Calibrating the End-Permian Mass Extinction
Shu-zhong Shen, et al.
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The end-Permian mass extinction was the most severe biodiversity crisis in Earth history. To better constrain the timing, and ultimately the causes of this event, we collected a suite of geochronologic, isotopic, and biostatigraphic data on several well-preserved sedimentary sections in South China. High-precision U-Pb dating reveals that the extinction peak occurred just before 252.28 ± 0.08 million years ago, after a decline of 2 per mil (‰) in δ13C over 90,000 years, and coincided with a δ18O excursion of ~5‰ that is estimated to have lasted ≤20,000 years. The extinction interval was less than 200,000 years and synchronous in marine and terrestrial realms; associated charcoal-rich and soot-bearing layers indicate widespread wildfires on land. A massive release of thermogenic carbon dioxide and/or methane may have caused the catastrophic extinction.

U-Pb geochronology. We established a chronology of the end-Permian extinction using U-Pb isotope dilution thermal ionization mass spectrometry (ID-TIMS) on 300 single grains of zircon and monazite from 29 volcanic ash beds in five marine, two marine-terrestrial transitional, and two terrestrial sections in South China (Figs. 1 and 2 and tables S1 and S2) (16). U-Pb geochronology of zircon from volcanic ash beds interlayered with fossil-bearing carbonate rocks can establish ages with uncertainties of ±60 to 120 ky (ky, thousand years) (2σ) for 250-Ma (Ma, millions of years ago) rocks. High-resolution ages strengthen the paleontologic correlation between these realms.

Previous estimates of the Permian-Triassic boundary (PTB) range from 251.4 to >254 Ma (17–19). We dated some samples reported in (17) and many new samples from well-known sections in four areas of South China (SOM text 1, Fig. 1 and fig. S1A, and table S1): (i) Meishan with two Global Stratotype Section and Points (GSSPs), (ii) Shangsi, (iii) Penglaitan and Tiegao, and (iv) several terrestrial and marginal marine sections (figs. S2 to S4). Dates from zircon are 206Pb/238U dates based on analyses of single grains (16). 207Pb/235U dates from monazite in two samples are used instead of zircon to interpret depositional ages because of considerable scatter in the zircon dates. The scatter is likely due to slight amounts of inheritance, Pb loss, or an extended period of residence in the magma (tables S1 and S2).

U-Pb dates from this study are considerably more precise than those from previous studies due to enhanced ionization efficiency in the mass spectrometer and a reduced amount of common Pb in our zircon analyses [0.48 pg, compared with 4.0 and 1.9 pg in (17, 18), respectively], leading to higher ratios of radiogenic Pb to common Pb. The average 2σ error on most of the individual 206Pb/238U dates that are neither xenocrysts nor contain a xenocrystalic component is ±0.23 My (0.09%), smaller than previous average errors on dates of ±1.0 to 1.2 My (17, 18). The improved precision enhances our ability to identify grains that have suffered slight Pb loss or contain a minor xenocrystalic component.

Weighted mean dates from beds 7 and 22 at Meishan are within error of those in (17), but dates from beds 25 and 28 near the PTB are 0.88 and 1.4 My older, respectively. The date from bed 25 agrees with that in (18), and the date from bed 28 is younger than that in (19). Dates from Penglaitan agree with those in (17), whereas the date from Heshan is 0.7 My older than three dates from (17). The discrepancy between our new dates and those of (17) is most likely due to Pb loss in grains dated by (17) that was not eliminated by mechanical abrasion, but has now been eliminated by chemical abrasion. Dates from Shangsi ash beds at ~0.3, ~12.8, and ~27.4 m below the PTB agree with those from (18) and are two to three times more precise. A decay-constant–adjusted 207Pb/235U monazite...
date from –2.9 m agrees with a zircon date from roughly the same interval in (18).

Age and duration of mass extinction. Because Meishan is the most intensively studied PTB section, we compared geochronologic dates and the carbon isotope record with a well-resolved conodont biostratigraphy (Fig. 2 and fig. S3). The following sequence of events can be distinguished: (i) a 5% negative δ13C isotopic anomaly over 5 cm that starts abruptly within bed 24e and ends in bed 25; (ii) the main extinction event between beds 24e and 28 (Fig. 3); and (iii) the PTB marked by the first appearance of *Hindeodus parvus* at bed 27c, 14 cm above bed 25. Geochronologic constraints are provided by ash beds at bed 25 dated at 252.28 ± 0.08 Ma and bed 28 (located 8 cm above the boundary) dated at 252.10 ± 0.06 Ma.

The duration of the sharp downturn in carbonate carbon isotopes is best estimated with the sediment accumulation rates from either beds 22 to 25 or beds 25 to 28. We favor the latter, which we project the composite species richness pattern through the Lopingian to Early Triassic (figs. S8 to S10). To calibrate the end-Permian extinction precisely, we project the combined record of dated ashes and species first and last occurrences into the stratal sequence at the most-intensively studied Meishan section.

Shangsi, and Zhongzhai and thus are consistent. Twelve richly fossiliferous sections from the Late Guadalupian to Early Triassic of South China span shallow-water carbonate platform, slope, and basinal habitats (table S3). Six sections from Tibet, Kashmir, and Pakistan record the southern temperate peri-Gondwanan region (20). This encompassed 1450 species from 16 fossil groups including cephalopods, brachiopods, foraminifers, fusulinids, conodonts, corals, bivalves, radiolarians, bryozoans, gastropods, ostracods, fish, calcareous algae, spores, and pollen, and plant macrofossils. We generated a composite species richness pattern through the Lopingian to Early Triassic (figs. S8 to S10).

Extinction patterns. To improve upon a previous species-level analysis based solely on Meishan (5), we pooled occurrence data from 18 biostratigraphically well-studied sections. Twelve richly fossiliferous sections from the Late Guadalupian to Early Triassic of South China span shallow-water carbonate platform, slope, and basinal habitats (table S3). Six sections from Tibet, Kashmir, and Pakistan record the southern temperate peri-Gondwanan region (20). This encompassed 1450 species from 16 fossil groups including cephalopods, brachiopods, foraminifers, fusulinids, conodonts, corals, bivalves, radiolarians, bryozoans, gastropods, ostracods, fish, calcareous algae, spores, and pollen, and plant macrofossils. We generated a composite species richness pattern through the Lopingian to Early Triassic (figs. S8 to S10). To calibrate the end-Permian extinction precisely, we project the combined record of dated ashes and species’ first and last occurrences into the stratal sequence at the most-intensively studied Meishan section.

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The full scope of the combined data set is 2584 serial estimates of species richness across >16 million years (SOM text 3 and fig. S8), of which 640 successive richness estimates occur in the portion of the time series that captures the end-Permian mass extinction.

The diversity data from 18 sections reveal a sharp drop in biodiversity over a very narrow time interval (Fig. 3 and figs. S8 to S10). Several ammonoid, bivalve, small foraminifer, and brachiopod species survived the extinction, but disappeared soon afterwards, accounting for the decreasing diversity in the earliest Triassic. Some spores and pollens in the Earliest Triassic from Meishan and a few new species, such as Claraia wangi and Hypophiceras sp., produce a trivial rise in diversity immediately after the PTB, but do not change the general trend of overall decreasing diversity. Although the proportional extinction rate stays high in the Early Triassic, the number of extinct species is very low, likely indicating continuing environmental deterioration. Raw, per-section, and rarefied taxon richness curves based on a wider interval demonstrate lack of significant sampling bias within the narrower interval of study spanning the extinction event. The previously repeated two- or multiple-stepped extinction derived from Signor-Lipps effect (21) is not supported below the 95% confidence threshold, and only one significant step remains (Fig. 3 and figs. S8 to S10). At Meishan, the main pulse of extinction in beds 24e to 28 is associated with and followed by cyanobacterial expansion with anoxic condition; the latter is a global occurrence (3, 13, 14).

The taxa projected into the Meishan section reinforce the species richness pattern derived from the Meishan pattern alone (3) after the Meishan local ranges are extended based on information from other sections that share these taxa (Fig. 3). At Meishan, U-Pb ages for ash beds indicate that the main extinction event began just before 252.28 ± 0.08 Ma (age of bed 25). After augmentation of information from all of the sections, Meishan constrains the major event to start no earlier than 252.30 Ma and end before 252.10 Ma; i.e., 200 ± 100 ky later—an absolute maximum for the duration of the extinction (Figs. 2 and 3).

Synchronous collapse of the end-Permian tropical terrestrial ecosystem. There is ongoing debate over whether the marine event coincides precisely with extinctions among plants and terrestrial vertebrates. The Gigantopteris floras of the Permian Paleotethys are interpreted as rainforest-type vegetation in the tropical ever-wet climatic zone. The Permian rainforest collapsed across the PTB, and recovery was delayed until the Middle Triassic (SOM text 4) (22). Detailed studies in the Karoo Basin of South Africa and Greenland indicated a catastrophic event for terrestrial vegetation and vertebrates in high paleolatitudes (23, 24), but there are few detailed investigations from tropical coastal and terrestrial P-T sections, and none are constrained by precise geochronology.

We investigated three terrestrial and two marine/nonmarine transitional sections (SOM text 2, Fig. 4, and figs. S1 and S5 to S7) on the eastern slope of a large (~300,000 km²) volcanic plateau (fig. S1A) formed by the late Guadalupian eruption of the Emeishan basalt. Correlation of the P-T transition is established by the first
occurrence of *Hindeodus parvus* and other conodonts, the negative carbon isotope shift, U-Pb zircon dating of PTB ash beds, and magnetostratigraphic data (SOM text 2 and Fig. 4).

At the marine/terrestrial transitional Chuanyan section, the topmost Changhsingian contains a diverse *Gigantopteris* flora, a 0.32-m-thick coal seam with an ash bed in the middle, an upper ash bed and a pyrite-rich bed with charcoal fragments, pyritized Triassic bivalves, and tiny gastropods; these represent high sulfidic input and transported remnants of a coal-forming tropical forest (fig. S5). Coal palynology (14 species in 18 genera) also reveals a typical Late Permian *Gigantopteris* flora. Twenty-six brachiopod species from the Changhsingian having multiple occurrences were used to locate the major marine extinction. Both the stratigraphic range data (figs. S5 and S6A) and the results of 50% confidence interval analysis for 23 species with multiple occurrences (fig. S7B) suggest that the marine mass extinction is coincident with the last coal.

The Lopingian *Gigantopteris* flora in South China consists of 94 genera and 261 species dominated by hygrophilous and thermophilous plant groups such as pecopterids, gigantopterids, lycopsiales, and equisetales. They mostly range up to the latest Changhsingian in South China (SOM text 4). At the Guanbachong section, foliar physiognomy analysis of 31 species 0.9 m below the most negative δ13Corg value indicates that plants with large leaves comprise 88% of the flora, and 77% have an entire margin; this is consistent with percentages found in the warm and humid conditions of modern tropical floras. Similar plant-rich horizons are found at the Longmendong, Chahe, and Chuanyan sections where latest Permian rocks, deposited before the isotopic negative shift, contain 95% of Late Permian or Paleozoic-type ferns and pteridosperms and 5% gymnosperm pollen. In the topmost Changhsingian, within the negative shift of carbon isotope, the abundance of fern and pteridosperm spores decreases to 61.2% whereas gymnosperm pollen increases to 38.8%. At the Longmendong section, 22 species in 23 genera are present in the PTB breccia bed. The immediately overlying lowest Triassic is barren of coal, plant fossils, and palynomorphs.

C-isotopic data of organic matter (δ13Corg) from three terrestrial sections show consistent values of ~23 to ~24‰ during the Lopingian, followed by sharp drops in δ13Corg ranging from ~5.8 to ~10‰ that coincide with mass extinction (Fig. 4). Such a rapid drop in δ13C slightly below the PTB has been also used to locate the PTB in nonmarine sequences in Australia, Antarctica, and South Africa, although in the absence of additional biostratigraphic or radiometric data, the correlations have been disputed (4, 24). The negative organic C isotope anomaly is apparently younger than 252.30 ± 0.07 Ma based on the age of the underlying ash bed (Chahe 68) in the Chahe section, which is nearly consistent in age with bed 25 at the Meishan section (Fig. 4 and table S4). Palynological study indicates a dramatic reduction in the diversity and abundance of the *Gigantopteris* flora above bed 68 at the Chahe section (25). Thus, the immediately overlying terrestrial extinction is consistent with those at the transitional Zhongzhai and Chuanyan sec-

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**Fig. 4.** Correlation of the disappearance of the *Gigantopteris* flora, charcoal layers, lithologic color shift, and carbon isotope excursions between the terrestrial and transitional PTB sequences on the eastern slope of the Emeishan volcanic plateau and the marine Meishan Section. Dashed blue line represents the correlated position between the stratigraphic sections which is just above the major extinction pulse. The carbon isotope profile at the Meishan section is from (2). The dates are U-Pb zircon 206Pb/238U ages of ash beds. Color of the lithology approximately represents the Munsell color of rocks measured in the field.
tions and the marine extinction at the Meishan section (5). The isotopic negative shift also coincides with the abrupt cessation of coal formation in southern high paleolatitudes (26). The δ^{13}C_{carb} and/or δ^{13}C_{org} and the floral data in South China suggest that a rapid collapse of the tropical rainforest occurred within the negative shift of δ^{13}C_{carb} very close to the PTB and that the disappearance of the highly diverse Gigantopteris flora is synchronous with the mass extinction of marine organisms (Fig. 4).

**Widespread wildfires.** Evidence of widespread deforestation close to the PTB comes from distinctive charcoal layers with abundant pyrofusinite at several localities in South China (Figs. 4 and 5 and fig. S11) (16). Fire-derived products have been recorded from PTB beds at the Meishan section (13, 27). Charcoal layers are also found from horizons correlated biostratigraphically and geochemically to the PTB at the Tieqiao section in Guangxi, South China, and near the PTB in Xinjiang Province and North China (Fig. 5). We interpret the pyrofusinite as transported from environments with charcoal and soot produced by burning of the rainforests in terms of its homogenized cell walls, three-dimensional cellular preservation with open lumina, pitted trachheid, and brittle fracture (Fig. 5). Other fire evidence was reported from the PTB beds in marine sections in Western Australia (28) and Canadian High Arctic (29). The widespread distributions of fire-derived products suggest that dramatic global warming and increasing aridity reached a climax coincident with the marine extinction, rapidly turned the ever-wet biome into a seasonally dry climate, and increased forest fire that was immediately followed by catastrophic soil erosion (30) and fungal virulence (31) due to rapid deforestation.

**Causes of the end-Permian mass extinction.**

A shift in latest Permian δ^{13}C_{carb} began with a gradual decline at the base of bed 23 at Meishan (Fig. 2), which could be interpreted as the collapse of the biological pump (32), an increase in continental weathering caused by sea-level fall, or massive volcanism (9, 17, 33). The gradual decline of C isotopes with a short duration (maximum duration of 90 ky) is followed by a brief (<20 ky) negative pulse of δ^{13}C_{carb} associated with the sharp drop of biodiversity between the uppermost part of bed 24 and bed 25, which is immediately followed by the negative shift of δ^{13}C_{org} (Figs. 2 and 3). Dates from Shangsi and Zhongzhai, the two other sections with dated ash beds bracketing the PTB, support this result. Biomarker and organic carbon isotopic studies are consistent with widespread continental weathering and transport of plant fragments and black carbon from wildfires, related to collapse and burning of terrestrial plants (27, 30, 34). The correlations between marine, marine-terrestrial transitional, and terrestrial sections (Fig. 4) indicate that the marine extinction was synchronous across South China at the ~0.2-My level with loss of the rainforest, wildfires, and the cessation of coal formation (24, 26). Integrated biomarker and organic C isotopic studies also indicate perturbations to the carbon cycle characterized by increased terrestrial weathering during and immediately after the collapse of terrestrial ecosystem and widespread introduction of sulfide waters into the photic zone (1, 12, 33) as indicated by the concentration of pyrite within the extinction horizon and cyanobacterial expansion (13).

Despite evidence for dysoxic and anoxic conditions in the deep ocean both just before and after the extinction (2, 3), the synchronicity of C_{carb} isotope excursion and extinction suggest a causal link between the introduction of the light carbon and the extinction. The simplest way to produce a widespread, large pulse of shallow-water anoxia and euxinia is by carbon dioxide and/or methane-induced global warming that leads to decreased oxygen solubility, intensification of continental weathering, and increased nutrient delivery to the oceans [e.g., (33)] with biodiversity decline coinciding with onset of a period of rapid warming.

The data presented here allow us to better constrain such hypotheses. The δ^{13}C_{carb} drops about 7‰ over roughly 100 ky, and about 5‰ in roughly the last 10 ky of those 100 ky, with the δ^{13}C_{org} decline immediately after the decline in δ^{13}C_{carb}. An understanding of such fast changes requires a model of isotopic evolution that explicitly considers rates of change. Here we use our new time scale to calculate how much additional light carbon of a fixed composition δ_i must be added to the system to reproduce the excursion as seen at Meishan, under the assumption that the isotopic changes occur in globally well-mixed oceans. The result provides the mass m' of additional light carbon, normalized by the assumed pre-existing size m* of the oceans’ reservoir of dissolved inorganic carbon (DIC) (fig. S12). As expected, lighter inputs require less flux. However, no known worldwide reservoir of light organic carbon contains greater than about 5000 Gt (35). The modern value for DIC, by contrast, suggests m* ~38000 Gt (36). Thus, the maximum conceivable modern value of m'/m* is about 0.13, somewhat less than the value of 0.16 that would be required for methane hydrates (δ_i = ~60‰), and much less than the value of 0.38 required from typical organic carbon (δ_i = ~28‰). Neither comparison disqualifies the scenario of a massive injection of light carbon. It instead indicates the unusual nature of the end-Permian environment.

The end-Permian extinction has long been linked to eruption of the massive Siberian flood basalt through production of large amounts of sulfates, CO_2, and possibly thermogenic methane (8, 9, 13, 14, 29, 33, 37). A previous U-Pb study of the flood basalts (8) shows that much of them are slightly younger than our interpreted extinction age. The age discrepancy could be due to...
REFERENCES AND NOTES

INTERLABORATORY BIAS RELATED TO CALIBRATION OF THE TRACER SOLUTIONS USED IN DIFFERENT LABORATORIES. MUNDL ET AL. (18) COMBINED RECALCULATED $^{40}$Ar/$^{39}$Ar DATES FOR BED 25 FROM MEISHAN (252.1 ± 0.4 MA) WITH THE EARLIER STUDY SHOWING THAT $^{40}$Ar/$^{39}$Ar DATES OF FLOOD BASALTS AND BED 25 ARE THE SAME (9) TO CONCLUDE THAT THE FLOOD BASALTS AND EXTINCTION ARE ESSENTIALLY SYNCHRONOUS. RECENT WORK HAS FOCUSED ON THE ROLE OF LARGE INTRUSIONS OF BASALTIC MAMMAGS THAT HAVE INTERACTED WITH ORGANIC-RICH SHALES AND PETROLEUM-BEARING EVAPORITES THAT MAY HAVE CAUSED LARGE QUANTITIES OF GREENHOUSE GASES TO BE RELEASED AT 252.0 ± 0.4 MA (38).

Our studies indicate that both marine and terrestrial ecosystems collapsed very suddenly, and massive release of thermogenic CO$_2$, as well as methane, is a highly plausible explanation (29, 39). Our data on the timing and pace of the end-Permian mass extinction are consistent with rapid CO$_2$ increase as indicated by distinct paleophysiological effects of the ecosystem (15), a sharp drop in O$_2$ (40), and substantial addition of atmospheric sulfate-bearing aerosols. These critical inputs could have resulted in increased continental aridity by rapid global warming, which caused widespread wildfires and accelerated deforestation in the world. Rapid deforestation further enhanced the continental weathering and finally resulted in a catastrophic soil erosion on the continent at PTB (30).

References and Notes

16. Materials and methods are available as supporting material on Science Online.

Imaging of Plasmodium Liver Stages to Drive Next-Generation Antimalarial Drug Discovery


Most malaria drug development focuses on parasite stages detected in red blood cells, even though, to achieve eradication, next-generation drugs active against both erythrocytic and exo-erythrocytic forms would be preferable. We applied a multifactorial approach to a set of >4000 commercially available compounds with previously demonstrated blood-stage activity (median inhibitory concentration < 1 micromolar) and identified chemical scaffolds with potent activity against both forms. From this screen, we identified an imidazolopiperazine scaffold series that was highly enriched among compounds active against Plasmodium liver stages. The orally bioavailable lead imidazolopiperazine confers complete causal prophylactic protection (15 milligrams/kilogram) in rodent models of malaria and shows potent in vivo blood-stage therapeutic activity. The open-source chemical tools resulting from our effort provide starting points for future drug discovery programs, as well as opportunities for researchers to investigate the biology of exo-erythrocytic forms.

**Malaria continues to present a major health challenge in many of the poorest countries in the world, with 225 million cases leading to an estimated 781,000 deaths in 2009 (1). In humans, malaria is caused by Plasmodium falciparum, P. malariae, P. ovale, P. vivax, and the simian parasite P. knowlesi (2). Plasmodium is naturally transmitted by the bite of an infected female Anopheles mosquito. During the bite, the sporozoites are injected with the mosquito’s saliva and find their way to the host liver. There the parasites multiply asexually as exo-erythrocytic forms (EEFs) during an asymptomatic incubation period of ~1 week.

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