High-precision U-Pb temporal constraints on the early Cambrian diversification of animal life from eastern Yunnan, China

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The Terreneuvian Epoch at the onset of the Cambrian marks the time of major biotic radiations and marine geochemical changes on the global scale. In order to understand the tempo of emergence of complex animal life as well as its interrelationships to the geologic environment, a robust correlation of the Terreneuvian intercontinental stratigraphic records is necessary. This correlation has been aided by long recognized patterns of perturbation in the ocean carbon cycle of presumed global extent. Here we report new high-precision U-Pb zircon geochronology (CA-ID-TIMS method) from interbedded volcanic ash beds in key stratigraphic sections of the eastern Yunnan Province in South China in order to calibrate the interval spanning the latest Ediacaran to the terminal Terreneuvian.

Samples from the top of the Ediacaran Dengying Formation and the base of the Cambrian Daibu Member of the Zhujiaqing Formation in the chemostratigraphically constrained Xiaotan section provide the best estimate for the age of the basal Cambrian negative carbon isotopic excursion (BACE), as well as the Ediacaran-Cambrian boundary. The new U-Pb age constraints for the boundary are on the order of 2 myr younger than the currently accepted age. Preliminary analyses of previously dated boundary ash beds from Oman and Namibia appear to support a revision of the boundary age, pending more comprehensive examination of the corresponding successions.

Further up stratigraphically, new high-precision age results from the base of Dahai Member of the Zhujiaqing Formation and the base of the Shiyantou Formation constrain the interval of the largest and most widely recognized positive carbon isotope excursion of the Terreneuvian, generally known as ZHUCE, to have occurred between ca. 527 Ma and ca. 526 Ma. Our new age results from the uppermost Dahai Member and basal Shiyantou Formation together constrain the beginning of the important negative carbon isotopic excursion known as SHICE. The latter also places maximum age limits on the first known appearance of trilobites and Chengjiang fauna. Our new calibration of the basal Cambrian biostratigraphy in South China places the base of Zone II (Siphogonuchites triangularis- Paragloborilus subglobosus Assemblage) and Zone III (Heraultipegma yunnanensis Assemblage) of the small shelly fossils at ca. 533 Ma and ca. 527 Ma, respectively, whereas the top of Zone III is constrained at ca. 526 Ma.

Keywords: U-Pb geochronology, Cambrian, Small shelly fossils, Biostratigraphy, Ediacaran-Cambrian boundary
Mass extinctions related to global cooling: A case study of the late Ordovician mass extinction using a multi isotope approach

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Except for the most severe mass extinctions, such as the Permian-Triassic (PT) and Cretaceous-Paleogene (K-Pg) boundary events, most moderate- to minor-class mass extinctions were related to global cooling rather than global warming [1]. The elevated extinction rates for the cooling-related mass extinctions were generally accompanied by a positive carbon isotope excursion, implying that major perturbations of the global carbon cycle might be involved. As it is very difficult to draw conclusions from carbon data alone, a multi-isotope approach is necessary to understanding the paleoenvironmental perturbations in such mass extinctions. Although there are some common characteristics for cooling-related mass extinctions, it is still unclear whether or not all of them were induced by a common trigger event, such as volcanic activity, meteorite impacts, or nearby supernova explosions. In this study, we discuss the environmental perturbations at the late Ordovician mass extinction as an example of a cooling-related mass extinction. Although the late Ordovician mass extinction was one of the “Big Five” mass extinction events in the Phanerozoic, the rate of species extinction was lower than those of the P-T and K-Pg boundary events [2]. The decline of biodiversity coincided with the onset of the Hirnantian glaciation, the inducing mechanisms for which are still unclear. In this study, isotopic ratios and concentrations of carbon and sulfur were analyzed in the Upper Ordovician to Lower Silurian shales from the Langkawi Islands in Malaysia. The results revealed that the weight ratios of organic carbon and pyritic sulfur (C/S) varied periodically from <1 to ~30. These periodic variations were interrupted by the position of the positive δ13C excursion. The excursion was accompanied by C/S ratios <0.1, lower than the minimum values during the periodical variations. Although the C/S ratios varied periodically, the minimum values for each C/S variation cycle gradually increased. This implies that the environmental perturbation recorded as very low C/S ratios repeated high and low intensities, but its fluctuation was attenuated overall.


Keywords: Ordovician-Silurian boundary, Stable isotopes, Global cooling
The redox history and nitrogen cycle in the pelagic Panthalassic deep ocean during the double-phased extinction interval across the Paleozoic-Mesozoic transition

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The end-Permian mass extinction, the largest catastrophic perturbation in the Phanerozoic life history, comprises two distinct extinctions; the first one across the Guadalupian-Lopingian (G-L) boundary and the second one across the Permian-Triassic (P-Tr) boundary. The appearance of prolonged global-scale anoxia during this interval was likely unfavorable for most animals and marine ecosystems. In order to constrain oceanic redox conditions and biological activity, carbon isotope ratios and redox proxies were measured in many sections; however, most of these studies have been undertaken on the sections from the Tethys Ocean, a region covered only 10-15% of the area of the global-ocean, and ignored the larger part of central Panthalassa, comprising 85-90% of the area of the Permian to Triassic global-ocean. The Permo-Triassic deep-sea pelagic cherts preserved in the on-land exposed Jurassic accretionary complex in Japan are ideal material for paleoenvironmental studies; however, the linkage between marine redox history and biological activity in the mid-Panthalassic deep ocean has not been well understood owing to limited data-set. We collected shales partings of bedded cherts of the Guadalupian to earliest Induan ages exposed at the Gujo-Hachiman section in central Japan. We determined the organic carbon ($\delta^{13}$C$_{org}$) and nitrogen ($\delta^{15}$N$_{TN}$) isotopic ratios, and major, trace and rare earth element abundances of the shales, in order to clarify changes in the redox history and nitrogen cycle in mid-Panthalassa for the double-phased mass extinction across the Paleozoic-Mesozoic transition.

Little enrichments of Mo, V, U, and TOC were detected from the Guadalupian to Lopingian shales, suggesting that the mid-Panthalassic deep ocean was dominated by an oxic-suboxic condition across the G-L transitional zone. In addition, the $\delta^{13}$C$_{org}$ and $\delta^{15}$N$_{TN}$ values across the G-L transitional zone exhibit little fluctuation, and the former is almost the same as those obtained from adjacent bedded cherts. In contrast, a negative $\delta^{15}$N$_{TN}$ shift and the extensive ocean euxinia are recognized in the Tethyan shallow marine strata. These lines of evidences indicate that the development of euxinia and nitrogen-limited conditions were limited only to shallow shelf domains of the Tethyan Ocean and had little influence to the mid-Panthalassic deep ocean across the G-L boundary.

High abundances of U, V, and Mo in the Induan black mudstones indicate the appearance of anoxic conditions in mid-Panthalassa. The $\delta^{13}$C$_{org}$ values during the Induan show a similar pattern to that reported in other deep-sea sites. On the other hand, the $\delta^{15}$N$_{TN}$ values in the Induan mudstones range from -2.0 to 0.7‰. These low $\delta^{15}$N$_{TN}$ values together with the emergence of anoxic condition suggest that a relative predominance of nitrogen fixation, which in turn means a nitrogen-limited condition in the mid-Panthalassa. Our $\delta^{15}$N$_{TN}$ profiles are similar to those reported from other P-Tr boundary sections, such as eastern Panthalassic and Tethyan Oceans. Therefore low $\delta^{15}$N$_{TN}$ values during the Induan was likely a global signature, and we concluded that the protracted oceanic nitrogen depletion during the Induan would have acted as an environmental stress on shallow and deep-sea biota.

Keywords: mass extinction, Panthalassa, organic carbon isotopes, nitrogen isotopes, redox-sensitive elements
Climate changes during mass extinctions by asteroid-comet impacts and large volcanic eruptions

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Cooling and associated drought induce mass extinctions. Warming is difficult to cause mass extinctions, because high latitude areas are good condition for life during hot surface of the Earth. Causes of cooling are soot and sulfate aerosols to cut sunshine. These aerosols in the troposphere fall out soon with rain, which do not cause global cooling, but stratospheric aerosols can live long to cause the global cooling and drought. Energy is needed to carry burned hydrocarbon and sulfur to the stratosphere. The energy can be provided by asteroid-comet impacts and large volcanic eruptions. Soot aerosols and sulfate aerosols are main causes of mass extinctions by the impacts and volcanic eruptions. Cooling on land reaches 1 month after the ejection on soot aerosol case, but one year after the ejection on sulfate aerosol case, followed by gradual recovery in 10 years on both cases. Warming subsequently occurred by CO$_2$ ejection by the impacts and volcanic eruptions in 10 to 1000 years after the events. The amount of CO$_2$ is usually smaller on the impact case than on the volcanic eruption case, resulting in no significant warming by the former, but significant warming may occur by the latter. Mass extinctions by the volcanic eruptions can be emphasized by subsequent warming events, resulting in stepwise extinctions.

Keywords: asteroid-comet impacts, large volcanic eruptions, climate changes, mass extinctions
Land ecosystem collapse followed by marine environmental stress spanning the Permian-Triassic mass extinction

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Abstract
The Permian–Triassic mass extinction was the most devastating extinction in the Phanerozoic Era. We investigated the biomarkers from the Shangsi section, South China, to identify changes in the biosphere and marine environments. We show that the collapse of land vegetation occurred before the latest Permian marine extinction at the Shangsi section. The stressful environmental conditions were persisted during the earliest Triassic rather than the latest Permian marine extinction. The second phase of stressful environmental conditions occurred in the late Griesbachian.

Keywords: Permian-Triassic, Mass extinction, Land plant, Environmental stress, Shangsi, Organic geochemistry
Neutral stochastic model of evolution and biodiversity: topological approach to phylogenetic tree

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Evolution and biodiversity are closely related to several environmental events in Earth history. Community ecology has played an important role in this subject, especially, ecological neutral theory has been recognized as one of the unified theory of biodiversity (e.g., Hubbell, 2001; Etirnne, 2005). This theory applied the concept of the neutrality in population genetics (Kimura, 1968) to the ecology such as the concept of the genetic drift corresponding to ecological drift (e.g., Alonso et al., 2006). The ecological neutral theory can explain the present structure of the evolution and the biodiversity without the assumption of the various interspecies action and the niche structure (e.g., Tilman, 2004; Suzuki and Chiba 2016). This suggests that the neutral model is also useful to understand the evolution and biodiversity in Earth science. The purpose of this work is to consider the topological property of the molecular phylogenetic tree based on the concept of the neutrality. Previous studies of real data with model results have not pay attention on the topological property of the molecular phylogenetic tree (e.g., Levinton, 1979; Harvey and Nee1994; Nee et al., 1995; Lieberman, 2011). Then, we apply the Horton analysis (Horton, 1945) to the phylogenetic tree and quantify the topological degree of it.

Data used in this paper are as following vertebrata: spiny-rayed fishes (Near et al., 2013), amphibian (Frost et al., 2006), turtles (Grawford et al., 2015), squamata (Pyron et al., 2013), avian (Burleigh et al., 2015) and placental mammals (Murphy et al., 2001). We applied the Horton analysis to these data and show that the Horton’s first law is valid in the molecular phylogenetic, and the mean value of the bifurcation ratio is estimated to be about 3.2. The value 3.2 is lower than the theoretical value: about 4.0 estimated by previous studies (e.g., Leopold and Langbein, 1962; Shreve, 1967). The causes of this are assumed as follows: (1) The bifurcation ratio of the molecular phylogenetic tree includes the effect of the non-neutral stochastic process. (2) The result of the joint model is different from that of the branch model.

Then we perform the neutral stochastic simulation of the branching with the two parameters: branching probability and time span. As a result, the value of the bifurcation ratio is found to be 3, which is very close to the date value 3.2. This means that the topological property of the molecular phylogenetic trees reflects the neutral stochastic process in evolution and biodiversity. In other words, the topological properties of the tree can be understood without the endemic events in Earth history.

Keywords: molecular phylogenetic tree, topological property, Horton analysis, bifurcation ratio, Neutral stochastic model, biodiversity
The Ediacaran period records one of the most dramatic biological episodes in Earth’s history. To track environmental changes occurring in the Ediacaran, multi-geochemical proxies have been reported by a number of studies. Ediacaran sedimentary rocks in South China figure prominently in such studies, because they are fossiliferous and accumulated at various depositional settings from shallow platform to basin facies. Recent extensive geochemical works for the Doushantuo Formation in South China demonstrate that $\delta^{13}C$ values of inorganic carbon were variable throughout the Ediacaran period. On the other hand, a drastic change in weathering influx from continents is thought to have major influences on the change in seawater composition and on biological activity. Its flux can be estimated from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonate rocks. However, the existing $^{87}\text{Sr}/^{86}\text{Sr}$ values are limited to shallow marine deposits, which leaves ambiguity in a variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in outer ocean.

We conducted drilling at Siduping, Tianping, and Weng’an sections in South China to obtain the Ediacaran complete sedimentary sequences deposited at slope and shoal facies. We newly report stratigraphic profiles of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the three sections. $^{87}\text{Sr}/^{86}\text{Sr}$ chemostratigraphy demonstrated some diachronous natures of $\delta^{13}C$ within the Doushantuo Formation. The enhanced continental weathering during Gaskiers glaciation likely promoted bacterial sulfate reduction and aerobic respiration of organic matter. These resulted in low $\delta^{13}C$ values of dissolved inorganic carbon and accumulations of phosphate and dissolved $\text{CO}_2$ species in seawater, and eventually induced the deposition of phosphorites at the shelf margin. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during the largest negative $\delta^{13}C$ anomaly in the Ediacaran can be also recognized in the continental slope sediment. This fact supports that globally high continental weathering rate led to massive remineralization of organic matter and a consequent significant negative $\delta^{13}C_{\text{carb}}$ excursion.

Keywords: radiogenic Sr isotopic ratio, South China, The Ediacaran
The Late Guadalupian (Permian) Kamura event revisited: carbon isotope stratigraphy of the topmost Iwaizaki limestone in NE Japan and the expansion of oceanic OMZ

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The major extinction of marine animals occurred in the Capitanian immediately before the Guadalupian-Lopingian boundary (Permian), of which detailed stratigraphy has been analyzed in low-latitude sections, e.g. in Texas, South China, and also in Japan. The sea-level drop and the coeval selective extinction of tropical fauna during the Capitanian suggest the appearance of global cooling. The Permian Iwaizaki limestone in the South Kitakami belt in NE Japan represents a shallow marine shelf carbonate sequence that record the development of a patch reef and subsequent collapse in the high-latitude side of subtropical zone. The occurrence of large-tested fusuline Lepidolina and extremely low Sr isotope ratios guarantee the Capitanian age of the uppermost part of the limestone. We analyzed the secular change in inorganic and organic carbon isotope ratios for drilled core from the topmost 40 m-thick interval of the limestone. We found out that δ¹³C values of the Capitanian seawater reached up to +5.8 ‰ during the extinction, and that organic matter had δ¹³Corg value as high as -22.5 ‰. The results confirm that the "Kamura event", originally proposed solely on inorganic carbon isotopic ratio, indeed implies the high primary productivity coupled with the efficient burial of organic matter. In order to drive Δ¹³C up to 30 ‰, additional contribution by methane-bacteria is necessary in carbon fixation, which can be best performed under reducing conditions. Similar high Δ¹³C values detected in coeval shallow marine limestones in the Brusane section in Croatia and the Senkina Shapka section in Far East Russia suggest the global nature of the Kamura event. This unique isotopic episode likely reflected the expansion of the oxygen minimum zone (OMZ) in the superocean, which may have caused the significant extinction at the end of the Guadalupian.

Keywords: mass extinction, Permian, Capitanian, C isotope ratio
Comparative study of mass extinction: end-Ordovician and and end-Guadalupian extinction events

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Among the so-called Big-5 mass extinctions of the Phanerozoic, those at the end-Permian and end-Ordovician stand out high as the largest and the second largest of magnitude. These two mass extinctions occurred respectively before and after the irreversible big change in the biosphere, i.e. the great land foresterization during the Devonian and Carboniferous. Characteristics of these two events are compared for searching possible common causes. The end-Permian extinction was two-folded; i.e. the first at the end of the Guadalupian (Middle Permian) and second at the end of the Permian. Some similarities exist between the end-Ordovician (Hirnanthian) event and the end-Guadalupian (Capitanian) event; such as the preferential elimination of sessile biota in tropics, sea-level drop, secular changes in seawater C and Sr isotope ratios. All these observations suggest that the Hirnanthian and Capitanian extinctions were triggered probably by global cooling resulted in significant glaciation and sea-level drop, although the cause of the global cooling has not yet been identified. In contrast, their mutual differences in screening pattern of biota etc. suggest that the background conditions were significantly different between the Ordovician and Permian cases. This comparison highlighted similar cause/processes but different background conditions and biotic responses.

Keywords: mass extinction, Ordovician, Permian, global cooling
Litho- and SSF stratigraphy of the lowermost Cambrian of the Hongjiachong and Xiaolantian sections in East Yunnan, South China

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Metazoans diversified dramatically in a short time during the latest Ediacaran and earliest Cambrian. Animal of small shelly fossils (SSF) were the first group that diversified much earlier than the well-known Burgess/Chengjiang faunas. Biostratigraphy of SSF was best analyzed in Yunnan, S. China (e.g. Meishucun, Laolin, Xiotan) because of the abundant occurrence of SSFs from various depositional environments from extremely shallow to deep basin. This study carefully examined litho- and SSF stratigraphy of Hongjiachong section and Xiaolantian section in Chengjiang area Yunnan. The two studied sections consist of the Zhijiaqing Fm, Shiyantou Fm, and Yu’anshan Fm, in ascending order. The Zhijiaqing Fm is subdivided into Daibu Mb, Zhongyicun Mb, and Dahai Mb. Although the first and second SSF assemblages were recovered at the Hongjiachong section (Sato et al., 2014), the boundary between these two assemblages was not identified yet. The first assemblage occurred in the lower Zhongicun Mb, but the overlying strata for ca. 20m thick are barren, except the second assemblage from the marker calcareous sandstone in the middle of Zhongicun Mb.

To date, the following results were obtained from the Hongjiachong section; 1) second SSF assemblage occurs from a phosphorite bed 1m lower than the previously claimed the lowest horizon at the marker sandstone in the middle of Zhongjicun Mb, 2) one unique SSF specimen with particular shell structure was extracted from a phosphorite bed ca. 4 m lower than the marker sandstone. This fossil piece is ca. 1.5 mm long and in an elongated oval shape, probably representing a fragment of nearly symmetrical shell. Along the axial cylindrical pillar, multiple small plates are aligned obliquely along one side. These features are similar to those of the SSF, *Sinosachites (Thambetolepis) delicaties* (JELL) reported from Lower Cambrian in S. Australia, which is correlated to relatively younger the Shiyantou and Yu’anshan formations in China. We will also report the litho- and SSF stratigraphy of drilled core samples (ca. 87 m deep) from the Xiaolantian section currently under analysis.

Keywords: Cambrian, SSF, Xiaolantian, Hongjiachong
Stable and radiogenic strontium isotope variation (δ\(^{88}\)Sr, \(^{87}\)Sr/\(^{86}\)Sr) in Middle-Upper Permian mid-oceanic paleo-atoll carbonates

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Stable strontium isotope ratios (δ\(^{88}\)Sr) of the Capitanian (late Guadalupian) to Wuchiapingian (early Lopingian) carbonates were measured by TIMS, by correcting isotope fractionation during mass spectrometry with \(^{87}\)Sr-\(^{84}\)Sr double spike. The studied carbonate section at Akasaka (Japan) in the Jurassic accretionary complex was originally deposited on a mid-Panthalassan paleo-seamount, which recorded a unique interval with extremely low \(^{87}\)Sr/\(^{86}\)Sr values (the Permian minimum for ca. 5 m.y. throughout the entire Capitanian). We also analyzed the Wuchiapingian section at Lianshan in S. China, which was deposited on the shallow shelf. Both in δ\(^{88}\)Sr and radiogenic \(^{87}\)Sr/\(^{86}\)Sr ratios, low values remained throughout the Guadalupian, whereas they increased rapidly in the Wuchiapingian. The newly obtained δ\(^{88}\)Sr profile of Middle-Late Permian seawater positively correlated with that of \(^{87}\)Sr/\(^{86}\)Sr ratio. As seawater δ\(^{88}\)Sr could sensitively reflect marine carbonate flux at the ocean floor, this correlation suggests that the valance between the Sr carbonate burial flux and Sr carbonate dissolution flux has changed sharply across the Guadalupian-Lopingian boundary. The Capitanian minimum and the following rapid increase in seawater \(^{87}\)Sr/\(^{86}\)Sr likely reflected a major change in continental flux, probably reflecting the rapid deglaciation together with enhanced erosion/weathering of continental crusts on a global scale.

Keywords: Sr isotope, Permian, carbonate
Change of the carbon cycle in G-L boundary using numerical value calculation

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The largest extinction of Big five in Phanerozoic is observed in end of Permian period. The large extinction include two step, Guadalupian- Lopingian boundary (GLB) and Permian- Triassic boundary (PTB) (Sepkoski, 1984; Knoll et al., 1996; Isozaki, 1997; Stanley and Yang, 1994; Kaiho et al., 2005). Therefore, we need to study from GLB to PTB, in order to understand the correlation between extinction and environmental changes. We study life cycle changes and influence to oceanic environment in extinction by changes of carbon isotope ratio.

There were many previous studies of carbonate and organic carbon isotope ratio from GLB to PDB. The carbon isotope records show over +6 permil before GLB, calling to Kamura event. The δ13Ccarb after Kamura event decrease to ca. 0 permil around GLB. Moreover, the δ13Ccarb 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). On the other hand, organic carbon isotope date show about -30^-28 permil in deep sea sediment (Nishikane et al., 2014). And decoupled carbonate and organic carbon isotope ratio is observed in Iwaizaki carbonate section, South of Kitakami belt. The section corresponds to the Kamura event before GLB (Tobita et al., in prep).

We discuss the change of carbon cycle to reproductive carbonate and organic carbon isotope changes by the numerical value calculate. We assume an inorganic and an organic reservoir in the sea. Flows (Photosynthesis and Remineralization, organic burial, carbonate burial) are a ratio of each reservoir’s size. The results suggested changing amount of organic matter in GLB. The changes might be triggered by large extinction. The large organic matter might cause a global expansion of oxygen minimum zone (OMZ).

Keywords: GL boundary, Carbon cycle, extinction