

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

OHNO, Sohsuke<sup>1\*</sup> ; KADONO, Toshihiko<sup>2</sup> ; KUROSAWA, Kosuke<sup>1</sup> ; HAMURA, Taiga<sup>3</sup> ; SAKAIYA, Tatsuhiro<sup>4</sup> ; SHIGEMORI, Keisuke<sup>4</sup> ; HIRONAKA, Yoichiro<sup>4</sup> ; SANO, Takayoshi<sup>4</sup> ; WATARI, Takeshi<sup>4</sup> ; OHTANI, Kazuto<sup>5</sup> ; MATSUI, Takafumi<sup>1</sup> ; SUGITA, Seiji<sup>3</sup>

<sup>1</sup>Planetary Exploration Research Center, Chiba Institute of Technology, <sup>2</sup>University of Occupational and Environmental Health, <sup>3</sup>University of Tokyo, <sup>4</sup>Osaka University, <sup>5</sup>Institut national de la recherche scientifique

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

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

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

FUJISAKI, Wataru<sup>1\*</sup> ; SAWAKI, Yusuke<sup>1</sup> ; YAMAMOTO, Shinji<sup>2</sup> ; YOKOYAMA, Tetsuya<sup>1</sup> ; MARUYAMA, Shigenori<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, <sup>2</sup>The University of Tokyo, <sup>3</sup>Earth-Life Science Institute, Tokyo Institute of Technology

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

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

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

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

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

ONOUÉ, Tetsuji<sup>1\*</sup> ; YAMASHITA, Daisuke<sup>1</sup> ; TOMINAGA, Takashi<sup>1</sup> ; SATO, Honami<sup>2</sup>

<sup>1</sup>Kumamoto University, <sup>2</sup>Kyushu University

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

Keywords: Triassic, Meteorite Impact, Radiolaria

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

KAIHO, Kunio<sup>1\*</sup> ; TAKAHASHI, Satoshi<sup>2</sup> ; GORJAN, Paul<sup>3</sup> ; CHEN, Zhong-qiang<sup>4</sup> ; TONG, Jinnan<sup>4</sup>

<sup>1</sup>Tohoku University, <sup>2</sup>University of Tokyo, <sup>3</sup>Washington University, <sup>4</sup>China University of Geosciences

Biotic recovery after the largest mass extinction at the end of the Permian (252.3 million years ago, Ma) became evident in early Spathian (250.1 Ma), Early Triassic, and was eventually completed in middle-late Anisian (ca. 244 Ma), early Middle Triassic. Recent studies showed that this much delayed recovery was impacted by several biocrises and associated environmental and climatic stresses during the Early Triassic. For instance, the end-Smithian extinction and associated thermal maximum and Smithian oceanic anoxia may have prevented biotic recovery initiated in early Smithian (251 Ma). Our new study not only confirmed the oceanic anoxia in late Smithian but also found an oxygenation event just after the Smithian thermal maxima (STM) using sulfur isotope fractionation between sulfate and sulfide. Newly obtained sulfur isotope ratios of carbonate-associated sulfate (d34SCAS) in the surface water and sulfide (d34Ssulfide) in the Panthalassic deep water during the late Permian to the Early Triassic compiled with published data show a significant increase in fractionation between the d34SCAS and d34Ssulfide during the early Spathian (41-51 permil to 62 permil). The latter indicates an increase in global oceanic dissolved oxygen levels, which also coincided with a climatic cooling and may have facilitated biotic recovery in late Early Triassic.

Keywords: Early Triassic, ocean dissolved oxygen, sulfur isotope

## Cyanobacterial proliferation during the Early Triassic

SAITO, Ryosuke<sup>1\*</sup> ; KAIHO, Kunio<sup>1</sup> ; OBA, Masahiro<sup>1</sup> ; TONG, Jinnan<sup>2</sup> ; CHEN, Zhong-qiang<sup>2</sup> ; TAKAHASHI, Satoshi<sup>3</sup> ; CHEN, Jing<sup>2</sup>

<sup>1</sup>Institute of Geology and Paleontology, <sup>2</sup>Institute of Geology and Paleontology, <sup>3</sup>Institute of Geology and Paleontology, <sup>4</sup>China University of Geosciences, <sup>5</sup>China University of Geosciences, <sup>6</sup>Department of Earth and Planetary Science, University of Tokyo, <sup>7</sup>China University of Geosciences

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

Keywords: biomarker, Early Triassic, extinction, cyanobacteria

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

TAKAHASHI, Satoshi<sup>1\*</sup>; YAMASAKI, Shin-ichi<sup>2</sup>; OGAWA, Yasumasa<sup>3</sup>; KIMURA, Kazuhiko<sup>4</sup>; KAIHO, Kunio<sup>5</sup>; YOSHIDA, Takeyoshi<sup>5</sup>; TSUCHIYA, Noriyoshi<sup>2</sup>

<sup>1</sup>Department of Earth and Planetary Science, the University of Tokyo, <sup>2</sup>Graduate School of Environmental Studies, Tohoku University, <sup>3</sup>Graduate School of Engineering and Resource Science, Akita University, <sup>4</sup>School of food, Agricultural and Environmental Science, Miyagi University, <sup>5</sup>Department of Earth Science, Graduate School of Science, Tohoku University

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

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

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

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

SAITOH, Masafumi<sup>1\*</sup> ; UENO, Yuichiro<sup>1</sup> ; NISHIZAWA, Manabu<sup>2</sup> ; ISOZAKI, Yukio<sup>3</sup> ; TAKAI, Ken<sup>2</sup>

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

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

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

KOFUKUDA, Daisuke<sup>1\*</sup>; ISOZAKI, Yukio<sup>1</sup>; IGO, Hisayoshi<sup>2</sup>; KANI, Tomomi<sup>3</sup>; ISHIMURA, Toyoho<sup>4</sup>

<sup>1</sup>The University of Tokyo, Komaba, <sup>2</sup>Institute of Natural History, <sup>3</sup>Kumamoto University, <sup>4</sup>AIST

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

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

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

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

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

KANI, Tomomi<sup>1\*</sup> ; KOFUKUDA, Daisuke<sup>2</sup> ; ISOZAKI, Yukio<sup>2</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, Kumamoto University, <sup>2</sup>Department of Earth Science and Astronomy, The University of Tokyo

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

Keywords: Permian, Sr isotope, seawater, limestone

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

ISOZAKI, Yukio<sup>1\*</sup> ; KASE, Tomoki<sup>2</sup>

<sup>1</sup>Dept. Earth Science & Astronomy, University of Tokyo, <sup>2</sup>National Science Museum

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

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

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

OZAKI, Kazumi<sup>1\*</sup>

<sup>1</sup>AORI, University of Tokyo

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

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

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

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

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

YAMADA, Kentaro<sup>1\*</sup> ; SASAKI, Kazunori<sup>2</sup> ; UENO, Yuichiro<sup>3</sup> ; YAMADA, Keita<sup>4</sup> ; YOSHIDA, Naohiro<sup>4</sup> ; MARUYAMA, Shigenori<sup>5</sup>

<sup>1</sup>Earth Sci. and Astro., the Univ. of Tokyo, <sup>2</sup>Human Metabolome Technologies Inc., <sup>3</sup>Earth and Planetary Sci., TITech, <sup>4</sup>Environmental Sci. and Tech., TITech, <sup>5</sup>Earth-Life Science Institute

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

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

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

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

## Ancient ocean environment in the Ediacaran to Cambrian.

SAWAKI, Yusuke<sup>1\*</sup> ; MARUYAMA, Shigenori<sup>1</sup>

<sup>1</sup>Tokyo Tech

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

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

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

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

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

ASANUMA, Hisashi<sup>1\*</sup>; OKADA, Yoshihiro<sup>1</sup>; SAWAKI, Yusuke<sup>1</sup>; YAMAMOTO, Shinji<sup>2</sup>; HIRATA, Takafumi<sup>3</sup>; MARUYAMA, Shigenori<sup>4</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, <sup>2</sup>Department of Earth and Astronomy Graduate School of Arts and Sciences The University of Tokyo, <sup>3</sup>Graduate School of Science, Kyoto University, <sup>4</sup>Earth-Life Science Institute, Tokyo Institute of Technology

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

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

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

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

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

## Deep-sea anoxia during the Marinoan Snowball Earth

SATO, Tomohiko<sup>1\*</sup>; OKADA, Yoshihiro<sup>1</sup>; ASANUMA, Hisashi<sup>1</sup>; MARUYAMA, Shigenori<sup>2</sup>; SHOZUGAWA, Katsumi<sup>3</sup>; MATSUO, Motoyuki<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Science, Tokyo Institute of Technology, <sup>2</sup>Earth-Life Science Institute, Tokyo Institute of Technology, <sup>3</sup>Graduate School of Arts and Sciences, The University of Tokyo

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

## Paleogeography of the Earth; Neoproterozoic

MARUYAMA, Shigenori<sup>1\*</sup> ; ISOZAKI, Yukio<sup>2</sup>

<sup>1</sup>ELSI Tokyo Institute of Technology, <sup>2</sup>University of Tokyo

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

### (1) Continent configuration

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

### (2) Environmental change

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

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

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

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

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

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

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

### (5) Role of Universe

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

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

SHIROZU, Hideko<sup>1\*</sup>; JOZEF, Michalik<sup>2</sup>; KUSAKA, Soichiro<sup>3</sup>; YAMASHITA, Katsuyuki<sup>4</sup>; YAMASHITA, Misa<sup>4</sup>; ONOUE, Tetsuji<sup>1</sup>

<sup>1</sup>Graduate School of Science and Technology, Kumamoto University, <sup>2</sup>Slovak Academy of Sciences, <sup>3</sup>Research Institute for Humanity and Nature, <sup>4</sup>Graduate School of Science and Technology, Okayama University

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

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

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

## Global paleogeography and life evolution: 1. Cenozoic

ISOZAKI, Yukio<sup>1\*</sup> ; MARUYAMA, Shigenori<sup>2</sup>

<sup>1</sup>Univ. Tokyo/Dept. Earth Sci. & Astronomy, <sup>2</sup>Tokyo Inst. Technology/ELSI

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

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

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

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

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

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