



# Carbon Isotope Chemostratigraphy Across the Permian-Triassic Boundary at Chaotian, China: Implications for the Global Methane Cycle in the Aftermath of the Extinction

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During the end-Permian extinction, a substantial amount of methane (CH<sub>4</sub>) was likely released into the ocean-atmosphere system associated with the Siberian Traps volcanism, although fluctuations in the global CH<sub>4</sub> cycle in the aftermath of the extinction remain poorly understood. The carbon (C) isotopic composition of carbonate ( $\delta^{13}\text{C}_{\text{carb}}$ ) across the Permian-Triassic boundary (P-TB) was analyzed at Chaotian, South China. The  $\delta^{13}\text{C}_{\text{carb}}$  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 (CO<sub>2</sub>) input to the surface oceans may also have contributed to the  $\delta^{13}\text{C}_{\text{carb}}$  decline. The magnitude of the  $\delta^{13}\text{C}_{\text{carb}}$  decrease (~3‰) is substantially smaller than the magnitude of a decrease in C isotopic composition of organic matter ( $\delta^{13}\text{C}_{\text{org}}$ ) in the same P-TB interval (~7‰). This apparent  $\delta^{13}\text{C}_{\text{carb}}-\delta^{13}\text{C}_{\text{org}}$  decoupling could be explained by proliferation of methanogen (“methanogenic burst”) in the sediments. A global  $\delta^{13}\text{C}$  compilation shows a large variation in marine  $\delta^{13}\text{C}_{\text{org}}$  records, implying that the “methanogenic burst” according to the Siberian Traps volcanism may have contributed, at least in part, to the  $\delta^{13}\text{C}_{\text{org}}$  variability and to the elevated CH<sub>4</sub> levels in the atmosphere. The present and previous observations allow us to infer that the global CH<sub>4</sub> cycle may have fluctuated substantially in the aftermath of the extinction.

**Keywords:** end-Permian extinction, global CH<sub>4</sub> cycle, methanogenesis, methanotrophy, anaerobic oxidation of methane (AOM), global warming, variable  $\delta^{13}\text{C}_{\text{org}}$  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., 2009; Burgess and Bowring, 2015) and the associated massive release of thermogenic gases (e.g., Wignall, 2001; Retallack and Jahren, 2008; Svensen et al., 2009; Shen et al., 2012; Polozov et al., 2016) and resulting global warming (e.g., Hallam and Wignall, 1997; Kidder and Worsley, 2004; Brand et al., 2012; Joachimski et al., 2012), oceanic anoxia (e.g., Wignall and Hallam, 1992; Wignall and Twitchett, 1996; Isozaki, 1997; Algeo et al., 2008; Shen et al., 2011c; Schobben et al., 2015) accompanied by H<sub>2</sub>S poisoning (e.g., Grice et al., 2005; Kump et al., 2005; Zhang et al., 2017; Zhou et al., 2017) and hypercapnia (Knoll et al., 1996, 2007), and oceanic acidification (e.g., Heydari et al., 2003; Payne et al., 2007; Clapham and Payne, 2011; Clarkson et al., 2015; Baresel et al., 2017; Garbelli 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 ( $\delta^{13}\text{C}_{\text{carb}}$ ) of P-TB rocks and documented a negative  $\delta^{13}\text{C}_{\text{carb}}$  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., 2000; 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  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease has been generally regarded as an original isotopic signal of seawater (Bagherpour et al., 2019).

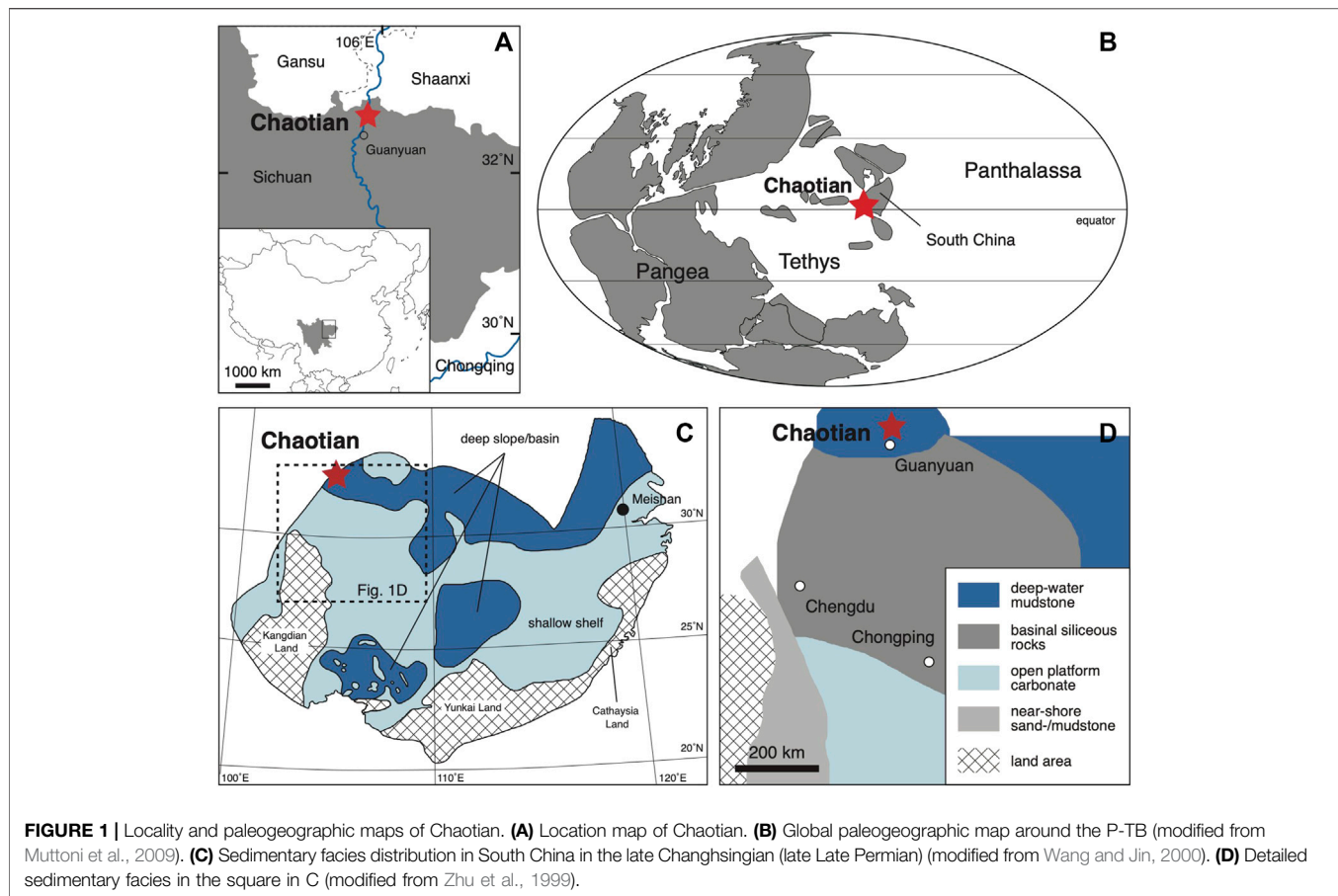
Considering a simple box model of the surface-ocean C pool, two principle mechanisms could explain the P-TB  $\delta^{13}\text{C}$  decrease in marine carbonates: 1) a decrease in the output and 2) an increase in the input of <sup>13</sup>C-depleted C (e.g., Korte and Kozur, 2010). A collapse in primary productivity and reduction in biological pump (“strangelove oceans”) corresponds to the former mechanism (e.g., Kump, 1991), although it may have produced only a ~3‰ negative  $\delta^{13}\text{C}_{\text{carb}}$  shift (Rampino and Caldeira, 2005) and might not be sufficient to explain larger P-TB  $\delta^{13}\text{C}$  declines commonly observed around the world. The increase in the input of <sup>13</sup>C-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 volcanogenic CO<sub>2</sub> emission involved in the Siberian Traps volcanism (e.g., Renne et al., 1995; Hansen, 2006), methane (CH<sub>4</sub>) 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., Kajiwarra et al., 1994; Knoll et al., 1996; Algeo et al., 2007a). Korte and Kozur (2010) comprehensively correlated the P-TB  $\delta^{13}\text{C}_{\text{carb}}$  records of shelf carbonates on a global scale. Based on a gradually decreasing trend toward the P-TB, the authors suggested that the  $\delta^{13}\text{C}_{\text{carb}}$  decrease was caused by a combination of the Siberian Traps volcanism and a shoaling of anoxic deep-waters onto shelves.

A negative shift of the C isotopic composition of organic C ( $\delta^{13}\text{C}_{\text{org}}$ ) across the P-TB has been reported in marine strata in many sections such as Arctic Canada (e.g., Grasby and Beauchamp, 2008; Algeo et al., 2012), Greenland (e.g., Twitchett et al., 2001), Spitsbergen (e.g., Wignall et al., 1998; Zuchuat et al., 2020), South China (e.g., Cao et al., 2002), Japan (e.g., Takahashi et al., 2010), and Australia (e.g., Morante, 1996). The marine  $\delta^{13}\text{C}_{\text{org}}$  decrease has been correlated normally with the negative  $\delta^{13}\text{C}_{\text{carb}}$  shift in shelf carbonates by assuming that the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  trends were parallel and the difference between the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values ( $\Delta^{13}\text{C}$ ) was consistent during the Permian-Triassic transition, although the  $\Delta^{13}\text{C}$  value is generally controlled by several factors such as carbon dioxide (CO<sub>2</sub>)-fixing enzymes and atmospheric CO<sub>2</sub> levels (*p*CO<sub>2</sub>) (e.g., Hayes et al., 1999). A parallel  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{carb}}$ - $\delta^{13}\text{C}_{\text{org}}$  decoupling across the P-TB. The  $\Delta^{13}\text{C}$  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  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  trends on land are generally variable compared to those of marine sediments, and the P-TB  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  records well with the marine  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  records.

Previous studies particularly suggested that a substantial amount of CH<sub>4</sub> 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.,



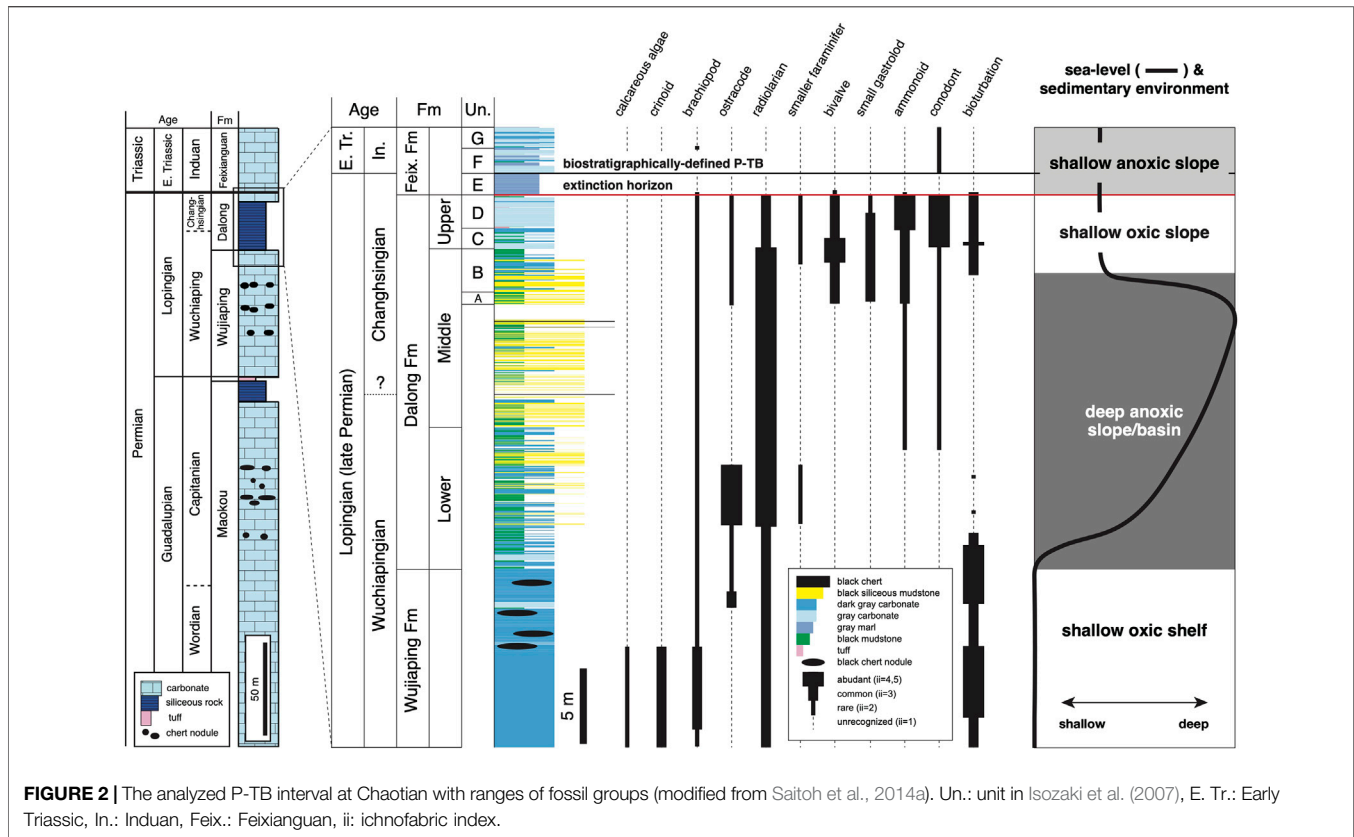
Krull et al., 2000; Krull et al., 2004; Brand et al., 2016), and enhanced microbial methanogenesis (“methanogenic burst”) (Rothman et al., 2014). As  $\text{CH}_4$  is a potent greenhouse gas, the huge  $\text{CH}_4$  input may have contributed to climate warming in the aftermath of the extinction (e.g., Hallam and Wignall, 1997; Joachimski et al., 2012; Sun et al., 2012; Cui and Kump, 2015). However, the global  $\text{CH}_4$  cycle during the Permian-Triassic transition has been poorly examined and constrained. In this study, we analyzed the  $\delta^{13}\text{C}_{\text{carb}}$  records of the P-TB carbonates at Chaotian in northern Sichuan, South China. Together with the previously reported  $\delta^{13}\text{C}_{\text{org}}$  records of the same interval, we examined the sedimentary C cycle in eastern Paleotethys during the Permian-Triassic transition. Moreover, we compiled the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  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  $\text{CH}_4$  cycle in the aftermath of the end-Permian 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 Guanyuan city in northern Sichuan (**Figure 1**;  $32^{\circ}37'N$ ,  $105^{\circ}51'E$ ; 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 Wujiaping 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



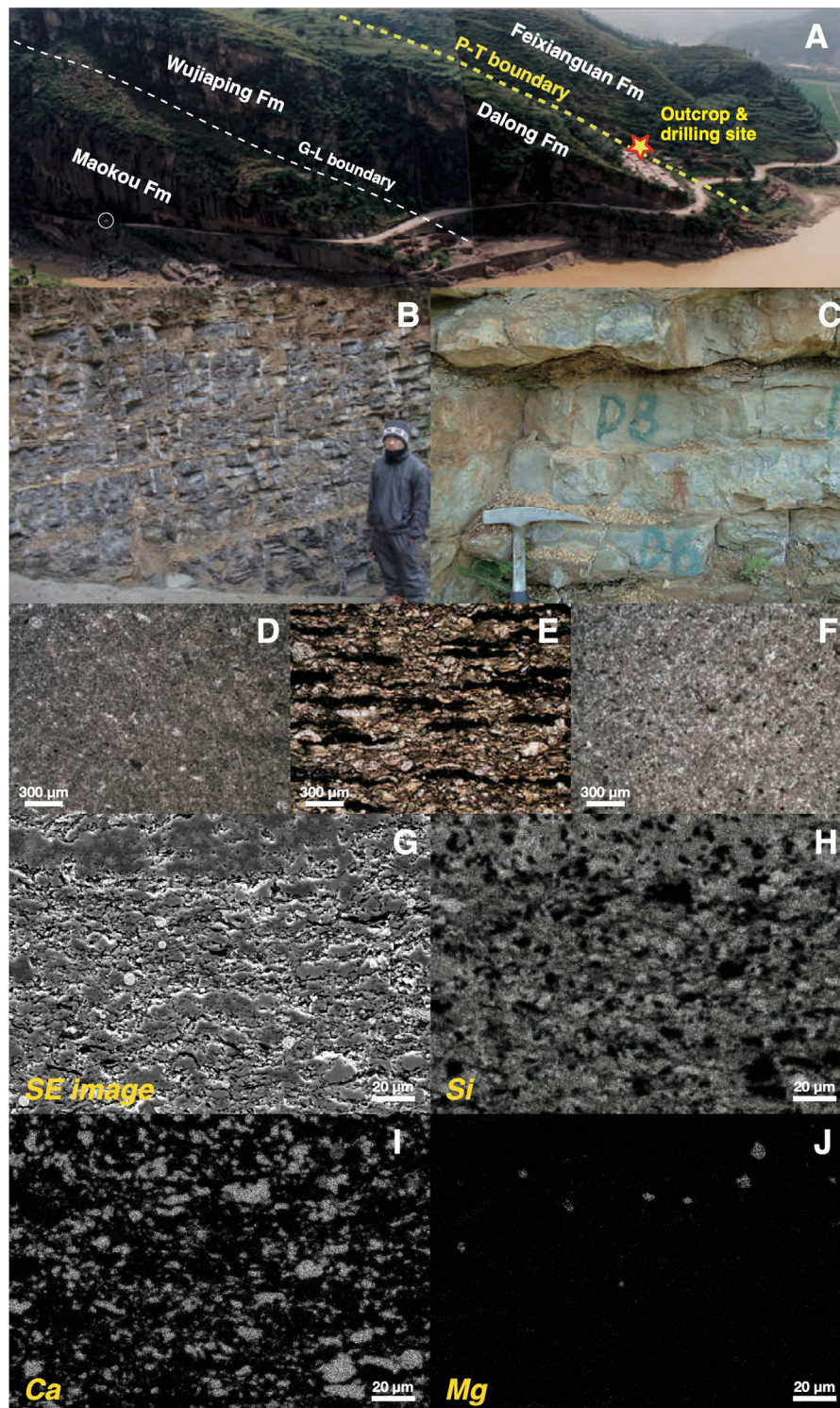
(~11 m thick) of the Maokou Formation is composed of thinly bedded black calcareous mudstone and black chert/siliceous mudstone with abundant radiolarians, conodonts, and ammonoids. The Wujiaping Formation (~70 m thick) is composed mainly of massive dark gray bioclastic limestone with black chert nodules/lenses, containing shallow-marine fossils such as fusulines, smaller foraminifer, rugosa corals, calcareous algae and brachiopods. At the base of the Wujiaping 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  $\delta^{13}\text{C}_{\text{carb}}$  values around the P-TB and found a negative  $\delta^{13}\text{C}$  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 Wujiaping Formation, 2) the Dalong Formation, and 3) the lowermost Feixianguan Formation, in ascending order. The upper Wujiaping 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 Wujiaping Formation. The upper Wujiaping 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 Wujiaping 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, black siliceous mudstone, dark gray muddy limestone, 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 and D' 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 framboids (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 euphotic 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 CO<sub>2</sub> 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 presented using the delta notation  $\delta^{13}\text{C} = ((^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1)$  and  $\delta^{18}\text{O} = ((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1)$ , respectively. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are reported in ‰ relative to the Vienna Pee Dee Belemnite (V-PDB) standard. The analytical reproducibility of the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values was better than 0.1 and 0.1‰, respectively.

## RESULTS

Table 1 lists all the measured  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values of the P-TB interval. Figure 4 shows chemostratigraphic profiles of the  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{18}\text{O}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$ , and  $\Delta^{13}\text{C}$  values and TOC contents. The  $\delta^{13}\text{C}_{\text{org}}$  values and TOC contents were previously reported in Saitoh et al. (2014a). Figure 5 shows a  $\delta^{13}\text{C}_{\text{carb}}$ - $\delta^{18}\text{O}_{\text{carb}}$  cross plot. The  $\delta^{13}\text{C}_{\text{carb}}$  values range from -6.9 to +4.3‰, with an average value of ca. 0‰. The  $\delta^{18}\text{O}_{\text{carb}}$  values range from -7.9 to -2.9‰, with an average value of ca. -5.9‰.

The  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  values increase slightly from ca. -2 to +1‰ upward except for some anomalously low (<-3‰) values (open symbols in Figure 4). The  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  results around the P-TB are generally identical to the results in Cao et al. (2010). The  $\delta^{18}\text{O}_{\text{carb}}$  values are somewhat variable in the upper Wujiaping limestones and are mainly around -7‰ in the overlying Dalong Formation. Above the P-TB, the  $\delta^{18}\text{O}_{\text{carb}}$  values are mostly around -6‰ in the lowermost Feixianguan Formation. The  $\Delta^{13}\text{C}$  values are mainly between 27 and 29‰ in the upper Wujiaping Formation and decrease slightly to ca. 26‰ in the Dalong Formation. The  $\Delta^{13}\text{C}$  values increase to ca. 30‰ in the overlying lowermost Feixianguan carbonates.

No linear correlation is observed between the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  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 <sup>13</sup>C-depleted C. Except for these anomalous values, the present  $\delta^{13}\text{C}_{\text{carb}}$  results represent a smooth chemostratigraphic trend in the analyzed interval. This trend may record secular changes in the  $\delta^{13}\text{C}$  value of dissolved inorganic carbon (DIC) in seawater ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in the Lopingian to earliest Triassic. Based on the C isotopic

**TABLE 1** | C and O isotopic composition of the analyzed P-TB interval at Chaotian. The  $\delta^{13}\text{C}_{\text{org}}$  values and TOC contents were reported in Saitoh et al. (2014a).

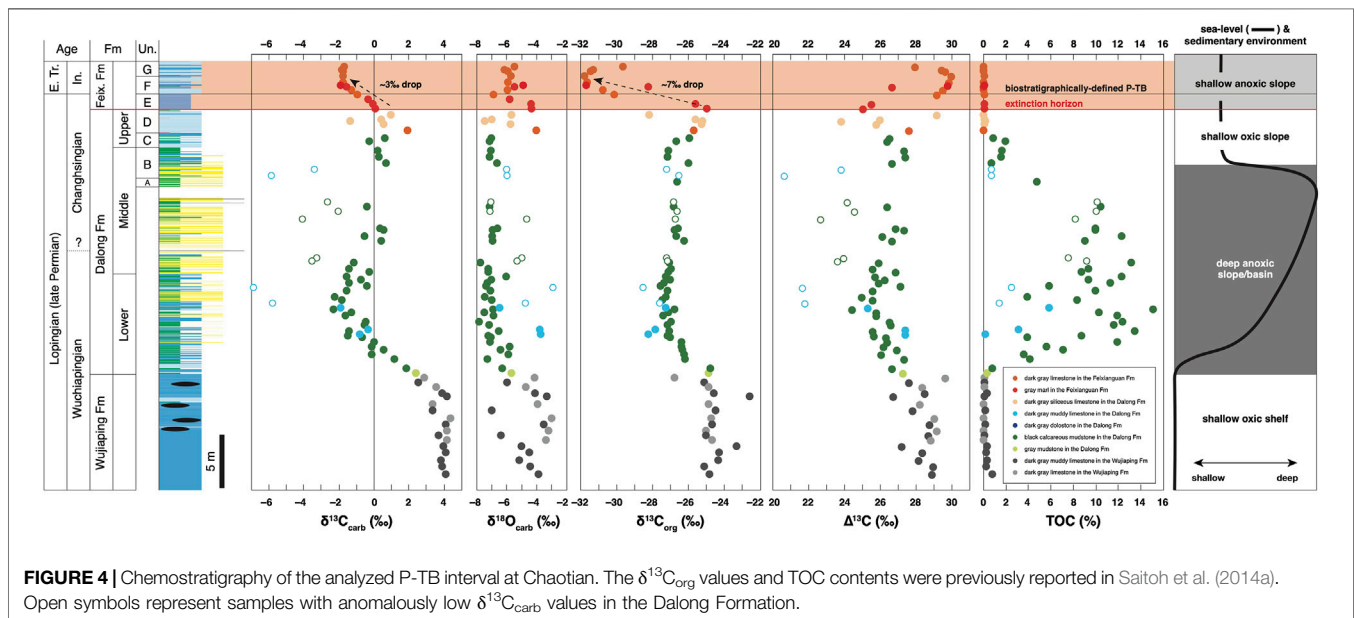
Formation	Sample ID	Lithology	Thickness (m)	$\delta^{13}\text{C}_{\text{carb}}$ vs. VPDB (‰)	$\delta^{18}\text{O}_{\text{carb}}$ vs. VPDB (‰)	$\delta^{13}\text{C}_{\text{org}}$ vs. VPDB (‰)	$\Delta^{13}\text{C}$ vs. VPDB (‰)	TOC (%)
Feixianguan	G8	dark gray limestone	38.3	-1.7	-5.5	-29.6	27.9	0.0
Feixianguan	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	C6	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	B26	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	24.6	-2.1	-7.1	-26.6	24.6	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	-3.6	-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	25.6	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	-7.9	-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)



**TABLE 1 |** (Continued) C and O isotopic composition of the analyzed P-TB interval at Chaotian. The  $\delta^{13}\text{C}_{\text{org}}$  values and TOC contents were reported in Saitoh et al. (2014a).

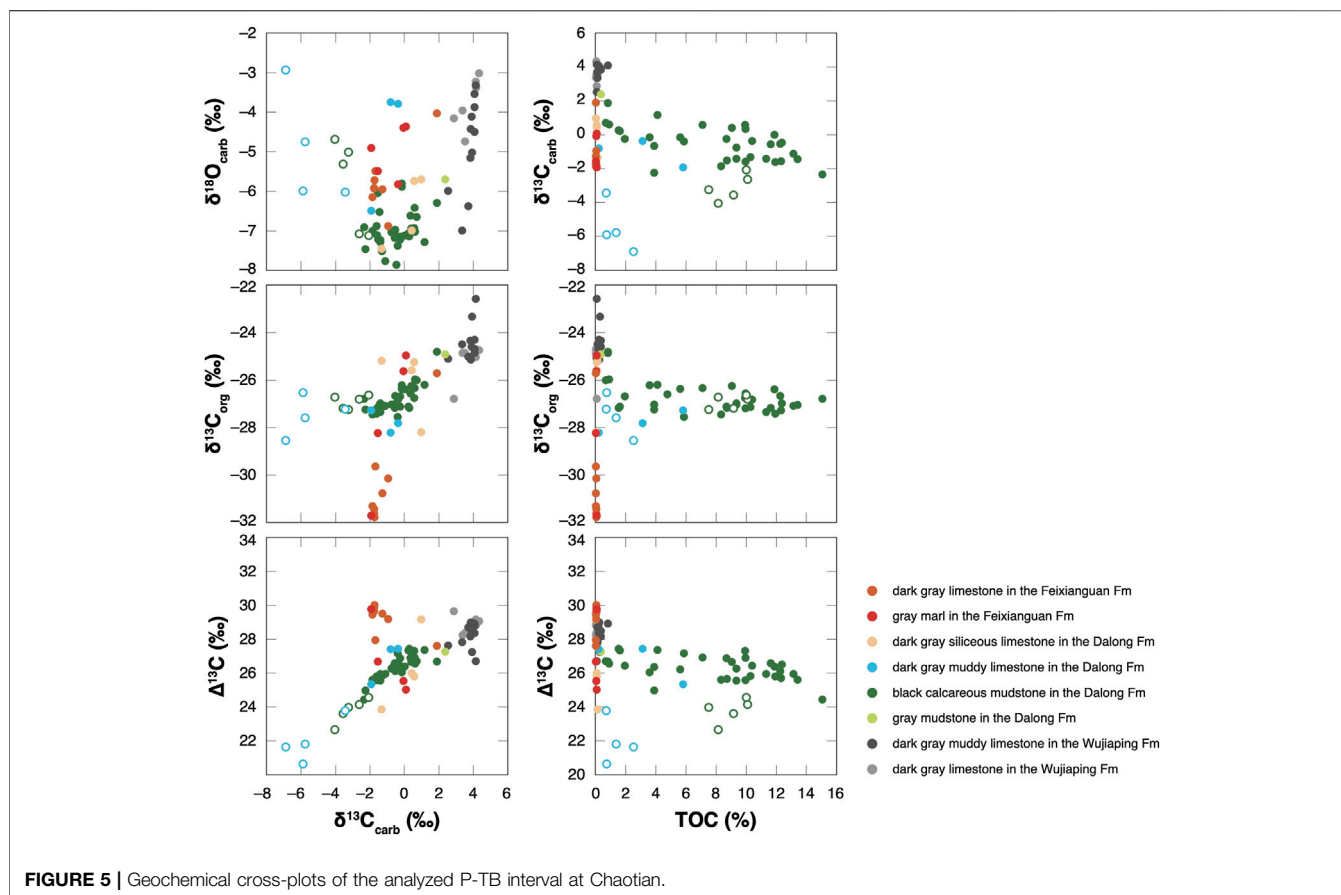
Formation	Sample ID	Lithology	Thickness (m)	$\delta^{13}\text{C}_{\text{carb}}$ vs. VPDB (‰)	$\delta^{18}\text{O}_{\text{carb}}$ vs. VPDB (‰)	$\delta^{13}\text{C}_{\text{org}}$ vs. VPDB (‰)	$\Delta^{13}\text{C}$ vs. VPDB (‰)	TOC (%)
Dalong	Dalong13	black mudstone	13.4	-1.4	-6.5	-27.0	25.6	13.4
Dalong	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	Dalong6	black mudstone	11.7	0.6	-6.4	-26.3	26.9	7.1
Dalong	Dalong5	black mudstone	11.2	-0.1	-5.9	-26.2	26.1	3.6
Dalong	Dalong3	black mudstone	10.8	1.2	-7.3	-26.2	27.4	4.1
Dalong	Dalong2	black mudstone	9.9	1.9	-6.3	-24.8	26.7	0.8
Dalong	Dalong1	gray 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

**FIGURE 4 |** Chemostratigraphy of the analyzed P-TB interval at Chaotian. The  $\delta^{13}\text{C}_{\text{org}}$  values and TOC contents were previously reported in Saitoh et al. (2014a). Open symbols represent samples with anomalously low  $\delta^{13}\text{C}_{\text{carb}}$  values in the Dalong Formation.

analyses of the P-TB carbonates in Iran, Schobben et al. (2016) suggested that the first-order  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  trend in the analyzed interval at Chaotian.





## DISCUSSION

### $\delta^{13}\text{C}$ Stratigraphy at Chaotian $\delta^{13}\text{C}_{\text{carb}}$ Decrease Around the Wuchiapingian-Changhsingian Boundary

The  $\delta^{13}\text{C}_{\text{carb}}$  values unidirectionally decrease from ca. +4 to  $-2\text{‰}$  across the Wujiaping/Dalong formation boundary at Chaotian (Figure 4). Although the timing of this negative  $\delta^{13}\text{C}_{\text{carb}}$  shift is not well constrained because of the poor occurrence of index fossils, the  $\delta^{13}\text{C}_{\text{carb}}$  shift likely occurred around the Wuchiapingian-Changhsingian boundary. This  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease likely records the Lopingian secular change in the  $\delta^{13}\text{C}_{\text{DIC}}$  value in the surface oceans in the eastern Paleotethys.

Two possible mechanisms could explain the  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease at Chaotian. However, the magnitude of the  $\delta^{13}\text{C}_{\text{carb}}$  drop ( $\sim 6\text{‰}$ ) seems to be too large to be caused solely by the collapse of primary productivity (e.g., Berner, 2002); thus the addition of  $^{13}\text{C}$ -depleted C to the DIC pool in the surface oceans likely contributed to the  $\delta^{13}\text{C}_{\text{carb}}$  drop. We emphasize that the sedimentary setting deepened from oxic shelf to anoxic slope/basin floor. The ubiquitous occurrence of small pyrite framboids 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  $^{12}\text{C}$  due to the anaerobic respiration; therefore, the injection of  $^{13}\text{C}$ -depleted C into the surface oceans via shoaling of the deep-water might have contributed to the negative  $\delta^{13}\text{C}_{\text{carb}}$  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  $\text{CO}_2$  and/or reoxidized sedimentary organic C during a eustatic sea-level fall is unlikely for the cause of the  $\delta^{13}\text{C}_{\text{carb}}$  drop at Chaotian.

Regional and global correlations would be useful to constrain the cause of the  $\delta^{13}\text{C}_{\text{carb}}$  decrease at Chaotian. Around the

Wuchiapingian-Changhsingian boundary, a ca. 6‰ negative  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{DIC}}$  decrease in eastern Paleotethys. Similar  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decreases (~2–5‰) is variable and smaller than that at Chaotian. At Abadeh in central Iran, Richoz (2006) found a negative  $\delta^{13}\text{C}_{\text{carb}}$  shift in the corresponding interval in the Hambast Formation, which was later re-confirmed by Liu et al. (2013). A similar negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion (~4‰) was also reported from the equivalent horizons of Julfa beds/Alibashi Formation boundary at Kuh-e-Ali Bashi in northwestern Iran (Shen et al., 2013). These almost co-eval negative  $\delta^{13}\text{C}_{\text{carb}}$  shifts around the Wuchiapingian–Changhsingian boundary in Iran are comparable to that at Chaotian. Moreover, a large negative  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{org}}$  shift, as well as the  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{org}}$  decreases may have likewise recorded fluctuations in the global C cycle; however, a negative  $\delta^{13}\text{C}_{\text{carb}}/\delta^{13}\text{C}_{\text{org}}$  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 above-mentioned sections in which a negative  $\delta^{13}\text{C}$  shift is recognized, the magnitude of and the trend in the  $\delta^{13}\text{C}$  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.

### $\delta^{13}\text{C}_{\text{carb}}$ Decrease Across the P-TB

The  $\delta^{13}\text{C}_{\text{carb}}$  values decrease from ca. +1 to –2‰ across the Dalong/Feixianguan formation boundary (P-TB) at Chaotian (Figure 4). This negative  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease: 1) collapse of primary productivity in the surface oceans and 2) addition of  $^{13}\text{C}$ -depleted C to the DIC pool in the surface oceans. The negative  $\delta^{13}\text{C}_{\text{carb}}$  shift occurs across the major extinction horizon, suggesting that the shift was driven by

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  $\delta^{13}\text{C}_{\text{carb}}$  decrease. Isozaki 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  $\text{CO}_2$  ( $\delta^{13}\text{C}$ : ~–5‰) may also have contributed to the  $\delta^{13}\text{C}_{\text{carb}}$  decrease. Weathering of sedimentary organic matter due to a large regression is another possible mechanism for the  $\delta^{13}\text{C}_{\text{carb}}$  decrease (e.g., Yin et al., 2014). However, the sea-level drop occurred significantly before the  $\delta^{13}\text{C}_{\text{carb}}$  shift at Chaotian (Isozaki 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  $\delta^{13}\text{C}_{\text{carb}}$  drop was negligible. Song et al. (2012a) proposed the existence of a large vertical  $\delta^{13}\text{C}_{\text{carb}}$  gradient in the end-Permian oceans, along which a deepening of the sedimentary setting possibly caused the observed  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease cannot be attributed to the assumed vertical  $\delta^{13}\text{C}_{\text{carb}}$  gradient in the water column.

### $\Delta^{13}\text{C}$ Increase Across the P-TB

Saitoh et al. (2014a) reported the  $\delta^{13}\text{C}_{\text{org}}$  chemostratigraphy of the P-TB interval at Chaotian and revealed that the  $\delta^{13}\text{C}_{\text{org}}$  values drop abruptly by 7‰ (from –25 to –32‰) immediately above the extinction horizon (Figure 4). This clear  $\delta^{13}\text{C}_{\text{org}}$  decrease is consistent apparently with the  $\delta^{13}\text{C}_{\text{carb}}$  shift documented in the present study, although the magnitude of the  $\delta^{13}\text{C}_{\text{org}}$  decrease (~7‰) is substantially larger than that of the  $\delta^{13}\text{C}_{\text{carb}}$  decrease (~3‰). The  $\Delta^{13}\text{C}$  ( $=\delta^{13}\text{C}_{\text{carb}}-\delta^{13}\text{C}_{\text{org}}$ ) values increase by 4‰ from +26‰ to +30‰ in the aftermath of the extinction at Chaotian. Two possible mechanisms may explain this  $\Delta^{13}\text{C}$  increase: 1) an increase in C isotopic fractionation of biological C fixation and 2) additional input of  $^{13}\text{C}$ -depleted C to the sedimentary organic matter. The high aqueous  $\text{CO}_2$  concentration ( $[\text{CO}_2(\text{aq})]$ ) generally promotes the large C isotopic fractionation during photosynthetic C fixation ( $\epsilon_p$ ) in the surface oceans (e.g., Rau et al., 1992; Rau et al., 1997; Kump and Arthur, 1999). The  $\Delta^{13}\text{C}$  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  $\text{CO}_2$  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  $[\text{CO}_2(\text{aq})]$  may have promoted greater  $\epsilon_p$  (e.g., Kump and Arthur, 1999).

The previous estimates of the amount of emitted  $\text{CO}_2$  and of the elevated  $p\text{CO}_2$  during the Permian-Triassic transition are useful to constrain the influence of  $\epsilon_p$  changes on the  $\delta^{13}\text{C}$  records. Cui and Kump (2015) estimated that  $p\text{CO}_2$  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  $p\text{CO}_2$  and  $\epsilon_p$  from

isotopic data of modern marine algae, with some assumptions:  $\varepsilon_p \approx 25 - 2,301/p\text{CO}_2$ . According to this relationship,  $\varepsilon_p$  with  $p\text{CO}_2$  of 500, 4,000, and 8,000 ppm is calculated apparently to be  $\sim 20.4$ ,  $\sim 24.4$ , and  $\sim 24.7\%$ , respectively. Thus, the relatively large  $\delta^{13}\text{C}_{\text{org}}$  decline ( $\sim 7\%$ ) compared to the  $\delta^{13}\text{C}_{\text{carb}}$  decrease ( $\sim 3\%$ ) at Chaotian can be explained by the enlarged  $\varepsilon_p$  according to the elevated  $p\text{CO}_2$ . However, it is obviously difficult to extrapolate the relationship formula between  $p\text{CO}_2$  and  $\varepsilon_p$  in Kump and Arthur (1999) directly to the end-Permian system, due to several reasons. First, several assumptions with large uncertainties are included in this simplified formula, such as the dissolved phosphate concentration in the surface seawater. Moreover,  $\varepsilon_p$  is controlled, not only by  $p\text{CO}_2$ , but also by temperature and the growth rate of phytoplankton, in general (e.g., Rau et al., 1997; Kump and Arthur, 1999). Second, this relationship formula was obtained empirically on the basis of data of modern haptophyte algae and seawater (Bidigare et al., 1997). Different coefficients on the formula would be more appropriate for the end-Permian phytoplankton communities with unknown physiology. Third, the relationship was obtained on the basis of observations of modern environments with relatively low  $[\text{CO}_2(\text{aq})]$  (calculated  $p\text{CO}_2 < 850$  ppm, assuming equilibration according to Henry's Law at  $25^\circ\text{C}$ ). It is uncertain whether the formula can be extrapolated to environments with substantially high  $[\text{CO}_2(\text{aq})]$ , 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  $p\text{CO}_2$  under high- $p\text{CO}_2$  conditions is probably essential (Rau et al., 1997; Kump and Arthur, 1999). Because the reciprocal dependence of  $\varepsilon_p$  on  $p\text{CO}_2$  is attributed theoretically to isotopic discrimination by diffusion of  $\text{CO}_2$  from the ambient seawater to the phytoplankton cell (Laws et al., 1995). It is also suggested that the sensitivity of  $\varepsilon_p$  to  $p\text{CO}_2$  of land plants is lower than that of marine phytoplankton (e.g., Popp et al., 1989). The estimated high  $p\text{CO}_2$  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  $\delta^{13}\text{C}$  records was not significant.

Additional input of  $^{13}\text{C}$ -depleted C to the sedimentary organic C pool is the other possible mechanism for the Chaotian P-TB  $\Delta^{13}\text{C}$  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  $\Delta^{13}\text{C}$  increase. Terrestrial plants are another possible C source for sedimentary organic matter in the Chaotian carbonates. In general, the  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{13}\text{C}$  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; Cao et al., 2019). 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). The terrestrial flux may have increased (rather than decreased) in the aftermath of the extinction, and thus the observed  $\Delta^{13}\text{C}$  increase cannot be attributed to the decreased terrestrial C flux. Also, the putative vertical  $\delta^{13}\text{C}_{\text{org}}$  gradient (Luo et al., 2014) cannot explain the  $\Delta^{13}\text{C}$  increase because the water depth of depositional site did not change substantially across the P-TB at Chaotian.

In summary, the P-TB  $\Delta^{13}\text{C}$  increase at Chaotian was most likely due to the proliferation of methanogen in the sediments during the Siberian Traps volcanism (Figure 4), corresponding to the "methanogenic burst" event at a local scale (Rothman et al., 2014).

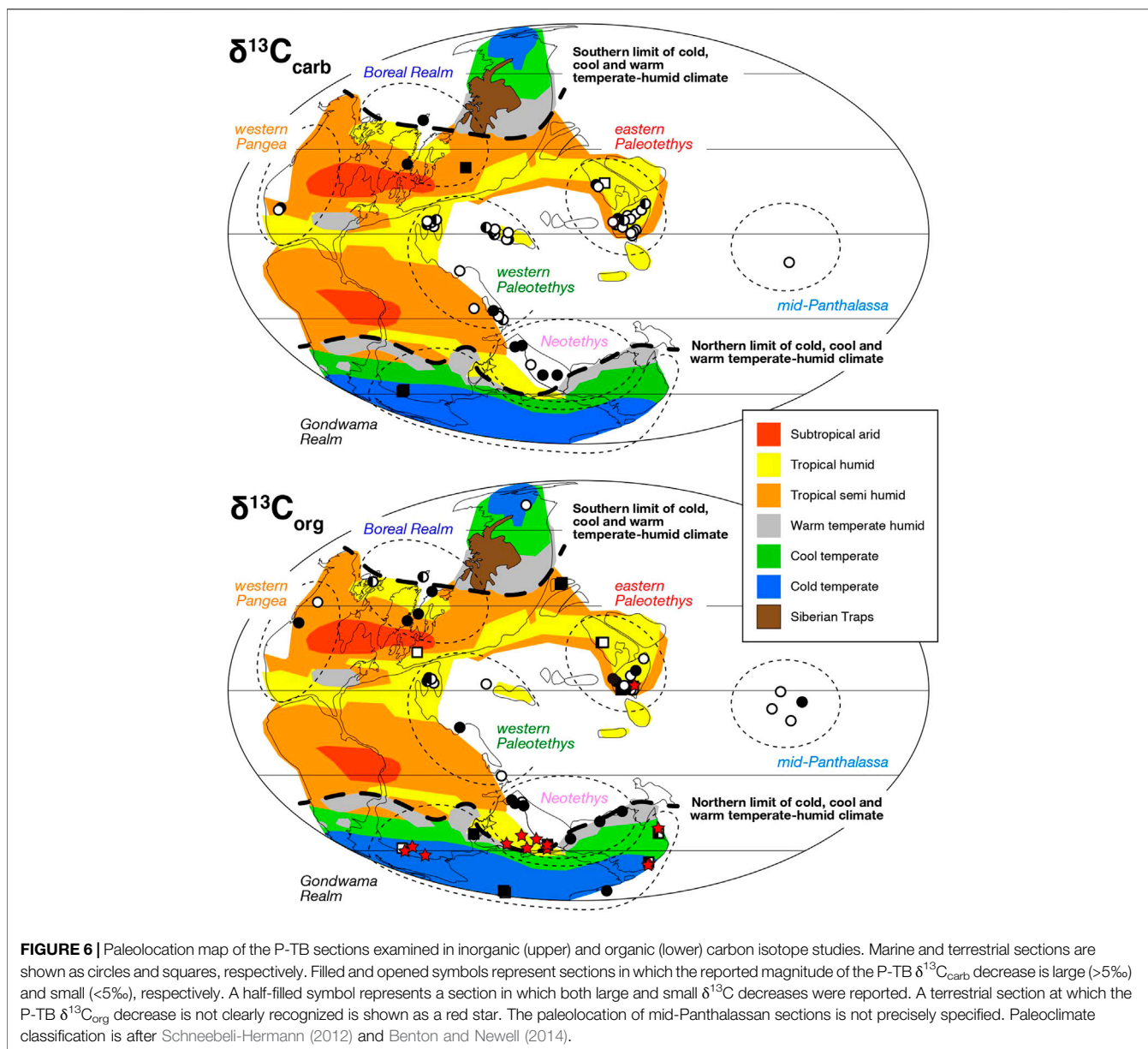
## Global $\delta^{13}\text{C}$ Correlations Around the P-TB Regional $\delta^{13}\text{C}$ Differences

The  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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 Paleotethys, western Pangea, mid-Panthalassa, Neotethys, and Gondwana (Figure 6).

### Marine Records

Previous  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease (Figure 7), suggesting a common  $\delta^{13}\text{C}_{\text{DIC}}$  decline throughout Paleotethys during the Permian-Triassic transition. The magnitude of the  $\delta^{13}\text{C}_{\text{carb}}$  decrease ranges mostly between 3 and 6‰ in those tropical regions. In the Boreal realm, the magnitude of the P-TB  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{org}}$  decrease varies substantially around the world (Figures 6, 7). In particular, a relatively large ( $\sim 7\%$ )  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  decrease in high latitudes was substantially larger than that of the  $\delta^{13}\text{C}_{\text{carb}}$  decrease in equatorial regions (e.g., Krull





et al., 2000; Krull et al., 2004; Korte and Kozur, 2010; Payne and Clapham, 2012; Saltzman and Sedlacek, 2013; Yuan et al., 2015).

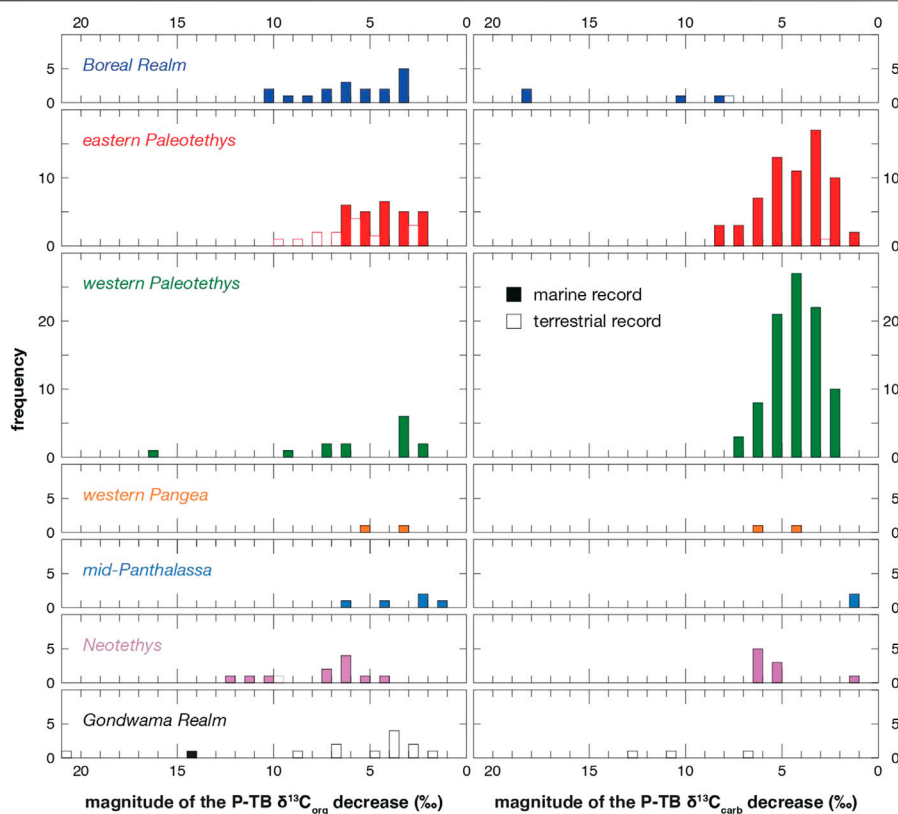
### Terrestrial Records

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

$\delta^{13}\text{C}_{\text{org}}$  decline is obscured frequently by sharp  $\delta^{13}\text{C}_{\text{org}}$  drops to  $-45\text{‰}$  (e.g., Krull and Retallack, 2000; Retallack et al., 2005).

### Variable $\Delta^{13}\text{C}$ Records

Magaritz et al. (1992) originally proposed a parallel  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  trends around the P-TB. For example, Riccardi et al. (2007) analyzed the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values of the P-TB carbonates at Meishan and Shangsi in South China, and compiled the  $\Delta^{13}\text{C}$  changes during the extinction in Iran, Slovenia, Japan, Austria,



**FIGURE 7** | Frequency histogram of the magnitude of the P-TB  $\delta^{13}\text{C}$  decrease in various regions.

and South China. They found a  $\Delta^{13}\text{C}$  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  $\Delta^{13}\text{C}$  decrease at Meishan. In contrast, the apparent  $\Delta^{13}\text{C}$  increase was reported at several sections in Italy (Siegert et al., 2011), South China (Shen et al., 2012; this study), and Pakistan (Schneebeil-Hermann et al., 2013). It is difficult to reconstruct the  $\Delta^{13}\text{C}$  changes in high latitudes as carbonates are generally scarce in those regions. Nonetheless, the present compilation illustrates that the  $\delta^{13}\text{C}_{\text{org}}$  records are substantially variable on a global scale particularly in high latitudes, in marked contrast to the rather consistent  $\delta^{13}\text{C}_{\text{carb}}$  records in equatorial Paleotethys (Figures 6, 7).

### Potential Causes of the Marine $\delta^{13}\text{C}_{\text{org}}$ Variability

Several possible mechanisms may explain the observed  $\delta^{13}\text{C}_{\text{org}}$  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  $p\text{CO}_2$ , and 5) “methanogenic burst”.

#### Eustatic Sea-Level Changes

The  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  variability of shallow-marine records, controlling the mixing ratio of  $^{13}\text{C}$ -enriched terrestrial and  $^{13}\text{C}$ -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  $\delta^{13}\text{C}_{\text{org}}$  decrease in the bulk sediments. Although the eustatic sea-level changes could have exerted a first-order control on the global  $\delta^{13}\text{C}_{\text{org}}$  variability of shallow-marine records, they do not fully explain the regionally variable  $\delta^{13}\text{C}_{\text{org}}$  records. For example, the  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  drop and  $\Delta^{13}\text{C}$  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;

Sephton et al., 2005), and intense continental weathering and increased continental flux to the oceans on a global scale (e.g., Algeo and Twitchett, 2010; Algeo et al., 2011; Cao et al., 2019). An increased flux of terrestrial plant C (with relatively high  $\delta^{13}\text{C}_{\text{org}}$  value) to the shelf sediments via the vegetation collapse and intense weathering may have increased the bulk  $\delta^{13}\text{C}_{\text{org}}$  values of sediments. However, this process generally decreases the bulk  $\Delta^{13}\text{C}$  value of shelf carbonates and cannot explain the P-TB  $\Delta^{13}\text{C}$  increase observed in several sections, including Chaotian, as discussed in the former section (Figure 4). Aged refractory organic matters may also have been derived into the sediments via the enhanced continental weathering and/or soil erosion (Hayes et al., 1989), though it is difficult to constrain their  $\delta^{13}\text{C}_{\text{org}}$  values. On the other hand, it is most likely that a terrestrial nutrient flux to the oceans also increased simultaneously via the intense continental weathering, which stimulated eutrophication and algal blooms in the coastal oceans (e.g., Xie et al., 2007; Algeo et al., 2011; Kaiho et al., 2016). The algal blooms may have resulted in an increased flux of marine C (with relatively low  $\delta^{13}\text{C}_{\text{org}}$  value) to the shelf sediments, offsetting the influence of increased terrestrial C flux on the bulk  $\delta^{13}\text{C}_{\text{org}}$  value of the sediments. Because of this offset effect, the net influence of the intense continental weathering on the marine  $\delta^{13}\text{C}_{\text{org}}$  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 Permian-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 ( $\sim 12.5\%$ ; 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  $\Delta^{13}\text{C}$  value of the sediments. Riccardi et al. (2007) reported the P-TB  $\Delta^{13}\text{C}$  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  $\Delta^{13}\text{C}$  increase observed in several sections, including Chaotian (Figure 4).

#### ***Enlarged C Isotopic Fractionation During Photosynthesis Under the Elevated $p\text{CO}_2$***

The increased  $[\text{CO}_2(\text{aq})]$  and  $\epsilon_p$  in the surface oceans is another potential mechanism for the observed  $\delta^{13}\text{C}_{\text{carb}}-\delta^{13}\text{C}_{\text{org}}$  decoupling (e.g., Rau et al., 1992; Rau et al., 1997). However, as discussed above for the Chaotian record, the influence of  $\epsilon_p$  change on the P-TB  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}_{\text{org}}$  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., Basiliko and Yavitt, 2001) and presumably enhanced microbial methanogenesis (“methanogenic burst”) on a global scale (Rothman et al., 2014).

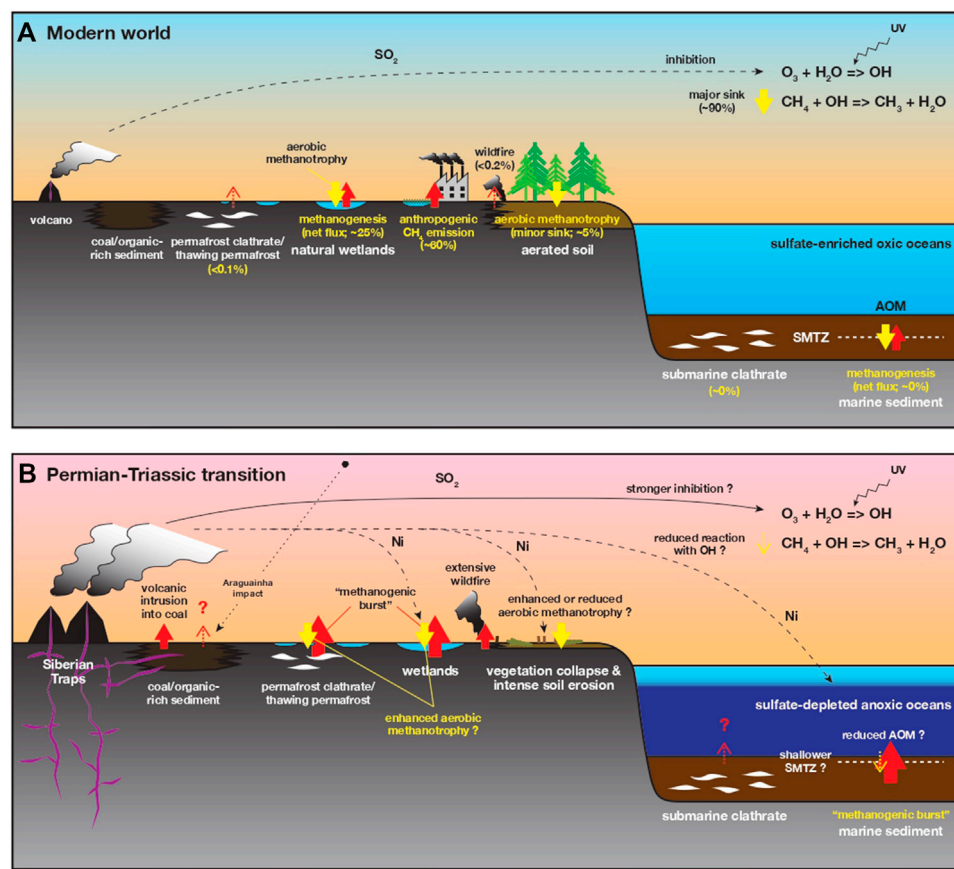
Methanogen generally fixes C via the reductive acetyl-CoA pathway, which can produce larger C isotopic fractionation up to 40‰ (e.g., Preuss et al., 1989), compared to the Calvin cycle (e.g., Schidlowski et al., 1983). Thus, according to the “methanogenic burst”, the increased organic-C flux from expanded methanogen biomass to the bulk organic-C pool in the local sediments may have caused the large  $\delta^{13}\text{C}_{\text{org}}$  decrease (Figures 6, 7). However, the activity of methanogen is generally regulated, not only by the Ni availability, but also by a number of environmental factors, such as temperature,  $\text{CO}_2$  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  $\delta^{13}\text{C}_{\text{org}}$  variability on a global scale. The elevated temperature and  $p\text{CO}_2$  may also have stimulated the “methanogenic burst”, because these factors generally increase the biogenic  $\text{CH}_4$  emissions in various environments (Supplementary Information; e.g., van Groenigen 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  $\delta^{13}\text{C}_{\text{org}}$  records quantitatively.

In summary, the P-TB  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  decrease in several sections, including the present Chaotian (Figure 4).

## **Implications for the Global $\text{CH}_4$ Cycle in the Aftermath of the Extinction**

A substantial amount of  $\text{CH}_4$  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  $\text{CH}_4$  was also produced by the incomplete combustion of organic carbon (e.g., Kirschke 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; Hudspeth et al., 2014; Vajda et al., 2020). The “methanogenic burst” likely contributed to the elevated  $p\text{CH}_4$  (Rothman et al., 2014). The claimed Araguainha impact event in Brazil (Tohver et al., 2013)





**FIGURE 8 |** Schematic diagram of the global CH<sub>4</sub> cycle in the modern world (A) and during the Permian-Triassic transition (B). CH<sub>4</sub> influx to and efflux from the atmosphere are shown as red and yellow arrows, respectively. In the modern system, the global atmospheric CH<sub>4</sub> budget is 0.4–0.5 Gt C/year (Supplementary Information; e.g., Conrad, 2009; Nazaries et al., 2013). During the Permian-Triassic transition, several processes may have contributed to the elevated pCH<sub>4</sub> and climate warming, although terrestrial responses to the elevated pCH<sub>4</sub> were probably complex. The elevated pCH<sub>4</sub> enhanced aerobic methanotrophy in local soils whereas the intense soil erosion decreased a net CH<sub>4</sub> efflux in the global budget. AOM: anaerobic oxidation of methane; SMTZ: sulfate-methane transition zone. See **Supplementary Information** for details.

may also have contributed to the CH<sub>4</sub> accumulation in the atmosphere, though its timing, magnitude, and effective time span for the global CH<sub>4</sub> cycle are not well-constrained. Together with other greenhouse gases like CO<sub>2</sub>, the elevated pCH<sub>4</sub> 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 SO<sub>2</sub>-induced cooling (Black et al., 2018).

Although there still remains large uncertainty, we infer fluctuations in the global CH<sub>4</sub> 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 δ<sup>13</sup>C<sub>org</sub> 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 δ<sup>13</sup>C<sub>org</sub> 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 δ<sup>13</sup>C<sub>org</sub> 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 CH<sub>4</sub> at that time. In the modern oceans enriched in sulfate (the SO<sub>4</sub><sup>2-</sup> concentration = 28 mM), almost all CH<sub>4</sub>, 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  $\text{SO}_4^{2-}$  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  $\text{CH}_4$  source compared to in the modern oceans, further contributing to the elevated  $p\text{CH}_4$ . The impact of “methanogenic burst” on the enhanced  $\text{CH}_4$  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  $\text{CH}_4$  to escape from the oceans to the atmosphere (e.g., Ryskin, 2003).

Finally, the global  $\text{CH}_4$  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  $\text{CH}_4$  emissions in high latitudes according to the warming (Nauta et al., 2015), whereas the massive soil erosion might also have contributed to the atmospheric  $\text{CH}_4$  accumulation as aerated terrestrial soils are a  $\text{CH}_4$  sink (Supplementary Information; Figure 8B).

## CONCLUSIONS

The carbon isotopic composition of carbonate ( $\delta^{13}\text{C}_{\text{carb}}$ ) 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 ( $\delta^{13}\text{C}_{\text{org}}$ ) of the same interval. The  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  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 ( $\text{CH}_4$ ) cycle during the Permian-Triassic transition. The following results were obtained:

- (1) The  $\delta^{13}\text{C}_{\text{carb}}$  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  $\delta^{13}\text{C}_{\text{carb}}$  decrease.

- (2) The magnitude of the  $\delta^{13}\text{C}_{\text{carb}}$  decline ( $\sim 3\%$ ) is substantially smaller than the magnitude of the  $\delta^{13}\text{C}_{\text{org}}$  decrease ( $\sim 7\%$ ) across the P-TB. This  $\delta^{13}\text{C}_{\text{carb}}-\delta^{13}\text{C}_{\text{org}}$  decoupling could be explained by an elevated  $\text{CO}_2$  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  $\delta^{13}\text{C}$  compilation shows a large variation in marine  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{13}\text{C}_{\text{org}}$  variability. The global  $\text{CH}_4$  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>.

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**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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