During the end-Permian extinction, a substantial amount of methane (CH₄) was likely released into the ocean-atmosphere system associated with the Siberian Traps volcanism, although fluctuations in the global CH₄ cycle in the aftermath of the extinction remain poorly understood. The carbon (C) isotopic composition of carbonate (δ¹³C_{carb}) across the Permian-Triassic boundary (P-TB) was analyzed at Chaotian, South China. The δ¹³C_{carb} values decrease from ca. +1 to −2‰ across the P-TB, possibly caused by a collapse of primary productivity associated with the shallow-marine extinction. The frequent intercalation of felsic tuff layers around the P-TB suggests that a volcanogenic carbon dioxide (CO₂) input to the surface oceans may also have contributed to the δ¹³C_{carb} decline. The magnitude of the δ¹³C_{carb} decrease (∼3‰) is substantially smaller than the magnitude of a decrease in C isotopic composition of organic matter (δ¹³C_{org}) in the same P-TB interval (∼7‰). This apparent δ¹³C_{carb}-δ¹³C_{org} decoupling could be explained by proliferation of methanogen (“methanogenic burst”) in the sediments. A global δ¹³C compilation shows a large variation in marine δ¹³C_{org} records, implying that the “methanogenic burst” according to the Siberian Traps volcanism may have contributed, at least in part, to the δ¹³C_{org} variability and to the elevated CH₄ levels in the atmosphere. The present and previous observations allow us to infer that the global CH₄ cycle may have fluctuated substantially in the aftermath of the extinction.

Keywords: end-Permian extinction, global CH₄ cycle, methanogenesis, methanotrophy, anaerobic oxidation of methane (AOM), global warming, variable δ¹³C_{org} records
INTRODUCTION

The end-Permian extinction was one of the largest biodiversity crises in the Phanerozoic (e.g., Erwin, 2006; Alroy, 2010; Shen et al., 2011a; Stanley, 2016), and many geologic events around the Permian-Triassic boundary (P-TB) have been proposed as the cause of the extinction, including a bolide impact (e.g., Xu et al., 1985; Becker et al., 2004), Siberian Traps volcanism (e.g., Renne and Basu, 1991; Campbell et al., 1992; Kamo et al., 2003; Reichow et al., 2007a; Horacek et al., 2007b; Korte and Kozur, 2010 and references therein; Shen et al., 2013; Schobben et al., 2016; Horacek et al., 2017; Jurikova et al., 2020). However, the ultimate trigger mechanisms of the extinction remain a topic of discussion (e.g., Payne and Clapham, 2012; Isozaki, 2019; Racki, 2020).

The global carbon (C) cycle was likely perturbed during the Permian-Triassic transition in association with those geologic events that potentially contributed to the extinction (e.g., Kump and Arthur, 1999). Stable C isotope geochemistry is useful to correlate sections in different regions and to reveal the changes in the global C cycle (e.g., Hayes et al., 1999). Plenty of studies analyzed the C isotopic composition of carbonate (δ13Ccarb) and organic carbon (δ13Corg) across the P-TB and documented a negative δ13Ccarb shift by ~5‰ during the extinction in various sections around the world, including South China, Iran, Armenia, northern Italy, Austria, Slovenia, and Pakistan (e.g., Magaritz et al., 1988; Baud et al., 1989; Holser et al., 1989; Jin et al., 2006; Richoz, 2006; Horacek et al., 2007a; Horacek et al., 2007b; Korte and Kozur, 2010 and references therein; Shen et al., 2013; Schobben et al., 2016; Joachimski et al., 2020). Although several studies pointed out a substantial diagenetic overprint and/or erosional unconformity on the P-TB δ13Ccarb records (e.g., Heydari et al., 2001; Heydari and Hassanzadeh, 2003; Grasby and Beauchamp, 2008; Yin et al., 2014; Schobben et al., 2016; Li and Jones, 2017), the widely recognized P-TB δ13Ccarb decrease has been generally regarded as an original isotopic signal of seawater (Baghperpour et al., 2019).

Considering a simple box model of the surface-ocean C pool, two principle mechanisms could explain the P-TB δ13C decrease in marine carbonates: 1) a decrease in the input and 2) an increase in the input of 13C-depleted C (e.g., Korte and Kozur, 2010). A collapse in primary productivity and reduction in biological pump (“strangelay oceans”) corresponds to the former mechanism (e.g., Kump, 1991), although it may have produced only a ~3‰ negative δ13Ccarb shift (Rampino and Caldeira, 2005) and might not be sufficient to explain larger P-TB δ13C declines commonly observed around the world. The increase in the input of 13C-depleted C to the surface oceans seems to be more important (e.g., Payne and Clapham, 2012), and several geologic events have been proposed for the C injection, including volcanicogenic CO2 emission involved in the Siberian Traps volcanism (e.g., Renne et al., 1995; Hansen, 2006), methane (CH4) release during destabilization of submarine and permafrost clathrates or thermal alteration of coal by volcanic intrusion (e.g., Erwin, 1993; Morante, 1996; Krull and Retallack, 2000; Berner, 2002; Sarkar et al., 2003; Retallack and Jahren, 2008), enhanced erosion and reoxidation of sedimentary organic matter or terrestrial soil (e.g., Baud et al., 1989; Holser et al., 1989; Ward et al., 2000; Sephton et al., 2005), and the oceanic overturn or shoaling of deep-water (e.g., Kajiwara et al., 1994; Knoll et al., 2005; Fielding et al., 2019). Moreover, the P-TB is generally not well correlated normally with the negative δ13Ccarb shift in shelf carbonates by assuming that the δ13Ccarb and δ13Corg trends were parallel and the difference between the δ13Ccarb and δ13Corg Values (Δ13C) was consistent during the Permian-Triassic transition, although the Δ13C value is generally controlled by several factors such as carbon dioxide (CO2)-fixing enzymes and atmospheric CO2 levels (pCO2) (e.g., Hayes et al., 1999). A parallel δ13Ccarb and δ13Corg decline has been reported in the P-TB intervals in Austria (Magaritz et al., 1992), Italy (Sephton et al., 2002), mid-Panthalassa (Musashi et al., 2001), and Kashmir (Algeo et al., 2007b). However, some studies pointed out a δ13Ccarb-δ13Corg decoupling across the P-TB. The Δ13C values apparently decrease in some sections in South China, Slovenia, and Iran (Riccardi et al., 2007), and increase in some other Chinese sections (e.g., Shen et al., 2012).

The δ13Corg decrease in a terrestrial P-TB succession has also been reported in South China (e.g., Shen et al., 2011a), South Africa (e.g., Ward et al., 2005; Gastaldo et al., 2020), Antarctica (e.g., Krull and Retallack, 2000), Australia (Morante, 1996), Madagascar (de Wit et al., 2002), and Germany (Scholze et al., 2017). However, the apparent δ13Corg trends on land are generally variable compared to those of marine sediments, and the P-TB δ13Corg decline is not clearly recognized in many terrestrial sections (e.g., Retallack et al., 2005; Fielding et al., 2019). Moreover, the P-TB is generally not well assigned in the terrestrial successions due to their poorer biostratigraphic constraints. Under these circumstances, it is still difficult to correlate the terrestrial δ13Corg records well with the marine δ13Corg and δ13Ccarb records.

Previous studies particularly suggested that a substantial amount of CH4 was released into the ocean/atmosphere during the Siberian Traps volcanism via several processes, including volcanic intrusion into coal (e.g., Retallack and Jahren, 2008; Shen et al., 2012; Rampino et al., 2017), destabilization of submarine and permafrost clathrates (e.g.,
Krull et al., 2000; Krull et al., 2004; Brand et al., 2016), and enhanced microbial methanogenesis (“methanogenic burst”) (Rothman et al., 2014). As CH$_4$ is a potent greenhouse gas, the huge CH$_4$ input may have contributed to climate warming in the aftermath of the extinction (e.g., Hallam and Wignall, 1997; Joachimski et al., 2012; Sun et al., 2012; Cui and Kump, 2015). However, the global CH$_4$ cycle during the Permian-Triassic transition has been poorly examined and constrained. In this study, we analyzed the $\delta^{13}$C$_{\text{carb}}$ records of the P-TB carbonates at Chaotian in northern Sichuan, South China. Together with the previously reported $\delta^{13}$C$_{\text{org}}$ records of the same interval, we examined the sedimentary C cycle in eastern Paleotethys during the Permian-Triassic transition. Moreover, we compiled the $\delta^{13}$C$_{\text{carb}}$ and $\delta^{13}$C$_{\text{org}}$ records of P-TB successions in various marine and terrestrial environments around the world, to examine whether the isotopic signal detected at Chaotian was a global one. Based on those results, we suggest fluctuations in the global CH$_4$ cycle in the aftermath of the end-Permain extinction.

**GEOLOGICAL SETTING AND STRATIGRAPHY**

During the Permian to early Triassic, South China was isolated from other continental blocks and located at low latitudes on the eastern side of Pangea (Figure 1B; Muttoni et al., 2009). Shallow-marine carbonates and terrigenous clastics with diverse fossils accumulated extensively on its platform (e.g., Zhao et al., 1981; Yang et al., 1987; Jin et al., 1998). In northern Sichuan along the northwestern edge of South China, carbonates and mudstones of deep-water facies accumulated on a slope/basin that faced on the eastern Paleotethys (Figure 1C; Zhu et al., 1999; Wang and Jin, 2000). The Chaotian section is located ca. 20 km to the north of Guangyuan city in northern Sichuan (Figure 1; 32°37′N, 105°51′E; Isozaki et al. 2004). At Chaotian, Guadalupian (middle Permian) to lowermost Triassic carbonates are continuously exposed along the bank of the Jialingjiang River in a narrow gorge called Mingyuexia. We mapped the eastern bank of the gorge on the southern limb of an E-W trending anticline.

The Permo-Triassic rocks at Chaotian (>300 m thick in total) are composed of the Guadalupian Maokou Formation, the Lopingian Wujiaaping and Dalong formations, and the lowermost Triassic Feixianguan Formation, in ascending order (Figure 2; Isozaki et al., 2004; Isozaki et al., 2007; Saitoh et al., 2013a; Saitoh et al., 2013b; Saitoh et al., 2014a). The Maokou Formation (>150 m thick) is composed mainly of massive dark gray bioclastic limestone with diverse shallow-marine fossils, such as calcareous algae, brachiopods, ostracodes, crinoids, rugosa corals, and fusulines. However, the uppermost part
The Maokou Formation (~11 m thick) of the Maokou Formation is composed of thinly bedded black calcareous mudstone and black chert/siliceous mudstone with abundant radiolarians, conodonts, and ammonoids. The Wujiaoping Formation (~70 m thick) is composed mainly of massive dark gray bioclastic limestone with black chert nodules/lenses, containing shallow-marine fossils such as fusulines, smaller foraminifer, rugosa corals, calcareous algae and brachiopods. At the base of the Wujiaoping Formation, a ca. 2 m thick tuffaceous Wangpo bed occurs. The Dalong Formation (~25 m thick) is composed mainly of thinly bedded black mudstone, black siliceous mudstone and dark gray limestone with radiolarians, ammonoids, bivalves, and brachiopods. The Feixianguan Formation (>30 m thick) is composed mainly of thinly bedded light gray micritic limestone containing few conodonts, ammonoids, and brachiopods.

Zhao et al. (1978) and Yang et al. (1987) originally described the overall biostratigraphy of the Chaotian section based on fusulines, conodonts, and ammonoids. Isozaki et al. (2004) and Isozaki et al. (2007) re-examined the stratigraphy of the section that spans across the two mass extinction intervals; i.e. the Guadalupian-Lopingian boundary (G-LB) and the P-TB in higher resolution. More analyses on the litho-, bio-, and chemo-stratigraphy of the Chaotian section added further information (Isozaki et al., 2008; Lai et al., 2008; Saitoh et al., 2013a; Saitoh et al., 2013b; Jost et al., 2014; Saitoh et al., 2014b; Saitoh et al., 2015; Saitoh et al., 2017). Isozaki et al. (2007) and Ji et al. (2007) constructed the detailed lithostratigraphy and conodont zonation for the ~12 m thick interval across the P-TB, and suggested that intermittent felsic volcanism may have contributed to the extinction. Cao et al. (2010) analyzed the $\delta^{13}$C_carb values around the P-TB and found a negative $\delta^{13}$C excursion around the extinction horizon. Saitoh et al. (2014a) analyzed the nitrogen and organic C isotopic composition of the ~40 m thick P-TB interval at Chaotian and suggested enhanced nitrogen fixation in the anoxic oceans throughout the Changhsingian.

In the present study, we focused on the ~40 m thick P-TB interval at Chaotian (Figure 2). This interval is identical to that analyzed in Saitoh et al. (2014a), which contains the ~12 m thick carbonates analyzed in Isozaki et al. (2007). Fresh rock samples, collected from outcrops and from core samples by scientific drilling to a depth of >30 m, were prepared as polished slabs and thin sections for describing microtextures by petrographical observations. The analyzed P-TB interval is composed of three stratigraphic units: 1) the upper Wujiaoping Formation, 2) the Dalong Formation, and 3) the lowermost Feixianguan Formation, in ascending order. The upper Wujiaoping Formation (~10 m thick) is composed mainly of massive dark gray limestone (lime mudstone/wackestone) with some sandy/muddy limestones (Figure 3D). Black chert nodules (<10 cm in diameter) occur in the uppermost part of the Wujiaoping Formation. The upper Wujiaoping limestones contain diverse shallow-marine fossils such as calcareous algae, crinoids, brachiopods, radiolarians,
FIGURE 3 | A distant view and photographs of the P-TB interval at Chaotian. (A) A distant view of Chaotian (circled car for scale). (B,C) Outcrops of the uppermost Dalong limestones. (D–F) Thin sections of bioclastic limestone in the upper Wujaping Formation (D), calcareous mudstone in the Dalong Formation (E), and lowermost Feixianguan limestone (F). (G–J) Secondary electron (SE) image (G) and element maps (H–J) of calcareous mudstone in the Dalong Formation. Carbonates in the mudstones are mainly finely-fragmented bioclasts with few secondary dolomites.
and ostracodes. Burrows frequently occur in the upper Wujiaping limestones.

The Dalong Formation (~25 m thick) is composed mainly of thinly bedded black calcareous mudstone, dark siliceous mudstone, and bedded gray limestone (lime mudstone/wackestone) (Figures 2, 3). The Dalong Formation contains abundant radiolarians with a minor amount of ostracodes, brachiopods, ammonoids, and conodonts, bivalves and small foraminifers. The uppermost (~3.5 m thick) part of the Dalong Formation mostly consists of bedded gray limestone (lime mudstone/wackestone) (‘Unit C’ in Isozaki et al., 2007). Thin (<10 cm thick) acidic tuff layers frequently occur in these limestones. Burrows are observed in the lower and upper Dalong Formation, although bioturbation is generally absent in the middle Dalong Formation. Small pyrite framboisoids (mostly 3–7 µm in diameter) occur abundantly throughout the Dalong Formation. The lowermost Feixianguan Formation (~5 m thick) is composed of thinly bedded gray marl and light gray micritic limestone with some sandy/muddy limestones. In particular, the lowermost (1.4 m thick) part (‘Unit E’ in Isozaki et al., 2007) is composed of gray marl. This marl unit is almost barren of fossil, although few ammonoids and bivalves occur from the basal part. The upper part of the lowermost Feixianguan Formation consists of light gray micritic limestone containing few conodonts and brachiopods. Few trace fossils are recognized in the lowermost Feixianguan Formation.

Based on index fossils (fusulines, conodonts, ammonoids, corals, and brachiopods), the analyzed P-TB interval at Chaotian is dated as follows (Figure 2; Zhao et al., 1978; Yang et al., 1987; Isozaki et al., 2004; Isozaki et al., 2007): The upper Wujiaping Formation is correlated with the Wuchiapingian (early Lopingian). The lower Dalong Formation is correlated with the late Wuchiapingian, whereas the middle Dalong Formation belongs to the late Wuchiapingian to early Changhsingian. The upper Dalong Formation is correlated with the late Changhsingian. The lowermost Feixianguan Formation is correlated with the latest Changhsingian to early Induan (early Early Triassic). The main extinction horizon is assigned at the base of the Feixianguan Formation (‘Unit D/E boundary’ in Isozaki et al., 2007), whereas the biostratigraphically defined P-TB is assigned at the base of the overlying micritic limestones (‘Unit E/F boundary’ in Isozaki et al., 2007). Based on the litho- and bio-facies, the sedimentary environments of the three stratigraphic units of the analyzed P-TB interval were reconstructed (Figure 2; Saitoh et al., 2014a). The upper Wujiaping limestones were deposited on the shallow eutrophic shelf under oxic conditions. In contrast, the lower and middle Dalong Formation was deposited on the relatively deep slope/basin under anoxic conditions. The upper Dalong limestones were deposited on the relatively shallow slope below the storm wave base under oxic conditions. The lowermost Feixianguan formations were deposited on a relatively shallow slope under anoxic conditions.

**ANALYTICAL METHODS**

Fresh rock samples were carefully chosen based on detailed observations of polished slabs and thin sections. Powdered sample was reacted with 100% phosphoric acid at 28°C for 24 h using a GasBench (Thermo Fisher Scientific). The extracted CO2 was separated in a chromatography line with a helium flow, and the carbon and oxygen isotope ratios were measured with a DELTA V PLUS mass spectrometer. The carbonate carbon and oxygen isotopic compositions are measured with a DELTA V PLUS mass spectrometer. The analytical reproducibility of the δ13C_carb and δ18O_carb values was better than 0.1 and 0.1‰, respectively.

**RESULTS**

Table 1 lists all the measured δ13C_carb and δ18O_carb values of the P-TB interval. Figure 4 shows chemostratigraphic profiles of the δ13C_carb, δ18O_carb, δ13C орг and Δ13C values and TOC contents. The δ13C_org values and TOC contents were previously reported in Saitoh et al. (2014a). Figure 5 shows a δ13C_carb–δ18O_carb cross plot. The δ13C_carb values range from −6.9 to +4.3‰, with an average value of ca. 0‰. The δ18O_carb values range from −7.9 to −2.9‰, with an average value of ca. −5.9‰.

The δ13C_carb values are consistently ca. +4‰ in the upper Wujiaping Formation and decrease from ca. +4‰ to −2‰ across the Wujiaping/Dalong formation boundary. In the Dalong Formation, the δ13C_carb values increase slightly from ca. −2 to +1‰ upward except for some anomalously low (<−3‰) values (open symbols in Figure 4). The δ13C_carb values decrease from ca. +1‰ to −2‰ across the Dalong/Feixianguan formation boundary (i.e., the P-TB) and are consistent around −2‰ in the lowermost Feixianguan carbonates. The present δ13C_carb results around the P-TB are generally identical to the results in Cao et al. (2010). The δ18O_carb values are somewhat variable in the upper Wujiaping limestones and are mainly around −7‰ in the overlying Dalong Formation. Above the P-TB, the δ18O_carb values are mostly around −6‰ in the lowermost Feixianguan Formation. The Δ13C values are mainly between 27 and 29‰ in the upper Wujiaping Formation and decrease slightly to ca. 26‰ in the Dalong Formation. The Δ13C values increase to ca. 30‰ in the overlying lowermost Feixianguan carbonates.

No linear correlation is observed between the δ13C_carb and δ18O_carb values (Figure 5). It indicates that secondary overprinting on the Chaotian carbonates is not significant (Knauth and Kennedy, 2009). In the chemostratigraphic profile, however, some δ13C_carb values in the Dalong Formation are anomalously low (<−3‰; open symbols in Figure 4) and these samples were likely affected at least partly by the secondary addition of 13C-depleted C. Except for these anomalous values, the present δ13C_carb results represent a smooth chemostratigraphic trend in the analyzed interval. This trend may record secular changes in the δ13C value of dissolved inorganic carbon (DIC) in seawater (δ13C DIC) in the Lopingian to earliest Triassic. Based on the C isotopic
| Formation | Sample ID | Lithology | Thickness (m) | \(\delta^{13}C_{\text{Carb}}\) vs. VPDB (%) | \(\delta^{18}O_{\text{Carb}}\) vs. VPDB (%) | \(\delta^{13}C_{\text{Org}}\) vs. VPDB (%) | \(\Delta^{13}C\) vs. VPDB (%) | TOC (%) |
|-----------|-----------|-----------|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-------|
| Feixianguan | G8        | dark gray limestone | 38.3 | -1.7 | -5.5 | -29.6 | 27.9 | 0.0 |
| Feixianguan | G6        | dark gray limestone | 38.0 | -1.9 | -6.1 | -31.3 | 29.5 | 0.0 |
| Feixianguan | G4        | gray limestone | 37.7 | -1.8 | -5.9 | -31.4 | 29.7 | 0.1 |
| Feixianguan | G1        | dark gray limestone | 37.3 | -1.7 | -5.7 | -31.8 | 30.0 | 0.1 |
| Feixianguan | F11       | gray limestone | 36.8 | -1.8 | -5.9 | -31.6 | 29.9 | 0.1 |
| Feixianguan | F7        | dark gray limestone | 36.5 | -1.9 | -4.9 | -31.7 | 29.8 | 0.1 |
| Feixianguan | F5        | gray marl | 36.3 | -1.6 | -5.5 | -28.2 | 26.7 | 0.0 |
| Feixianguan | F3        | gray limestone | 36.0 | -1.3 | -6.0 | -30.8 | 29.5 | 0.0 |
| Feixianguan | F1        | gray limestone | 35.7 | -0.9 | -6.9 | -30.1 | 29.2 | 0.1 |
| Feixianguan | E11       | gray marl | 35.1 | -0.4 | -5.8 | | | |
| Feixianguan | E7        | gray marl | 34.8 | -0.1 | -4.4 | -25.6 | 25.5 | 0.1 |
| Feixianguan | E2        | gray marl | 34.4 | 0.1 | -4.4 | -25.0 | 25.0 | 0.1 |
| Dalong | D19        | gray limestone | 33.7 | 1.0 | -5.7 | -28.2 | 29.2 | 0.0 |
| Dalong | D15        | gray limestone | 33.3 | 0.4 | -7.0 | -25.6 | 26.0 | 0.1 |
| Dalong | D13        | gray limestone | 33.1 | -1.3 | -7.5 | -25.2 | 23.8 | 0.2 |
| Dalong | D9         | gray limestone | 32.8 | 0.6 | -5.7 | -25.2 | 25.8 | 0.1 |
| Dalong | D3         | gray limestone | 32.2 | 1.9 | -4.0 | -25.7 | 27.6 | 0.0 |
| Dalong | C8         | black mudstone | 31.6 | 0.6 | -7.0 | -26.0 | 26.6 | 0.9 |
| Dalong | D6         | black mudstone | 31.2 | -0.2 | -7.2 | -26.7 | 26.4 | 2.0 |
| Dalong | B33        | black mudstone | 30.3 | 0.2 | -7.1 | -27.1 | 27.3 | 1.6 |
| Dalong | B30        | black mudstone | 29.7 | 0.3 | -7.1 | -27.2 | 27.4 | 1.5 |
| Dalong | B20        | dark gray muddy limestone | 29.2 | 0.7 | -6.7 | -26.0 | 26.7 | 0.7 |
| Dalong | B10        | dark gray muddy limestone | 28.5 | -3.4 | -6.0 | -27.2 | 23.8 | 0.7 |
| Dalong | B3         | dark gray muddy limestone | 28.0 | -5.9 | -6.0 | -26.5 | 20.6 | 0.7 |
| Dalong | A11        | black mudstone | 27.4 | | | -26.6 | 4.8 |
| Dalong | Dalong49    | black mudstone | 25.5 | -2.6 | -7.1 | -26.8 | 24.2 | 10.1 |
| Dalong | Dalong48    | black mudstone | 25.1 | -0.4 | -7.2 | -26.8 | 26.4 | 10.4 |
| Dalong | Dalong47    | black mudstone | 24.8 | -2.1 | -7.1 | -26.6 | 26.4 | 10.0 |
| Dalong | Dalong46    | black mudstone | 24.0 | -4.1 | -4.7 | -26.7 | 22.7 | 8.1 |
| Dalong | Dalong45    | black mudstone | 23.1 | 0.4 | -6.6 | -26.6 | 26.9 | 10.0 |
| Dalong | Dalong44    | black mudstone | 22.9 | 0.6 | -6.9 | -26.8 | 27.3 | 9.9 |
| Dalong | Dalong43    | black mudstone | 22.4 | -0.5 | -7.0 | -26.7 | 26.1 | 12.3 |
| Dalong | Dalong42    | black mudstone | 21.9 | 0.4 | -6.9 | -26.2 | 26.7 | 9.0 |
| Dalong | Dalong41    | black mudstone | 20.3 | -3.2 | -5.0 | -27.2 | 24.0 | 7.5 |
| Dalong | Dalong40    | black mudstone | 20.0 | -3.8 | -5.3 | -27.2 | 23.6 | 9.2 |
| Dalong | Dalong39    | black mudstone | 19.8 | -1.1 | -7.8 | -27.1 | 25.9 | 13.2 |
| Dalong | Dalong38    | black mudstone | 19.3 | -1.4 | -7.2 | -27.0 | 26.5 | 9.4 |
| Dalong | Dalong37    | black mudstone | 19.0 | -0.2 | -7.2 | -27.1 | 26.9 | 8.7 |
| Dalong | Dalong36    | black mudstone | 18.5 | -1.6 | -6.0 | -27.3 | 25.7 | 12.3 |
| Dalong | Dalong34    | black mudstone | 18.2 | -0.7 | -7.0 | -27.0 | 26.3 | 9.4 |
| Dalong | Dalong33    | black mudstone | 17.9 | -1.4 | -7.3 | -27.3 | 25.9 | 11.3 |
| Dalong | Dalong31    | black mudstone | 17.7 | -0.4 | -7.4 | -27.6 | 27.2 | 5.9 |
| Dalong | Dalong30    | dark gray muddy limestone | 17.6 | -6.9 | -2.9 | -28.5 | 21.6 | 2.5 |
| Dalong | Dalong29    | black mudstone | 17.2 | -1.6 | -7.1 | -27.2 | 25.6 | 10.0 |
| Dalong | Dalong28    | black mudstone | 16.6 | -2.3 | -7.5 | -27.2 | 25.0 | 3.9 |
| Dalong | Dalong27    | black mudstone | 16.3 | -1.8 | -7.0 | -27.4 | 25.6 | 8.3 |
| Dalong | Dalong26    | dark gray muddy limestone | 16.1 | -5.8 | -4.7 | -27.6 | 21.8 | 1.4 |
| Dalong | Dalong25    | dark gray muddy limestone | 15.6 | -1.9 | -6.5 | -27.3 | 25.3 | 5.8 |
| Dalong | Dalong23    | black mudstone | 15.5 | -2.3 | -6.9 | -26.8 | 24.5 | 15.1 |
| Dalong | Dalong21    | black mudstone | 15.2 | -1.3 | -7.5 | -27.1 | 25.8 | 10.3 |
| Dalong | Dalong20    | black mudstone | 14.8 | -1.6 | -6.9 | -27.4 | 25.8 | 11.9 |
| Dalong | Dalong18    | black mudstone | 14.3 | -0.5 | -7.8 | -27.0 | 26.5 | 12.4 |
| Dalong | Dalong17    | black mudstone | 14.0 | -0.6 | -7.2 | -27.2 | 26.6 | 11.6 |
| Dalong | Dalong14    | dark gray muddy limestone | 13.6 | -0.4 | -3.8 | -27.8 | 27.4 | 3.1 |

(Continued on following page)
analyses of the P-TB carbonates in Iran, Schobben et al. (2016) suggested that the first-order $\delta^{13}$C$_{\text{carb}}$ trend in the bulk carbonates is robust, although small-scale isotopic fluctuations may be due to secondary alteration. In the following discussion, we focus solely on the first-order $\delta^{13}$C$_{\text{carb}}$ trend in the analyzed interval at Chaotian.

| Formation | Sample ID | Lithology | Thickness (m) | $\delta^{13}$C$_{\text{carb}}$ vs. VPDB (%) | $\delta^{18}$O$_{\text{carb}}$ vs. VPDB (%) | $\delta^{13}$C$_{\text{org}}$ vs. VPDB (%) | $\Delta^{13}$C vs. VPDB (%) | TOC (%) |
|-----------|-----------|-----------|---------------|---------------------------------------------|------------------------------------------|---------------------------------------------|------------------------------------------|--------|
| Dalong    | Dalong13  | black mudstone | 13.4          | −1.4                                       | −6.5                                    | −27.0                                      | 25.6                                      | 13.4   |
| Dalong    | Dalong12  | dark gray muddy limestone | 13.2          | −0.8                                       | −3.8                                    | −28.2                                      | 27.4                                      | 0.2    |
| Dalong    | Dalong11  | black mudstone | 13.0          | −1.5                                       | −7.2                                    | −27.2                                      | 25.7                                      | 8.7    |
| Dalong    | Dalong10  | black mudstone | 12.8          | −0.7                                       | −7.1                                    | −27.0                                      | 26.4                                      | 3.9    |
| Dalong    | Dalong9   | black mudstone | 12.5          | 0.0                                        | −7.1                                    | −26.4                                      | 26.4                                      | 11.9   |
| Dalong    | Dalong8   | black mudstone | 12.0          | −0.1                                       | −5.8                                    | −26.4                                      | 26.2                                      | 5.6    |
| Dalong    | Dalong7   | black mudstone | 11.7          | 0.6                                        | −6.4                                    | −26.3                                      | 26.9                                      | 7.1    |
| Dalong    | Dalong6   | black mudstone | 11.2          | −0.1                                       | −5.9                                    | −26.2                                      | 26.1                                      | 3.6    |
| Dalong    | Dalong5   | black mudstone | 10.8          | 1.2                                        | −7.3                                    | −26.2                                      | 27.4                                      | 4.1    |
| Dalong    | Dalong4   | black mudstone | 9.9           | 1.9                                        | −6.3                                    | −24.8                                      | 26.7                                      | 0.5    |
| Dalong    | Dalong3   | black mudstone | 9.4           | 2.4                                        | −5.7                                    | −24.9                                      | 27.3                                      | 0.4    |
| Wujiaping | Wujiaping20 | dark gray limestone | 9.0           | 2.9                                        | −4.2                                    | −26.8                                      | 29.7                                      | 0.1    |
| Wujiaping | Wujiaping19 | dark gray limestone | 8.6           | 2.5                                        | −6.0                                    | −25.1                                      | 27.6                                      | 0.1    |
| Wujiaping | Wujiaping18 | dark gray limestone | 8.2           | 3.5                                        | −4.7                                    | −24.9                                      | 28.4                                      | 0.1    |
| Wujiaping | Wujiaping17 | dark gray limestone | 7.6           | 3.9                                        | −4.1                                    | −24.6                                      | 28.5                                      | 0.3    |
| Wujiaping | Wujiaping16 | dark gray limestone | 7.2           | 4.2                                        | −3.3                                    | −22.6                                      | 26.7                                      | 0.1    |
| Wujiaping | Wujiaping15 | dark gray limestone | 6.6           | 3.4                                        | −4.0                                    | −24.9                                      | 28.2                                      | 0.0    |
| Wujiaping | Wujiaping14 | dark gray limestone | 6.0           | 3.4                                        | −7.0                                    | −24.5                                      | 27.8                                      | 0.1    |
| Wujiaping | Wujiaping13 | dark gray limestone | 5.2           | 4.3                                        | −3.0                                    | −24.7                                      | 29.1                                      | 0.1    |
| Wujiaping | Wujiaping12 | dark gray limestone | 4.6           | 4.1                                        | −3.5                                    | −24.7                                      | 28.8                                      | 0.2    |
| Wujiaping | Wujiaping11 | dark gray limestone | 4.1           | 4.2                                        | −3.2                                    | −25.0                                      | 29.2                                      | 0.1    |
| Wujiaping | Wujiaping10 | dark gray limestone | 3.6           | 3.7                                        | −6.4                                    | −25.0                                      | 28.7                                      | 0.1    |
| Wujiaping | Wujiaping9  | dark gray limestone | 3.1           | 4.2                                        | −3.4                                    | −24.7                                      | 28.9                                      | 0.0    |
| Wujiaping | Wujiaping8   | dark gray limestone | 2.6           | 3.9                                        | −5.0                                    | −23.3                                      | 27.2                                      | 0.3    |
| Wujiaping | Wujiaping7   | dark gray limestone | 2.0           | 4.1                                        | −4.5                                    | −24.3                                      | 28.4                                      | 0.2    |
| Wujiaping | Wujiaping6   | dark gray limestone | 1.3           | 3.8                                        | −5.2                                    | −24.3                                      | 28.2                                      | 0.4    |
| Wujiaping | Wujiaping5   | dark gray limestone | 0.8           | 3.9                                        | −4.4                                    | −25.1                                      | 29.0                                      | 0.2    |
| Wujiaping | Wujiaping4   | dark gray limestone | 0.0           | 4.1                                        | −3.9                                    | −24.8                                      | 28.9                                      | 0.8    |
DISCUSSION

$\delta^{13}C$ Stratigraphy at Chaotian

$\delta^{13}C_{\text{carb}}$ Decrease Around the Wuchiapingian-Changhsingian Boundary

The $\delta^{13}C_{\text{carb}}$ values unidirectionally decrease from ca. +4 to $-2\%_o$ across the Wujiaping/Dalong formation boundary at Chaotian (Figure 4). Although the timing of this negative $\delta^{13}C_{\text{carb}}$ shift is not well constrained because of the poor occurrence of index fossils, the $\delta^{13}C_{\text{carb}}$ shift likely occurred around the Wuchiapingian-Changhsingian boundary. This $\delta^{13}C_{\text{carb}}$ decrease apparently coincides with the deepening of the sedimentary setting from a shallow shelf to relatively deep slope/basin floor. However, we emphasize that carbonates in the Dalong Formation of deep-water facies comprise mainly finely fragmented bioclasts and few secondary dolomite (Figures 3E, G-J). Thus, regardless of the lithofacies change, this prominent $\delta^{13}C_{\text{carb}}$ decrease likely records the Lopingian secular change in the $\delta^{13}C_{\text{DIC}}$ value in the surface oceans in the eastern Paleotethys.

Two possible mechanisms could explain the $\delta^{13}C_{\text{carb}}$ decrease: 1) collapse of primary productivity in the surface oceans and 2) addition of isotopically light C into the DIC pool of the surface oceans. As certain shallow-marine taxa went extinct across the Wuchiapingian-Changhsingian boundary (e.g., Knoll et al., 1996; Bambach, 2006), extinction-related productivity deficiency may have contributed to the $\delta^{13}C_{\text{carb}}$ decrease at Chaotian. However, the magnitude of the $\delta^{13}C_{\text{carb}}$ drop ($\sim 6\%_o$) seems to be too large to be caused solely by the collapse of primary productivity (e.g., Berner, 2002); thus the addition of $^{13}C$-depleted C to the DIC pool in the surface oceans likely contributed to the $\delta^{13}C_{\text{carb}}$ drop. We emphasize that the sedimentary setting deepened from oxic shelf to anoxic slope/basin floor. The ubiquitous occurrence of small pyrite framboinds in the Dalong Formation suggests the dominance of sulfate reduction in an anoxic deep-water mass on the slope/basin. The DIC in the deep-water mass would have become enriched in $^{12}C$ due to the anaerobic respiration; therefore, the injection of $^{13}C$-depleted C into the surface oceans via shoaling of the deep-water might have contributed to the negative $\delta^{13}C_{\text{carb}}$ shift. It is noteworthy that no eruption of a large igneous province or substantial sea-level change occurred on a global scale around the Wuchiapingian-Changhsingian boundary (e.g., Haq and Schutter, 2008; Bond and Wignall, 2014). An input of volcanogenic excess CO$_2$ and/or reoxidized sedimentary organic C during a eustatic sea-level fall is unlikely for the cause of the $\delta^{13}C_{\text{carb}}$ drop at Chaotian.

Regional and global correlations would be useful to constrain the cause of the $\delta^{13}C_{\text{carb}}$ decrease at Chaotian. Around the
Wuchiapingian-Changhsingian boundary, a ca. 6‰ negative δ13C_carb shift was reported at Shangsi, ca. 60 km southwest of Chaotian, in northern Sichuan (Bai et al., 2008; Shen et al., 2013), which is almost identical in magnitude to that at Chaotian. Therefore, the deep-water carbonates in northwestern South China probably record the common δ13C_DIC decrease in eastern Paleotethys. Similar δ13C_carb declines were also reported from other sections in South China, including Dukou in Sichuan, Shiligou in Chongqing, Zhuqiao in Hubei, and Heshan and Matan in Guangxi (Shao et al., 2000; Shen et al., 2013; Yang et al., 2019); nonetheless, the magnitude of the δ13C_carb decreases (~2–5‰) is variable and smaller than that at Chaotian. At Abadeh in central Iran, Richoz (2006) found a negative δ13C_carb shift in the corresponding interval in the Hambast Formation, which was later re-confirmed by Liu et al. (2013). A similar negative δ13C_carb excursion (~4‰) was also reported from the equivalent horizons of Jufa beds/Alibashi Formation boundary at Kuh-e-Ali Bashi in northwestern Iran (Shen et al., 2013). These almost co-eval negative δ13C_carb shifts around the Wuchiapingian-Changhsingian boundary in Iran are comparable to that at Chaotian. Moreover, a large negative δ13C_carb excursion (~7‰) was demonstrated in the Bellerophon Formation at the Reppwand section in the Carnic Alps, Austria (Buggisch et al., 2015), which is also correlative to the negative shift at Chaotian.

A negative δ13C_org shift, as well as the δ13C_carb drop, around the Wuchiapingian-Changhsingian boundary has been documented in several sections in South China and Arctic Canada (e.g., Bai et al., 2008; Beauchamp et al., 2009; Wei et al., 2015; Liao et al., 2016). These δ13C_org decreases may have likewise recorded fluctuations in the global C cycle; however, a negative δ13C_carb/δ13C_org shift around the Wuchiapingian-Changhsingian boundary is not clear in the rest of the Permian world (e.g., Baud et al., 1996; Korte et al., 2004; Richoz, 2006; Baud et al., 2012). Even at the abovementioned sections in which a negative δ13C_C5H4 shift is recognized, the magnitude of and the trend in the δ13C_C5H4 decrease vary substantially (Shen et al., 2013). Under the circumstances, we infer that the C cycle in the surface oceans around the Wuchiapingian-Changhsingian boundary was not globally uniform but rather widely variable possibly owing to local factors, such as primary productivity and oceanic circulation along the continental margins. More studies with high chemo- and bio-stratigraphic resolutions in various sections around the world are necessary to reveal the fluctuations in the global C cycle around the Wuchiapingian-Changhsingian boundary.

Δ13C Increase Across the P-TB
Saitoh et al. (2014a) reported the δ13C_org chemostratigraphy of the P-TB interval at Chaotian and revealed that the δ13C_org values drop abruptly by 7‰ (from ~25 to ~32‰) immediately above the extinction horizon (Figure 4). This clear δ13C_org decrease is consistent apparently with the δ13C_carb shift documented in the present study, although the magnitude of the δ13C_org decrease (~7‰) is substantially larger than that of the δ13C_carb decrease (~3‰). The Δ13C (δ13C_carb−δ13C_org) values increase by 4‰ from +26‰ to +30‰ in the aftermath of the extinction at Chaotian. Two possible mechanisms may explain this Δ13C increase: 1) an increase in C isotopic fractionation of biological C fixation and 2) additional input of 13C-depleted C to the sedimentary organic matter. The high aqueous CO2 concentration ([CO2 (aq)]) generally promotes the large C isotopic fractionation during photosynthetic C fixation (ε) in the surface oceans (e.g., Rau et al., 1992, Rau et al., 1997; Kump and Arthur, 1999). The Δ13C values are ~26‰ in the middle to upper Dalong Formation at Chaotian, which are consistent with the typical Calvin cycle (e.g., Schidlowski et al., 1983), although the values increase substantially to ca. 30‰ above the P-TB (Figure 4). It should be noted that a substantial amount of CO2 was released during the Siberian Traps volcanism around and mostly after the P-TB (Supplementary Information) (e.g., Renne et al., 1995; Hansen, 2006; Cui et al., 2013; Cui and Kump, 2015). The increased [CO2 (aq)] may have promoted greater ε (e.g., Kump and Arthur, 1999).

The previous estimates of the amount of emitted CO2 and of the elevated pCO2 during the Permian-Triassic transition are useful to constrain the influence of ε on the Δ13C records. Cui and Kump (2015) estimated that pCO2 rose from 500 to 4,000 ppm to ~8,000 ppm during the extinction (Supplementary Information). Kump and Arthur (1999) derived a simplified relationship between pCO2 and ε from the collapse of primary productivity during the extinction. The addition of isotopically light C to the shallow-marine DIC pool is another plausible candidate for the cause of the δ13C_carb decrease. Ioszaki et al. (2007) found frequent intercalations of thin felsic tuff layers across the extinction horizon at Chaotian and suggested volcanic stress on the shallow-marine biota during the extinction. An excess input of volcanogenic CO2 (δ13C: ~−5‰) may also have contributed to the δ13C_carb decrease. Weathering of sedimentary organic matter due to a large regression is another possible mechanism for the δ13C_carb decrease (e.g., Yin et al., 2014). However, the sea-level drop occurred significantly before the δ13C_carb shift at Chaotian (Ioszaki et al., 2007; Saitoh et al., 2014a), without any evidence for shallowing across the extinction horizon (Figure 4). This suggests that a contribution of reoxidized organic C to the δ13C_carb drop was negligible. Song et al. (2012a) proposed the existence of a large vertical Δ13C_carb Gradient in the end-Permian oceans, along which a deepening of the sedimentary setting possibly caused the observed δ13C_carb decrease. At Chaotian, however, the upper Dalong and lowermost Feixianguan carbonates across the P-TB were deposited on a relatively shallow slope without abrupt sea-level changes. Thus the δ13C_carb decrease cannot be attributed to the assumed vertical δ13C_carb gradient in the water column.

δ13C Carboxylic Acid Decrease Across the P-TB
The δ13C_carb values decrease from ca. +1 to ~2‰ across the Dalong/Feixianguan formation boundary (P-TB) at Chaotian (Figure 4). This negative δ13C_carb shift is identical to that previously reported at Chaotian in Cao et al. (2010). Likewise, two possible mechanisms should be considered for the cause of this δ13C_carb decrease: 1) collapse of primary productivity in the surface oceans and 2) addition of 13C-depleted C to the DIC pool in the surface oceans. The negative δ13C_carb shift occurs across the major extinction horizon, suggesting that the shift was driven by the addition of isotopically light C to the shallow-marine DIC pool.
The organic C from methanogenic biomass may have reductive acetyl-CoA pathway, which can produce greater C uptake of CO2 (aq) (calculated according to Henry’s Law at 25°C). It is uncertain whether the formula can be extrapolated to environments with substantially high [CO2 (aq)], which are particularly supposed in the aftermath of the end-Permian extinction (Cui et al., 2013; Cui and Kump, 2015). Nonetheless, the low sensitivity of $\varepsilon_p$ to $p$CO2 under high-$p$CO2 conditions is probably essential (Rau et al., 1997; Kump and Arthur, 1999). Because the reciprocal dependence of $\varepsilon_p$ on $p$CO2 is attributed theoretically to isotopic discrimination by diffusion of CO2 from the ambient seawater to the phytoplankton cell (Laws et al., 1995). It is also suggested that the sensitivity of $\varepsilon_p$ to $p$CO2 of land plants is lower than that of marine phytoplankton (e.g., Popp et al., 1989). The estimated high $p$CO2 up to 4,000 ppm before the end-Permian extinction (Brand et al., 2012; Cui et al., 2013; Cui and Kump, 2015) allows us to postulate that the influence of $\varepsilon_p$ change on the Chaotian $\delta^{13}$C records was not significant.

Additional input of $^{13}$C-depleted C to the sedimentary organic C pool is the other possible mechanism for the Chaotian P-TB $\Delta^{13}$C increase. Rothman et al. (2014) suggested that increased Ni input to the ocean/atmosphere during the Siberian Traps volcanism promoted methanogen proliferation in the oceans (“methanogenic burst”). Methanogens generally fix C via the reductive acetyl-CoA pathway, which can produce greater C isotopic fractionation than the Calvin cycle (e.g., Preuss et al., 1989). The organic C from methanogenic biomass may have contributed, at least partly, to the $\Delta^{13}$C increase. Terrestrial plants are another possible C source for sedimentary organic matter in the Chaotian carbonates. In general, the $\delta^{13}$Corg value of Permian terrestrial plant is thought to be higher than the value of marine phytoplankton (e.g., Faure et al., 1995; Foster et al., 1997; Korte et al., 2001). Thus, if the terrestrial C flux decreased across the P-TB, the bulk $\delta^{13}$Corg and $\Delta^{13}$C values of the sediments would have decreased and increased, respectively. However, two lines of evidence exclude the possibility of the decreased terrestrial flux at Chaotian. First, as discussed above, the water depth of depositional site did not change substantially across the P-TB, and a large change in terrestrial flux owing to sea-level changes is unlikely. Second, previous studies suggested enhanced chemical weathering and increased continental flux during the Permian-Triassic transition (Algeo and Twitchett, 2010; Algeo et al., 2011; Cui et al., 2013). At Chaotian, the enhanced chemical weathering is supported by the increased supply of clay minerals/micas around the P-TB based on bulk nitrogen isotope records (Saitoh et al., 2014a).

Global $\delta^{13}$C Correlations Around the P-TB Regional $\delta^{13}$C Differences

The $\delta^{13}$C profile across the P-TB at Chaotian is here relatively perceived through global correlation, in the context of global C cycle during the Permian-Triassic transition. We focused particularly on the apparent magnitude of the $\delta^{13}$C decrease across the P-TB in previous studies and examined its frequency distribution on a global scale (Figures 6, 7). All the reference sections in the current compilation are summarized in Table 2. We categorize the compiled sections geographically into seven realms; i.e., Boreal, eastern Paleotethys, western Paleothetys, western Pangea, mid-Panthalassa, Neothetys, and Gondwana (Figure 6).

Marine Records

Previous $\delta^{13}$Ccarb studies are concentrated mostly in eastern (China) and western Tethys realms (Iran to Italy) (Figures 6, 7; Table 2), where extensive carbonate platforms developed under warm tropical climate. These two realms share almost the same frequency distribution of the magnitude of the P-TB $\delta^{13}$Ccarb decrease (Figure 7), suggesting a common $\delta^{13}$DIC decline throughout Paleothetys during the Permian-Triassic transition. The magnitude of the $\delta^{13}$Ccarb decrease ranges mostly between 3 and 6‰ in those tropical regions. In the Boreal realm, the magnitude of the P-TB $\delta^{13}$Ccarb decrease in few marine records is substantially large (to 19‰), which indicates a diagenetic overprint onto the original isotopic signal from seawater (Mii et al., 1997). In contrast, the magnitude of the P-TB $\delta^{13}$Corg decrease varies substantially around the world (Figures 6, 7). In particular, a relatively large (~7‰) $\delta^{13}$Corg decline has been reported in several marine sections in high latitudes such as Greenland, Spitsbergen, Australia, and Antarctica (e.g., Retallack and Jahren, 2008; Nabbefeld et al., 2010). It is consistent with the previous notion that the magnitude of the $\delta^{13}$Corg decrease in high latitudes was substantially larger than that of the $\delta^{13}$Ccarb decrease in equatorial regions (e.g., Krull...
Terrestrial Records

The present \(\delta^{13}C\) compilation also demonstrates that the P-TB \(\delta^{13}C\)org decrease is not clearly recognized in a number of terrestrial sections, especially around the Neotethys and in Gondwana realms (Figure 6). The \(\delta^{13}C\)org decline is not clearly recognized in previous studies at 14 out of 49 terrestrial sections (Table 2). In these sections, the \(\delta^{13}C\)org values are sometimes substantially scattered and no smooth \(\delta^{13}C\)org trend is observed (e.g., de Wit et al., 2002; Retallack et al., 2005; Coney et al., 2007). In other Gondwanan sections, the \(\delta^{13}C\)org decline is recognized and the apparent magnitude of the \(\delta^{13}C\)org decrease is mostly not large (Figure 7). However, the \(\delta^{13}C\)org decline is obscured frequently by sharp \(\delta^{13}C\)org drops to \(-45\%\) (e.g., Krull and Retallack, 2000; Retallack et al., 2005).

Variable \(\Delta^{13}C\) Records

Magaritz et al. (1992) originally proposed a parallel \(\delta^{13}C\)carb and \(\delta^{13}C\)org trend on the basis of the P-TB isotope profile of the Gartnerkofel Core from the Carnic Alps, Austria, and later studies confirmed similar parallel trends not only in the Tethyan but also in the Panthalassan realms (e.g., Musashi et al., 2001; Algeo et al., 2007b; Luo et al., 2014). However, other studies pointed out a decoupling between the \(\delta^{13}C\)carb and \(\delta^{13}C\)org trends around the P-TB. For example, Riccardi et al. (2007) analyzed the \(\delta^{13}C\)carb and \(\delta^{13}C\)org values of the P-TB carbonates at Meishan and Shangsi in South China, and compiled the \(\Delta^{13}C\) changes during the extinction in Iran, Slovenia, Japan, Austria,
and South China. They found a Δ¹³C decrease across the extinction horizon in these regions and suggested that it was due to proliferation of green sulfur bacteria with photic zone euxinia (e.g., Grice et al., 2005; Zhang et al., 2017). Kaiho et al. (2009) confirmed the Δ¹³C decrease at Meishan. In contrast, the apparent Δ¹³C increase was reported at several sections in Italy (Siegert et al., 2011), South China (Shen et al., 2012; this study), and Pakistan (Schneebeli-Hermann et al., 2013). It is difficult to reconstruct the Δ¹³C changes in high latitudes as carbonates are generally scarce in those regions. Nonetheless, the present compilation illustrates that the δ¹³Corg records are substantially variable on a global scale particularly in high latitudes, in marked contrast to the rather consistent δ¹³Ccarb records in equatorial Paleotethys (Figures 6, 7).

**Potential Causes of the Marine δ¹³Corg Variability**

Several possible mechanisms may explain the observed δ¹³Corg variability in marine records on a global scale during the Permian-Triassic transition: 1) eustatic sea-level changes, 2) intense continental weathering, 3) proliferation of green sulfur bacteria, 4) elevated pCO₂, and 5) "methanogenic burst".

**Eustatic Sea-Level Changes**

The δ¹³Corg value of terrestrial plant was generally thought to be higher than the value of marine phytoplankton in the Permian (e.g., Faure et al., 1995; Foster et al., 1997; Korte et al., 2001). Eustatic sea-level changes during the Permian-Triassic transition may have been responsible for the δ¹³Corg variability of shallow-marine records, controlling the mixing ratio of ¹³C-enriched terrestrial and ¹³C-depleted marine C in the shelf sediments. The Permian-Triassic transition is marked by a major transgression on a global scale (e.g., Hallam and Wignall, 1999; Erwin et al., 2002; but also see; Yin et al., 2014). It is therefore likely that shelf sediments of proximal facies shifted to be of more distal facies during the transgression, and that the terrestrial C flux to the depositional setting reduced, which resulted in the apparent δ¹³Corg decrease in the bulk sediments. Although the eustatic sea-level changes could have exerted a first-order control on the global δ¹³Corg variability of shallow-marine records, they do not fully explain the regionally variable δ¹³Corg records. For example, the δ¹³Corg records of terrestrial to marine transitional sections in western South China do not record a simple mixing of terrestrial and marine C, despite of a regional transgression, but rather the atmospheric C isotopic signal (Cui et al., 2017). Moreover, the P-TB δ¹³Corg drop and Δ¹³C increase at the present Chaotian cannot be attributed to the sea-level changes, because the water depth of depositional site did not change substantially across the P-TB, as discussed above (Figure 4).

**Intense Continental Weathering and Increased Terrestrial C Flux**

The Permian-Triassic transition is characterized by extensive vegetation collapse on lands (e.g., Retallack et al., 1996; Benton and Newell, 2014), massive soil erosion (e.g., Retallack, 2005;
An increased fractionation (tricarboxylic acid (TCA) cycle, which can produce smaller C isotopic values) may have resulted in the increased terrestrial C (with relatively high $\delta^{13}C_{\text{org}}$ value) to the shelf sediments, offsetting the influence of increased terrestrial C flux on the bulk $\delta^{13}C_{\text{org}}$ value of the sediments. Because of this offset effect, the net influence of the intense continental weathering on the marine $\delta^{13}C_{\text{org}}$ records is highly uncertain.

**Proliferation of Green Sulfur Bacteria With Photic Zone Euxinia**

Characteristic green sulfur bacteria (GSB) may have proliferated under photic-zone euxinic conditions during the Permain-Triassic transition (e.g., Grice et al., 2005). They generally fix C via the reverse tricarboxylic acid (TCA) cycle, which can produce smaller C isotopic fractionation (~12.5‰; van Breugel et al., 2005), than the Calvin cycle (variable but mostly 25–35‰) (e.g., Schidlowski et al., 1983). Thus, the proliferation of GSB and an increased contribution of GSB biomass to the bulk organic-C pool in the shelf sediments would have decreased the $\Delta^{13}C$ value of the sediments. Riccardi et al. (2007) reported the P-TB $\Delta^{13}C$ decrease in various sections in the peri-Tethyan realm and attributed it to the GSB proliferation. Nonetheless, the proliferation of GSB cannot explain the apparent $\Delta^{13}C$ increase observed in several sections, including Chaotian (Figure 4).

**Enlarged C Isotopic Fractionation During Photosynthesis Under the Elevated pCO₂**

The increased [CO₂ (aq)] and $\varepsilon_p$ in the surface oceans is another potential mechanism for the observed $\delta^{13}C_{\text{carb}}$-$\delta^{13}C_{\text{org}}$ decoupling (e.g., Rau et al., 1992, Rau et al., 1997). However, as discussed above for the Chaotian record, the influence of $\varepsilon_p$ on the P-TB $\Delta^{13}C$ records may not have been significant.

**Methanogenic Burst**

In addition to the several potential mechanisms discussed above, we emphasize here that the “methanogenic burst” may also have contributed to the variable $\delta^{13}C_{\text{org}}$ records on a global scale (Figures 6, 7). A substantial amount of Ni was presumably released into the atmosphere during the Siberian Traps volcanism (Le Vaillant et al., 2017; Rampino et al., 2017). Because Ni is a key element for microbial methanogenesis (e.g., Diekert et al., 1981), the temporary input of excess Ni was likely favorable for methanogens (e.g., Basliko and Yavitt, 2001) and presumably enhanced microbial methanogenesis (“methanogenic burst”) on a global scale (Rothman et al., 2014).

Methanogen generally fixes C via the reductive acetyl-CoA pathway, which can produce larger C isotopic fractionation up to 40‰ (e.g., Preuss et al., 1989), compared to the Calvin cycle (e.g., Schidlowski et al., 1983). Thus, according to the “methanogenic burst”, the increased organic-C flux from expanded methanogen biomass to the bulk organic-C pool in the local sediments may have caused the large $\delta^{13}C_{\text{org}}$ decrease (Figures 6, 7). However, the activity of methanogenesis is generally regulated, not only by the Ni availability, but also by a number of environmental factors, such as temperature, CO₂ levels, and availability of organic substrates (Supplementary Information; e.g., Singh et al., 2010; Nazaries et al., 2013). Although the excess Ni input during the Siberian Traps volcanism likely promoted methanogenesis, the variable activity of methanogen in the local sediments may have been responsible for the observed $\delta^{13}C_{\text{org}}$ variability on a global scale. The elevated temperature and pCO₂ may also have stimulated the “methanogenic burst”, because these factors generally increase the biogenic CH₄ emissions in various environments (Supplementary Information; e.g., van Groeningen et al., 2011; Yvon-Durocher et al., 2014; Aben et al., 2017). The “methanogenic burst” may have occurred not only in marine sediments but also in terrestrial wetlands (Figure 8). Nonetheless, it is still difficult to estimate the total amount of released Ni during the Siberian Traps volcanism (Le Vaillant et al., 2017), and to evaluate the influence of the “methanogenic burst” on the global $\delta^{13}C_{\text{org}}$ records quantitatively.

In summary, the P-TB $\delta^{13}C_{\text{org}}$ variability in marine records on a global scale may have been attributed to several potential mechanisms, including the eustatic sea-level changes, intense continental weathering, and GSB proliferation. We infer that the “methanogenic burst” was also involved, at least in part, in the substantial $\delta^{13}C_{\text{org}}$ decrease in several sections, including the present Chaotian (Figure 4).

**Implications for the Global CH₄ Cycle in the Aftermath of the Extinction**

A substantial amount of CH₄ was presumably released into the atmosphere during the Siberian Traps volcanism (Figure 8B), via volcanic intrusion into coal (e.g., Retallack and Krull, 2006; Retallack and Jahren, 2008; Grasby et al., 2011; Shen et al., 2012; Rampino et al., 2017; Elkins-Tanton et al., 2020), and via destabilization of submarine and permafrost clathrates (e.g., Krull et al., 2000; Krull et al., 2004). Pyrogenic CH₄ was also produced by the incomplete combustion of organic carbon (e.g., Kirshke et al., 2013) and emitted during extensive wildfire events around the P-TB both in the northern and southern hemispheres (e.g., Shen et al., 2011b; Hudspith et al., 2014; Vajda et al., 2020). The “methanogenic burst” likely contributed to the elevated pCH₄ (Rothman et al., 2014). The claimed Araguainha impact event in Brazil (Tohver et al., 2013)
may also have contributed to the CH₄ accumulation in the atmosphere, though its timing, magnitude, and effective time span for the global CH₄ cycle are not well-constrained. Together with other greenhouse gases like CO₂, the elevated pCH₄ may have contributed to the climate warming during the earliest Triassic (e.g., Hallam and Wignall, 1997; Joachimski et al., 2012; Sun et al., 2012; Cui and Kump, 2015), although the long-term warming may have been disturbed intermittently by short-term SO₂-induced cooling (Black et al., 2018).

Although there still remains large uncertainty, we infer fluctuations in the global CH₄ cycle in the aftermath of the extinction based on the present and previous observations (Figure 8B). Firstly, aerobic methanotrophy may have prevailed in aerated terrestrial soils in the Gondwana and peri-Gondwanan realms (Figure 8B; Krull and Retallack, 2000). The present compilation illustrates that the P-TB δ¹³Corg decrease is not clearly recognized in a number of terrestrial sections, especially around the Neotethys and in Gondwana realms (Figure 6; Table 2). The highly scattered and variable δ¹³Corg records in the terrestrial successions were likely due to local-scale and short-term organic C dynamics in soils, including vegetation, selective microbial decomposition of sedimentary organic matters with C isotopic fractionation, and addition of microbial biomass to the sedimentary C pool (e.g., Krull and Retallack, 2000; Korte and Kozur, 2010). The locally enhanced methanotrophy might have been involved, at least in part, in the soil C dynamics and in the scattered δ¹³Corg records in the Gondwana and peri-Gondwanan realms (Krull and Retallack, 2000), possibly according to the warming and permafrost thaw (Supplementary Information; e.g., Oh et al., 2020).

Secondly, the oceanic sediments may have been a significantly large source for atmospheric CH₄ at that time. In the modern oceans enriched in sulfate (the SO₄²⁻ concentration = 28 mM), almost all CH₄ produced in deeper sediments, is consumed by anaerobic oxidation of methane (AOM) in the sulfate-methane transition zone (SMTZ) (Figure 8; Supplementary Information; e.g., Reeburgh, 2007). However, AOM would be substantially suppressed when the sulfate concentration is <0.5 mM (Knittel and Boetius, 2009). The Permian-Triassic transition interval is characterized by the substantially low
sulfate concentration in the oceans (0.6–2.8 mM) (Luo et al., 2010; Schobben et al., 2017; Stebbins et al., 2019). This estimated SO$_4^{2-}$ range is slightly higher than the threshold of the AOM rate. Nonetheless, the porewater sulfate concentration in the sediments may have quickly become <0.5 mM at a very shallow depth, due to sulfate consumption via decomposition of other organic substrates. The sedimentary AOM was consequently suppressed and the oceanic sediments might have been a larger CH$_4$ source compared to in the modern oceans, further contributing to the elevated $p$CH$_4$. The impact of “methanogenic burst” on the enhanced CH$_4$ emissions should have been significant under such sulfate-depleted conditions with less AOM. Prevailing oceanic anoxia (e.g., Wignall and Hallam, 1992; Isozaki, 1997; Song et al., 2012b) also helped CH$_4$ to escape from the oceans to the atmosphere (e.g., Ryskin, 2003).

Finally, the global CH$_4$ budgets may have been disturbed by the terrestrial devastation and intense continental weathering (e.g., Algeo and Twitchett, 2010; Cao et al., 2019). The Permian-Triassic transition is characterized by the extensive vegetation collapse on lands and massive soil erosion on a global scale (Figure 8B; e.g., Retallack, 2005; Sephton et al., 2005; Benton and Newell, 2014). The destruction of terrestrial ecosystems and the decay of land plants in the aftermath of the extinction was claimed to bring the well-known Early Triassic “coal gap” (Retallack et al., 1996). Although the release of substantial amounts of Ni into the ocean-atmosphere during the Siberian Traps volcanism may have caused the “methanogenic burst”, it may also have contributed to the vegetation collapse because excess Ni is generally toxic to plants (Fielding et al., 2019). The vegetation collapse could have stimulated the destabilization of permafrost and the CH$_4$ emissions in high latitudes according to the warming (Nauta et al., 2015), whereas the massive soil erosion might also have contributed to the atmospheric CH$_4$ accumulation as aerated terrestrial soils are a CH$_4$ sink (Supplementary Information; Figure 8B).

CONCLUSIONS

The carbon isotopic composition of carbonate ($\delta^{13}$C$_{carb}$) across the Permian-Triassic boundary (P-TB) was analyzed at Chaotian, Sichuan, South China, and was correlated to the chemostratigraphy of the carbon isotopic composition of organic carbon ($\delta^{13}$C$_{org}$) of the same interval. The $\delta^{13}$C$_{carb}$ and $\delta^{13}$C$_{org}$ records at Chaotian were further integrated into the records from various marine and terrestrial environments all around the world, to examine fluctuations in the global methane (CH$_4$) cycle during the Permian-Triassic transition. The following results were obtained:

1. The $\delta^{13}$C$_{carb}$ values decrease from ca. +1 to −2‰ across the P-TB, possibly reflecting the shallow-marine extinction and the collapse of primary productivity in the oceans. The frequent intercalation of felsic tuff layers around the extinction horizon suggests that volcanic activity also contributed to the $\delta^{13}$C$_{carb}$ decrease.

2. The magnitude of the $\delta^{13}$C$_{carb}$ decline (~3‰) is substantially smaller than the magnitude of the $\delta^{13}$C$_{org}$ decrease (~7‰) across the P-TB. This $\delta^{13}$C$_{carb}$-$\delta^{13}$C$_{org}$ decoupling could be explained by an elevated CO$_2$ concentration in the ocean/atmosphere and/or proliferation of methanogen (“methanogenic burst”) in the sediments, according to the Siberian Traps volcanism.

3. A global P-TB $\delta^{13}$C compilation shows a large variation in marine $\delta^{13}$C$_{org}$ records, which could be attributed to several potential mechanisms including eustatic sea-level changes and proliferation of green sulfur bacteria. We infer that the “methanogenic burst” may also have contributed, at least in part, to the $\delta^{13}$C$_{org}$ variability. The global CH$_4$ cycle might have fluctuated substantially in the aftermath of the extinction.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

MS designed the study. YI provided the samples for the analyses. MS and YI conducted the lithofacies description. MS conducted the isotopic analyses. MS and YI wrote the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2020.596178/full#supplementary-material.
REFERENCES

Aben, R. C. H., Barros, N., van Donk, E., Frenken, T., Hilt, S., Kazanjian, G., et al. (2017). Cross continental increase in methane ebullition under climate change. Nat. Commun. 8, 1682. doi:10.1038/s41467-017-01535-y

Algeo, T. J., Chen, Z. Q., Fraiser, M. L., and Twitchett, R. J. (2011). Terrestrial–marine teleconnections in the collapse and rebuilding of Early Triassic marine ecosystems. Palaeogeogr. Palaeoclimatol. Palaeoecol. 308, 1–11. doi:10.1016/j.palaeo.2011.01.011

Algeo, T. J., Ellwood, B., Nguyen, T. K. T., Rowe, H., and Maynard, J. B. (2007a). The Permain–Triassic boundary at Nhi Tao, Vietnam: evidence for recurrent influx of sulfidic watermasses to a shallow-marine carbonate platform. Palaeogeogr. Palaeoclimatol. Palaeoecol. 252, 304–327. doi:10.1016/j.palaeo.2006.11.055

Algeo, T. J., Hannigan, R., Rowe, H., Brookfield, M., Baud, A., Krystyn, L., et al. (2007b). Sequencing events across the permain–triasic boundary, guryul ravine (Kashmir, India). Palaeogeogr. Palaeoclimatol. Palaeoecol. 252, 328–346. doi:10.1016/j.palaeo.2006.11.050

Algeo, T. J., Henderson, C. M., Ellwood, B., Rowe, H., Elsick, E., Bates, S., et al. (2012). Evidence for a diachronous Late Permian marine crisis from the Canadian Arctic region. GSA Bull. 124, 1424–1448. doi:10.1130/B30505.1

Algeo, T. J., Shen, Y., Zhang, T. G., Lyons, T. W., Bates, S., Rowe, H., et al. (2008). Association of δ34S-depleted pyrite layers with negative carbonate δ13C excursions at the Permian-Triassic boundary: evidence for upwelling of sulfidic deep-ocean water masses. Geochim. Geophys. Geosyst. 9, Q04025. doi:10.1029/2007GC001823

Bambach, R. K. (2006). Phanerozoic biodiversity mass extinctions. Science 313, 1276–1284. doi:10.1126/science.1139910

Bagherpour, B., Bucher, H., Vennemann, T., Schneebeli-Hermann, E., Yuan, D. X., et al. (2017). Cross-continental increase in methane ebullition under climate change. Palaeoceanogr. Palaeoclimatol. Palaeoecol. 328, 1–11. doi:10.1002/2016GC006199

Basiliko, N., and Yavitt, J. B. (2001). In Bambach, R. K. (2006). Phanerozoic biodiversity mass extinctions. Science 313, 1276–1284. doi:10.1126/science.1139910

Berner, R. A. (2002). Examination of hypotheses for the Permo–Triassic boundary extinction by carbon cycle modeling. Proc. Natl. Acad. Sci. USA 99, 4172–4177. doi:10.1073/pnas.0320991199

Bidigare, R. R., Fuegge, A., Freeman, K. H., Hanson, K. L., Hayes, J. M., Hollander, D., et al. (1997). Consistent fractionation of 13C in nature and in the laboratory: growth-rate effects in some haptophyte algae. Glob. Biogeochem. Cycles 11, 279–292. doi:10.1029/96gb03939

Black, B. A., Neely, R. R., Lamarque, J., Elkins-Tanton, L. T., Kiehl, J. T., Shields, C. A., et al. (2018). Systemic swings in end-Permian climate from Siberian Traps carbon and sulfur outgassing. Nat. Geosci. 11, 949–954. doi:10.1038/s41561-018-0261-y

Bond, D. P. G., and Wignall, P. B. (2014). "Large igneous provinces and mass extinctions: an update." in Volcanism, impacts, and mass extinctions: causes and effects. Spec. Pop., Editors G. Keller and A. Kerr, Geol. Soc. Am. Vol. 505, 29–55. doi:10.1130/2014.2505p0(2)

Brand, U., Blamey, N., Garbelli, C., Grissabher, E., Posenato, R., Angiolini, L., et al. (2016). Methane Hydrate: killer cause of Earth’s greatest mass extinction. Palaeoworld 25, 496–507. doi:10.1016/j.palwor.2016.06.002

Cao, C. Q., Yang, Y. C., Shen, S. Z., Wang, W., Zheng, Q. F., and Summons, R. E. (2015). Timing of global regression and microbial bloom linked with the Permain-Triassic boundary in the meishan section, zhejiang province, China. Chin. Sci. Bull. 47, 1125–1129.

Cao, C. Q., Yang, Y. C., Shen, S. Z., Wang, W., Zheng, Q. F., and Summons, R. E. (2010). Pattern of δ34S, and implications for geological events during the Permain-Triassic transition in South China. Geol. J. 45, 186–194. doi:10.1002/ gji.1220

Cui, Y., Xia, Y., Song, H., Algeo, T. J., Chu, D., Du, Y., Tian, L., et al. (2019). Intensified chemical weathering during the Permain–Triassic transition recorded in terrestrial and marine successions. Palaeogeogr. Palaeoclimatol. Palaeoecol. 519, 166–177. doi:10.1016/j.palaeo.2018.06.012

Cui, Y., Kump, L. R., and Ridgwell, A. (2013). Initial assessment of the carbon isotope excursions of local or of global significance. Glob. Biogeochem. Cycles 27, 677–677. doi:10.1002/2013GC005278

Cui, Y., Kump, L. R., and Ridgwell, A. (2013). Initial assessment of the carbon isotope excursions of local or of global significance. Glob. Biogeochem. Cycles 27, 677–677. doi:10.1002/2013GC005278

Cui, Y., Bercovici, A., Yu, J. X., Kump, L. R., Freeman, K. H., Su, S. G., et al. (2017). Ocean acidification and the Permo-Triassic mass extinction. Science 348, 229–232. doi:10.1126/science.aaa1093

Coney, L., Reimold, W. U., Hancock, P. J., Mader, D., Koeberl, C., McDonald, I., Struck, U., Vajda, V., and Kamo, S. L. (2007). Geochemical and mineralogical investigation of the Permain–Triassic boundary in the continental realm of the southern Karoo Basin, South Africa. Palaeoworld Rep. 16, 67–104.

Conrad, R. (2009). The global methane cycle: recent advances in understanding the microbial processes involved. Environ. Microbiol. Rep. 1, 285–292. doi:10.1111/j.1758-2229.2009.00383.x

Cui, Y., Bercovici, A., Yu, J. X., Kump, L. R., Freeman, K. H., Su, S. G., et al. (2017). Ocean acidification and the Permo-Triassic mass extinction. Glob. Biogeochem. Cycles 28, 272–285. doi:10.1002/2015GB005303

de Wit, M. J., Ghoosh, J. G., de Villiers, S., Rakotosolofo, N., Alexander, J., Tripathi, A., et al. (2002). Multiple organic carbon isotope reversals across the Permain–
Triassic boundary of terrestrial Gondwana Sequences: clues to extinction patterns and delayed ecosystem recovery. *J. Geol.* 110, 227–240.

Dikert, G., Konheiser, U., Pischull, K., and Thauer, R. K. (1981). Nickel requirement and factor F430 content of methanogenic bacteria. *J. Bacteriol.* 148, 459–464.

Elkins-Tanton, L. T., Grasyb, S. E., Black, B. A., Veselovskiy, R. V., Ardanaki, O. H., and Goodarzi, F. (2020). Field evidence for coal combustion links the 252 Ma Siberian Traps with global carbon disruption. *Geology* 48, 986–991. doi:10.1130/G47365.1

Erwin, D. H., Bowring, S. A., and Yogan, J. (2002). “End-Permian mass extinctions: a review.” in *Catastrophic events and mass extinctions: impacts and beyond: Boulder, Colorado*. Editors C. Koeberl, and K. G. MacLeod, (Boulder: Geol. Soc. Am. Spec. Pap.) 356, pp. 363–383.

Erwin, D. H. (2006). Extinction: how life on Earth nearly ended 250 million years ago. New Jersey, United States: Princeton Univ. Press, 296 p.

Erwin, D. H. (1993). *The great paleozoic crisis*. New York, United States: Columbia Univ. Press, 327 p.

Faure, K., de Wit, M. J., and Willis, J. P. (1995). Late Permian global coal hiatus linked to 13C-depleted CO2 flux into the atmosphere during the final consolidation of Pangaea. *Geology* 23, 507–510.

Fielding, C. R., Frank, T. D., McLoughlin, S., Vajda, V., Mays, C., Tevyaw, A. P., Erwin, D. H., Bowring, S. A., and Yugan, J. (2002).

Heydari, E., Wade, W. J., and Hassanzadeh, J. (2001). Diagenetic origin of carbon and oxygen isotope compositions of Permian—Triassic boundary strata. *Geol. Soc. Geology* 143, 191–197. doi:10.1130/S0007-0738(01)00095-1

Holser, W. T., Schönlaub, H.-P., Attrep, M., Boeckelmann, K., Klein, P., Magaritz, M., et al. (1989). A unique geochemical record at the Permian/Triassic boundary. *Nature* 337, 39–44.

Horacek, M., Brandner, R., and Abar, R. (2007b). Carbon isotope record of the P/T boundary and the Lower Triassic in the Southern Alps: evidence for rapid changes in storage of organic carbon. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 252, 347–354. doi:10.1016/j.palaeo.2006.11.049

Horacek, M., Richoz, S., Brandner, R., Krystyn, L., and Spoél, C. (2007a). Evidence for recurrent changes in Lower Triassic oceanic circulation of the Tethys: the δ13C record from marine sections in Iran. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 252, 355–369. doi:10.1016/j.palaeo.2006.11.052

Hudspith, V. A., Rimmer, S. M., and Belcher, C. M. (2014). Latest Permian chars may derive from wildfires, not coal combustion. *Geology* 42, 879–882. doi:10.1130/G35920.1

Isozaki, Y. (2019). “End-paleozoic mass extinction: hierarchy of causes and a new cosmoclimatological perspective for the largest crisis.” in *Astrobiology*. Editors A. Yamagishi, T. Kakegawa, and T. Usui. (Singapore: Springer), 273–301. doi:10.1007/978-981-13-3639-3_18

Isozaki, Y. (1997). Permo-Triassic boundary Superanoxia and stratified superocean: records from lost deep-sea. *Science* 276, 235–238. doi:10.1126/science.276.5310.235

Isozaki, Y., Shimizu, N., Yao, J. X., Ji, Z. S., and Matsuda, T. (2007). End-Permian extinction and volcanism-induced environmental stress: the Permian—Triassic boundary interval of lower-slope facies at Chaotian, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 252, 218–238. doi:10.1016/j.palaeo.2006.11.051

Isozaki, Y., Yao, J. X., Ji, Z. S., Saitoh, M., Kobayashi, N., and Sakai, H. (2008). Rapid sea-level change in the late guadalupian (permian) on the tethyan side of South China: litho- and biostратigraphy of the chaotian section in sichuan. *Proc. Ipn. Acad. Ser. B* 84, 344–353. doi:10.2183/pjab.84.344

Isozaki, Y., Yao, J. X., Matsuda, T., Sakai, H., Ji, Z. S., Shimizu, N., et al. (2004). Stratigraphy of the middle-upper permian and lowermost triassic at chaotian, sichuan, China. –Record of late permian double mass extinction event—. *Proc. Ipn. Acad. Ser. B* 80, 10–16. doi:10.2183/pjab.80.10

Ji, Z. S., Yao, J. X., Isozaki, Y., Matsuda, T., and Wu, G. C. (2007). Conodont biostratigraphy across the permian—triassic boundary at chaotian, in northern sichuan, China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 252, 39–55. doi:10.1016/j.palaeo.2006.11.033

Jin, Y. G., Mei, S. L., Wang, W. W., Wang, X. D., Shen, S. Z., Shang, Q. H., et al. (1998). On the Lopingian series of the Permian system. *Palaeoworld* 9, 1–18.

Jin, Y. G., Wang, W. W., Wang, X. D., Shen, S. Z., and Erwin, D. H. (2000). Pattern of marine mass extinction near the Permian—Triassic boundary in South China. *Science* 289, 432–436. doi:10.1126/science.289.5478.432

Joachimski, M. M., Alekseev, A. S., Grigoryan, A., and Gatovsky, Y. A. (2020). Siberian Trap volcanism, global warming and the Permian—Triassic mass extinction: new insights from Armenian Permian-Triassic sections. *GSA Bull.* 132, 427–443. doi:10.1130/B35310.1

Joachimski, M. M., Lai, X. L., Shen, S. Z., Jiang, H. S., Luo, G. M., Chen, B., et al. (2020). Climate warming in the latest Permian and the Permian—Triassic mass extinction. *Geology* 40, 195–198. doi:10.1130/G32707.1

Jost, A. B., Mundil, R., He, B., Brown, S. T., Alten, D., Sun, Y. D., et al. (2014). Constraining the cause of the end-Guadalupian extinction with coupled records of carbon and calcium isotopes. *Earth Planet Sci. Lett.* 396, 201–212. doi:10.1016/j.epsl.2014.04.014

Jurikova, H., Gutjahr, M., Wallmann, K., Flögel, S., Liebetrau, V., Posenato, R., et al. (2020). Triassic marine crisis. *J. Geol.* 118, 147–163. doi:10.1002/jgs2.2541

Kaiho, H., Aki, K., Eiji, K., Ito, K., Miyaji, T., Bae, F. S., Tian, L., et al. (2016). Effects of Late Permian (251 Ma) carbon isotope excursions on the stable carbon isotope ratio before, during and after the end-Permian mass extinction. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 489, 217–230. doi:10.1016/j.palaeo.2017.05.002

Kajiwara, Y., Yamakita, S., Ishida, K., Ishiga, H., and Imai, A. (1994). Development of euxinic ocean in the Permian–Triassic boundary of terrestrial Gondwana Sequences: clues to extinction patterns and delayed ecosystem recovery. *Lithos* 33, 39–48. doi:10.1016/0024-4937(94)90064-2

Kaiho, H., Chen, Z. Q., and Sawada, K. (2009). Possible causes for a negative shift in the stable carbon isotope ratio before, during and after the end-Permian mass extinction in Meishan, South China. *Aust. J. Earth Sci.* 56, 799–808. doi:10.1080/0812000900302615

Kaiho, K., Saito, R., Ito, K., Miyaji, T., Biswas, R., Tian, L., et al. (2016). Effects of soil erosion and anoxic–euxinic ocean in the Permian–Triassic marine crisis. *Helyon* 2, e00137. doi:10.1080/20710326.2016.600137

Kajiwara, Y., Yamakita, S., Ishida, K., Ishiga, H., and Imai, A. (1994). Development of a largely anoxic stratified ocean and its temporary massive mixing at the Permian—Triassic boundary supported by the sulfur isotopic record.
Rothman, D. H., Fournier, G. P., French, K. L., Alm, E. J., Boyle, E. A., Cao, C. Q., Riccardi, A., Kump, L. R., Arthur, M. A., and D...
van Groeningen, K., Osenberg, C., and Hungate, B. (2011). Increased soil emissions of potent greenhouse gases under increased atmospheric CO₂. Nature 475, 214–216. doi:10.1038/nature10176

Wang, Y., and Jin, Y. (2000). Permian palaeogeographic evolution of the jiangan basin, south China. Palaeogeogr. Palaeoclimatol. Palaeoecol. 160, 35–44. doi:10.1016/S0031-0182(00)00432-3

Ward, P. D., Botha, J., Buick, R., De Kock, M. O., Erwin, D. H., Garrison, G. H., et al. (2005). Abrupt and gradual extinction among Late Permian land vertebrates in the Karoo Basin, South Africa. Science 307, 709–714. doi:10.1126/science.1107068

Ward, P. D., Montgomery, D. R., and Smith, R. (2000). Altered river morphology in South Africa related to the Permian–Triassic extinction. Science 289, 1740–1743. doi:10.1126/science.289.5485.1740

Wei, H., Yu, H., Wang, J. G., Qiu, Z., Xiang, L., and Shi, G. (2015). Carbon isotopic shift and its cause at the Wuchiapingian–Changhsingian boundary in the Upper Permian at the Zhaojiaba section, South China: evidences from multiple geochemical proxies. J. Asian Earth Sci. 105, 270–285. doi:10.1016/j.jseaes.2015.01.011

Wignall, P. B., and Hallam, A. (1992). Anoxia as a cause of the Permian/Triassic mass extinction: facies evidence from northern Italy and the western United States. Palaeogeogr. Palaeoclimatol. Palaeoecol. 93, 21–46. doi:10.1016/S0031-0182(92)90182-5

Wignall, P. B. (2001). Large igneous provinces and mass extinctions. Earth-Sci.Rev. 53, 1–33. doi:10.1016/S0012-8252(00)00037-4

Wignall, P. B., Morante, R., and Newton, R. (1998). The Permo–Triassic transition in Spitsbergen: δ¹³Ccarb chemostратigraphy, Fe and S geochemistry, facies, fauna and trace fossils. Geol. Mag. 135, 47–62. doi:10.1017/S0016756879008121

Wignall, P. B., and Twitchett (1996). Oceanic anoxia and end Permian mass extinction. Science 272, 1155–1158. doi:10.1126/science.272.5265.1155

Xie, S. C., Pancost, R. D., Huang, J. H., Wignall, P. B., Yu, J. X., Tang, X. Y., et al. (2007). Changes in the global carbon cycle occurred as two episodes during the Permian–Triassic crisis. Geology 35, 1083–1086. doi:10.1130/G2424A.1

Xu, D. Y., Ma, S. L., Chai, Z. F., Mao, X. Y., Sun, Y. Y., Zhang, Q. W., et al. (1985). Abundance variation of iridium and trace elements at the Permian/Triassic boundary at Shansi in China. Nature 314, 154–156.

Yang, B., Li, H. X., Wignall, P. B., Jiang, H. S., Niu, Z. J., Ye, Q., et al. (2019). Latest wuchiapingian to earliest triassic conodont zones and δ¹³Ccarb isotope excursions from deep-water sections in western Hubei province, south China. J. Earth Sci. 30, 1059–1074. doi:10.1007/s12583-019-1018-2

Yang, Z. Y., Yin, H. F., Wu, S. B., Yang, F. Q., Ding, M. H., and Xu, G. R. (1987). Permian–triassic boundary. Stratigraphy and faunas of South China. Ministry of geology and mineral resources, Geol. Mem. Ser. 26, 1–379 (in Chinese with English abstract).

Yin, H. F., Jiang, H. S., Xia, W. C., Feng, Q. L., Zhang, N., and Shen, J. (2014). The end-Permian regression in South China and its implication on mass extinction. Earth-Sci.Rev. 137, 19–33. doi:10.1016/j.earscirev.2013.06.003

Yuan, D. X., Chen, J., Zhang, Y. C., Zheng, Q. F., and Shen, S. Z. (2015). Changhsingian conodont succession and the end-Permian mass extinction event at the Daijiagou section in Chongqing, Southwest China. J. Asian Earth Sci. 105, 234–251. doi:10.1016/j.jseaes.2015.04.002

Yvon-Durocher, G., Allen, A., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., et al. (2014). Methane fluxes show consistent temperature dependence across microbial to ecosystem scales. Nature 507, 488–491. doi:10.1038/nature13164

Zhang, G. J., Zhang, X. L., Hu, D. P., Li, D. D., Algeo, T. J., Farquhar, J., et al. (2017). Redox chemistry changes in the Panthalassic ocean linked to the end-Permian mass extinction and delayed Early Triassic biotic recovery. Proc. Natl. Acad. Sci. USA 114, 1806–1810. doi:10.1073/pnas.1609331114

Zhao, J. K., Liang, X. L., and Zheng, Z. G. (1978). Late Permian cephalopods of South China. Palaeontol. Sinica, N.S. 12, 1–194 (in Chinese with English abstract).

Zhao, J. K., Sheng, J. Z., Yao, Z. Q., Liang, X. L., Chen, C. Z., Rui, L. et al. (1981). The changhsingian and permian-triassic boundary of South China. Bull. Nanjing Inst. Geol. Palaeontol. Acad. Sinica 2, 1–112 (in Chinese).

Zhou, W. F., Algeo, T. J., Ruan, X. Y., Luo, G. M., Chen, Z. Q., and Xie, S. C. (2017). Expansion of photic-zone euxinia during the Permian–Triassic biotic crisis and
its causes: microbial biomarker records. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 474, 140–151. doi:10.1016/j.palaeo.2016.06.027

Zhu, T. X., Huang, Z. Y., and Hui, L. (1999). *The geology of late permian period biothermal facies in upper yangtze tableland*. Beijing, China: Geol. Pub. House, (in Chinese).

Zuchuat, V., Sleveland, A. R. N., Twitchett, R. J., Svensen, H. H., Turner, H., Augland, L. E., et al. (2020). A new high-resolution stratigraphic and palaeoenvironmental record spanning the End-Permian Mass Extinction and its aftermath in central Spitsbergen. *Svalbard Palaeogeogr. Palaeoclimatol. Palaeoecol.* 554, 109732. doi:10.1016/j.palaeo.2020.109732

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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