

BPT002-01

Room:201B

Time:May 25 08:30-08:45

Intraspecific Variations in Carbon and Oxygen Isotope Compositions of a Modern Brachiopod Collected off Okinawa-jima

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Carbon ($d^{13}C$) and oxygen ($d^{18}O$) isotope compositions in rhynchonelliform brachiopod shell calcite have been widely used as proxies of $d^{13}C$ of dissolved inorganic carbon (DIC) and $d^{18}O$ of ancient seawater, respectively. The use of brachiopods as a paleoenvironmental proxy is based on the presupposition that the shell calcite is precipitated in isotopic equilibrium with ambient seawater. Recently, it was shown that the modern brachiopod calcite display variable carbon and oxygen isotope offsets from the range of equilibrium calcite (= calcite precipitated in isotopic equilibrium with ambient seawater) even within a single shell and degree of the disequilibrium varies from species to species [e.g., Auclair *et al.*, 2003, *Chem. Geol.*, 202, 59-78; Yamamoto *et al.*, 2010a, *Palaeo-3.*, 291, 348-359; Yamamoto *et al.*, 2010b, *G-cubed*, 11, Q10009]. However, a single specimen was examined for each species in the previous studies that dealt with within-shell variations. Therefore, further geochemical investigations are needed to reveal intraspecific variations in isotopic compositions to establish the isotopic compositions of brachiopod shells as a much more reliable paleoenvironmental proxy.

This study presents intraspecific variations in carbon and oxygen isotope profiles along the growth axis of modern brachiopod shells of *Basiliola lucida* collected from shelf to shelf slope environments (180-320 m water depth) off Okinawa-jima and Amami-o-shima, southwestern Japan. The $d^{13}C$ and $d^{18}O$ values of each shell are rather constant with no significant variations. The $d^{13}C$ values are greater than those of equilibrium calcite with two outlier shells. The $d^{18}O$ profiles show enrichment in ^{18}O relative to equilibrium calcite throughout the growth axis, which underestimates seawater temperature, although the differences in the $d^{18}O$ values among the samples correspond to those of seawater temperatures among the brachiopod growth sites. Significant offsets of $d^{13}C$ and $d^{18}O$ values from the range of equilibrium calcite indicate that the isotopic compositions in the shells of *B. lucida* are influenced by vital effects that are generally explained by kinetic fractionation and metabolic effects. However, the degrees of the effects on $d^{13}C$ and $d^{18}O$ values are comparatively constant in each individuals. In conclusion, the use of *B. lucida* as a proxy of ancient seawater temperature is not very recommend. However, if water depths of the brachiopod-yielding horizons are determined independently by other fossils (e.g., benthic foraminifers) in a given geologic section, $d^{18}O$ value of *B. lucida* can be used as a proxy to determine depth gradient of seawater temperature for the past.

Keywords: brachiopod, carbon isotope composition, oxygen isotope composition, off Okinawa-jima, off Amami-o-shima

BPT002-02

Room:201B

Time:May 25 08:45-09:00

Geochemistry of sediments from the Ganges and Brahmaputra Rivers

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World-scale big rivers play an important role in the transportation of river water and particles to the ocean. The Ganges and Brahmaputra rivers are especially important for reconstruction of Himalayan monsoon climate. Chemical compositions of the Ganges and Brahmaputra River sediments have been determined to investigate their provenance and source area weathering conditions.

Major and trace element concentrations normalized to upper continental crust (UCC) show the sediments in both rivers are depleted in CaO, K₂O, Na₂O, Sr, MgO, Al₂O₃ - Sc and Fe₂O₃ and enriched in Zr, Th, Ce, SiO₂, Y, TiO₂ and Cr. Silica enrichment is caused by quartz concentration, mineral sorting and/or enhanced compositional maturity during fluvial transportation. Chemical Index of Alteration (CIA) ratios in the river sediments (Ganges, ~64 and Brahmaputra, ~60) are low compared to those of Miocene Sylhet sediments in Bangladesh (mostly ~70-87). CIA ratios are low in the river samples because they mostly contain fresh sandy material within the active channels, while highly weathered fine-grained detritus has been transported by the river waters into the ocean. Major element and trace element ratio plots indicate the sediments in both rivers were derived from felsic continental crust sources. A - CNK - FM relationships further suggest minimal weathering of the modern sediments, major contribution from felsic materials, and minor ferromagnesian mineral content. Chemical similarity of the river sediments, the Sylhet and the equivalent Siwalik sequence sedimentary rocks in Nepal represents homogenization of material derived from the Himalayan source, and no major compositional changes have occurred in the source during the last 20 million years.

Keywords: river, sediments, climate, weathering

BPT002-03

Room:201B

Time:May 25 09:00-09:15

Age models of stalagmite from Shimochibaru cave in Kume Island, using radiocarbon dating

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Speleothem is a unique archive of past climate and has been used for paleoclimate studies. Advancement of analytical chemistry using mass spectrometry enable us to establish the record of past precipitation, temperature, and vegetations of various terrestrial regions. The most commonly used measure of radiometric age determination is Uranium series dating which can establish high precision age models. Although radiocarbon dating is powerful tool to determine the past climate events up to 50,000 years ago recorded in geological samples, nature of speleothem deposition processes make this method to be difficult to apply. It is so called dead carbon effect that groundwater dissolve much older carbon (ie. no radiocarbon) before it precipitates as speleothems other than ambient atmospheric CO₂. However several previous studies have attempted to correct this effect and an example from Bahama using coupled measurements of radiocarbon and U-series dating reveal constant contribution of dead carbon for the last 50,000 years (Beck et al., 2001), yet few studies reported using this strategy. In this study, we measured more than 30 of AMS (Accelerator Mass Spectrometry) radiocarbon dates for 2 speleothems collected from Kume Island in Okinawa, Japan. All the radiocarbon ages are stratigraphically in order and no age reversals were observed. Several newly formed speleothems on cave floor suggested that approximately 20 percent dead carbon contamination shift radiocarbon concentrations in spelethems as is consistent with Bahama and other records reported from similar geological settings. Corrected radiocarbon ages suggested that two speleothems preserve early to mid Holocene records. It will be therefore useful for studies of past Monsoon reconstructions since the period overlapped with the time when Monsoon activities were stronger than today according to Chinese cave records (eg., Wang et al., 2005). We conclude that systematic radiocarbon dating can be utilized as reliable age determination tools if the dead carbon content corrections are properly applied.

Keywords: stalagmite, radiocarbon age, dating, Kume Island

Japan Geoscience Union Meeting 2011

(May 22-27 2011 at Makuhari, Chiba, Japan)

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BPT002-04

Room:201B

Time:May 25 09:15-09:30

Reconstruction of temperature and oxygen isotopes in the surface water of the Mid-Holocene tropical western Pacific

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Oxygen isotope ratios ($d^{18}\text{O}$) in foraminifera from deep sea cores have been used successfully to reconstruct continental ice volume, sea level and deep-ocean temperatures throughout the last glacial-interglacial cycle. Yet there is still considerable debate regarding the relative contributions of changes in the oxygen isotopic composition of seawater in the tropical surface ocean. Obtaining accurate estimate of the past $d^{18}\text{O}$ distribution in tropical surface waters is crucial to establishing the role of the tropical oceans in global climate change. In this study, Sr/Ca ratios and $d^{18}\text{O}$ values in a fossil coral collected from Vanuatu with the age of 5.2 ka were measured to reconstruct past sea surface temperature (SST) and $d^{18}\text{O}$ in seawater. XRD analysis and SEM observation revealed that skeletal material was composed of only aragonite and the age determination was precisely conducted using U-Th dating method. Then Sr/Ca and $d^{18}\text{O}$ were analyzed with an approximate time resolution of 2 month. As a result, slightly higher mean SST and about 0.4 per mil enrichment of $d^{18}\text{O}$ relative to modern seawater have shown from 5.2 ka coral. The result is corresponding to the previous study from Great Barrier Reef which has suggested that the temperature increase enhanced the evaporative enrichment of ^{18}O in seawater.

Keywords: western Pacific, coral Sr/Ca, oxygen isotope, Holocene

Japan Geoscience Union Meeting 2011

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BPT002-05

Room:201B

Time:May 25 09:30-09:45

Detecting Antarctic melting during the Holocene using sea-level information from Sri Lanka

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Mid to Late Holocene sea-level change can be used for evaluating long-term stability of the Antarctic ice sheet since the most of the Northern hemisphere major ice sheets disappeared by approximately 8,000 years ago. Ongoing global warming may trigger disintegration of this ice sheet, with collapse of the West Antarctic Ice Sheet alone potentially producing a more than 3 to 4 m global sea-level rise. Relative sea level records from sites far away from former ice sheet regions (far-field) provide information on total volume of the ocean mass change, which can be interpreted as global ice volume change. Here we report Holocene sea-level records from Sri Lanka compared with glacio-hydro-isostatic modeling to better understand the melting history of Antarctic ice sheet during the Holocene.

Keywords: Sea Level, Holocene, Antarctica, Isostasy, sediment core, Radiocarbon dating

BPT002-06

Room:201B

Time:May 25 09:45-10:00

Effects of ocean acidification on calcification of symbiont-bearing reef foraminifers

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Ocean acidification (decreases in carbonate ion concentration and pH) 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. Large, algal symbiont-bearing benthic foraminifers, which are important primary and carbonate producers in coral reefs, produce high-Mg calcite shells, whose solubility can exceed that of aragonite produced by corals, making them the "first responder" in coral reefs to the decreasing carbonate saturation state of seawater. Here we report results of culture experiments performed to assess the effects of ongoing ocean acidification on the calcification of symbiont-bearing reef foraminifers using a high-precision pCO₂ control system. Living clone individuals of three foraminiferal species (*Baculogypsina sphaerulata*, *Calcarina gaudichaudii*, and *Amphisorus hemprichii*) were subjected to seawater at five pCO₂ levels from 260 to 970 ppm. Cultured individuals were maintained for about 12 weeks in an indoor flow-through system under constant water temperature, light intensity, and photoperiod. After the experiments, the shell diameter and weight of each cultured specimen were measured. Net calcification of *Baculogypsina* and *Calcarina*, which secrete a hyaline shell and host diatom symbionts, increased under intermediate levels of pCO₂ (580 and/or 770 ppm) and decreased at a higher pCO₂ level (970 ppm). Net calcification of *Amphisorus*, which secretes a porcelaneous shell and hosts dinoflagellate symbionts, tended to decrease at elevated pCO₂. These different responses among the three species are possibly due to differences in calcification mechanisms (in particular, the specific carbonate species used for calcification) between hyaline and porcelaneous taxa, and to links between calcification by the foraminiferal hosts and photosynthesis by the algal endosymbionts. Our findings suggest that ongoing ocean acidification might favor symbiont-bearing reef foraminifers with hyaline shells at intermediate pCO₂ levels (580 to 770 ppm) but be unfavorable to those with either hyaline or porcelaneous shells at higher pCO₂ levels (near 1000 ppm).

Japan Geoscience Union Meeting 2011

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BPT002-07

Room:201B

Time:May 25 10:00-10:15

Speed of environmental change and ocean acidification

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Warm tropical ocean is analogy of those in Cretaceous and the Paleocene/Eocene transition. But both showed different features. In the late Albian, the deep sea temperature is estimated at about 15 degree C in the equatorial Pacific and atmospheric CO₂ concentrations is suggested to vary between about 2 and 5 times more than that at present atmospheric pCO₂. Larger oceanic alkalinity content can also be argued from the perspective of the production of calcifying organisms at the surface. Recently Zondervan et al. (2001) pointed out that an acidification of the ocean slows or prevents growth of calcifying primary producers. So the fact that we see some carbonate preservation during the Albian suggests that the ocean surface was sufficiently basic, despite higher atmospheric pCO₂, to allow growth of calcifying producers. In contrast, The P/En is characterized by large excursion in the oxygen and carbon isotope records due to the disintegration of methane hydrate and the most dramatic extinction of 35-50% of cosmopolitan benthic foraminifera in the past 100 m.y.. ODP Leg 199 Site 1220 provides a continuous sedimentary section across the P/E boundary in the carbonate-bearing sediments on 56-57 Ma oceanic crust. The methane is expected to be rapidly oxidized to carbon dioxide. Because of an acidic gas, CO₂ will lead to a reduction in deep-sea pH. A pH decrease was very likely responsible for the emergence of agglutinated foraminiferal fauna as calcareous fauna was eliminated by acidification at the P/E transition at Site 1220.

Keywords: Speed, nvironmental change, ocean acidification

BPT002-08

Room:201B

Time:May 25 10:45-11:15

Subtropical coral records of Northern Hemisphere climate variability and abrupt surface ocean salinity changes

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Subtropical corals provide an ultra-high resolution archive of past temperature and salinity variations at the sea surface. In contrast to tropical corals, which primarily document interannual variability associated with the El Niño-Southern Oscillation, subtropical coral records document mid- to high-latitude atmosphere-ocean variability. Due to their sub-seasonal resolution, these coral records allow to reconstruct climate variability for individual seasons such as boreal winter, which is still underrepresented in high-resolution proxy reconstructions of the last millennium. The northern Red Sea and the western North Pacific Ocean represent unique locations at the western and eastern margins of the Asian continent, where ocean currents transport warm tropical waters to higher latitudes, enabling coral reef growth at subtropical latitudes. Coral oxygen isotope records in the northern Red Sea (28-29 deg N) were shown to reflect a combined signal of aridity and temperature variations and document atmospheric variability of the Arctic Oscillation/North Atlantic Oscillation (AO/NAO). Coral Sr/Ca and U/Ca records in the western subtropical North Pacific Ocean (27 deg N) were shown to reflect temperature variations and document the oceanic variability of the Pacific (inter)Decadal Oscillation (PDO). Combined analysis of oxygen isotope and Sr/Ca (U/Ca) ratios in corals enables to reconstruct past changes in salinity at annual or higher resolution. Surface ocean salinity is a major component in climate dynamics. However, continuous salinity observations in the surface ocean are scarce prior to 1970, and the magnitude of salinity changes during the last centuries is largely unknown. A coral record from the western subtropical North Pacific indicates that an abrupt regime shift toward fresher surface ocean conditions in this region occurred during the early 20th century, between 1905 and 1910 A.D.. This abrupt freshening resulted from a combination of atmospheric and oceanic advection processes, including a weakening of the westerlies that transport dry continental air from Asia to the North Pacific. New coral Sr/Ca data from the northern Red Sea, in combination with oxygen isotopes, reveal that an abrupt regime shift toward fresher surface ocean conditions occurred in this region at the end of the Little Ice Age, between about 1850 and 1855 A.D.. Possible mechanisms for this abrupt freshening in the northern Red Sea, such as the re-organization of the Northern Hemisphere atmospheric circulation at the end of the Little Ice Age, will be discussed.

Keywords: coral paleoclimatology, oxygen isotopes, trace elements, Northern Hemisphere, Last centuries, Porites corals

BPT002-09

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Time:May 25 11:15-11:30

Tropical South Pacific Climate Variability Inferred from Tahiti Fossil Corals: IODP Expedition 310 -Tahiti Sea Level-

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Massive Porites corals, living in shallow waters of the tropical to subtropical oceans, precipitate annually-banded aragonite skeletons. These colonies provide robust chronological control and allow sampling at subseasonal resolution. Ages of fossil corals can be determined accurately by radiocarbon and uranium/thorium dating. Coral strontium/calcium (Sr/Ca) ratio has been widely used as a robust paleothermometer (e.g., Beck et al., 1992). Coral oxygen isotopes (d18O) reflect variations in sea surface temperature and seawater d18O 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., Tudhope et al., 1995). Therefore, coupled determinations of Sr/Ca and d18O in a coral enable the construction of proxy records for both sea surface temperature and salinity (e.g., Gagan et al., 1998, Felis et al., 2009). Fossil corals were shown to provide subseasonally-resolved proxy records of sea surface temperature and salinity for time windows of the Holocene, the last glacial period and older interglacials. However, most fossil reefs of glacial age are located today at water depths of >100 m, as a result of the lower sea level caused by ice sheet build-up during glacial periods (e.g., Bard et al., 1990). Therefore, it has been difficult to collect corals of glacial and deglacial age for paleoclimatic studies.

In 2005, the Integrated Ocean Drilling Program (IODP) Expedition 310 (Tahiti Sea Level), conducted by the European Consortium for Ocean Research Drilling-Science Operator using the mission-specific platform (DP Hunter), drilled the coral reef system off Tahiti (French Polynesia), an island located in the central tropical South Pacific (Camoin et al., 2007). During the expedition, massive fossil coral colonies, mostly of Porites, were recovered in-situ at depths of about 40 to 150 m below modern sea level. We present monthly resolved Sr/Ca and d18O records from well-preserved fossil corals recovered during the expedition (Asami et al., 2009). Our coral-based estimates of sea surface temperature and seawater d18O document thermal and hydrologic variations around Tahiti for selected time windows during the Quaternary, furthering our understanding of tropical South Pacific climate change that accompanied the sea-level change.

Keywords: coral skeleton, Tahiti, oxygen isotope composition, paleothermometer, tropical South Pacific, IODP

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BPT002-10

Room:201B

Time:May 25 11:30-11:45

PDO- and East Asia Winter Monsoon-related variability detected in coral records from 4 islands in the North Pacific Gyre

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Decadal variations in the East Asian Monsoon, Pacific Decadal Oscillation (PDO), as well as El Nino Southern Oscillation (ENSO), are considered to play an important role for the regional climate of the NW Pacific. Their interactions may evolve under the progress of the global warming. However, our knowledge on the future climate is limited mostly due to the lack of long-term and precise records. Here we compared the centennial-long $d^{18}O$ and Sr/Ca records in modern *Porites* corals from four sites along the North Pacific Gyre in order to examine past changes in the relationship among the major climate variability. By applying a possible regime shift detection method, it was revealed that evident PDO pattern dominated in the records from the mid-ocean sites, Ogasawara (27 6'N, 142 11'E) and Guam (13 35 N, 144 50 E). In contrast, corals from Ishigaki (12 10'N, 124 20'E) and Bicol (13 03'N, 124 01'E), proximal sites to the continent, indicated strong influence of the East Asian Winter Monsoon, with an evident decreasing trend in its decadal component. Interestingly, both Ishigaki and Bicol records during the 19th century showed significant covariation linked to the PDO, suggesting the PDO as the ruling variability all over the NW Pacific in the past. Weakening of the decadal component of winter monsoon intensity and PDO influence in the marginal sites of the NW Pacific may be associated to impaired Siberian High development during winter while the Aleutian Low remains unchanged under the global warming trend in the 20th century.

Keywords: Pacific Decadal Oscillation, East Asian Winter Monsoon, coral skeletal climatology, North Pacific Gyre, climatic regime shift

BPT002-11

Room:201B

Time:May 25 11:45-12:00

A 432-year-long paleoceanographic record in *Porites* coral in Kikai Island, Southern Japan

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In June 2009, we obtained a long modern core from a coral reef in Kikai Island, Japan. The island is located on the eastern boundary of the East China Sea in the northwestern Pacific. The coral core is approximately 440 cm long and dates back to 432 years (1578-2009 A.D.) including the Little Ice Age (LIA).

The LIA was a time when Europe and other regions neighboring the North Atlantic experienced colder conditions between the 16th to mid-19th centuries. It is reported that this was characterized by the most extensive period of mountain glacier expansion in the recent past. However, owing to the sparseness of the available proxy data during the LIA, there is still no consensus concerning its spatial pattern, timing and cause. In particular, there is a lack of records in the Pacific during the LIA. Thus our 432-year-long coral record from Kikai Island is a useful tool to understand the global-scale picture of climate change during the LIA.

Here we show a continuous 432-year record of sea surface temperature and other parameters based on coral paleo-climate proxies including trace elements, such as Sr, U, and Ba. We analyzed the skeletal elements using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This is a very powerful tool to handle long-term records since it requires a relatively brief experimental time compared with analysis using isotope dilution or thermal ionization ICP-MS. Based on these results, we discuss the paleoceanographic conditions in the northwestern Pacific during the LIA.

Keywords: Coral, Laser Ablation ICP-MS, Little Ice Age, East Asian Monsoon, Pacific Decadal Oscillation

BPT002-12

Room:201B

Time:May 25 12:00-12:15

Mg isotope fractionations 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 (Bohm 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

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(May 22-27 2011 at Makuhari, Chiba, Japan)

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BPT002-13

Room:201B

Time:May 25 12:15-12:30

Growth-rate influences on coral climate proxies tested by multiple clone culture experiment

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While coral-based climate reconstruction has been increasingly reported from many tropical sites, potential ambiguity of oxygen isotope thermometer intrinsic in biomineralization process attracts much attention, including so-called "vital effects", "growth-rate-related kinetic effect", "[CO₃²⁻] effect" and so on. Here we study growth-rate influences on skeletal oxygen and carbon isotope ratios based on a long-term culture experiment using *Porites australiensis* clone colonies. The oxygen isotope ratios of colonies showed negligible influence of growth rate over a large variation (2 - 10 mm yr⁻¹) based on the comparison of the seasonal minimum oxygen isotope values during summer. Intercolony variation in the winter extremes can be attributed to growth slowdown / cessation during the cold months. Positive shift in carbon isotope ratios for slower-growing corals was found, and it can be attributed to a kinetic behavior of calcification reaction. Seasonal fluctuation pattern in carbon isotope ratios did not correspond to light intensity. These lines warrant the signal recording ability of coral skeletal oxygen isotope ratios from a long-lived colony of clonal growth as paleo-climate archives, and pose implication for the proper interplication of carbon isotope ratio records.

Keywords: coral, oxygen isotope ratio, Sr/Ca ratio, skeleton

BPT002-14

Room:201B

Time:May 25 12:30-12:45

Nitrogen isotope of coral skeletons: A new proxy for nitrogenous nutrients in subtropical and tropical ocean

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Coral skeleton could be a high resolution recorder of past nutrient dynamics in tropical and subtropical ocean 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. However, nitrogen isotope of coral skeletons had problems to be a paleoenvironmental proxy. Reef corals uptake various nitrogen compounds such as (1) dissolved inorganic nitrogen (DIN) assimilated by zooxanthellae, (2) coral consumption of particle and dissolved organic nitrogen (PON, DON), and (3) nitrogen fixation of symbiotic cyanobacteria. In this study, we developed a new method for coral nitrogen isotope analysis and demonstrated which nitrogen sources controlled nitrogen isotope in coral skeletons. For nitrogen isotope analysis of coral skeletons, each 28 mg powder samples were decalcified. Then, all of organic matter in coral skeleton resolved to nitrate and converted into nitrous oxide to introduce into continuous-flow isotope ratio mass spectrometry. The standard deviation of sample measurements was less than 0.2 permil (1sigma). We compared distribution of coral nitrogen isotope with that of nitrate nitrogen isotope in Shiraho coral reef, Ishigaki Island. We sampled the coral cores from five coral colonies distributed from the mouth of Todoroki River that flow into the coral reef to the reef edge. Seawater samples for nitrate were taken at 50 m intervals along the parallel line of coral sampling. Distribution of coral nitrogen isotope was decreasing from +8.6 permil to +3.0 permil toward off-shore. Nitrogen isotope of nitrate was also decrease from +9.0 permil at river mouth to +2.3 permil at reef edge, which showed similar trends with coral nitrogen isotope. Nitrogen isotope of nitrate near the river mouth was originated from nitrate in river water (nitrogen isotope: +8.2 permil). This result suggested that nitrogen source for reef corals was mainly DIN in reef water, and coral skeleton recorded nitrogen isotope of nitrate. Time series of coral nitrogen isotope has a possibility to reconstruct seasonal to interannual variations of nitrate sources to coral reef such as land-derived nitrogen, nitrogen fixation, and upwelled nitrate. In this presentation, we also introduce application examples of a nitrogen isotope proxy to corals alive in coastal reef and open ocean.

Keywords: coral skeleton, nitrogen isotope, nitrate, terrestrial input, nitrogen fixation, upwelling

BPT002-P01

Room:Convention Hall

Time:May 25 14:00-16:30

Sources of plutonium to the tropical Northwest Pacific Ocean since the mid-20th century: a natural coral archive

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The main source of plutonium (Pu) to the Pacific Ocean is fallout from atmospheric nuclear weapons testing between 1945 and 1980. Other sources (e.g. discharges from the nuclear industry, radioactive waste dumping and burn-up of nuclear powered satellites) have only made a relatively minor impact. Between 1945 and 1980, 543 atmospheric weapons tests were carried out worldwide with an estimated total released fission energy yield of 189 Mt (UNSCEAR, 2000). Due to the well-defined spatial and temporal inputs of Pu and its physical and chemical properties, Pu can be used a tracer for various oceanic processes such as water mass transport, particle fluxes and scavenging (Lindahl et al., 2010 Mar. Environ. Res.). Massive Porites corals, living in tropical/subtropical shallow waters, have annually-banded aragonite skeletons with high- and low-density increments and grow rapidly, which can provide chronological control and allow high-resolution sampling. Because of such benefits, geochemical composition in coral skeletons has been most widely used as paleoclimate proxies for temperature and chemical composition of seawater in many studies. Plutonium is incorporated in the coral skeleton during growth with a constant relationship between Pu in the coral and Pu in the surrounding seawater. Therefore, the historical Pu signal in the surrounding seawater can be reconstructed by analyzing well-dated coral cores

Here we determine the total Pu activity concentrations and Pu atom ratios in the annual growth bands of an accurately dated modern coral core from Guam Island using multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to reconstruct the 1943-1999 Pu records in the tropical Northwest Pacific (Lindahl et al., 2011 Geochim. Cosmochim. Acta). The coral chronology was established in previous works (Asami et al., 2004 Palaeogeogr. Palaeoclimatol. Palaeoecol.; 2005 J. Geophys. Res.), in which coral $\delta^{18}O$ was determined with high-temporal resolution (biweekly to monthly) over the period 1787-2000. Dating of the coral was based on visual observations of soft X-radiograph images, which showed well-developed annual high- and low-density skeletal growth bandings. Selections relating to annual skeletal growth increments (approximately from January to December) were then assigned. The Pu atom ratios in the coral bands were used to distinguish the source(s) of Pu contamination and characterize the isotopic input from notable nuclear tests. Close-in fallout from the former US Pacific Proving Grounds (PPG) in the Marshall Islands and global fallout were identified as the two main sources. The Guam site was dominated by PPG close-in fallout in the 1950s. In addition, a higher Pu atom ratio was observed that could be attributed to fallout from the Ivy Mike thermonuclear detonation in 1952. The atom ratio decreased in the 1960s and 1970s due to increase in the global fallout with a low Pu atom ratio. Recent coral bands (1981-1999) are dominated by the transport of remobilized Pu, with high Pu atom ratios, from the Marshall Islands to Guam Island along the North Equatorial Current. This remobilized Pu was estimated to comprise 69% of the total Pu in the recent coral bands, although its contribution was variable over time.

Keywords: coral skeleton, annually-dated bands, plutonium, tropical Pacific Ocean, nuclear weapons test, North Equatorial Current

BPT002-P02

Room:Convention Hall

Time:May 25 14:00-16:30

Variation of expression of Ca^{2+} -ATPase and skeletal growth of cultured corals (*Porites australiensis*)

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Trace elements, such as Sr/Ca and Mg/Ca ratios, of coral skeleton is a commonly used for reconstructing paleoenvironment, especially it has been used to estimate past sea surface temperatures. However the processes controlling trace elements incorporation in coral aragonite are poorly understood and recently it has been reported that skeletal growth might be altered variation of trace element rather than temperature. In zooxanthellate corals, Ca^{2+} is transported transcellularly to the calcification site by both calcium channels and by the carrier protein Ca^{2+} -ATPase. The pump enzyme Ca^{2+} -ATPase has a higher affinity for Ca^{2+} than for Sr^{2+} , and the Ca^{2+} -ATPase pump is activated by exposure of the polyp to light, suggesting that the skeletal Sr/Ca of rapid calcifiers might be lower than that of slow calcifiers because of differences in the Sr/Ca ratio in the bulk calcifying solution. However, there has been no study investigating the relationship between Ca^{2+} -ATPase and Sr/Ca and Mg/Ca in the skeleton of *Porites* coral which is dominantly used for the study on paleoclimate. In this study, *Porites australiensis* were cultured under controlled temperature and pH settings and expression level of Ca^{2+} -ATPase in each cultured corals was estimated. Also Sr/Ca and Mg/Ca ratios in the same coral colony were analyzed. We will discuss the relationship between skeletal growth rate and expression of Ca^{2+} -ATPase.

Keywords: coral skeleton, Ca^{2+} -ATPase, growth rate, culture

BPT002-P03

Room:Convention Hall

Time:May 25 14:00-16:30

Biological controls on Sr/Ca, Ba/Ca and Carbon isotope in freshwater pearl mussel *Hyriopsis* sp.

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Biogenic skeletons of marine and freshwater organisms are important archives of paleoenvironmental information. Bivalves occur in various environments from polar region to low latitude region, in freshwater and marine, and have carbonate shells which are formed by addition growth. So they have the potential to contain the paleoenvironmental information within their isotope and elemental compositions. Freshwater environment sensitively reacts to the climate changes and is well known as a role of the material transportation from continental regions to seawater following chemical and physical weathering. So freshwater bivalves gather much attention as time-series paleoenvironmental archives. By this time, there are many reports on elemental and isotope fractionation of marine bivalves, but little is known about freshwater bivalves.

In this study, we analyzed the trace element (Sr/Ca and Ba/Ca) and stable isotope (oxygen and carbon) ratios of a commercially cultured freshwater pearl mussel *Hyriopsis* sp. shells (*Bivalvia* Unionidae) and ambient water in Lake Kasumigaura. Our aim was to assess what is the factors influencing Sr/Ca, Ba/Ca, and carbon isotope ($d^{13}C_{SHELL}$) ratios freshwater bivalve shells.

Element ratios (Sr/Ca and Ba/Ca) in the three shell specimens were measured with a quadrupole ICP-MS and stable isotope ratios ($d^{18}O_{SHELL}$ and $d^{13}C_{SHELL}$) with an isotope ratio mass spectrometer. Shell structures were observed by the microscope and by inspection of the external shell. Trace element ratios (Sr/Ca and Ba/Ca) of water samples were calculated from the Ca, Sr and Ba concentrations, which were measured with an ICP-AES. $d^{13}C_{DIC}$ was measured by isotope ratio mass spectrometer. We compare the element/isotopic profiles of shells among various parameters such as water temperature, annual growth rate, and elemental/carbon isotope ratios of ambient water.

Sr/Ca ratios of water remained relatively constant throughout years. Clear annual Sr/Ca cycles of shell suggest that Sr was incorporated into the shells at a high rate during warm seasons. If the Sr incorporation is governed by thermodynamic control, Sr/Ca profiles show a negative correlation with ambient temperature. However, between Sr/Ca and $d^{18}O$ profiles negative correlation is found. That indicates primary controlling factor of a Sr incorporation into *Hyriopsis* shell is not thermodynamic partition. All three examined shells showed a clear decrease in annual average Sr/Ca with age. Inter- and intra-annual trends suggest that Sr incorporation was higher during periods of faster growth.

The Ba concentration and the Ba/Ca ratio of ambient water showed neither an annual periodicity nor a seasonal trend. In contrast to the findings of an inorganic aragonite precipitation experiment, Ba/Ca was positively correlated with ambient temperature. In addition, Ba/Ca and Sr/Ca ratios were positively correlated with each other. These results suggest that not thermodynamic equilibrium partitioning but the shell growth rate controls Ba incorporation into *Hyriopsis* shells.

The $d^{13}C_{DIC}$ showed a wide range fluctuation from -14.63 to -8.62 per mill. The enrichment of $d^{13}C$ was observed in summer samples. On the other hand, the $d^{13}C_{SHELL}$ varied mainly from -12 to -9 per mill and its pattern was not symmetric and sinusoidal like the water temperature profile. A carbon isotopic mixing equation presented by McConnaughey et al. [1997] describes the combination of respired and environmental carbon incorporated into the precipitating carbonate. The calculated values of $d^{13}C_{SHELL}$ under equilibrate with $d^{13}C_{DIC}$ are ranged from -11.93 to -9.41 per mill and are consistent with observed shell data. Thus, the primary factor controlling the value of $d^{13}C_{SHELL}$ is not the respired effects but the carbon isotope fluctuations of ambient DIC.

*McConnaughey, T. A., J. Burdett, J. F. Whelan, and K. P. Charles (1997), *Cosmochim. Acta*, 61, 611-622.

Keywords: freshwater bivalve, Sr/Ca, Ba/Ca, Carbon isotope