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General Introduction

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General introduction of the session.

Keywords: biomineralization

Calcification mechanisms in foraminifera and proxy incorporation

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Anthropogenic carbon emissions have now been recognized to not only cause global warming but also ocean acidification (OA), anoxia, ocean stratification, changes in biogeochemical cycles, ecosystem functioning etc. At the end, our carbon hunger may turn out to be one of the biggest challenges faced by future society. Although, the impacts of global warming have been studied for some time now, other aspects of carbon perturbations such as OA are still in its infancy. To investigate and understand the impacts of the present carbon perturbation, it is of utmost importance to exploit proxy records in Earth history in order to understand its consequences on longer timescales.

Calcifying organisms, such as pteropods, bivalves, corals and foraminifera are not only among the first victims of ongoing OA but also provide a rich resource for pale-oceanographers and climatologists because their geochemical make-up (proxies) can be used to reconstruct past ocean history and evolution during and after natural carbon perturbations. However, it has been shown for all geochemical proxies that the main assumption of only one environmental variable controlling a target proxy is too simple. Empirical calibrations introduce a lot of uncertainty because the mechanisms of proxy incorporation are not well understood. The major problem is that the calcification mechanisms are still a black box. In this presentation I will review the current knowledge of calcification in foraminifera.

Keywords: foraminifera, biomineralization, calcification, proxy

Foraminiferal cellular Calcium and pH distribution under laboratory culture experiment

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Foraminifera have been considered as one of the major carbonate producer in ocean. Their calcareous tests are broadly utilized as paleo-environmental indicators in various studies of earth science because their tests have been archived as numerous fossil in sediment for long time and various environmental information are brought by population, morphology and geochemical fingerprints.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 knowledge about the cytological process on carbonate precipitation has been described for couples of decade using by OM, SEM and TEM. Foraminiferal management of calcium and carbonate ion uptake into foraminiferal tests from ambient seawater are of great interest. Our previous 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. Observed results show that foraminifera controls very detailed timing of pH variation and concentration of calcium at any stage of chamber formation dynamically. These observations results will help to consider how the geochemical compositions arranging on the foraminiferal test, sensitivity of pH proxy of boron and others.

Keywords: foraminifera, biomineralization

Impacts of ocean acidification on foraminiferal calcification

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Anthropogenic carbon dioxide emissions result in ocean acidification through net flux of atmospheric CO₂ into sea surface waters. This process reduces pH and carbonate ion concentration, resulting in a decrease of the calcium carbonate saturation state of seawater. More often than not calcifying organisms are particularly vulnerable to ocean acidification. Traditional experimental protocols such as the dissolved inorganic carbon manipulation method lead to a change in every parameter of the carbonate system apart from one (in this case total alkalinity). Therefore these protocols are not suited to determine the parameter of the carbonate system which causes observed effects.

In order to accurately predict foraminiferal calcification at reduced seawater pH and to isolate the effects of pH and carbonate ion concentration we cultured juvenile specimens of the shallow water, benthic foraminifer *Ammonia tepida* in seawater with altered carbonate chemistries: 1) varying pH, stable carbonate ions concentration and 2) varying carbonate ion concentration, stable pH. Growth rates, shell thickness, weight and trace element partitioning will be presented.

Keywords: foraminifera, ocean acidification, calcification

Effects of ocean acidification on trace elements ratio (Mg/Ca, Sr/Ca, Ba/Ca and U/Ca) in two foraminifer species

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It has been concerned that accelerations of anthropogenic CO₂ release will result not only warming the surface of earth but also acidify the ocean. Decrease of carbonate ion concentration and pH in the ocean affects marine calcifying organisms. Reef-dwelling benthic foraminifera, which secrete high-magnesium calcite test, could be categorized as first responders to the ocean acidification as high-magnesium calcite is more soluble than aragonite or calcite, however a limited number of studies focus on their adaptation to ocean acidification. One such study is Fujita et al (2011) and they reported the changing in the calcification rates measuring the diameter and the weight of three different species of large, algal symbiont-bearing benthic foraminifera. The result seems to show the positive correlations between the calcification rate and pCO₂ in the intermediate level, whereas negative correlations are seen in the high pCO₂ (970 micro-atm) condition. However the degree of importance for calcifications seems to have species dependence (i.e. hyaline vs. porcelaneous shell, different type of symbionts, diatom vs. dinoflagellate). The present study use these samples in order to investigate the effects on trace elements in the calcium carbonate shells as is often used for proxies to reconstruct paleoceanography. We analyzed Mg/Ca, Sr/Ca, Ba/Ca and U/Ca by high resolution sector field laser ablation inductively coupled plasma-mass spectrometer (HR-SF-ICPMS) on *Baculogypsina sphaerulata* (perforate and hyaline shell and diatom endosymbiont) and *Amphisorus hemprichii* (imperforate and porcelaneous shell and dinoflagellate endosymbiont) cultured at five different pCO₂ (260, 360, 580, 770 and 970 micro-atm). We will present the preliminary results of the measurements during the talk.

References:

Fujita, K., M. Hikami, A. Suzuki, A. Kuroyanagi, K. Sakai, H. Kawahata, and Y. Nojiri. 2011. Effects of ocean acidification on calcification of symbiont-bearing reef foraminifera. *Biogeosciences*, 8, 2089-2098.

Keywords: ocean acidification, trace element, LASER ICP-MS, foraminifer

Mg isotope fractionation in Porites coral skeletons: evaluation of a new climate proxy from culture experiments

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Recent developments in inorganic mass spectrometry have allowed new stable isotope systems to be explored by paleoceanographers. In the field of low-latitude climate reconstruction, proxy developments in massive hermatypic corals are still highly desirable for more accurate temperature reconstructions. Stable isotope compositions of the major and minor constituents, such as Ca and Sr, of coral aragonite are potentially new proxies for environmental studies (Boehm et al., 2006; Fietzke and Eisenhauer, 2006). These studies have focused on the temperature dependency of isotope fractionation during the precipitation of biogenic carbonates, because water temperature is the most fundamental parameter controlling the earth's surface environment. Although Sr/Ca is regarded as useful temperature proxy, Mg/Ca is thought to mainly reflect the growth rate (e.g., Inoue et al., 2007). Evaluation of Mg isotope fractionation process in hermatypic coral aragonite must be addressed in order to understand a coral biomineralization and develop a new palaeoceanographic proxy. Many researchers have analyzed Ca isotopes in biogenic and inorganic calcium carbonates, with the first objective being to evaluate them as a potential new paleothermometer. They have found a small but resolvable temperature dependence of Ca isotope fractionation (e.g., Gussone et al., 2009). Strontium is important minor element in CaCO₃, and in inorganic aragonite and cultured hermatypic corals, it displays similar isotope fractionation mechanisms to those of Ca (Fietzke and Eisenhauer, 2006). Previous studies have reported some steeper temperature dependence (slopes) in Ca and Sr isotope fractionation of biogenic CaCO₃ and the differences in temperature slopes are interpreted as a large kinetic isotopic effects depending on how fast the crystal growing rate and relative mass difference (rmd) among isotopes. Growth effects on Mg isotope are expected to be highly concerned since Mg/Ca is known to clearly dependent on growth rates (Inoue et al., 2007). In this study, we performed high-precision Mg isotope measurements in Porites coral cultured in thermostated tanks. We here evaluate the plausible factors controlling Mg isotope fractionation in coral CaCO₃ skeletons and present the relationships between Mg isotope values and e.g., water temperature, minor elemental concentrations, growth rates.

Keywords: hermatypic coral, magnesium isotope, MC-ICP-MS, culture experiment

Seasonal changes in shell microstructures of the bloody clam, *Scapharca broughtonii* (Mollusca: Bivalvia)

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Molluscan shells have various shapes, sizes of crystals, and their arrangement, and these variable characters are called as shell microstructure. Shell microstructure has been studied mainly in the light of taxonomy and phylogeny, and its function, however, the formation of shell microstructure is also affected by environmental and phylogenetic factors. If we can detect environments from the microstructure of fossil specimens, we can establish new paleoenvironmental or paleoecological proxies. This study demonstrated seasonally controlled changes in shell microstructures in *Scapharca broughtonii* (Mollusca: Bivalvia). We conducted the observations of shell microstructures and stable oxygen isotope analyses to reveal the factors controlling cyclical microstructural changes in *S. broughtonii*. We used recent specimens collected in Aomori, Miyagi, Ishikawa, Fukui, Yamaguchi, and Nagasaki Prefectures around Japan to compare geographic variation. Shell microstructure was observed by light microscopy of acetate peels and scanning electron microscope. The stable carbon and oxygen isotopic composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of *S. broughtonii* shells were measured, using an isotope ratio mass spectrometer (Micromass ISOPRIME, Manchester, UK) at the National Institute of Advanced Industrial Science and Technology (AIST).

Scapharca broughtonii has outer and inner layers that are divided by the myostracum. The outer layer is subdivided into composite prismatic structure on the exterior side and crossed lamellar structure on the interior side with a transitional boundary. The proportion of two structures in the outer layer changes cyclically with ontogeny. After the positions of the peaks where the crossed lamellar structure is thickened, growth breaks are observed in most specimens. From the oxygen isotope profiles, the fluctuations of the proportions of the thickness of two microstructures are synchronized with the fluctuations of the shell $\delta^{18}\text{O}$. Crossed lamellar structure is thickened at high water temperatures in summer.

Annual shell growth rate that was estimated based on oxygen isotopic and shell microstructural fluctuation. Southern specimens have longer cycles of the proportion of the thickness of two structures than northern specimens. From shell isotopic records, it appears that the clams can form their shells at over about 12 °C. Annual shell growth rate was decreased in around three-year-old specimens. The change in shell growth is probably caused by sexual maturity. Growth breaks are observed after the peaks of high water temperatures may be formed as spawning break, since they correspond to spawning season.

The proportion of the thickness of shell microstructures can directly indicate the fluctuation of water temperature. This method contributes to age determination, criteria of seasons of shell growth, and understanding paleo-climate.

Keywords: Bivalve, shell microstructure, SEM, stable oxygen isotope, Seasonal change

Carbon- and oxygen-isotope compositions of a modern brachiopod collected from east coast of Sokcho, Korea

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Carbon- ($d^{13}C$) and oxygen-isotope ($d^{18}O$) compositions of fossil brachiopods have been regarded as one of important data source for delineating their secular variations of the Phanerozoic seawater, especially those of the Paleozoic, because it has been believed that brachiopods secrete their shells in isotopic equilibrium with ambient seawater. Recent studies, however, demonstrated that their $d^{13}C$ and $d^{18}O$ values are highly variable within a single shell as well as among taxa and that shell calcite may or may not be precipitated in isotopic equilibrium with ambient seawater. These are due to the degree of kinetic and metabolic effects that may vary depending upon the shell portions and among taxa. However, enough sequential high resolution isotopic data are still lacking to generalize this theory. Therefore, more information is needed to clarify which brachiopod taxa and shell portions reliably record past ocean environments.

We show within-shell variations of $d^{13}C$ and $d^{18}O$ values using a modern brachiopod, *Coptothyris grayi*, collected at a water depth of 8.8 m in eastern coast of Sokcho, Korea. Although many fossil brachiopod shells are ornamented with fine radial costae, the detailed isotopic analyses of modern brachiopods have been performed for those without such ornamentation. Therefore, our research is expected to provide useful information on paleoenvironmental condition based on stable isotope compositions of fossil brachiopods, especially of Paleozoic age.

Keywords: brachiopod, carbon isotope, oxygen isotope, Korea

Application of coral ^{15}N proxy: interannual variability of water mass in Tatsukushi Bay due to Kuroshio volume changes

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The Kuroshio Current transports a large amount of warm and low nutrient seawater northward in the western north Pacific and its variability has been discussed the relationship with global climate change in decadal scales. Coral skeletons have been used as high resolution recorder of past nutrient dynamics with decades to millennia time scales. Nitrogen isotope of organic matter in the coral skeleton could vary with that of nitrogenous sources and be a potential to capture nitrogen isotope changes in marine nitrate. In this study, we tried to detect poor nitrate water mass of Kuroshio through the time series of nitrogen isotope in coral cores from Tatsukushi Bay, Kochi, Japan.

Coral drilling performed in October, 2008 and we took three cores 1.5 meter long from the same *Porites* coral. According to observation of annual bands in x-radiographs of coral cores, that *Porites* colony alive more than 216 years. For nitrogen isotope analysis of coral skeletons, the microsampling from the coral slabs 5 mm thick performed along the major growth axis at 4 mm intervals. Each 28 mg powder samples were then decalcified, and all of organic matter in coral skeleton resolved to nitrate and converted into nitrous oxide to introduce into continuous-flow isotope ratio mass spectrometry. We also determined the time axis of coral cores using coral oxygen isotopes and annual bands in x-radiographs.

Coral nitrogen isotopes varied between +3 and +10. We compared coral nitrogen isotopes with Kuroshio volume observed by Japan meteorological Agency from 1973 to 2008. The 2-year moving averages of coral nitrogen isotopes had inverse variation with that of Kuroshio volume. Coral nitrogen isotope was decreased by intensified Kuroshio volume. We measured nitrogen isotope of nitrate in the mouth of Tatsukushi Bay, which results were +9.5 on June 2011 when Kuroshio leave from the bay, and +6.1 on October 2011 when Kuroshio came close to the bay. This result suggested nitrate in Kuroshio water had low nitrogen isotope composition originated from tropical oceans. As Kuroshio volume decreased, upwelling nitrate with heavier nitrogen isotope supplied Tatsukushi Bay. Coral nitrogen isotopes recorded nitrate isotope composition varied with Kuroshio volumes. In this presentation, we also report time series of coral nitrogen isotope with precipitation anomaly in the northern hemisphere for 160 years. From 1973 to 2008, they have negative correlation ($r=-0.48$) and varied with Kuroshio volume. Using coral nitrogen isotope, we discuss the effect of Kuroshio volume changes to climate in northern hemisphere and their decadal cycle.

Keywords: coral skeletons, nitrogen isotope, nitrate, Kuroshio

Detecting algal photosymbiosis from ontogenetic isotope analyses of living planktonic foraminiferal test from Sagami Bay

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Some modern planktonic foraminifers harbor photosynthetic algae in their cells throughout their life. This symbiosis contributes to foraminiferal nutrition through the exchange of metabolic and/or photosynthetic products between foraminifers and algae. Therefore, in the evolutionary history of planktonic foraminifers, development of photosymbiotic ecology is expected to enable foraminiferal species to radiate into oligotrophic ocean habitats unexplored by then. Thus, for further understanding of the dynamics of paleobiodiversity in planktonic foraminifers, it is significantly important to identify photosymbiotic ecology of extinct species.

In order to disclose the photosymbiotic signal, some previous authors have analyzed ontogenetic variations of stable isotopic compositions in foraminiferal tests. Among those studies, cultural experiments indicated that symbiont-bearing species show characteristic increasing trend in $d^{13}C$ through the individual ontogeny¹⁾. This is because symbiont's photosynthesis makes seawater surrounding foraminifers enriched in ^{13}C by preferential uptake of ^{12}C . This effect becomes more prominent along host's size increase through ontogeny. Therefore, isotopic variations with respect to ontogenetic stages of foraminifers would be a possible candidate as a proxy for identifying the photosymbiotic ecology even for fossilized specimens. Although the proxy seems to be plausible in laboratory-cultured specimens, we should test it with modern wild specimens obtained from natural environment.

Here, we show ontogenetic isotopic variations from a single foraminiferal test recovered by a plankton tow. Four species, *Globigerinoides sacculifer*, *Globigerinoides conglobatus*, *Neogloboquadrina dutertrei*, and *Globorotalia inflata* recovered at Sagami Bay were utilized for the analyses. Cytoplasm of each specimen was decomposed with sodium hypochlorite and residual tests were dissected chamber-by-chamber with micro-scalpels under a binocular microscope. Isotopic measurements were performed on each single chamber using the customized continuous-flow IRMS (IsoPrime) at Geological Survey of Japan (AIST), which enables measurements of micro-volume samples as small as 1.5 micro grams of carbonate²⁾.

Continuous increases in $d^{13}C$ with growth are observed in two species; by 1.1 permil in *Gs. sacculifer* and by 1.4 permil in *Gs. conglobatus*. In comparison, *Gr. inflata* exhibits much smaller isotopic variation for both $d^{13}C$ and $d^{18}O$. On the contrary, *Nq. dutertrei* shows significant positive correlation between $d^{13}C$ and $d^{18}O$. The median of $d^{18}O$ of *Gr. inflata* is obviously ^{18}O -enriched than those of the other three species.

Successive increase with growth and rather positively deviated value from isotopic equilibrium in $d^{13}C$ of *Gs. sacculifer* and *Gs. conglobatus* represent classic signals of algal photosymbiosis observed in cultural experiments. Since these two species are known to be symbiont-bearing species, this result shows that we successfully detected the photosymbiotic signal from ontogenetic isotope analyses in live-caught wild specimens.

1) Spero and Lea, 1993, Marine Micropaleontology, DOI:10.1016/0377-8398(93)90045-Y.

2) Ishimura et al., 2004, Rapid Comm. Mass Spectrom., DOI:10.1002/rcm.3571.

Keywords: modern planktonic foraminifers, photosymbiosis, stable isotopes, ontogeny, Sagami Bay, plankton tow

Genetic populations of planktic foraminifera in the Northwest Pacific

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Molecular phylogenetic analyses have revealed significantly high genetic diversity within planktic foraminifer morphospecies. Molecular studies of planktic foraminifera suggest these genotypes exhibit distinct ecological preferences. Moreover, the differences of their ecology and habitats among genotypes could affect their calcification and potentially affect the test morphology. The distribution patterns of genotypes show correlation to the water mass structure and the phylogeography of these planktic foraminifera genotypes could be affected by the paleoceanic and geographic events. In order to examine the correlation between the divergence and oceanographic /geographical factors, we investigated the genetic variability of planktic foraminifera in the Pacific based on partial small subunit ribosomal RNA gene.

Implications for paleo-reconstruction based upon oxygen isotopic ratio of different sized polar planktonic foraminifera

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Planktonic foraminifera provide a record of the ocean surface environment through the isotopic and chemical composition of their calcite shells. Shell oxygen isotopic composition ($d^{18}O$) is commonly used to reconstruct the paleo-environment, including temperature, salinity, and water column structure. *Neogloboquadrina pachyderma* is a common polar-subpolar planktonic foraminifer, thus it is an important species for the reconstruction of paleo-oceanography in the high latitude. Foraminifera in sediment trap samples are particularly useful for examining changes in ($d^{18}O$) over time, and for determining which seasons and depths are most represented. In the study, we examined seasonal variation in $d^{18}O$ of different sized *N. pachyderma* (sin.) using sediment trap samples collected over 3.5 years in the northwestern North Pacific Ocean. Shell $d^{18}O$ of small (125-180 μm) and large (180-250 μm) *N. pachyderma* (sin.) exhibited similar seasonal variation, with minimum values during September-October and maximum values during April-May. In the study, vital offset values were approximately -1 permil for both size classes throughout the study, except during 2000 (-0.8 permil). However, in the reconstruction of paleo-temperature, offset values should be examined from viewpoints of the equation used as oxygen isotope-temperature relationship and the presence of genotypes. $d^{18}O$ differences between size classes of *N. pachyderma* (sin.) in the present study varied seasonally, not a consistent offset; suggesting that the differences were due mainly to oceanographic conditions in the water column rather than to size-specific kinetic/metabolic effects. During summer, when the water column is stratified, large and small individuals appeared to mainly calcify near the pycnocline, at 25-35 m and approximately 45 m, respectively. During winter, when the water column is not stratified or only weakly stratified, both size classes calcified at or slightly above the pycnocline, at 45-65 m. Because the seasonal peaks in flux coincide with minimum and maximum water temperatures and contribution of the flux peaks is approximately equal, flux-weighted values of all (125-250 μm) and small (125-180 μm) shell size are in good agreement with the mean annual values (no flux-weighted) of small (125-180 μm) individuals. Thus, the fossil $d^{18}O$ data of *N. pachyderma* (sin.) most likely record the annual mean oceanographic environment around pycnocline depth, and size-specific differences in $d^{18}O$ reflect water column stratification.

Keywords: planktonic foraminifer, oxygen isotope ratio, *Neogloboquadrina pachyderma*, sediment trap, northwestern North Pacific

ECOLOGY OF LIVE BENTHIC FORAMINIFERA FROM THE WHITTARD CANYON (NE ATLANTIC)

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Living (Rose Bengal stained) benthic foraminifera were investigated at 18 deep-sea stations sampled in the Whittard Canyon area (NE Atlantic). The stations were positioned along 4 bathymetric transects ranging from 300 to 3000 m depth: two along the main canyon axes (Western and Eastern branches) and two along adjacent open slopes (Western and Eastern slopes). The aim of this study was to assess changes of foraminiferal standing stock, diversity and microhabitat in relation to the physico-chemical conditions prevailing at and below the sediment-water interface. Minimal oxygen penetration depths and maximal diffusive oxygen uptake were recorded at upper canyon stations suggesting a higher mineralisation rate in the canyon heads. It is confirmed by high phytopigment concentrations measured in the sediment of the upper canyon axes. Foraminiferal abundance is positively correlated with (1) species richness, (2) diffusive oxygen uptake and (3) phytopigment concentration in the sediment. It suggests the key role of organic matter fluxes on the foraminiferal communities (standing stock and diversity). Foraminiferal abundance is generally higher along the canyon axis compared to open-slope sites at comparable water depths. It confirms a preferential transport of organic detritus into the canyons. The species composition varies (1) with water depth along all of the four transects and (2) between canyon branches and adjacent slopes. Higher abundances of agglutinated taxa such as *Reophax* spp., *Eggerella bradyi*, *Ammobaculites agglutinans* are observed at the open slope stations, whereas calcareous species dominate the canyon branches. This faunal difference may be related to food scarcity on the slopes, and suggests that the dominant calcareous taxa are strongly favoured by a higher supply of labile food particles. The silty/sandy intercalations at many of the deeper canyon stations may have been rapidly deposited by fairly recent gravity flows. At station 51WB (3002 m), the faunal characteristics (strong dominance, shallow infaunal microhabitats) suggest that the foraminiferal community is in an early state of ecosystem colonisation after these recent sedimentation events, which would have supplied the important amounts of phytopigments.

Keywords: benthic foraminifera, NE Atlantic, Ecology, Canyon, Open slope

TEX₈₆ and seasonal distributions of archaeal membrane lipids across the chemocline in the modern shallow coastal ocean

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Aquatic ecosystems in the shallow coastal ocean would be quite sensitive to the ongoing global warming. In fact, anomalous occurrences of many macro fauna have been reported in these decades in the Seto Inland Sea. For predicting the biological responses to the global warming, it is really important to analyze precise sea surface temperature (SST) records and micro and/or macro faunal abundances in the shallow coastal ocean. However, since historical records of instrumental SSTs are very scarce in the Seto Inland Sea, we need to employ an appropriate paleotemperature proxy for historical SST analyses. Nonetheless, conventional paleotemperature proxies of oxygen isotope and alkenone paleothermometry are practically inapplicable in the Seto Inland Sea. Therefore, we need to rely on the organic paleotemperature proxy of TEX₈₆. On the other hand, since TEX₈₆ has rarely been systematically applied to the paleothermometry in the shallow coastal ocean, we need to test the applicability of TEX₈₆ in the Seto Inland Sea.

Here we present relationships between the distribution of thaumarcaetol isoprenoid glycerol dibiphytanyl glycerol tetraethers (GDGTs) and *in situ* SST, and abundances of GDGT and nutrient/chlorophyll, on the basis of time-series analyses of particulate organic matters (POMs) in Beppu Bay, the Seto Inland Sea. Because Beppu Bay is the archetypal enclosed basin, bottom water is decoupled from surface and intermediate water, resulting in bottom water anoxia through summer to autumn. Within the anoxic water mass, ammonium is extremely concentrated, accompanied by the significant chemocline at the redox boundary, which is disappeared on January by vigorous mixing of a water column. Then, we sampled POMs within a water column on October, November, showing bottom water anoxia, and March, representing the month of phytoplankton blooming.

Calculated temperatures derived from TEX₈₆^H and TEX₈₆^L show significant positive correlation with *in situ* temperatures, indicating that TEX₈₆ paleothermometry can be firmly applicable to the shallow coastal ocean. On the other hand, the relationship observed in Beppu Bay shows slight difference from that reported by Kim et al. (2010), suggesting that TEX₈₆^H and TEX₈₆^L in open ocean might not be representatives of true SSTs as implied by Wuchter et al. (2005). In addition to the thermometry, concentrations of total GDGTs within a water column were also analyzed on October, November, and March. Total GDGTs in the anoxic water mass are significantly higher than those in overlying oxic layers, whereas particulate organic carbon (POC) concentrations show no increase in the anoxic water mass, indicating enhanced biosynthesis of GDGTs within the anoxia. On the other hand, although POC concentrations are elevated at the depth showing chlorophyll maximum, GDGTs indicate no increase at the chlorophyll maximum. In addition, GDGT concentrations show no correlation with chlorophyll concentrations in any samples analyzed, while they indicate significant correlation with ammonium concentrations. Although the heterotrophic physiology has been reported for the marine mesophilic Archaea, our results demonstrate that the Archaea, which produced GDGTs analyzed in this study, is assumed to have grown by chemoautotrophic ammonium oxidation.

Kim et al. (2010) *Geochimica et Cosmochimica Acta*, v. 74, no. 16, p. 4639-4654.

Wuchter et al. (2005) *Paleoceanography*, v. 20, no. 3., PA3013.

Keywords: Thaumarchaeota, TEX₈₆, paleotemperature, chemoautotroph, Seto Inland Sea

The effect of high pCO₂ seawater on foraminiferal oxygen and carbon isotopes

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Ocean acidification in response to rising atmospheric pCO₂ is generally expected to reduce rates of calcification by reef calcifying organisms, with potentially severe implications for coral reef ecosystems. Various studies have revealed potentially dramatic responses in a variety of calcareous organisms to the range of pCO₂ values projected to occur over this century. In our previous culture experiment with two algal symbiont bearing, reef dwelling foraminifers, *Amphisorus kudakajimensis*, which hosts dinoflagellate symbionts, and *Calcarina gaudichaudii*, which host diatom symbionts, in seawater under five different pCO₂ conditions, net calcification of *A. kudakajimensis* was reduced under higher pCO₂, whereas calcification of *C. gaudichaudii* generally increased with increased pCO₂. These different responses among the two species are possibly due to differences in calcification mechanisms (in particular, the specific carbonate species used for calcification), and to links between calcification by the foraminiferal hosts and photosynthesis by the algal endosymbionts. However, knowledge about the factors of different calcification responses is poorly understood. To shed light on the factors leading to different calcification response to ocean acidification between perforate and imperforate, we analyzed the stable isotope composition of reef-dwelling foraminifers: *Amphisorus hemprichii*, belong to imperforate species, *Baculogypsina sphaerulata* and *C. gaudichaudii* belong to perforate species, subjected to five varied acid seawater for twelve weeks almost same as above-mentioned culture experiment. Oxygen isotope ratio value of cultured foraminiferal tests under five varied pCO₂ seawater, which temperature and intensity of light was adjusted constantly for experimental period, indicated no significant correlation to pCO₂. The results show that oxygen isotope ratio stay constant within narrower range from CO₃²⁻ concentration (111 to 264 μmol/kg). On the other hand, carbon isotope ratio of foraminiferal tests indicated heavy trend with increasing pCO₂. Alteration of carbonate chemistry result from ocean acidification may be effect strongly on carbon isotope composition relate to metabolic system (i.e. photosynthesis and respiration). In perforate species, both of oxygen isotope ratio and carbon isotope ratio was lighter than that in imperforate. For oxygen isotope ratio variation possibility among species would be caused by their Mg-content concentration in calcite shells. The distinct difference in the level of carbon isotope ratio values between imperforate and perforate foraminifera indicates different amounts of metabolic CO₂ used for shell construction. Therefore, oxygen and carbon isotopes ratio of foraminiferal test have the potential to reveal calcification mechanism of two species.

Keywords: ocean acidification, reef-dwelling foraminifera, culture experiment, oxygen and carbon isotopes, calcification

Differing utilization of nitrate nitrogen in shallow-water benthic foraminiferal cells under oxic/anoxic conditions

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Some benthic foraminiferal species have been reported to respire nitrate under dysoxic conditions. However, it is still unknown whether they can actually respire nitrate or symbiotic bacteria contribute to the nitrate respiration. We incubated a shallow water benthic foraminifera, *Ammonia beccarii*, under oxic or anoxic conditions to see their nitrate utilizations. We added nitrate intermittently to the cultured bottles and incubated them for 1 month. After the incubation, we measured the $\delta^{15}N$ of amino acids from cytoplasm and organic matters embedded in carbonate test. The measured nitrogen isotopic ratios indicated that enhanced utilization of nitrate under anoxic conditions. Trophic levels of *A. beccarii* under anoxic conditions suggest large contribution of prokaryotes to the observed nitrate utilizations.

Keywords: Sediment-water interface, Benthic foraminifera, Nitrate, isotope tracer, Amino acid isotopes

Element profile and chemical environment of sulfur in clam shell: insights from micro-XRF and XANES

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Element profiles of sulfur and strontium in the inner layer of a clam shell (*Hippopus hippopus*) were investigated by means of micro X-ray fluorescence, and sulfur *K*-edge X-ray absorption near-edge structure (XANES) were used to evaluate the local environment of sulfur in aragonitic and calcitic bivalve shells. The spectra of S *K*-edge XANES collected from bivalve shells and S-bearing organic and inorganic reference materials indicated that inorganic sulfate was present in calcitic bivalve shells. However, XANES results did not permit us to discriminate between organic and inorganic sulfate in aragonitic shells. Strontium fluctuations and thin section observations suggested that Sr was incorporated into the shells at high growth rates during warm seasons. The first-order fluctuations of sulfur in the inner shell layer showed clear annual fluctuations, with sulfur concentrations being lower during periods of faster growth. Bivalve shells consist of well-crystallized CaCO₃ and amorphous CaCO₃ containing organic matter, and the proportion of crystalline CaCO₃ increases during the high growth season. Our results suggest that trace sulfur profiles in aragonitic shells could be the result of cyclic changes of shell crystallization related to bivalve physiology and environmental factors.

Keywords: Sulfur, micro-XRF, Synchrotron radiation, XANES, Strontium