Reconstruction of Permian-Triassic ocean redox conditions based on laminae preservation and pyrite framboids from the pelagic Panthalassic Ocean

Akane Mizutani[1], *Satoshi Takahashi[1], Jun Ishida[1], Shinji Yamamoto[1], Masayuki Ikeda[2], Kazumi Ozaki[3], Megumi Saitoh[4], Nozomi Suzuki[4], Ryuji Tada[1]

1.Department of Earth and Planetary Science, University of Tokyo, 2.Shizuoka University, 3.Atmosphere and Ocean Research Institute.University of Tokyo, 4.Division of Paleoenvironment and Paleoecology Department of Geology and Paleontology National Museam of Nature and Science

Widespread oceanic anoxia has been implicated as an important factor in the Permian -Triassic mass extinction and the delayed recovery of Early Triassic marine ecosystems. This study investigates the composite columnar section of the deep-sea Permian-Triassic boundary section preserved in the accretionary complex in Northeast Japan. This columnar section consists of the Upper Permian bedded chert and siliceous claystone, and overlying the end-Permian to earliest Triassic black claystone. The mass extinction horizon places in the base of the black claystone, and top of the reconstructed black claystone corresponds to 226.7 kilo year after the extinction event based on sedimentation rate estimated by Takahashi et al. (2014). The careful observation of polished cross sections identified thinly laminated structures in the end-Permian to earliest Triassic claystone interval. Our observation on the polished specimen revealed small and well sorted framboids (average diameters are 4 μm and their standard deviations are 1.1 μm) suggesting that sulfidic water column prevailed during the end Permian mass extinction and subsequent time interval corresponding to the overlying 30 cm. Well preserved laminae occur within the same stratigraphic interval, suggesting stagnant benthos activity due to anoxic bottom water condition under sulfidic water column. On the other hand, well preserved laminae appear again in the overlying earliest Triassic horizon, but size of pyrite framboids are not so small (average diameters are more than 7μm), suggesting anoxic but non-sulfidic water column condition. These facts indicate water column sulfidic episodes sustained for less than 50 kilo years in the pelagic Panthalassa.

Keywords: Permian, Triassic, Mass extinction, Pelagic deep sea, Pyrite Framboids

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Redox conditions of late Early Triassic oceanic region around the South Kitakami Microcontinent

*Kazuko Yoshizawa[1], Satoshi Takahashi[1], Masayuki Ehiro[2], Takanobu Tsuihiji[1], Shun Muto[1], Takayuki Tashiro[1], Tsuyoshi Iizuka[1], Masato Tanaka[1], Yoshio Takahashi[1]

1.Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 2.The Tohoku University Museum, Tohoku University

After the end-Permian mass extinction (EPME), biotic recovery required more than 5 million years during the Early Triassic. Evidence of recovery such as the emergence of complex ecosystems and high biodiversity appeared in the late Early Triassic to Middle Triassic (Chen and Benton, 2012). The fossil evidence of a complex food chain was reported from shallow-marine strata of late Olenekian (Spathian), late Early Triassic age, in the South Kitakami Microcontinent that was located in the low-latitude Tethys-Panthalassa border (Ehiro, 2001). These strata belong to the Osawa Formation in the South Kitakami Belt, now distributed in Northeast Japan, and are characterized by well-preserved parallel laminae and the occurrence of the oldest ichthyosaurs (Shikama et al., 1978; Yamanaka and Yoshida, 2007). However, the depositional environment of these strata has been poorly understood. The present study aims to reveal detailed redox conditions in the Spathian shallow marine region around the South Kitakami Microcontinent based on observation of the sedimentary structure (laminae preservation), mode of occurrence of pyrite, and geochemical proxies (redox-sensitive elements). Referring to the type columnar sections described by Kamata and Takizawa (1992), four lithologic sections corresponding to the lower, middle, and upper parts of the Osawa Formation were identified. From these sections, 49 rock samples were collected for thin sections, polished specimens, and geochemical analyses (ICP-AES and ICP-MS). Observation of polished rock specimens indicates that laminae were well-preserved in mudstone from the middle part of the Osawa Formation whereas laminae were not visible in the lowermost and uppermost parts. These trends indicate that the middle part of the Osawa Formation was deposited under conditions of lower benthos activity than the lowermost and uppermost parts. Mode of occurrence of pyrite in the studied sections is divided into euhedral pyrite and aggregations of framboidal pyrite, of which the latter are formed around organic matter. These types of pyrite were observed in almost all the horizons. These modes of occurrence indicate that pyrite formed within the sediment, suggesting a reductive condition during their diagenesis (Wignall et al., 2010; Bond and Wignall, 2010; Gallego-Torres et al., 2013; Wang et al., 2013). Measured concentrations of redox-sensitive elements from bulk samples provide further information on the redox condition. V and U show values close to average upper continental crust (AUCC) value (Taylor and McLennan, 1985) throughout the study sections. Mo values are lower than AUCC in most horizons, but slightly high in the middle part of the Osawa Formation, which is consistent with laminae preservation. Among the modern examples of various redox conditions (Algeo et al., 2009; Tribovillard et al., 2012), the combination of U and Mo concentrations in the Osawa Formation is in agreement with those from the dysoxic condition (not sufficiently oxic but not reaching a strong reductive condition). Accordingly, the depositional environment of the Spathian shallow marine region around the South Kitakami Microcontinent is regarded as possibly reductive, as suggested by low benthic activity, and remaining at the level of a dysoxic condition. It is implied that, after the EPME, recovery of complex marine ecosystems during Early Triassic proceeded under such mildly reducing oceanic environment.

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Keywords: late Early Triassic, South Kitakami, redox condition, Osawa Formation

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Paleoenvironmental reconstruction by organic matter analyses of Triassic-Jurassic highly mature sediments from North America and Inuyama, Japan.

*Yuki Tateshita[1], Ken Sawada[1], Masayuki Ikeda[2]

1.Department of Natural History Sciences, Faculty of Science, Hokkaido University, 2.Faculty of Science, Shizuoka University

Paleoenvironmental reconstruction has been extensively performed using sedimentary organic matter, but paleoenvironmental and paleontological records were hardly preserved in ancient sediments that are of high maturity. In highly mature ancient sediments, a very small quantity of molecular fossils (biomarkers) in solvent extractable components (bitumen) and insoluble organic matter (kerogen, geomacromolecule) are possibly applicable as paleoenvironmental and paleoecological tools. The kerogen has been known to be well preserved as major organic component in ancient sediment. In the present study, we analyzed Triassic-Jurassic highly mature sediments from North America and Inuyama, Japan to improve biomarker and kerogen analyses for reconstructing paleoenvironments, and to examine variations of terrestrial and marine environments during the Triassic-Jurassic.

We used 1) lacustrine sediments (black shales and red sandstones) deposited during Triassic-Jurassic boundary from North America, and 2) Anisian to Toarcian (T-OAE2) pelagic sediments (black shales and cherts) of accretionary zone in Inuyama. Whole rock samples were crushed to a ‘rice’-sized (diameter 2–5 mm) grain in an agate mortar. Crushed rock samples (5–10 g) were extracted with ultrasonication, by successive treatment with organic solvents. Thereafter, residues were treated sequentially in a water bath shaker with HCl and HF. We analyzed pyrolysis and thermochemolysis of kerogen by using GC-MS equipped Curie-point pyrolyzer. Thermochemolysis was performed with tetramethylammonium hydroxide (TMAH).

Organic matter in sediments from both North America and Inuyama are confirmed to be of high maturity that were reached oil window. We identified β-carotane (lacustrine algae origin) and 2-methyl hopanes (marine cyanobacteria origin) in sediments from North America and Inuyama, respectively. Interestingly, phenol compounds released from kerogens are mainly detected in black shale from the East Berlin Formation in Hartford basin. These results suggest that terrestrial plant-derived materials were more efficiently transported and deposited by environmental change.

Keywords: Triassic-Jurassic boundary, biomarker, kerogen, termochemolysis, highly matured sediment

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Environmental change and morphological variability in mid-Cretaceous planktic foraminifer, *Muricohedbergella delrioensis*

*Eri Takahashi[1], Kazuyoshi Moriya[1]

1.Dep. Earth Sciences, Waseda University

The mid-Cretaceous climate maximum (CCM) (approximately 90–98 Ma) is one of the typical examples of the green house intervals. Comparing to the modern Earth system, there must be significantly different interactions between Earth's surface environment and marine biota in this extreme condition. Oceanic Anoxic Events (OAEs), which are accompanied by extinction of surface dwelling microorganisms, e.g. planktic foraminifers, radiolarians, etc., are one of the well known perturbations in the CCM (e.g. Leckie et al., 2002). The other minor events have also been identified in the CCM. For example, mid-Cenomanian Event (MCE) is considered as a precursor event of OAE2 at the Cenomanian/Turonian boundary. However, precise interactions between oceanic surface environment and planktic foraminifers at the MCE are still poorly understood.
We here examined morphological variability, the maximum diameter and the total number of chambers, of the mid-Cretaceous planktic foraminifers, *Muricohedbergella delrioensis*, across the MCE. The specimens were obtained from ODP Site 1258 at Demerara Rise, equatorial Atlantic. Carbon and oxygen isotopic data from the same samples we utilized, published by Moriya et al. (2007), enabled us to compare our results on morphological variability with those isotopic records. The maximum diameter becomes smaller in the sequence younger than the MCE, which is accompanied by decrease in the total number of chambers within a single individual. According to the modern cultivation experiments, the maximum dimeter and the total number of chambers become greater with increase in feeding frequency (Bé et al., 1981). These results indicate that *M. delrioensis* older than the MCE might have more feeding opportunity than those younger than the MCE. Additionally, we analyzed a coiling (sinistral/dextral) ratio of *M. delrioensis*. The coiling ratio shows a significant correlation with the oxygen isotopic composition, hence temperature. The correlation between the coiling ratio of *M. delrioensis* and temperature has also been reported by Desmares et al. (2016). Our results reconfirm their implication. Considering modern examples showing genetic discrepancy between sinistral and dextral morphotypes in the species having a correlation between a coiling ratio and ambient temperature (Darling et al., 2006), the coiling direction of *M. delrioensis* might indicate existence of potential cryptic (sub)species.

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Keywords: Cretaceous, Planktic foraminifer, Morphological evolution

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Evaluation of ‘paleo’ red-tide during the mid-Cretaceous Oceanic Anoxic Event (OAE) 2.

*Takuto Ando[1], Ken Sawada[1], Reishi Takashima[2], Hiroshi Nishi[2]

1.Department of Natural History Sciences, Faculty of Science, Hokkaido University, 2.Tohoku University Museum, Tohoku University

Red-tide is known as blooming of marine phytoplankton, especially dinoflagellate, under eutrophication, and severely influence on aquatic resources as natural toxins, harmful effects, and depletion of dissolved oxygen. Moreover, evidence for ‘paleo’ red-tide in the warming period can give understands for occurrence of red-tide associated with global warming in future. Dinoflagellate *Apectodinium* increased during the Paleocene/Eocene Thermal Maximum (PETM) characterized by global warming (Slujis et al., 2007). However, micropaleontological investigation of dinocyst demonstrated that productivity of dinoflagellate presumably decreased as a result of the warming during the mid-Cretaceous Oceanic Anoxic Event (OAE) 2 (Pearce et al., 2009). Paleothermometer such as TEX_{86} indicate the OAE2 include twice warming and once cooling phases (Forster et al., 2007), and detailed carbon isotope stratigraphy in that interval could enable to comparison between different localities. In this study, we focus on dinoflagellate biomarker (triaromatic dinosteroid) and very small dinoflagellate-like acritarchs, and compare these trends between the Yezo Group (YG; Hokkaido, Japan) and Vocontian Basin (VB; SE France) sediments. Values of dinoflagellate production proxy (triaromatic dinosteroid index; TADS) increase at twice during the OAE2 interval, the onset of 1st build-up phase and from the Trough to 2nd build-up phases, in both YG and VB sediments. These results are synchrous with global warming trend estimated by TEX_{86} and suggest elevated contribution of dinoflagellate for primary production in different two sections located at NW Pacific and Tethys. Huber et al. (1999) reported ‘collapse’ of vertical stratification during the warming phase of the OAE2. These changes related to global warming presumably caused enhanced nutrient supply from intermediate and bottom water masses and global expansion of suitable condition for dinoflagellate. Moreover, marine palynomorphs are mainly composed of very small (< 20μm diameter) spiny acritarchs (*Micrhystridium*) in the higher TADS samples in both two sections. It was reported that *Micrhystridium*-accumulated fraction of the Cambrian sediments have high concentration of dinosteane (Talyzina et al., 2000), although the origin of these acritarchs are uncertain. These acritarchs are similar to Gonyaulacoid dinocyst in the morphology and smaller than these cysts, which suggest original species of these acritarch are autotrophic and r strategist such as modern red-tide species. From these results, it is implied that frequent occurrences of red-tides by small dinoflagellate were triggered by global warming and eutrophication, and promoted efficient deposition of organic matter and consequently expansion of anoxic water mass.

Keywords: Cretaceous, Dinoflagellate, red-tide, Oceanic Anoxic Events, acritarch

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Draught in the low latitudes and cooling by global soot aerosols led to the mass extinction at the Cretaceous-Paleogene boundary

*Kunio Kaiho[1], Naga Oshima[2], Kouji Adachi[2], Yukimasa Adachi[2], Takuya Mizukami[1], Megumu Fujibayashi[3], Ryosuke Saito[1]

1.Graduate School of Science, Tohoku University, 2.Meteorological Research Institute, Tsukuba, Japan, 3.Ecological Engineering Laboratory, Tohoku University

The extinction of the dinosaurs at the Cretaceous/Paleogene boundary led to the macroevolution of mammals and appearance of humans. The current hypothesis for the extinction of the dinosaurs is that an asteroid impact at Chicxulub, present-day Mexico, formed condensed aerosols in the stratosphere, which caused the cessation of photosynthesis and global near-freezing conditions. Here, we propose a new hypothesis that latitude-dependent climate changes caused by the soot aerosols in the stratosphere could consistently explain both the extinction of the dinosaurs and the survival of the crocodilians. Our geochemical data show that stratospheric soot aerosols were ejected from the oil-rich area by the asteroid impact and spread globally, coinciding with the devastation of land plants. Our model calculation and biological interpretation indicate that the soot aerosols caused sufficiently colder climates at the mid-high latitudes for several years, inducing the extinction of the dinosaurs and crocodilians in those areas. However, the climate still remained warm enough for their survival and the weak sunlight was still sufficient for plant photosynthesis at low latitudes, but the substantial decreases in precipitation occurred at low latitudes over several years resulting in draught, which may have affected their eventual extinction or survival.
More than 90% species of planktonic foraminifera, which inhibited the global seas, became extinct coinciding with the asteroid impact at the Cretaceous/Paleogene boundary. Our model calculation indicates that the soot aerosols caused 7–11°C, 4–8°C, and 3–6°C cooling at most in the 2 m, 50 m, and 100 m water depths in the low-middle latitude ocean. The rapid global cooling may have caused the marine extinctions.

Keywords: mass extinction, dinosaurs, planktonic foraminifera, Cretaceous-Paleogene boundary, soot, climate

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Ontogenetic stable isotope records of Eocene planktic foraminifers: Comparison to modern symbiotic species observation

*Haruka TAKAGI[1], Kazuyoshi Moriya[2], Toyoho Ishimura[3]

1.Graduate School of Creative Science and Engineering, Waseda University, 2.Department of Earth Sciences, Waseda University, 3.National Institute of Technology, Ibaraki College

Many planktic foraminiferal species in the Eocene epoch are thought to have symbiotic algae in their cytoplasm. Detection of photosymbiosis is achieved from ontogenetic isotopic signature; the $\delta^{13}C$ of symbiont-bearing species yields more ^{13}C-enriched values than the asymbiotic species, reflecting selective incorporation of ^{12}C by the symbiont photosynthesis. Because foraminiferal tests grow intermittently by adding a new chamber on the preformed test, each chamber holds information of the symbiont photosynthesis at the time of the chamber calcification. Recently, we have proposed chamber-by-chamber isotope analyses to investigate ontogenetic development of the photosymbiotic relationship. Here, we show the preliminary results of ontogenetic trends of isotopic values of Eocene species, and discuss the profiles from our observational results of cultured modern species.
Three Eocene species recovered by IODP Exp. 342 (U1407) were analyzed to examine ontogenetic isotopic profiles; *Morozovella*, *Acarinina* (symbiotic), and *Subbotina* (asymbiotic). Each individual test was dissected into chambers by using a micro-blade, then analyzed by the customized continuous-flow mass spectrometry system that can measure micro-volume carbonate as small as a single chamber.
The $\delta^{13}C$ values of *Morozovella* and *Acarinina* tended to show the ontogenetic positive shifts until the penultimate chamber. Then the final chamber showed more ^{13}C-depleted $\delta^{13}C$ value drastically by 0.5–1.0 ‰. In contrast to these species, *Subbotina* showed comparatively ^{13}C-depleted $\delta^{13}C$ values whole through its ontogeny. We can say that the progressive ^{13}C-enrichment of the chambers $\delta^{13}C$ with growth, excluding the last chamber, seen in *Morozovella* and *Acarinina* probably reflected the increase of the effect of symbiont photosynthesis. The contrasting relatively constant $\delta^{13}C$ values through ontogeny seen in *Subbotina* is in good agreement with the known asymbiotic nature of this species. The notable thing is that the last chamber of the two symbiotic species showed comparable $\delta^{13}C$ value to that of *Subbotina*. It indicates that the two symbiotic species had already lost their symbionts, or their photosynthesis was not active at the time of the last chamber calcification.
Our recent culture experiments of modern species (*Globigerinoides sacculifer* and *Globigerinella siphonifera*) to investigate symbiont photosynthesis through ontogeny showed that the chlorophyll content of the foraminifers, thus the symbiont content, drastically decreased to almost zero at the time or just before the gametogenesis. It sometimes occurred during the last chamber calcification. These modern observations indicate that the more ^{13}C-depleted $\delta^{13}C$ value in the final chamber in Eocene symbiotic species could reflect the digestion or lysis of symbionts. If so, it can be said that each individual had to acquire the symbionts from the environment at some time during the ontogeny as the modern obligate symbiotic species do.

Keywords: Eocene, Planktic foraminifer, Carbonate stable isotopes, Photosymbiosis

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Radiolarian faunal turnover across the early/middle Miocene boundary in the eastern equatorial Pacific Ocean

*Shin-ichi Kamikuri[1]

1.Faculty of Education, Ibaraki University

The lower to middle Miocene sequence was drilled at IODP Site U1335 (5°18.735'N, 126°17.002'W, water depth 4328 m) in the eastern equatorial Pacific Ocean. In the modern ocean, Site U1335 is located under the North Equatorial Current, and the biogenic silica fluxes to the sea-floor sediments are comparatively high in this area. The sediments recovered from Site U1335 are predominantly nannofossil ooze with siliceous microfossils such as diatoms and radiolarians.
230 morphotypes of radiolarians were identified at this site. Because the low latitude species commonly occurred at this site, the tropical Cenozic zonation of radiolarians proposed by Sanfilippo and Nigrini (1998) was adopted. The studied sequence was divided into four zones, consisting of the RN2 (the *Stichocorys delmontensis* Interval Zone), RN3 (the *Stichocorys wolffii* Interval Zone), RN4 (the *Calocycletta costata* Interval Zone), and RN5 (the *Dorcadospyris alata* Interval Zone) at Site 1335. In the standard zonal scheme, the early/middle Miocene boundary corresponds to the top of C5Cn.1n with an age estimate of 16.268 Ma (Pälike et al., 2010; Gradstein et al., 2012). Hence, this boundary was placed at 189.6 mcd at Site 1335.
Radiolarian fauna was divided into three assemblages based on variations in the composition of dominant species: an early Miocene assemblage (20.0 to 16.8 Ma), a transitional assemblage (16.8 to 13.4 Ma) and a middle Miocene assemblage (13.4 to 12.0 Ma). The early Miocene assemblage is characterized by two dominant species of *S. delmontensis*, *S. wolffii,* and *Tholospyris anthophora*. The transitional assemblage consists of three dominant species of *S. delmontensis, Calocycletta robusta* group, and *T. anthophora.* The four dominant species of the middle Miocene assemblage present in this assemblage are *Stylodictya* sp. A, *Lophocyrtis aspera*, *Disolenia* spp. and *Collosphaera* spp. The most significant faunal turnover of radiolarians is marked at the boundary between the transitional/middle Miocene assemblages.

Keywords: radiolaria, Miocene, eastern equatorial Pacific

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Geologic age of the whale fossil-bearing calcareous float concretion from the Hae River, Hokkaido, Japan, based on radiolarian and diatom analyses

*Isao Motoyama[1], Toshiaki Maruyama[1], Tomohiro Nishimura[2], Kazuhiko Sakurai[2], Akane Kasukawa[1], Kenji M. Matsuzaki[3]

1.Department of Earth and Environmental Sciences, Yamagata University, 2.Hobetsu Museum, 3.Geological Survey of Japan, AIST

Radiolarian and diatom fossils have been used to constrain the age of calcareous concretion collected from the Hae River, Hidaka Town, southern central Hokkaido, Japan. The calcareous concretion contains whale fossils and was discovered as a float during the riparian works in 2005. Recovered radiolarian and diatom assemblages indicate the *Lipmanella redondoensis* Zone (9.0 to 7.4 Ma) and the *Rouxia californica* Zone (7.7 to 6.5 Ma), respectively. Thus the concretion can be dated as 7.7 to 7.4 Ma. This age is concordant with the age range of the Nina Formation which is distributed near the locality of the concretion and was previously dated as ca. 10.1 to 3.5 Ma based on the diatom stratigraphy in the surrounding area. We will examine some samples collected from the Nina Formation exposed along the Hae River to confirm the origin of the concretion.

Keywords: whale fossil, Radiolaria, Diatom

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The extinct pinniped *Allodesmus* (Mammalia: Carnivora) from the Miocene of Hokkaido, northern Japan, and its implications for phylogeny and postcranial morphology

*Wataru Tonomori[1], Hiroshi Sawamura[2], Tamaki Sato[3], Naoki Kohno[1,4]

1.Graduate School of Life and Enviromental Sciences, University of Tsukuba, 2.Ashoro Museum of Paleontology, 3.Department of Astronomy and Earth Sciences, Tokyo Gakugei University, 4.Department of Geology and Paleontology, National Museum of Nature and Science

Allodesmus is an extinct pinniped that is known from the Middle and Late Miocene of the North Pacific and belongs in the family Desmatophocidae, which became extinct in the early Late Miocene. According to the previous studies, *Allodesmus* has at least five species and is divided into three subgroups: i.e., “Basal”, “Broad head” and “Long head” subgroups. However, the phylogenetic study of *Allodesmus* has been limited until now, and therefore, the evolutionary history of the Desmayophocidae is also still unclear. Moreover, a study of postcranial bones of *Allodesmus* nor the Desmatophocidae is almost nothing because of insufficient skeletal material for those taxa.

In this study, we described a specimen of *Allodesmus* (AMP25) collected in 1991 from the Middle Miocene Okoppezawa Formation, Hokkaido, northern Japan. AMP25 contains 83 bones consisting of a skull, fore- and hind-limbs, ribs and vertebrae. To demonstrate the paleobiological importance of this specimen, we performed cladistic analysis to locate the new specimen in the phylogenetic framework. We used PAUP 4.0 and Mesqueite 3.03, and then, we based on 97 morphological characters and 15 species, with the enigmatic musteloid *Potamotherium*, and the basal pinnipeds *Enaliarctos* and *Pteronarctos* as out-group.

As a result, previously recognized “Long head” subgroup was supported as a monophyletic group, but the “Broad head” subgroup was not recognized as a monophyletic group in our analysis. As for AMP25, it didn’t have any synapomorphy of the “Long head” subgroup and nested with *Allodesmus packardi* and *A. naorai* as unresolved polytomy. On the other hand, AMP25 has an autoapomorphy in that the supraorbital process is located at the anterior portion of the interorbital bar in our analysis. From the above and additional observations, we have concluded that AMP25 belongs to an unknown species. Importantly, some postcranial bones of AMP25 also show very different character combination, differentiating it from *A. kernensis* among the Desmatophocidae. In particular, morphology of the calcaneum (that is one of the component of the ankle bones) of AMP25 is remarkably distinguishable from that of *A. kernensis*. For example, the calcaneum of AMP25 is more slender than that of *A. kernensis*, and its peroneal tubercle is more developed than that of *A. kernensis*. These characters were distinguishable not only among the species of *Allodesmus* but among all other pinnipeds. It means that some postcranial characters other than characters that we used for the phylogenetic analysis in this study also have potential phylogenetic values as well as its functional importance.

Keywords: pinnipeds, Allodesmus, phylogeny, postcranium

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Evaluation of early diagenetic influence on nitrogen isotopes within fossil amino acids: Towards estimation of ancient food webs

*Daijiro Hagehashi[1], Robert Jenkins[2], Akiko S. Goto[2], Yoshito Chikaraishi[3], Takashi Hasegawa[2]

1.Division of Environmental Science and Engineering, Graduate school of Natural Science and Technology, Kanazawa University, 2.School of Natural System, College of Science and Engineering, Kanazawa University, 3.Japan Agency for Marine-Earth Science and Technology

Compound-specific isotope analysis (CSIA) of nitrogen within amino acids is a relatively new tool to estimate the tropic level of organisms (Chikaraishi et al. 2009; Limnol Oceanogr Meth). It would be applicable as a new technique to the trophic and ecological study of fossils. Hard parts (e.g. shells and bones) usually contain amino acids, which can be extracted and identified in a number of previous studies. However, amino acids in fossils would be influenced by diagenesis, including thermal maturation, racemization, and degradation. Thus, it is important to evaluate whether or not the amino acids within the shell keep the original isotopic composition of organisms. Thus, this study aim to evaluate consistency of the estimated trophic level based on the CSIA of amino acids in shells with respect to early diagenesis. We use modern and fossil *Turbo cornutus* (Gastropoda), which is presumably primary consumer, i.e. trophic level should be 2.0. Fossil *Turbo* were obtained from Yuigahama archaeological site (Kanagawa Pref., Kamakura Era, 13-14th century, ca. 800 years ago) and Torihama archaeological site (Fukui Pref., Jyomon Era, ca. 4000 years ago). The modern materials were obtained from Hakui, Ishikawa and Kaneda, Chiba. Some of the modern materials were heated at 200 and 400 °C in oven.
Prior to the isotope analysis, the samples were examined in several ways, including X-ray diffraction pattern analysis, SEM observations of shell microstructures, D/L ratio of amino acids within the shells to evaluate the preservation of the samples. *Turbo cornutus* shell was composed of three layers. Our observation reveal that the outer layer of the shell contaminated by encrusting biota. Middle layer, consists of nacreous structure, sometimes had erosion by microbes. Moreover, microstructures of the modern sample heated at 400 °C were partially dissolved and recrystallized, and no amino acid was found in there. Amino acid composition in these aged samples was similar to the clean modern ones. Based on those results, we used several fossil samples, which remained original microstructures, for the isotope analysis. We also analyzed modern samples, including those heated at 200 °C and invaded by microbes.
As a result, all the samples analyzed show around 1.9-2.3 for the trophic level estimated based on the CSIA of amino acids. It is indicated that the early diagenesis wouldn't affect to the nitrogen isotopes of amino acids in shells at least for 4000 years.

Keywords: Trophic level, fossil, amino acids, stable nitrogen isotope ratios, early diagenesis

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Effects of carbonate chemistry and metabolism induced by ocean acidification on stable isotope fractionation in molluscan shell carbonate

*Kozue Nishida[1,2], Masahiro Hayashi[3], Akari Nagoshi[4], Hodaka Kawahata[4], Mizuho Sato[1,5], Atsushi Suzuki[1]

1.National Institute of Advanced Industrial Science and Technology, 2.The University Museum, UTokyo, 3.Marine Ecology Research Institute, 4.AORI, UTokyo, 5.Asahi Geo-Survey Co. Ltd

Stable oxygen and carbon isotope compositions of biogenic carbonate have been widely used for many paleoclimate, paleoecological, and biomineralization studies. Oxygen isotope compositions of carbonate, a commonly used proxy of seawater temperature and oxygen isotope compositions of seawater, are also affected by seawater carbonate chemistry, but the knowledge of its dependency on stable isotope fractionation of both synthetic and biogenic aragonite is still limited. It has also been reported that carbon isotope compositions of molluscan shells are affected by carbon isotope compositions of seawater carbonate chemistry and metabolic carbon. Several studies reported effects of ocean acidification on metabolism of molluscs, and thus the metabolic changes could potentially influence the stable isotope compositions of metabolic carbon. Here, we have focused on stable oxygen and carbon isotopic responses of moluscan shells to CO_2-driven seawater acidification for understanding of the contribution of environmental and metabolic effects. Two species of clams (*Scapharca broughtonii*, *Pseudocardium sachalinense*) and two species of abalones (*Haliotis discus discus*, *Haliotis gigantea*) were cultured in seawater chemically manipulated to vary pCO_2 condition using CO_2 control system of the Demonstration Laboratory, Marine Ecology Research Institute (MERI), in Kashiwazaki City, Niigata Prefecture, Japan.

Stable oxygen isotope compositions of *S. broughtonii* had significant negative correlations with pH (-0.48‰ /pH, at 17°C; -0.61‰ / pH, at 25 °C). These of *P. sachalinense*, *H. discus discus*, and *H. gigantea* showed non-significant relationships with pH and small variations (within 1 per mil). The oxygen isotope fractionation in four species of our study are smaller than that of synthetic calcite (-1.42‰ / pH, Zeebe et al., 1999).

The significant negative correlations between stable carbon isotope compositions and pH appeared in *S. broughtonii*, *H. discus discus*, and *H. gigantea* which had non-significant pH effects on calcification, and the slopes of these relationships of shell carbonate were lower than these of dissolved inorganic carbon (DIC) of seawater. We estimated the equilibrium values of carbon isotope compositions at each pCO_2 treatment, and the difference between the carbon isotope compositions of shell carbonate and equilibrium values showed gradual increases of carbon isotope values with decreasing pH in *S. broughtonii*, *H. discus discus*, and *H. gigantea*. Thus, the pCO_2-induced change in metabolism might appear in carbon isotopes of shells of these species as the metabolic effect. On the other hand, in *P. sachalinense* which showed a decrease in calcification in our culture experiment of ocean acidification, the difference between the carbon isotope compositions of shell carbonate and equilibrium values did not indicate a significant pH dependency. This result might be attributable to differences in metabolic responses to acidified seawater.

The findings of our study will contribute to the correction of isotopic paleotemperature of biogenic carbonate and the understanding of acidification effects on metabolism of marine calcifiers.

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