeared and quickly evolved. The origin and early evolution of Metazoa are very attractive firstly because the events suddenly happened after very long calmness, over 2000 m.y. since the emergence of eukaryotes, and proceeded very quickly, and secondly because appearance of new phylum was limited to this period (Cambrian explosion). Recent paleontology, biomarker study and molecular biology suggested early origin, especially of sponges and cnidarians, and cryptic evolution of the metazoans (e.g. Maloof et al., 2010; Love et al., 2010; Peterson et al., 2008; Sperling et al., 2010, Erwin et al., 2011). On the other hand, recent comprehensive study of multi-elemental and multi-isotopic chemostratigraphies of drill core samples in Three Gorges, Tianping and Beidoushan areas revealed that redox condition and bioessential element contents of seawater such as P, Ca,  $\text{NO}_3^-$ , Fe, Mn, Mo, and Sr drastically changed from the Neoproterozoic to the Early Cambrian. Sr isotope values display positive excursions at ca. 580, 570-550 and 540 Ma, indicating repeated high continental influxes at those times. P contents of carbonate minerals were very high until ca. 550 Ma, and then decreased, suggesting the seawater was enriched in phosphorus before 550 Ma and then depleted due to oxidation of seawater and deposition of phosphorite. High nitrogen isotope values of organic matter and high Ca isotope values of carbonate rocks indicate that seawater was depleted in  $\text{NO}_3^-$  and Ca contents until ca. 550 Ma, and then increased. Mo isotopes of black shale, and Fe and Mn contents and REE patterns of carbonate rocks indicate that seawater became more oxic since ca. 550 Ma. In addition, the Mo contents of black shale increased in the Late Ediacaran and Early Cambrian, indicating Mo content of seawater increased due to the oxidation of seawater. On the other hand, iron and manganese contents of carbonate rocks decreased, suggesting that iron and manganese contents of seawater decreased because of the oxidation of seawater.

Comparison of the geochemical evidence with biostratigraphy suggests that the emergence of Metazoan in the Early Ediacaran was caused under the relatively less oxic and P-rich condition, whereas their diversification occurred under oxic,  $\text{NO}_3^-$  and Ca-rich condition. Especially, the transition from phosphorus-rich to  $\text{NO}_3^-$ -rich seawater possibly increased Redfield ratio, and contributed to diversification of more actively mobile multicellular animals. In addition, the comparison of geochemical and paleontological evidence indicates that the biological evolution occurred just after the environmental changes, especially the timing of increase in nutrients, allowing a new insight of biological evolution of multicellular animals. The quick response of biological evolution to the environments suggests that the fundamental innovation for biological functions was already established long before the environmental changes. The quick adaptation implies that early metazoans or a common ancestor have genomes for the functions before they acquired the functions, indicating genome duplication plays important role on the early evolution of metazoans.

Keywords: Biological evolution, paleoenvironmental change, Ediacaran, Nutrients of seawater, Evolution of Metazoa and Cambrian explosion, Genome duplication

## Reconstruction of the gene sets for the developmental signaling ligands in ancestral protostome animals

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Recently, a draft genome sequence of the pearl oyster *Pinctada fucata* was reported, enabling to infer a possible evolutionary scenario of the gene sets that are important for body plan formation in protostomes including both lophotrochozoans and ecdysozoans. We report the results of phylogenetic character mapping carried out for the gene families that encode developmental signaling ligands (Fgf, Hedgehog, PDGF/VEGF, TGF- $\beta$ , and Wnt families) to reconstruct possible copy numbers of signaling molecule-coding genes for hypothetical ancestral protostomes. Our reconstruction suggests that *P. fucata* retains the ancestral protostome gene complement, providing further justifications for the use of this taxon as a model organism for developmental genomics research.

Keywords: paleogenomics, metazoan evolution, evo-devo, signaling ligand genes, Cambrian explosion, lophotrochozoans

## Reconstruction of paleo genomic information of metazoan based on a microsynteny analysis

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Since a variety of metazoan genome decoding, the conservation of gene order on the DNA (synteny) is recognized as a common event in the metazoan. For example, Putnam reported the some amounts of signatures of macrosynteny between human and sea anemone (*Nematostella vectensis*) (Putnam et al 2007). Subsequently, Irimia reported their hypothesis that two adjacent genes that shared their 5' cis region (head to head) may restraint their translocation. Because of this situation, I'm trying to use these syntenic constraint for reconstructing the ancient genome. To the start of such reconstruction analyses, I'm compared among the genome of Hemichordate, Sea urchin and Amphioxus. These analyses revealed their possible common developmental mechanisms kept since their common ancestor.

Keywords: metazoan, genome, microsyntey, reconstruction

## A close relationship between global oceanic environmental changes and seafloor mineral deposition during the Phanerozoic

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Metal deposition on seafloor is strongly controlled by marine redox conditions. Fe-Mn and Mn oxide deposits are formed under oxygenated oceans. In striking contrast, Cu and Zn-bearing sulfide deposits are stable under anoxic oceans. Seafloor mineral deposits in turn are good indicators to redox conditions or redox changes of modern and ancient oceans.

There are numerous strata-bound ore deposits in the Japanese accretionary complexes. These deposits are mainly divided into three types; umber (Fe-Mn), Mn-rich, and volcanogenic massive sulfide (VMS; Besshi-type). The Mn-rich deposits are further divided into two subtypes that are associated with greenstone and NOT associated. Ages of these deposits provide us important constraints for a secular change of marine redox conditions over the past ~360 Myr. Depositional ages of umber and Mn deposits were previously determined by microfossils including radiolarians and conodonts. On the other hand, ages of the Besshi-type deposits are determined by Re-Os method (Nozaki et al., 2013). Oxide ore deposits such as umbers and Mn deposits were very likely precipitated in the modern-style oxygenated deep-sea. In contrast, Mn carbonate and VMS deposits were precipitated in the stagnant, O<sub>2</sub>-deficient deep-sea during the Triassic and Jurassic periods. Seafloor mineral deposition closely related to global oceanic environmental changes may give us a hint for exploring the causes of mass extinction, and further for elucidating the evolution of life.

Nozaki, T., Y. Kato, K. Suzuki (2013) Late Jurassic ocean anoxic event: evidence from voluminous sulphide deposition and preservation in the Panthalassa. *Scientific Reports*, 3: 1889; doi:10.1038/srep01889.

Keywords: oceanic environmental change, seafloor mineral deposit, Japanese accretionary complexes, marine redox condition, Phanerozoic

## Global paleogeography and life evolution: 2. Mesozoic

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The Mesozoic witnessed the Pangean breakup. Since the Triassic, the southern half of Gondwana successively rifted/separated, kicking out numbers of continents northward to form Laurasia, i.e., the northern half of Pangea, ca. 200 Ma. Multiple collisions among the Russian platform, Kazakhstan, Siberia, N. China, S. China, Indochina, Tarim, and other minor continental blocks were completed mostly in the Triassic or in the Early Jurassic at the latest. Gondwana has started to be fragmented immediately after its birth at 540Ma, except the collision of Laurentia at 430 Ma. The apparent supercontinent Pangea formed when Laurasia came in shape by 200 Ma. Its disassembly began first by the opening of the central Atlantic domain induced by the eastward moving of Africa for ca. a few thousands of km. The birth of South Atlantic Ocean was delayed until ca. 120Ma, whereas the opening of Northern Atlantic already started. The separation of S. America from Africa occurred ca. 120Ma. There was a pulse period of Pacific superplume ca. 120-85Ma when the production rate of MORB was 150-300 % higher than the rest of the Mesozoic. Numbers of huge oceanic plateaus were formed in the Pacific domain, including the Caribbean plateau. The birth of Indian Ocean occurred at ca. 100-120Ma by the separation of India from Gondwana. It is composed of 4 distinct oceanic lithospheres (separated by NS-trending major transform faults) behaved uniquely. The sea-level was kept relatively high according to such Mesozoic global tectonics; warm period without global glaciation but with oceanic anoxia and remarkable production of oil, gas, and coal. The climate was generally dryer than the Cenozoic, with higher production of evaporites. The mammalian diversification was triggered by the ca. 120Ma separation of the final bridge among Africa, S. America, and Laurasia. The appearance of the fox monkey in Madagascar, and of new-world monkeies in S. America, was likely connected to Indian migration and narrow arc bridge to S. America.

Keywords: paleogeography, Mesozoic, supercontinent, Pangea, Atlantic Ocean, evolution

## Recent results of foraminiferal calcification

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Foraminifera, marine unicellular organism, have been thought as one of the major carbonate producer in ocean. Their calcareous tests are commonly utilized as paleo-environmental indicators in various studies of earth science because their tests have been archived as numerous fossil in sediment for long time and various environmental information are brought by population, morphology and geochemical fingerprints. The calcareous test itself is interested by many foraminifer scientists. The knowledge about the cytological process on carbonate precipitation has been described for couples of decade using by many legacy technology. Cellular regulations of ions uptake into calcareous tests from seawater are of great interest for broad fields of earth science. Our recent studies showed the potential to understanding the biomineralization of foraminifera by the application of fluorescent indicators. Recently, we visualize the spatial distributions of cytological calcium and pH in living cell at same time under several pH conditions (7.5-8.1). Observed results show that foraminifera controls very detailed timing of pH variation and concentration of calcium at any stage of chamber formation dynamically even ambient pH are varied. These observations results will help to consider how the geochemical compositions arranging on the foraminiferal test, sensitivity of pH proxy of boron and others.

## Left-right reversal in unicellular eukaryotes, planktonic foraminifera

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Aquatic unicellular organisms are little motile and passively disperse in general. Holoplankton, which spend their entire life-cycle floating in the water column, are likely carried by water flow and exposed to diverse conditions of environment. Their morphology may vary over wide distribution ranges by phenotypic plasticity or allelic variation. Among these organisms, planktonic foraminifera are an excellent system to examine diversity and evolution in cellular responses to the environment because of two reasons: (1) occurrence in every ocean and (2) visible asymmetry in coiled shell. Both left- and right-coiled forms are often found within single morphospecies. Their coiling direction has traditionally been thought to change phenotypically depending on environmental factors, especially water temperature, based on coil-morph distributions but without statistical evidence. Molecular phylogenetic studies have revealed that morphospecies often contain multiple cryptic species. The arguments on the role of temperature for coil reversal most probably confused cryptic species into single taxa. In the present study, we examined the dependence of morph frequency on temperature by focusing on populations that are dimorphic for coiling direction and occur across wide ranges of temperature. *Globorotalia truncatulinoides* includes five genetically isolated species, and each of them is dimorphic for coiling direction. The statistically meaningful regression analysis was possible in three species that are distributed in global ranges. The results showed that morph frequency does not depend on water temperature in warm or cold seasons or on the annual mean temperature. Moreover, the geographic patterns of frequency variation among water masses in these species suggest that gene flow affects morph frequency. The majority exhibits the same coiling direction among populations that inhabit water masses connected by ocean circulation system. In contrast, morph frequency greatly varies between unconnected water masses regardless of climatic conditions. The present results, therefore, reject temperature-dependence of coiling direction and suggest the presence of genetic basis for coiling direction in planktonic foraminifera. Our study provides a base to explore the evolution on left-right asymmetry in unicellular eukaryotes.

Keywords: left-right asymmetry, coiling direction, cryptic species, unicellular eukaryote

## Were marine microplankton in the Japan Sea geographically isolated during the Last Glacial Maximum?

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The Japan Sea is connected by three straights (the Soya, Tsugaru, and Tsushima Straights) to the Sea of Okhotsk and Pacific Ocean with the shallow sill depth (140 m). During the last glacial maximum (LGM: 23-19 kilo years before present), the sea-level was decreased at least 120 m lower than today and the Japan Sea was almost isolated from surrounding seas. It is possible that such geographic isolation reduced and/or impeded gene flow of marine organisms between the Japan Sea and surrounding seas. Previous phylogeographic studies of coastal vertebrates (only whose larval stage is planktonic) have actually suggested that the Japan Sea was closed during the LGM. However, there is no phylogeographic study with marine microplankton, which inhabit the water column throughout their entire life cycle.

Radiolaria, the major marine planktonic protists, are passively transported in the pelagic ocean. Their geographic distribution would be easily affected by geographic changes through geological time. Moreover, their siliceous shells have been preserved in marine sediments and form a good fossil record. The sensitivity to geographic changes and well-preserved fossil record of Radiolaria could allow us to elucidate a past geographic isolation of marine microplankton. *Larcopyle buetschlii*, a morphospecies of radiolarians analyzed in the present study, is found in the surface waters in the Pacific Ocean, whereas it has a characteristic distribution vertically ranged from the surface to deep layers in the Japan Sea. In addition, its fossil specimens are continuously observed in the Japan Sea before the LGM. Therefore, *L. buetschlii* could be a good model to study a link between geographic isolation during the LGM and reproductive isolation of marine microplankton.

Heterogeneity of internal transcribed spacer regions of ribosomal DNA (ITS1 and ITS2) is observed in many eukaryotes (e.g., vertebrates, dinoflagellates, and diatoms). The ITS1 and ITS2 regions are spliced out during the maturing process of ribosome, causing a nucleotide substitution rate higher than ribosomal DNA coding regions. Nevertheless, the ITS1 and ITS2 sequences are functionally important for their splicing, because the premature transcript composed of 18S, 28S, 5.8S rRNA, ITS1, and ITS2 is folded into a secondary structure followed by the self-splicing of ITS1 and ITS2. Based on the secondary structures of ITS1 and ITS2 sequences, compensatory base changes (CBCs: base changes occurring on both sides of a double-stranded portion) and hemi-CBCs (HCBCs: base changes occurring on one side of a double-stranded portion) are often observed among closely related species. The correlation between CBCs and HCBCs in the ITS2 sequences likely reflects sexual compatibility among individuals of a closely related species. Thus, the CBCs/HCBCs correlation is a useful marker to infer whether geographically isolated populations are reproducible.

We demonstrated that there is heterogeneity of the ITS2 sequences within an individual of *L. buetschlii* and that all individuals of *L. buetschlii* collected from the surface to deep layers in the Japan Sea do not have a significant difference in the CBCs/HCBCs of the ITS-2 sequences. Furthermore, the CBCs/HCBCs of the ITS-2 sequences do not show a significant difference between individuals of the Japan Sea and Pacific Ocean. These findings suggest that *L. buetschlii* in the Japan Sea and Pacific Ocean likely forms a reproducible single population. Thus, the geological isolation during the LGM is unlikely effective for the reproductive isolation of this radiolarian species.

Keywords: Japan Sea, *Larcopyle buetschlii*, Radiolaria, secondary deep-sea plankton

## Non-coding sequences conserved independently in four different mammalian orders

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Conserved noncoding sequences (CNSs) of vertebrates are considered to be closely linked with protein-coding gene regulatory functions. We examined the abundance and genomic distribution of CNSs in four mammalian orders: primates, rodents, carnivores, and cetartiodactyls. We defined the two thresholds for CNS using conservation level of coding genes; using all the three coding positions and using only first and second codon positions. The abundance of CNSs varied among lineages, with primates and rodents having highest and lowest number of CNSs, respectively, whereas carnivores and cetartiodactyls had intermediate values. These CNSs cover 1.3-5.5% of the mammalian genomes and have signatures of selective constraints that are stronger in more ancestral than the recent ones. Evolution of new CNSs as well as retention of ancestral CNSs contribute to the differences in abundance. The genomic distribution of CNSs is dynamic with higher proportions of rodent and primate CNSs located in the introns compared with carnivores and cetartiodactyls. In fact, 19% of orthologous single-copy CNSs between human and dog are located in different genomic regions.

If CNSs can be considered as candidates of gene expression regulatory sequences, heterogeneity of CNSs among the four mammalian orders may have played an important role in creating the order-specific phenotypes. Fewer CNSs in rodents suggest that rodent diversity is related to lower regulatory conservation. With CNSs shown to cluster around genes involved in nervous systems and the higher number of primate CNSs, our result suggests that CNSs may be involved in the higher complexity of the primate nervous system. This study was published in *Genome Biology and Evolution* (Babarinde and Saitou, 2013; vol. 5:2330-2343).

Keywords: genome, mammals, Primates, Rodents, Artiodactyla, Carnivores

## Development for new hyphenated analytical technologies for paleogenomics research

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Cytometry is the analytical technique, basically applied for quantitative analysis of cells and cell systems. In general, cytometry measures optical properties of cells, and most often uses fluorescence to measure specific antigen molecules, intracellular ions and DNA/RNA. Cells may be live or fixed, depending on the application, and individual cells can often be physically sorted. ? Other optical signals can be measured, including light scatter. The cytometry has blossomed to become the key technique to evaluate the nutritional status or to understand the elemental metabolism for animals. Several advantages can be derived by the cytometry, such as analysis speed, detection sensitivity, the ability to measure many parameters simultaneously, and the ability to sort individual cells (i.e., single cell spectroscopy). Recently, new generation cytometry utilizing the sensitive mass spectrometers (i.e., mass cytometry) was described. With the mass cytometry, further sensitive detection of ions or proteins and higher capability for the multiparameter analysis of individual adherent cells (e.g.,; Benfall et al., *Science*, 2011; Bodenmiller et al., *Nature Biotechnology*, 2012). With the extensive number of information collected from cells or samples through the cytometry, reliable and objective evaluation for the changes in biochemical functions could be achieved. This approach can also be applied to understand the solar system evolution based on the numerous number of age data. In recent ten years, we have demonstrated the unique study approach using the distribution pattern of sample ages based on the series of precise age data collected from large number of samples (i.e., age-cytometry) (e.g., Rino et al., *PEPI*, 2008; Iizuka et al., *Geology*, 2008; Iizuka et al., Iizuka et al., *Chem. Geol.*, 2009; Iizuka et al., *GCA*, 2010). The mass cytometry will become a powerful tool to promote the big-data science for various research fields such as metallomics, medical sciences or the geochemistry. For elemental or isotopic analysis of trace- or ultratrace-elements, plasma ion source mass spectrometry (ICP-MS) has been widely employed because of its high analytical capabilities such as high-elemental sensitivities, minimal sample preparation procedures, high-analysis throughput or user-friendly operations (Bandura et al., *Anal. Chem.*, 2009). With the laser ablation sample introduction technique, distribution of both the elemental and isotopic data for trace- or ultratrace-elements can be successfully derived directly from large-sized solid samples (>10cm). Despite the obvious success in obtaining elemental and isotopic data (age data), it should be noted that stable isotope ratio data for light elements (e.g., C and O) could not be derived by the present LA-ICPMS technique because of serious contribution mass spectrometric interferences on C and O isotopes, which provides key information concerning the physico-chemical conditions for the sample formation. To overcome this, we would like to develop a new analytical technique to measured the C isotopes, at a same time with elemental analysis using the LA-ICPMS technique. Newly developed spectroscopy technique combined to the LA-ICPMS technique can become a major analytical tool to expand the analytical capability for mass cytometry for biochemical samples and geochemical samples through precise, reliable and uniform quality data. The analytical technique develop here will promote the big-data science for various research fields including geochemistry and biochemistry.

Keywords: mass spectrometry, laser ablation, paleogenomics, hyphenated technology, analytical chemistry, geochemistry

## Conditions for photic zone euxinia deduced from ocean biogeochemical cycle model

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It is widely thought that atmospheric oxygen concentration has been kept in a level of the same order of magnitude as that of today over the Phanerozoic, based on both charcoal records and geochemical cycle modeling.

On the other hand, several lines of geological/geochemical evidence indicate that the oceans below photic zone were strongly de-oxygenated on a global scale at some geological intervals. Such oxygen deficient events are known as "Oceanic Anoxic Events (OAEs)."

In the anoxic water column, hydrogen sulfide is produced via bacterial sulfate reduction. Therefore, if sulfate and metabolizable organic matter are sufficient, hydrogen sulfide builds up in some cases, which is called "ocean euxinia."

Biomarkers derived from photosynthetic green sulfur bacteria have been discovered in the sedimentary rocks deposited during the Mesozoic OAEs(e.g., early-Triassic superanoxia and Cretaceous OAE2) indicating that hydrogen sulfide existed in the photic zone (~100m) at those intervals. However, the conditions required to generate the photic zone euxinia remains unrevealed.

Here we investigate the conditions required for occurrence of photic zone euxinia, using an ocean biogeochemical cycle model developed by Ozaki and Tajika (2013). We further improve the model to have the surface ocean with higher resolution to evaluate the vertical profiles of H<sub>2</sub>S, NO<sub>3</sub>, HPO<sub>4</sub>, and O<sub>2</sub>. We try to understand the changes of marine primary producer during photic zone euxinia quantitatively.

Keywords: oceanic anoxic events, biogeochemical cycles, phosphorus cycle, anoxia/euxinia, photic zone euxinia

## Partial pressure of atmospheric CO<sub>2</sub> during the Paleoproterozoic global glaciation

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The Paleoproterozoic Makganyene Glaciation is a particular enigmatic geologic event in that ice covered the oceans even at low latitude (Snowball Earth). This event might have drastically curtailed biological productivity but melting of the oceanic ice presumably induced a cyanobacterial bloom, leading to an acceleration of global oxygenation. It has been predicted that this event occurred as a result of the drawdown of greenhouse gases in the atmosphere. However, atmospheric CO<sub>2</sub> levels at that time are still under debate. Here, we constrained the CO<sub>2</sub> concentration in seawater based on fluid inclusions in seafloor hydrothermal quartz deposits from the 2.2 billion years (Gyr) old Ongeluk volcanics, South Africa, in which the ancient water and carbon dioxide are preserved. The quantitative analysis of the concentration and stable carbon isotopes of CO<sub>2</sub> in the fluid inclusions revealed that the CO<sub>2</sub> concentration in the seawater was limited to be less than 7 mmol/kg. Because the Ongeluk seawater was locally open to the atmosphere, atmospheric CO<sub>2</sub> level was also estimated to be lower than 33 times the present atmospheric level (PAL) ( $<1.3 \times 10^2$  bar) assuming equilibrium between the Ongeluk seawater and atmosphere. This CO<sub>2</sub> level was not enough to compensate the faint young sun and keep the ocean temperature sufficiently above freezing point by itself. Although the behavior of other greenhouse gases is still unknown, our results demonstrate that the deficient atmospheric CO<sub>2</sub> level was a significant contributing factor to the 2.2 Gyr global glaciation.

## Impact-driven ocean acidification as a mechanism of Cretaceous?Palaeogene mass extinctions

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The Cretaceous?Paleogene (K?Pg) mass extinction event at 65.5 Ma triggered by a meteorite impact is one of the most drastic events in the history of life on the Earth. Many hypotheses have been proposed as killing mechanisms induced by the impact, including global darkness due to high concentrations of atmospheric silicate dust particles, global wildfires, greenhouse warming due to CO<sub>2</sub> release, and global acid rain. However, the actual mechanism of extinction remains highly controversial. One of the most important clues for understanding the extinction mechanism is the marine plankton record, which indicates that plankton foraminifera, living in the near-surface ocean, suffered very severe extinction in contrast to the high survival ratio of benthic foraminifera. No proposed extinction mechanism can account for this globally observed marine extinction pattern. Here, we show that SO<sub>3</sub>-rich impact vapor was released in the K-Pg impact and resulted in the occurrence of global acid rain and sudden severe ocean acidification at the end of the Cretaceous, based on the new results of impact experiments at velocities much higher than previous works (>10 km/s) and theoretical calculations on aerosol coagulation processes. Sudden severe ocean acidification can account for many of the features of various geologic records at the K?Pg boundary, including severe extinction of plankton foraminifera. This extinction mechanism requires impact degassing of SO<sub>3</sub>-rich vapor, which is not necessarily found at impact sites other than Chicxulub, suggesting that the degree of mass extinction was controlled greatly by target lithology.

Keywords: K/Pg mass extinction, impact, laboratory experiment, acid rain, ocean acidification, mass spectroscopy

## Platinum group element anomalies in the Triassic-Jurassic deep-sea sediments

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One of the biggest mass extinctions in the Phanerozoic occurred at the Triassic-Jurassic (T-J) boundary. The large magmatic activity associated with the breakup of Pangaea (CAMP event) or a bolide impact attract interests as causes of the mass extinction at the T-J boundary. However, the cause of the mass extinction is still controversial because of insufficient geological evidences. PGE abundances and radiogenic Os isotope ratios are powerful tracers that potentially distinguish ancient basaltic magmatism from the effect from extraterrestrial.

We conducted detailed geological survey at the Inuyama area, where Triassic to Jurassic deep-sea sediments well crop out. We developed detailed a geological map of the study area and reconstructed ocean plate stratigraphy. We collected ca. 70 siliceous shale samples bed-by-bed were also collected to measure PGEs concentration and Os isotopes with a high spatial resolution. The rock powder was spiked with <sup>190</sup>Os, <sup>185</sup>Re, <sup>191</sup>Ir, <sup>99</sup>Ru, <sup>194</sup>Rt, and <sup>105</sup>Pd and digested by 2:1 mixture of HNO<sub>3</sub> and HCl in a sealed Carious tube at 240oC for 48 hours. After chemical separation using an anion exchange resin, the isotope ratios of PGE were measured by a quadrupole type ICP-MS at Tokyo Tech. The Os isotope ratios were determined by N-TIMS (Triton plus) at Tokyo Tech.

PGEs concentrations and Os isotope composition are determined from 28 siliceous shale samples across the T-J boundary. Re and Os contents varies from 14.7 to 128.6 pg/g and from 4.9 to 99.2 pg/g, respectively. <sup>187</sup>Os/<sup>188</sup>Os decreases from 0.77 to 0.34 before the T-J boundary. The <sup>187</sup>Os/<sup>188</sup>Os values in the Jurassic siliceous shales fluctuated around ca. 0.5. The highest Os concentration and negative Os isotope anomaly corresponds to the first occurrence of Jurassic type radiolarian. Also, Ir/Pt vs Pd/Pt cross plot and C1 chondrite-normalized PGE patterns of siliceous shales across the T-J boundary show similar trend to CAMP and upper continental crust (UCC). This indicates that the origin of PGEs detected from siliceous shales are the mixture of CAMP and UCC, and that extraterrestrial influence at the T-J boundary was minor.

Keywords: T-J boundary mass extinction, deep-sea sediments, platinum group element

## Impact event and radiolarian faunal turnover across the middle-upper Norian transition at Sakahogi section in Japan

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Anomalously high platinum group element (PGE) concentrations have been reported for Upper Triassic (middle Norian) deep-sea claystone layer in the Sakahogi section, central Japan, which have been interpreted to be derived from an extraterrestrial impact event that formed the 90 km Manicouagan crater in Canada. Here we report middle to upper Norian radiolarian biostratigraphy from the Sakahogi section across the impact ejecta layer. Based on the radiolarian biostratigraphy from the Sakahogi section, three radiolarian zones are recognized in ascending order as follows: Capnodocoe?Trialatus zone, Trialatus robustus?Lysemelas olbia zone, and Lysemelas olbia zone. Detailed high-resolution sampling and biostratigraphical data allowed us to date precisely the ejecta layer, which occur in the base of the radiolarian Trialatus robustus?Lysemelas olbia zone. Our biostratigraphic analysis suggests that there was no mass extinction of radiolarians across the impact event horizon. Only one species became extinct at the ejecta horizon and the extinction rate of radiolarians (extinct species divided by total species at the same level) is estimated to be about 5% at the horizon. Major turnovers of radiolarians occur above the ejecta horizon within the Trialatus robustus?Lysemelas olbia zone. Biostratigraphic analysis shows that 20 radiolarian species became extinct in this zone and the extinction rate is estimated to be 83%. This turnover is associated with a deposition of spicular chert, suggesting temporal changes in marine ecosystems after the impact event. Given that the average sedimentation rate of the middle to upper Norian chert succession is 2.7 mm per thousand years, this turnover occurred 400 kyr after the impact event. Thus the meteorite impact did not directly cause of radiolarian extinction event.

Keywords: Triassic, Meteorite Impact, Radiolaria

## A global ocean oxidation event immediately after the Early Triassic thermal maximum

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Biotic recovery after the largest mass extinction at the end of the Permian (252.3 million years ago, Ma) became evident in early Spathian (250.1 Ma), Early Triassic, and was eventually completed in middle-late Anisian (ca. 244 Ma), early Middle Triassic. Recent studies showed that this much delayed recovery was impacted by several biocrises and associated environmental and climatic stresses during the Early Triassic. For instance, the end-Smithian extinction and associated thermal maximum and Smithian oceanic anoxia may have prevented biotic recovery initiated in early Smithian (251 Ma). Our new study not only confirmed the oceanic anoxia in late Smithian but also found an oxygenation event just after the Smithian thermal maxima (STM) using sulfur isotope fractionation between sulfate and sulfide. Newly obtained sulfur isotope ratios of carbonate-associated sulfate ( $d_{34}SCAS$ ) in the surface water and sulfide ( $d_{34}S_{sulfide}$ ) in the Panthalassic deep water during the late Permian to the Early Triassic compiled with published data show a significant increase in fractionation between the  $d_{34}SCAS$  and  $d_{34}S_{sulfide}$  during the early Spathian (41-51 permil to 62 permil). The latter indicates an increase in global oceanic dissolved oxygen levels, which also coincided with a climatic cooling and may have facilitated biotic recovery in late Early Triassic.

Keywords: Early Triassic, ocean dissolved oxygen, sulfur isotope

## Cyanobacterial proliferation during the Early Triassic

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Recent studies have shown that microbes bloomed in the aftermath of several major Phanerozoic biocrises. Microbial proliferation, as indicated by widespread microbialites, characterized marine ecosystems after the end-Permian mass extinction, which constituted the most severe biocrisis for life on Earth. The microbialite builders, including cyanobacteria and other unknown microalgae or bacteria, acted as primary producers in the trophic structure of the earliest Triassic marine ecosystem. However, the stratigraphic distributions of cyanobacteria and eukaryotic algae during the Permian-Triassic transition remain unknown. Thus, we conducted studies for the interval from the latest Permian to the Middle Triassic using the monomethyl heptadecane ratio (MHR) and 2-methyl hopane index (2-MHI) as cyanobacterial proxies, and the n-alkyl-cyclobenzene ratio (ACBR) as a biomarker for eukaryotic algae. We detected a proliferation of eukaryotic algae during the latest Permian and early Middle Triassic, whereas cyanobacteria flourished during most of the Early Triassic. The new findings are consistent with previously determined stratigraphic distributions of microbialites and the species richness of eukaryotic algae. The erosion intensity and temperature fluctuated in conjunction with changes in the populations of cyanobacteria and eukaryotic algae. Therefore, we postulate that these population changes were primarily the result of enhanced water turbidity from elevated bedrock erosion and lethally hot temperatures.

Keywords: biomarker, Early Triassic, extinction, cyanobacteria

## Mo depleted ocean after the end Permian mass extinction referred from Mo and U behaviors in pelagic deep-sea sedimentary

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The end-Permian mass extinction was the largest biotic catastrophe of the Phanerozoic, and evidence of global oceanic anoxia during this event has been reported (e.g. Wignall and Twitchett, 1996). Such anoxic/euxinic conditions have also been revealed by enrichments of redox-sensitive elements (Fio et al., 2010; Grasby et al., 2009, 2011; Algeo et al., 2012). Among redox-sensitive elements, uranium increased in sediments and finally result uranium drawdown, suggested by a decrease in sedimentary uranium isotope ratio ( $^{238}/^{235}\text{U}$ ) and a increase in Th/U ratio from the shallow marine carbonates (Brennecke et al., 2011). In this presentation, we will show the possible evidence of Mo drawdown after the mass extinction event from the continuous deep-sea Permian-Triassic boundary section which located in the low latitude pelagic Panthalassa (Akkamori section-2; Takahashi et al., 2009).

High resolution ICP-MS analysis using sedimentary rock samples from the study section (Takahashi et al., in review) indicates vertical distribution of UEF and MoEF (Enrichment factor of U and Mo), the Mo/U ratio. MoEF and UEF show a synchronous increase from the Upper Permian bedded chert to the overlying siliceous claystone, while the Mo/U ratio increases from 3.9 to 47.3 showing continuous elevation from the  $1.0 \times$  modern seawater Mo/U ratio to  $9.0 \times$  the modern ratio. Accepting the previous study's criteria (Algeo and Tribouillard, 2009), increased Mo/U ratios that clearly exceed 9 (3 times the value of modern seawater) suggest the presence sulphidic bottom water at that time. Considering possibility of U drawdown suggested by Brennecke et al. (2011), decrease in seawater U concentration (possibly up to 1/7) would also help the rise of Mo/U ratio. Further elevations of MoEF and the Mo/U ratio reach values of more than 1000, and MoEF reaches values of several thousands from Upper Permian siliceous claystone to the basal 20cm end-Permian black claystone, indicating that sulphidic bottom water was increasingly developed and that Mo transportation by the particulate shuttle was activated. The particulate shuttle, proposed by Algeo and Tribouillard (2009), is a process by which Mn oxyhydroxides absorb molybdate oxyanions above the oxic/euxinic chemocline in the water column and then sink and finally dissolve on or just below the sediment-water interface, releasing Mo to the sediments. Additionally, in such a developed sulphidic water column, syngenetic pyrite formation in the euxinic water column could possibly have contributed to Mo transportation to the sediment (Algeo and Maynard, 2004). Above the 20 cm horizon of the black claystone, MoEF decreases to values lower than 100 and the Mo/U ratio takes values of more than 3 but less than 20. These values could be interpreted to indicate that sulphidic bottom water was still present but that the particle shuttle had subsided to some extent after the time of the mass extinction. Low Mo/U values occur in earliest Triassic siliceous claystone bed, despite high MoEF and UEF values. Because MoEF and UEF are high, reducing bottom water conditions still existed. Thus, the decrease in Mo/U does not indicate a return to oxic conditions, but rather a Mo drawdown in the earliest Triassic seawater. The study examples of such trace-metal drawdown in geologic past have been reported by Algeo (2004) and Hetzel et al. (2009). In fact, the trend of low Mo/U values with high MoEF and UEF is consistent with that of the Mo-depleted seawater condition identified in the modern Black Sea (Algeo and Tribouillard, 2009), suggesting a drawdown of seawater Mo in the pelagic ocean.

Keywords: molybdenum, mass extinction, Permian, Triassic, deep-sea, Panthalassa

## Nitrogen isotope chemostratigraphy across the Permian-Triassic boundary at Chaotian, Sichuan, South China.

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Nitrogen isotopic compositions of upper Permian to lowermost Triassic rocks were analyzed at Chaotian in northern Sichuan, South China, in order to clarify changes in the oceanic nitrogen cycle during the Changhsingian (Late Late Permian) prior to the end-Permian extinction. The analyzed interval across the Permian-Triassic boundary (P-TB) at Chaotian consists of three stratigraphic units: the upper Wujiaping Formation, the Dalong Formation, and the lowermost Feixianguan Formation, in ascending order. The upper Wujiaping Formation is mainly composed of dark gray limestone with diverse shallow-marine fossils deposited on the shallow shelf. In contrast, the overlying Dalong Formation is mainly composed of thinly bedded laminated black mudstone and black siliceous mudstone containing abundant radiolarians, deposited on the relatively deep slope/basin under anoxic condition. The lowermost Feixianguan Formation is composed of thinly bedded gray marl and micritic limestone with minor fossils deposited on the shallow shelf.  $\delta^{15}\text{N}$  values are in positive values in the upper Wujiaping Formation implying denitrification and/or anammox in the ocean.  $\delta^{15}\text{N}$  values gradually decrease in the lower Dalong Formation and are consistently low in the middle Dalong to lowermost Feixianguan Formation. In particular, no clear  $\delta^{15}\text{N}$  shift is recognized across the extinction horizon. The consistently low  $\delta^{15}\text{N}$  values at Chaotian suggest the enhanced nitrogen fixation in the ocean during the entire Changhsingian to early Induan (Early Early Triassic), accompanied with the emergence of anoxic condition. The  $\delta^{15}\text{N}$  trend at Chaotian was possibly a regional isotopic signature in northwestern South China and not a global one, because the composite  $\delta^{15}\text{N}$  profiles document that no  $\delta^{15}\text{N}$  trend similar to that at Chaotian is observed in other P-TB sections around the world. Nonetheless, the protracted oceanic nitrogen depletion during the Changhsingian suggested by the present results at Chaotian may have acted as a stress to shallow-marine biota.

## A remarkable sea-level drop and global cooling in the late Middle Permian: record from the mid-superoceanic limestone

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For clarifying the global environmental changes relevant to the Guadalupian-Lopingian boundary (G-LB) extinction, i.e. the first major biodiversity drop during the Permian, litho-, bio-, and chemo- stratigraphy of  $\delta^{13}C_{carb}$  and  $^{87}Sr/^{86}Sr$  were analyzed in the Middle-Upper Permian paleo-atoll limestone at Akasaka in central Japan, which was derived from a paleo-atoll complex deposited primarily in the low latitude in the mid-Panthalassa. Between the Capitanian (upper Middle Permian) black limestone (the *Yabeina* fusuline Zone) and the Wuchiapingian (lower Upper Permian) light gray limestone (the *Codonofusiella-Reichelina* Zone), a unique black-white striped limestone is intercalated, of which top marks the G-LB horizon.

The major extinction occurred in the uppermost black limestone, large-tested fusuline and large bivalve that were adapted to low-latitude extremely warm conditions sharply became extinct. Most parts of the Akasaka Limestone consist of shallow marine wackestone/packstone deposited in low-energy settings of the subtidal zone likely within a lagoon on the top of a seamount.

We newly identified 1) a remarkable hiatus with erosional features at the top of the striped limestone, 2) large-scale cross-beddings in the striped limestone immediately below the hiatus, and 3) the dominance of grainstone in the basal light gray limestone immediately above the hiatus. These lines of evidence altogether suggest that a remarkable sea-level drop has occurred around the G-LB in the mid-oceanic paleo-atoll complex, and that a cool climate has appeared in the Capitanian. The isotope stratigraphy for the Capitanian interval with extremely high  $\delta^{13}C_{carb}$  values over +5 ‰ and the extremely low  $^{87}Sr/^{86}Sr$  ratios below 0.7070 indicate the high productivity in the superocean and the suppressed continental weathering on Pangea, respectively. Both isotope signatures can be concordantly explained by the appearance of a putative global cooling in the Capitanian. After all, the litho-, bio-, and chemostratigraphical records from the Permian mid-superocean positively suggest a possible link between the Capitanian global cooling and the end-Capitanian extinction.

Keywords: G-L boundary, mid-superoceanic limestone, sea-level drop, cooling, carbon isotope, strontium isotope

## Middle to Late Permian seawater Sr isotope variation linked to the glaciation/deglaciation

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We report the detailed secular change of the Middle to Late Permian seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the Akasaka and Iwato limestone in SW Japan. The studied two sections were originally deposited as paleo-atoll complexes on the low-latitude, mid-Panthalassa seamounts. We also analyzed coeval sections at Sizipo and Liangshan deposited on the shallow marine shelf of South China. Commonly in the four studied sections, extremely low values ( $<0.7069$ ; the lowest values of the Phanerozoic) continued from upper Wordian (middle Middle Permian) to the topmost Capitanian (upper Middle Permian) immediately below the Middle-Late Permian boundary. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increased to 0.7072 in the early Late Permian. This increase recorded the most rapid in the entire Phanerozoic. The ca. 5 m.y.-long minimum interval and the following rapid increase in Sr isotope ratio can be explained by the remarkable changes in continental erosion/weathering rate; in particular, by the onset of glaciation and the following deglaciation, that is supported by global sea level change, in addition to the initial doming/rifting of Pangea. After the Capitanian cooling, the long-term climatic regime shifted to a warmer one during which covering ice was removed from continents to expose crustal silicates for to erosion/weathering. The continental rifting with new drainage systems likely increased decisively the highly radiogenic continental flux to the superocean.

Keywords: Permian, Sr isotope, seawater, limestone

## A unique low-latitude-type molluskan assemblage from the Permian Iwaizaki limestone in the S. Kitakami belt, NE Japan

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Permian large gastropod "*Pleurotomaria*" *yokoyamai* was found for the first time from the Capitanian (Upper Guadalupian) Iwaizaki limestone in the South Kitakami belt, NE Japan. A smaller planispiral gastropod *Porcellia* sp. was also associated. These taxa have been scarcely reported, except from the coeval Akasaka limestone in SW Japan. The Akasaka Limestone was deposited as a low-latitude atoll on a mid-Panthalassan seamount, whereas the Iwaizaki limestone as a patch reef within terrigenous clastics-dominant facies on a shallow marine continental shelf. The occurrence of this unique gastropod assemblage, together with large bivalves and large-tested fusulines, suggests that the Iwaizaki Limestone was originated also in a Permian low-latitude domain, and that the South Kitakami belt likely formed a part of the continental margin of South China representing its eastern extension to NE Japan.

Keywords: Permian, bivalve, gastropod, South Kitakami belt, South China

## Mechanisms regulating the redox state of an atmosphere-ocean system during the Paleozoic

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There is now a great interest in understanding paleoredox conditions of an atmosphere-ocean system because it is essential for investigating links between oxygenation of biosphere and major biological innovation/extinction. Therefore, understanding the regulating mechanism(s) of secular (over millions of years) changes of redox state of Earth's surface environments is one of the fundamental topics. Early Paleozoic is marked by the prominent biological evolution/diversification events (i.e., Cambrian explosion, Great Ordovician Biodiversification Event, and advent of land plants). On the other hand, multiple lines of geological and geochemical evidence (such as black shale deposition, low C/S ratio of buried sediments, low molybdenum isotopic value, and iron speciation data) suggest that oxygen-depleted waters were generally more common and widespread in the ocean interior than they are today until the Devonian. Among these, recent finding of an increase in molybdenum isotopic value from ~1.4 ‰ to ~2.0 ‰ between ~440 Ma and ~390 Ma (Dahl et al., 2010 PNAS) attracts the attention because it implies the oceanic redox transition to a well-oxygenated condition. However, the ultimate cause of this transition remains uncertain.

Considering the fact that the ocean oxygenation event correlates with the diversification of land plants since the Late Ordovician, causal linkage between them are intriguing; an enhanced chemical weathering on the continent by land plants could lead to an increase in the burial rate of terrigenous organic matter, giving rise to an oxygenation of an ocean-atmosphere system. However, it remains unclear whether the radiation of land plants is necessary to cause such redox transition.

The evolution of atmospheric oxygen concentration has been studied intensively, but reconstructed atmospheric oxygen evolution varies widely between models, demonstrating that further understanding on the mechanisms controlling atmospheric oxygen level is still required. Because oxygen is most likely regulated by a combination of several feedbacks in the Earth system, it is essential to evaluate the impact of plant diversification on the oxygenation state of an ocean-atmosphere system with the aid of a biogeochemical cycle model. In this study, a model is designed to explore the roles of several feedback mechanisms regulating the redox state of the atmosphere and oceans during the early Paleozoic, and to reconstruct the paleoredox history of an ocean-atmosphere system during the early Paleozoic. The results of systematic sensitivity experiment demonstrate that (1) oceans before the advent of land plant had been kept in suboxic-anoxic condition, that (2) the diversification of land plant since Late Ordovician could cause an increase in atmospheric oxygen level to >16% by the Devonian and ocean could be oxygenated by the Middle Devonian, and that (3) a redox dependent burial efficiency of phosphorus at sediment-water interface and degradability of particulate organic matter (POM) play substantial roles in atmospheric oxygen level before the advent of land plant. The modeling results confirm the causal linkage between plant diversification and the oxidation of Earth's surface environments. Our result also highlights the need for more quantitative and process-based knowledge of the decomposition process of POM in order to reveal the redox evolution of atmosphere-ocean system during the Paleozoic.

Keywords: Paleozoic, atmospheric oxygen level, biogeochemistry, land plant evolution, biogeochemical cycle model

## Compound-specific carbon isotope ratios from the Ediacaran-lower Cambrian in the Three Gorges area, South China

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In order to reveal the organic carbon cycle in the early Cambrian ocean, compound-specific carbon isotope ratios of aliphatic hydrocarbons which records the change of the composition of organic matters derived from phototrophs were first measured for the drill cores from the Three Gorges area. The differences between the carbon isotope ratios of short chain n-alkanes and pristane ( $\Delta_{ap}$ ) show relatively high ( $\sim$ -3-4 ‰) in the Ediacaran, decreased down to  $\sim$ -6 ‰, and subsequently increased up to  $\sim$ 6 ‰ in the early Terreneuvian (the earliest Cambrian; 541-521 Ma), and again decreased down to  $\sim$ -4 ‰ in the Epoch 2 (the early Cambrian; 521-509 Ma). The differences between the carbon isotope ratios of pristane and phytane ( $\Delta_{pp}$ ) were  $\sim$ 0 ‰, decreased down to  $\sim$ -5 ‰ in the Terreneuvian, and increased up to  $\sim$ 6 ‰ in the Epoch 2. <sup>13</sup>C-depleted  $\beta$ -carotane was found only from the black shale at the Series 2.

$\Delta_{pp}$  indicate that a single phototroph community has existed in the Ediacran, whereas multiple phototroph communities existed in the early Cambrian. The decrease in  $\Delta_{ap}$  indicates enhanced burial of lipids derived from eukaryotic phototrophs, probably in response to the emergence of faecal pellets, which has consumed the large dissolved organic carbon reservoir. <sup>13</sup>C-depleted  $\beta$ -carotane and negative  $\Delta_{pp}$  values indicate that the anaerobic phototrophs utilized CO<sub>2</sub> derived from degraded organic matters.

Thus, the aerobic phototrophs and the anaerobic phototrophs coexisted on the continental shelf in the early Cambrian. An anoxic water reached on to the photic zone on the continental shelf, and that lasted until Epoch 2. The increase of the burial of lipids derived from aerobic phototrophs is consistent with the intensified biological pump by the radiation of SSFs in the early Terreneuvian.

Keywords: Ediacaran, Cambrian, oxygen level, molecular fossil, South China

## Ancient ocean environment in the Ediacaran to Cambrian.

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The Ediacaran to Cambrian period is one of the most important intervals for the evolution of life. However, the scarcity of well-preserved outcrops of Ediacaran and Cambrian rocks still leaves ambiguity in deciphering ambient surface environmental changes and biological evolution.

Recent paleontologists, mainly Chinese scientists, revealed that life on the Earth have evolved through multiple stages. Some of the metazoan fossils were discovered from Ediacaran sedimentary rocks. This suggests that so-called Cambrian Explosion already started from the Ediacaran, not from the Cambrian. Therefore, unraveling surface environmental changes during the Ediacaran attract interests.

The Ediacaran to Cambrian strata in South China are almost continuously exposed and contain many fossils, which is suitable for study of environmental and biological changes in the Ediacaran and Cambrian. We (Tokyo Institute of Technology and The University of Tokyo) conducted on-land drilling through the Nantuo, Doushantuo, Dengying, Yanjiahe, Shuijintuo, Shipai and Tianheban Fms at six sites in the Three Gorges area to obtain continuous samples. We systematically analyzed some kinds of isotope ratios (carbon isotope ratios of carbonate and organic carbon, oxygen isotope ratios, nitrogen isotope ratios of organic matter, radiogenic strontium isotope ratios, calcium isotope ratios, molybdenum isotope ratios and iron isotope ratios of pyrite) and elemental concentrations (cerium, phosphorus, manganese and iron concentration in carbonate), using these core samples. The combination of these detailed chemostratigraphies enables us to decipher the surface environmental changes in the Ediacaran and Cambrian. The most important discovery is that surface environment also had evolved through multiple stages during the Ediacaran and the Cambrian.

I will talk about summary of our comprehensive work in the speech.

## Neoproterozoic accretionary complex exposed in the Anglesey island and Lleyn peninsula, northwestern Wales

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Accretionary complex is formed by subduction of oceanic plate, and records a history of the subduction. Subduction-related Precambrian rocks crop out in central England to Wales. The subduction with eastward polarity is considered to have continued from the Neoproterozoic to the Ordovician. Those are supported by three evidences: existences of (1) 680-480 Ma calc-alkaline volcano-plutonic complexes, (2) a high-P/T metamorphic belt formed by regional metamorphism, which has barroisite <sup>40</sup>Ar/<sup>39</sup>Ar ages of 560-550 Ma (peak ages), (3) pelagic to hemipelagic-sedimentary rocks and mafic to ultramafic rock in Monian Supergroup. Based on these evidences, previous studies suggested that the region from the central England to the Wales had been formed by subduction-related orogeny. However, there have been a few constraints on a depositional age in the Monian Supergroup. The age constraint is necessary to reveal tectonic history of the central England to the Wales.

The Monian Supergroup is exposed in the Anglesey island and Lleyn peninsula, northwestern Wales. This complex is divided into three groups; South Stack Group (Gp), New Harbour Gp and Gwna Gp. This study focuses on Gwna Gp because sedimentary rocks consist of lower to middle Cambrian acritarchs. The Gwna Gp has been described as melange since 1919 and is located at structural top than the other two groups. The Gwna melanges include pillow basalts, bedded or jaspery cherts, carbonates, mudstones, sandstones and quartzites, and these rocks are typical rocks of an ocean plate stratigraphy (OPS). At eight areas in the Lleyn peninsula, we conducted geological survey to reconstruct OPSs. In addition, we determined U-Pb ages of zircons from tuffs, mudstones, claystones or sandstones with LA-ICP-MS at the University of Kyoto.

Twenty-six OPSs are reconstructed, and then repetitions of the OPSs by layer-parallel thrusts are confirmed. We separated zircons from three tuffs, two mudstones, four claystones and three sandstones of each OPS. The U-Pb ages of the zircons range from  $637 \pm 13$  Ma (the oldest) to  $541 \pm 16$  Ma (the youngest). We constrained arrival time of each OPS to a trench by the youngest age of detrital zircons.

Although the Gwna Gp has been treated as a single unit, this group can be divided into three types based on the arrival times. The arrival times of Type1, Type2 and Type3 are 630-610 Ma, 610-570 Ma and younger than 560 Ma, respectively. This result indicates the structural upper sequence is older than the lower. This structurally downward growth is the characteristic of typical accretionary complex, and was formed by the eastward subduction. This trend is also supported by the spatial and temporal relation of both volcano-plutonic complexes and regional metamorphic belt. From these evidences, we concluded that the Gwna Gp is the accretionary complex formed by a series of the subduction-related orogeny.

Keywords: Wales, Neoproterozoic, U-Pb age of detrital zircon, Accretionary complex, Subduction-related orogeny

## Deep-sea anoxia during the Marinoan Snowball Earth

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The oxidation of the deep ocean in the Earth's history is regarded to have occurred in the Neoproterozoic, coincident with the metazoan diversification; however, the geological record of the Neoproterozoic environment has been restricted only to shallow-sea sediments. Here we present the discovery of the Neoproterozoic deep-sea sediments in the accretionary complex in Llyen Peninsula, Wales, UK. In the studied section, the oceanic plate stratigraphy consists of mid-ocean ridge basalts, bedded dolostones, ca. 10 m-thick black mudstones, hemipelagic siliceous mudstones and turbidite sandstone, in ascending order. The detrital zircons separated from sandstone give the youngest age of 637±13 Ma. Within ca. 10 m-thick black mudstones, lithological changes are observed; (1) alternating black mudstone and dolomitic carbonate layers, (2) black mudstone with less developed lamination, (3) pyrite-enriched black mudstone, and (4) rhythmically bedded black mudstone, and gradually turns into bedded greenish gray chert sequence. The overlying greenish gray cherts show red color in some place. We analyzed these mudstones and cherts by <sup>57</sup>Fe Mossbauer spectroscopy, and identified six iron species, i.e., hematite, pyrite, two paramagnetic Fe<sup>3+</sup>, and two paramagnetic Fe<sup>2+</sup> with different quadrupole splittings. About a quarter of iron content in the black mudstones consist of pyrite, and other component belong to paramagnetic Fe<sup>2+</sup> or occasionally paramagnetic Fe<sup>3+</sup>. The overlying red cherts contain hematite as the main iron mineral. In the analyzed samples, hematite and pyrite never co-existed. The occurrence of hematite in deep-sea chert essentially indicates a primary oxidizing depositional condition, and that of pyrite a reducing one, respectively. The present results confirmed that a reducing condition persisted in the Neoproterozoic deep-sea through the interval of the black mudstone deposition. The overlying partly-red hematite-bearing cherts give evidence of recover from reducing to oxidizing condition before the arrival to the trench. Here we propose that the black mudstone in Llyen Peninsula shows the global-scale oceanic anoxic event during the Marinoan Snowball Earth, and name this event the 'Marinoan Superanoxia'. During the black mudstone deposition, the whole ocean may have turned into anoxic like the Permo-Triassic boundary Superanoxia; although further discussions for the depositional model based on other geochemical proxies are needed.

## Paleogeography of the Earth; Neoproterozoic

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Neoproterozoic Earth was a transient state to bridge Precambrian mono-cellular world to Phanerozoic Earth of metazoans and plants. The snowball Earth from 770Ma to the onset of Cambrian time, was another environmental pressure to force the life evolution.

### (1) Continent configuration

Supercontinent Rodinia was consolidated ca. 1.0Ga around the equatorial region, and began to be rifted in Neoproterozoic. After ca.600Ma, it became fragmented by rising superplume in the center to give a birth of Pacific Ocean. Immediately after the fragmentation, continents were removed to the South Pole to assemble again to make a semi-supercontinent Gondwana by 540Ma.

### (2) Environmental change

Owing to the leaking Earth (Maruyama and Liou, 2005; Maruyama et al., 2014), the rapid emergence of huge landmass caused the rapid diversification of surface environment and birth of metazoans, as well as algae evolution. Preceding to the Cambrian explosive evolution of life, the snowball Earth event which was a warm-cold fluctuation, GCR-triggered cloud cover, rapid sea-level change, nutrients supply, and probably wet and dry climate change, forced the rapid evolution of life. The first appearance of sponge was between Sturtian and Marinoan snowball Earth event, but the most explosive diversification of metazoans occurred between 540 and 520Ma.

Chemostratigraphy more than 10 were completed for the drilled cores in S. China and the detailed environmental changes were analyzed (Special issue in GR, 2014). Weakened paleomagnetic intensity caused severe radiation for the evolving life on the surface of the Earth.

### (3) Life-evolution and mass extinction

By this reason, and presumably the rift volcanism related to atomic bomb magma caused local mass extinction to promote mutation-induced quick evolution to diversify life.

### (4) Biomass, Ecosystem, mass extinction

Sr isotopic change recorded in platform carbonate clearly indicate the huge amount of nutrients supply for continents and sea-level drop caused the birth of paradise of metazoans on the continental visible platform with enough nutrients supply. A new diversified ecosystem was appeared.

The most extensive mass extinction occurred during the Ediacaran to Cambrian time, more than 10 times in this restricted period, from 635Ma to 488Ma.

### (5) Role of Universe

This could be due to the starburst in our Milky Way Galaxy, and promoted volcanic eruption of atomic bomb magma along the continental rifts on the Rodinia and Gondwana.

## Spherules layer of the uppermost Triassic (Rhaetian) limestone sequence in the Kardolina section, Slovakia

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Triassic/jurassic (T/J) boundary of approximately 201 million years ago is known as a stratigraphic boundary recorded one of the big five Phanerozoic mass extinctions. Catastrophic processes such as widespread eruption of the Central Atlantic Magmatic Province (CAMP) flood basalts and extraterrestrial impacts have been proposed to account for the mass extinction event. Here we show the results of our analysis of enigmatic spherules in the Upper Rhaetian of the Kardolina section, Slovakia. The Kardolina section is situated on a steep western slope of the Mt Palenica in the Belianske Tatry Mts as the most continuous section of the uppermost Triassic (Rhaetian) Fatra Formation. The Fatra Formation is shallow marine carbonate sequence and is overlain with a sharp contact by marine shale of the lowermost Jurassic (Hettangian) Kopieniec Formation. The Kopieniec Formation consists of a sequence of brown claystone with sandstone and limestone intercalations. The position of the T/J boundary is constrained by foraminiferal assemblages.

The limestone sequence containing the spherules exists in the upper part of Fatra Formation. A negative  $\delta^{13}\text{C}$  excursion and a positive  $\delta^{18}\text{O}$  peak have been known from spherules layers. Analysis of the foraminiferal assemblages showed the diversity of foraminifera have decreased in spherules layers. Spherules are found in at least six sedimentary layers in the Fatra limestone. The size of spherules is approximately 200-300  $\mu\text{m}$ . Spherules are contained ~10 % in the layers and the other component grains consist of lithoclasts, bivalves, and crinoids. These grains were relatively rounded and have reworked fabrics. The results of SEM-EDS analysis indicated that spherules were composed mainly of Si, Al and Mg, and contain small sulfide particles with Fe, Zn, and Cu. Such a geochemical composition was clearly different from ooids and peloids in Fatra Formation, though the origin of spherules in Kardolina section remains uncertain.

Keywords: Triassic/Jurassic boundary, Rhaetian, limestone, spherule, extinction

## Global paleogeography and life evolution: 1. Cenozoic

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Continental configuration in the Phanerozoic were synthesized, by the integration of not only continents and oceans, but also, plates, ridge-transform system, ocean current, desert, glacier, major rivers, plume-driven bulge, rifts, mountain belts, lakes, vegetation, and the location of first fossils appeared on the Earth. Methods employed here are as follows; plate reconstruction after Scotese (1996, 2002, 2008), for the oceans by Engebretson et al. (1985; 1992), Cogne and Humler (2006), and Seton et al. (2012), and OIB by Utsunomiya et al. (2008).

The Earth system has been changed drastically at 20 Ma under the strong influence by the internal phenomena of solid-Earth, in particular, by the generation of 410 km-depth swarm of hydrous plumes immediately above the "2nd continents". The Cenozoic is clearly divided into the two periods at ca. 20 Ma on the basis of the secular change in seawater Sr isotopic composition (Veizer et al., 1999). This sharp change reflects the increased material flux from continental crusts to ocean by the plume-driven topographic elevations and collision orogeny along the Himalayan-Tethyan domain all the way from Europe to Papua New Guinea. It should be emphasized that the former is nearly 10 times greater in magnitude than the latter. The uplifted regions include Tibet-East Asia, Rocky Mtn./Colorado plateau/Basin-and-Range/Rio Grande Rift in North America, and Middle America. The A-subduction of the main S. America block caused the uplift of the Andean Mtn. The separation

of S. America from Antarctica was critical to have isolated Antarctica around the South Pole to have triggered the glaciation by virtue of cold-water circulation around the Antarctica.

The rapid glaciation both in Arctic and Antarctica started the Quaternary Period at 1.8 Ma, although the Cenozoic glaciation had already started on Antarctica back to 20 Ma. The ultimate cause of the Quaternary glaciation can be blamed to the encounter of our galaxy with a small "dark cloud" since 20 Ma, and to that with nearby supernovae since 1.8 Ma. The low-temperature on the planet surface and the resultant glaciation was triggered likely by the increased galactic cosmic radiation (GCR) through the extensive development of cloud.

The appearance of the cold weather initiated two independent but critical driving forces for nutrient supply in ocean; i.e., cold-water formation in high-latitudes coupled with accelerated upwelling, and intensified the Hadley atmospheric circulation induced by the plume-driven development of topographic highs on-land closer to the altitude of basal stratosphere, as monitored by the secular curve of seawater Sr isotope ratio. As to the changes in ecosystem after the end-Cretaceous extinction, the promoted nutrients supply caused the increased volume of biomass and various biological innovations; e.g., replacement of radiolarians by diatom, the appearance of C4 plants etc. The collision of India against Asia, caused the species mixing between two continents. On the other hand, the resultant Tibetan uplift and birth of Asian Monsoon brought contrasting climate within Eurasia. The birth of human being along the Rift Valley in E. Africa ca. occurred 5-7Ma was caused likely by the episodic eruption of "atomic bomb" magma along the prominent rift zone. In addition to the local mass extinction by radiations, this led the episodic human escapes from Africa into Eurasia in multiple times after 1.2 Ma.

Keywords: paleogeography, Cenozoic, Pacific Ocean, land bridge, evolution