

Diagenetic signatures of the Gaskies glaciation and their implication to the Ediacaran stratigraphy

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The isotopic excursion of inorganic carbon that repeatedly happened in Earth history were linked to biological evolutions and extinctions as well to the significant environmental changes. During the Ediacaran period when multicellular animals dramatically evolved, several distinct isotopic excursions recorded from the stratigraphic sections. The Ediacaran platform in South China exposes well-preserved sedimentary rocks, and high-resolution carbonate carbon isotopic data have been extensively studied (e.g., Sawaki et al., 2010). Although most of the excursions were global, a negative excursion in the middle Doushantuo Formation is unique in South China and presumably correlated with the Gaskiers glaciation (Tahata et al., 2013). These data could have reflected characteristic oceanic structure and influenced by oceanic oxidation in Ediacaran, those causes have been not fully understood. This study investigated a negative excursion observed in the Yangjiaping section in NE Hunan, which records large fluctuation in inorganic carbon isotope (e.g. Kunimitsu et al., 2011). The unique excursion was developed in middle to upper parts of Doushantuo Formation Unit 3. Here, we found that the calcite cement exhibit lower isotopic values than bulk component, by 25 permil for carbon and by 2 permil for oxygen. A reasonable process for these observations was most likely decomposition of organic matter in a meteoric diagenetic environment. Co-occurrence of pyrite implies that the process would be coupled with sulfate reduction in an anoxic condition. Yangjiaping section was located in the shallowest part of the platform together with the famous Wengan section in Guizhou province, and was easily exposed subaerially during the sea-level fall. Some characteristics of this negative excursion were commonly seen in the middle Doushantuo in the type section, and an excursion below the paleokarst in Wengan. Thus, the subaerial exposure was associated with the Gaskiers glaciation in the middle Ediacaran period (580 Ma). Thick phosphoric sediments in the Doushantuo Unit 3 imply intensified upwelling during the glaciation. The Gaskiers glaciation enhances ocean circulation that distributes nutrients and oxygen in the water column and induced the animal evolution in late Ediacaran.

Kunimitsu et al., 2011. *Precambrian Research*, 191, 194-208.

Sawaki et al., 2010. *Gondwana Research* 14, 134-147.

Tahata et al., 2013. *Gondwana Research* 23, 333-353.

When did the "Cambrian agronomic revolution" start?

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A variety of benthic animals have appeared in the Cambrian, marine bottom sediments have started to be subjected to bioturbation, and microbial mats, which had widely covered the sea floor in the Proterozoic, have generally declined except for special environment. This phenomenon is known as "the Cambrian agronomic revolution" (Seilacher and Pflüger, 1994), and this is one of the major evolutionary changes caused by the evolution of benthic animals. Previous studies showed that this kind of substrate change has started only after the early Cambrian. However, we have discovered a new evidence that indicate existence of deep burrows made by benthic animals from the Ediacaran of western Mongolia.

Upper Proterozoic to Cambrian deposits are widely distributed in the Gobi Altay area in western Mongolia. In the Bayan Gol valley, we found large-sized *Arenicolites* isp. with vertical burrows from as many as 11 horizons in the Ediacaran bedded limestones. These burrows reaches 4 cm in maximum in vertical orientation. We collected rock samples in 2 m interval, for the carbon isotope stratigraphy.

The horizons with *Arenicolites* isp. are in the bedded limestone of the upper Tsagaan Oloom Formation. They are located at 190-140 m lower than the base of the Cambrian determined by the first occurrence of the ichnofossil *Treptichnus pedum* in this section, and at 120-70 m lower than the horizon of the "BACE event", which is characterized by a clear negative excursion and is correlated approximately to the horizon of the Pc/C boundary. It is clarified that the ichnofossil *Arenicolites* isp. with vertical structure certainly occurs from the Ediacaran as opposed to the previous interpretation. This shows that "The Cambrian agronomic revolution" had already begun in Ediacaran in western Mongolia. This early start of this revolution can be attributed to the geographic position of Mongolia in late Ediacaran-early Cambrian, because Mongolia was located near the equator under warm environment during this interval.

Keywords: Ediacaran, Cambrian, ichnofossil, Cambrian explosion, Cambrian agronomic revolution

Soil erosion event during the Late Devonian mass extinction recorded at the GSSP section

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The Late Devonian mass extinction occurred in a stepwise manner and culminated close to the Frasnian-Famennian (F-F) boundary (372 million years ago). Organic-molecular indices from marine sedimentary rocks at the GSSP section at Coumiac, France, indicate that the sequence of soil erosion and euxinia occurred close to this boundary. The increased concentrations of organic molecules indicating combustion and soil erosion measured in the Coumiac section suggest that terrigenous organic matter flowed into the ocean at this time, leading to reduction of the ocean that caused marine extinctions. Since this soil erosion event simultaneously occurred at the Sinsin section in Belgium (Kaiho et al., 2013), expansion of the reducing environment of the ocean due to soil inflow is thought to have occurred in a wide area. The study of sedimentary organic molecules presents several lines of evidence to link reduction of the ocean due to soil erosion to the Late Devonian mass extinction.

Kaiho, K., Yatsu, S., Oba, M., Gorjan, P., Casier, J.-G., Ikeda, M., 2013. A forest fire and soil erosion event during the Late Devonian mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 392, 272-280.

Keywords: mass extinction, Devonian, Soil erosion

Assessment of mode of extinction and recovery based on changes in morphospace and species-abundance relationship

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Morphological disparity has been attracting attention as a clue for understanding mode of mass extinction because selective extinctions readily reduce the disparity than do random extinctions. In recent years, changes in morphospace occupation are also used to assess selectivity of extinction and subsequent recovery. However, hitherto approaches to this subject have been based on among-species variation and have omitted abundance of each species. Recent developments of database systems such as the Paleobiology Database allow us to utilize data of collection-based occurrences as a proxy of abundance of each species. Here I would propose a method to determine which model of extinction and recovery best explains the observed data on species-abundance relationship as well as on the patterns of morphospace occupation. In the present method, the mode of mass extinction and subsequent recovery is categorized into three models: 1) random extinction and random recovery, 2) selective extinction and random recovery and 3) selective extinction and selective recovery. The method is based on a statistical model selection in which each model is rated in terms of congruence with observed data according to an information criterion. Likelihood functions are computed for various model conditions through simulations of extinction and origination. Prior to the simulations, the morphological values and the number of fossil occurrences are provided for each species through measurements and tabulation of database information. In the simulation of mass extinction, a given percentage of actual occurrences are stochastically removed from the morphospace. In the case of selective extinction, fitness is defined as a function of a morphological variable to determine the probability of removal for each occurrence with a value of the variable. The recovery process is simulated by adding new hypothetical occurrences to the morphospace such that the total number of species is same as the actual data. An addition of new occurrence originates a new species or just increases abundance of a preexisting species randomly chosen. In the former case, morphological values of the new species are stochastically determined so that the new species is located in the neighborhood of the ancestral species in the morphospace. In the selective recovery model, the fitness function defined above also determines where a new occurrence is likely to be introduced in the morphospace. Maximum-likelihood estimation of model parameters requires vast number of simulations with various conditions for each model. In order to select the best model among the three scenarios, the present method refers to the Akaike Information Criterion and its modified version for a small sample sizes.

Keywords: morphospace, disparity, mass extinction and recovery, statistical model selection

Changes in biofacies and environments at the end-Gudalupian: response in mid-latitude

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The Guadalupian-Lopingian boudnary (Permian) recorded the most significant environmental change in the Paleozoic on all aspects; i.e. major global cooling, biodiversity decline, ocean chemistry, and even geomagnetism. Previous studies focused mostly on the fossiliferous limestones deposited in low-latitude domains both in peri-Pangean shelves and mid-oceanic atoll complexes. In order to check the relevant environmental changes in mid-latitude, the Iwaizaki Limestone in the South Kitakami Blet, NE Japan, was analyzed in litho-, bio-, and isotope stratigraphy. In particular, the top part of the limestone, ca. 50 m-thick interval, recorded the collapse of a patch reef complex. Except the Capitanian fusulines from the basal part of this interval, most of the interval lacks index fossil. The present Sr isotope analysis newly identified the uniquely low Sr-ratio, as low as 0.7068, throughout the interval, confirming the Capitanian age. The collapse of reef occurred during the Capitanian in accordance with the Kamura cooling event, but probably much earlier than the low-latitude domains.

Keywords: Permian, Capitanian, cooling, Sr isotope ratio, South Kitakami, shelf limestone

The collapse of a Capitanian (Middle Permian) reef: Sr-isotope profile at Iwaizaki, NE Japan

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The Iwaizaki Limestone in the South Kitakami Belt, NE Japan, represents shallow-marine shelf carbonates deposited along the Guadalupian (Middle Permian) South China margin. The main part of the limestone is composed of massive fossiliferous limestone (ca. 100 m) of reef complex, while the upper part (ca. 35 m thick) consists of interbedded limestone and mudstone. This facies transition corresponds to the onset of reef collapse, and the disappearance of tropical fauna. The main part and the lowermost upper part yielded Capitanian (Upper Guadalupian) fusulines but the rest of the upper limestone is barren of index fossils. As the overlying black mudstone yields Late Permian (Lopingian) ammonoids, the extinction-related G-L boundary exists somewhere within the uppermost limestone or in much higher mudstones. In order to constrain the age of the fossil-free uppermost limestone, we analyzed ⁸⁷Sr/⁸⁶Sr stratigraphy of the Iwaizaki Limestone, and correlated with the global secular trend. The present results confirmed that the topmost Iwaizaki limestone, as well as the main part, has the same low ⁸⁷Sr/⁸⁶Sr ratio of 0.7068-0.7069. The extremely low ⁸⁷Sr/⁸⁶Sr ratio (<0.7069; the lowest values of the Phanerozoic) continued to the topmost bedded limestone in the section. The coeval limestones in the world, including those at Akasaka and Kamura in Japan, recorded a unique interval of extremely low ⁸⁷Sr/⁸⁶Sr ratio (0.7068-0.7070) as called the "Capitanian minimum". Therefore, the topmost Iwaizaki Limestone no doubt belongs to Capitanian, suggesting that the collapse of reef started clearly before the G-L boundary, probably by the onset of the putative Capitanian cooling.

Keywords: Permian, Sr isotope, shelf, South Kitakami belt, reef

Sulfur and carbon isotope study for understanding environmental changes across the Middle/Late Permian boundary

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The mass extinction at the end of the Paleozoic Era has been recognized as the most severe extinction event in the history of life. Such severe diversity loss could be attributed to the combined consequences of two successive mass extinctions, which occurred at the Guadalupian-Lopingian (G-L) (Middle-Late Permian) boundary (260 Ma) and the Permian-Triassic (P-T) boundary (250 Ma). Drastic environmental change during this time likely started immediately before the G-L boundary and reached a maximum around the P-T boundary. In order to understand paleoenvironmental change in oceans across the G-L boundary, we analyzed secular changes in sulfur and carbon isotope ratios of Middle-Upper Permian carbonates of an accreted mid-oceanic paleoatoll complex at Kamura in central Kyushu, Japan.

Negative correlations were observed between $\delta^{34}\text{S}_{CAS}$ and $\delta^{13}\text{C}_{carbonate}$ values for Guadalupian and Lopingian carbonates, respectively. These correlations imply that the bottom water anoxia expanded to the open oceans before and after the G-L boundary. In such environments, organic matter was oxidized by sulfate-reducing bacteria in the water column, which produced negative $\delta^{34}\text{S}_{CAS}-\delta^{13}\text{C}_{carbonate}$ correlations.

The slopes of the negative correlations varied at the G-L boundary. This implies that the supply processes of carbon and sulfur into the oceans changed at the boundary. This finding suggests that the magmatic chemistry changed at the boundary from sulfur-rich type to CO_2 -rich type.

Keywords: Guadalupian-Lopingian boundary, mass extinction, oceanic anoxia, carbonate-associated sulfate, Panthalassan paleoatoll carbonates

Perturbations of the nitrogen cycle in mid-Panthalassa in the Late Guadalupian (Middle Permian)

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To examine the changes in the oceanic N cycle and their possible relationships to the extinction at the end-Guadalupian (Middle Permian), we analyzed the N isotopic compositions ($d^{15}N$) of the upper Guadalupian paleo-atoll limestone, accumulated on the top of a mid-oceanic seamount in the superocean Panthalassa, at Akasaka in central Japan. The $d^{15}N$ values of the limestone are substantially high (ca. +20 permil on average) throughout the analyzed interval. These values are the highest in the previously reported $d^{15}N$ records throughout the entire Phanerozoic. The substantially high $d^{15}N$ values suggest enhanced oceanic denitrification/anammox in the Capitanian (Late Guadalupian). Moreover, the present results revealed remarkably large $d^{15}N$ fluctuations in the analyzed limestone at Akasaka. We interpret that periodic expansion and reduction of the oxygen minimum zone (OMZ) in mid-Panthalassa caused the observed $d^{15}N$ fluctuations in the Capitanian. The suggested OMZ expansions may have been attributed to the high productivity 'Kamura event' in the surface oceans enhancing a biological pump. Chemostratigraphic correlations imply that the enhanced denitrification in the expanded OMZ may have been a global phenomenon in the Capitanian. Widespread developments of the anoxic deep-waters prior to the extinction may have stressed the shallow-marine biota by upwelling at the end-Guadalupian.

A unique Cr-enriched bed across the Guadalupian-Lopingian boundary (Permian) in mid-Panthalassan paleo-atoll carbonates

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We examined in detail the chemical composition of a thin clayey bed (~1 cm) recognized at the Guadalupian-Lopingian boundary (G-LB) in the mid-oceanic paleo-atoll limestone in Japan (Kamura and Akasaka sections), to clarify whether or not the clayey bed is the product of a large-scale explosive volcanism that led to the end-Guadalupian mass extinction (Isozaki and Ota, 2001; Isozaki, 2007). Results of X-ray mapping and ICP-MS analyses revealed that the clay materials both in Kamura and Akasaka are roughly identical in compositions and are characterized by high-chromium contents (ca. 3000 ppm in anhydrous basis). This contradicts the previous notion that the bed represents rhyo-dacitic tuff brought by explosive eruption of acidic magma. Despite this, the widespread occurrence of Cr-enrichment at the G-LB horizon is inferred from the fact that the G-LB mudstones in continental shelf limestone in South China (Wangpo Bed at Chaotian and Shangsi sections) have geochemical affinity to the Cr-rich clayey bed at Kamura and Akasaka sections deposited in western Panthalassa. From these data, together with the normal platinum-group element signatures throughout the G-LB samples, we invoke a global fall-out of Cr-rich air-borne ash originated from mafic or ultramafic magma, most likely related to the mantle plume-derived large igneous provinces (LIPs). This might be possible at the initial phase of intrusion/eruption of basaltic to picritic magma that formed the Emeishan LIP in South China (~260 Ma) or other continental LIPs emplaced during the breakup of the supercontinent Pangea, if such high-temperature magmas were effectively carbonated and hydrated through the reaction with the thick sedimentary piles of limestones and shales.

Keywords: geochemistry, ICP-MS, clayey bed, Guadalupian-Lopingian boundary, mass extinction, Emeishan flood basalts

Organic carbon isotope changes at P-T boundary in Gujohachiman, Japan

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There was large extinction from Guadalupian- Lopingian boundary (GLB) to Permian- Triassic boundary (PTB), ca. 260- ca. 251Ma (Sepkoski, 1984; Knoll et al., 1996; Isozaki, 1997; Stanley and Yang, 1994; Kaiho et al., 2005). The extinction will have correlation with Oceanic environment (e.g. oxic level in ocean, climatic change). Black shale layer is observed in chert of accretionary complex in Japan and Canada. The layers indicate anoxic in entire Ocean (Oceanic Anoxic Events) (Isozaki, 1997). However, the correlation between extinction and environmental changes is not known. Therefore, we need to study life cycle changes and influence to oceanic environment in extinction by changes of carbon isotope ratio.

The stable isotope ratios $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ are believed to reflect the change in the global status of photosynthesis, since biological organisms preferentially use light carbon during photosynthesis. When the biological mass with light-carbon content becomes large, the inorganic carbon (mantle CO_2) in the atmosphere and ocean become heavier. In other words, carbon isotope changes in carbonate and organic carbon will reflect carbon cycle changes by extinctions (Rothman et al., 2003; Tahata et al., 2014).

There were many previous studies of carbonate carbon isotope ratio from GLB to PDB. The carbon isotope records show over +6 permil before GLB, calling to Kamura event. The $\delta^{13}\text{C}_{\text{carb}}$ after Kamura event decrease to ca. 0 permil around GLB. Moreover, the $\delta^{13}\text{C}_{\text{carb}}$ decreases from ca. +3 permil to ca. -2 permil at PTB and shows large excursions from PTB to middle Triassic (Isozaki et al., 2007a,b; Korte et al., 2005a,b; Payne et al., 2008). As the carbonate carbon isotope records, there are no continuous carbon isotope records of organic carbon from GLB to PTB, because the carbonate-rich rocks have low organic contents and difficult to analyze organic carbon isotope ratio.

Accretionary complex in Gujohachiman, Gifu-ken, Japan constitute of alternation of chert and shale. The sediments show continuous depositions in deep sea from GLB to PTB. We analyze organic carbon isotope ratio from continuous shale layers in Gujohachiman, because the shale layers between chert layers have organic-rich.

The results of organic carbon ratio show coupling to carbonate carbon isotope changes, except for GLB. Organic carbon isotope records in GLB decouple carbonate carbon isotope ratio. The carbon isotope change indicate to reflect to carbon cycle changes by extinction.

Abrupt surface-water reduction accompanied with massive soil inflow during the end-Permian mass extinction

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The largest mass extinction of biota in Earth history occurred at the end of the Permian Period, which led to a turnover of biosphere from Paleozoic Fauna to Modern Fauna. Siberian volcanism is the most possible cause, however, the direct causal mechanism for the mass extinction is unclear. We report that the worst redox condition in the shallow sea appeared during the mass extinction on the way to a gradual reduction of deep sea. An abrupt decrease in oxygen in the shallow sea is thought to be a direct cause of the marine mass extinction. A significant decrease in atmospheric oxygen should also have occurred during the mass extinction to explain the shallow surface water reduction and land mass extinction.

A soil erosion event occurring at the end-Permian mass extinction has already been reported. However, those records are restricted in a few near-shore sequences. We demonstrate that a organic-molecule soil-erosion proxies have peaks during the end-Permian mass extinction throughout the inner continental shelf to the upper continental slope in Paleotethys and a sea mount in the central Panthalassic ocean, and in contrast to this, no peaks at isolated platform area in Paleotethys and deep Panthalassic ocean. Furthermore, we found high DBF/Phe ratio values throughout the inner continental shelf to the upper slope and a sea mount, and low values at isolated platform, its slope, and in central deep ocean during the mass extinction. This phenomenon is supported by other organic molecule proxies sourced from land. The distribution of soil erosion proxies in the end-Permian sea clarifies that massive soil erosion event surly occurred during the end-Permian mass extinction.

In summary, abrupt surface-water reduction accompanied with massive soil inflow occurred during the end-Permian mass extinction.

Keywords: oceanic reduction, soil, Permian, Triassic, mass extinction

Osmium isotope composition in the deep pelagic Panthalassa ocean during the Toarcian Oceanic Anoxic Event

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The Toarcian Oceanic Anoxic Event (T-OAE) represents one of the most significant paleo-environmental perturbations in the Phanerozoic, which resulted in marked disruption to both the climate system and marine ecosystem. The causes for this widespread deposition of organic carbon-rich sediments under the reducing condition are still controversial. Several mechanisms have been proposed to explain the occurrence of T-OAE including; abrupt seawater warming, an increase in continental weathering rates, enhanced rates of biotic turnover, atmospheric pCO₂ changes, and ocean acidification. In particular, volcanic activities in the large igneous Karoo-Ferrar province have been considered as the most fundamental trigger for the Toarcian perturbations. Radiogenic Os isotope compositions of sedimentary rocks are useful for estimating the influx from both ancient basaltic magmatism and continental weathering. However, the relationship between biotic crisis, anoxic event, and the volcanic activity in the deep pelagic environment is still ambiguous because of the lack of detailed Os isotope records during T-OAE. In this study, we reconstructed a detailed lithological column in the Inuyama area where the Pliensbachian to Toarcian deep-sea cherts well crop out along the Kiso river. For Os isotope analysis, we collected 12 chert samples from a section where two black bedded chert intervals T-OAE1 and T-OAE2 were observed.

The rock powder was spiked with ¹⁹⁰Os and ¹⁸⁵Re prior to digestion. The sample was digested by CrO₃-H₂SO₄ in a sealed Carius tube at 240 °C for more than 48 hours. Subsequently, Os was separated by solvent extraction using CCl₄ and back-extracted from CCl₄ into HBr, followed by the final purification using the micro-distillation method. The Os isotope ratios were determined by N-TIMS at Tokyo Tech. Re-bearing solution after the CCl₄ extraction was stored in a Teflon vessel, and Cr⁶⁺ in the solution was completely reduced to Cr³⁺ by the addition of ethanol in order to avoid the disturbance of the elution profile of the following chromatography due to the coexistence of Cr⁶⁺. After this process, Re was purified by chemical separation using an anion exchange resin, and the isotopic composition was determined using a quadrupole-type ICP-MS at Tokyo Tech. The Os and Re concentrations were determined by the isotope dilution method.

The Re and Os abundances in 12 chert samples across T-OAE varied from 2.1 to 128.6 ng/g, and from 32.8 to 2284.3 pg/g, respectively. The ¹⁸⁷Os/¹⁸⁸Os ratio in the samples before T-OAE1 decreased from 0.44 to 0.27, resulting in the minimum value of 0.24 at the onset of T-OAE1. However, the ¹⁸⁷Os/¹⁸⁸Os ratio increased abruptly to be 0.77 towards the end of T-OAE1, and decrease down to 0.30 at the interval between T-OAE1 and T-OAE2. During T-OAE2, the ¹⁸⁷Os/¹⁸⁸Os ratio gradually increased up to 0.56. Take into account organic carbon isotope record in the same section by Grocke et al. (2011), we envisage the following scenario for the cause of Os and C isotopic variation during T-OAE observed in the chert samples: The Karoo-Ferrar volcanic activity induced an anoxic condition, which resulted in negative ¹⁸⁷Os/¹⁸⁸Os before T-OAEs. The Karoo-Ferrar volcanism released significant amount of CO₂, which triggered the global warming and continental erosion during T-OAE1. Subsequent gradual increase of Os isotope ratios most likely reflects its aftermath. These indicate that the Karro-Ferrar volcanism played an important role for inducing anoxic condition and global warming during Toarcian in the deep pelagic Panthalassa ocean.

Keywords: Toarcian Oceanic Anoxic Event, deep pelagic Panthalassa ocean, osmium isotope, Karoo-Ferrar volcanism

Birth place and migration history of primates: Proposal of new model

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The origin and evolution of ancestor of human being, so-called Primates, has not been well known yet, although several conflicting models were proposed so far. Here, a new model is proposed to satisfy (1) genomic phylogeny, (2) fossil evidence, and (3) paleogeographic constraints based on not only ocean-floor age constraints but also surface geology.

Birth place of Primates must have been a rift in the Gondwana ca. 100Ma, which was 25 m.y. earlier than 75Ma that was estimated by most genome biologists. The existence of new world monkey (Platyrrhini) in South America can be explained assuming the birth place of ancestor of new world monkey was between Antarctica and South America at 100Ma, migrated to South America and land bridge was disconnected at 34Ma between Antarctica and S. America. On the other hands, lemur and aye-aye in Madagascar could be migrated from northward-moving Indian continent around 65Ma to intercross with ancestral primates originated in Madagascar that was migrated southward from Northeastern margin of African continent. Land bridge between those two islands was generated as the result of rising plume at 65Ma between these two islands. Also, primates in the Indonesian region could have been transported by fragmented continents disconnected from Antarctica-Australia (origin of Borneo). Primates on the Indian continent arrived at Central South Asia at 50Ma, and highly diversified ecosystem was generated by crown evolution which is the most bio-diverse region since then.