



# Middle–Upper Permian carbon isotope stratigraphy at Chaotian, South China: Pre-extinction multiple upwelling of oxygen-depleted water onto continental shelf

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## ABSTRACT

In order to examine the causal relationships between the carbon cycle in a shallow euphotic zone and the environmental changes in a relatively deep disphotic zone at the end-Guadalupian (Middle Permian), isotopic compositions of carbonate carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ) of the Guadalupian–Lopingian (Upper Permian) rocks were analyzed in the Chaotian section in northern Sichuan, South China. By analyzing exceptionally fresh drill core samples, a continuous chemostratigraphic record was newly obtained. The ca. 65 m-thick analyzed carbonate rocks at Chaotian comprise three stratigraphic units, i.e., the Limestone Unit of the Guadalupian Maokou Formation, the Mudstone Unit of the Maokou Formation, and the lower part of the Wuchiapingian (Lower Lopingian) Wujiaping Formation, in ascending order. The Limestone Unit of the Maokou Formation is characterized by almost constant  $\delta^{13}\text{C}_{\text{carb}}$  values of ca. +4‰ followed by an abrupt drop for 7‰ to −3‰ in the topmost part of the unit. In the Mudstone Unit of the Maokou Formation, the  $\delta^{13}\text{C}_{\text{carb}}$  values are rather constant around +2‰, although distinct three isotopic negative excursions for 3‰ from ca. +2 to −1‰ occurred in the upper part of the unit. In the lower part of the Wujiaping Formation, the  $\delta^{13}\text{C}_{\text{carb}}$  values monotonously increase for 5‰ from ca. 0 to +5‰. The present data newly demonstrated four isotopic negative excursions in the topmost part of the Maokou Formation in the Capitanian (Late Guadalupian) at Chaotian. It is noteworthy that these negative excursions are in accordance with the emergence of an oxygen-depleted condition on the relatively deep disphotic slope/basin on the basis of litho- and bio-facies characteristics. They suggest multiple upwelling of oxygen-depleted waters with dissolved inorganic carbon of relatively low carbon isotope values along the continental margin, from the deeper disphotic slope/basin to the shallower euphotic shelf, slightly before the end-Guadalupian extinction. Although the negative excursions at Chaotian are apparently correlated with the previously proposed large negative excursion in the middle Capitanian in South China, the age difference according to the biostratigraphic constraints clearly exclude this interpretation. The isotopic negative excursions at Chaotian are unique and no similar isotopic signal in the same period has been reported elsewhere. The multiple upwelling of oxygen-depleted waters onto the euphotic shelf may have represented local phenomena that occurred solely around northwestern South China.

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## 1. Introduction

The Permian mass extinction was the largest biodiversity crisis in the Phanerozoic (e.g., Erwin, 2006; Alroy, 2010). Although the catastrophe has been traditionally regarded as a single event, it comprises two distinct extinctions; i.e., the first occurred at the

end-Guadalupian (Middle Permian), ca. 260 million years ago (Ma), and the second at the end-Changhsingian (Late Permian), ca. 252 Ma. The end-Changhsingian extinction has been traditionally well known; however, the older end-Guadalupian extinction has been later focused since Jin et al. (1994) and Stanley and Yang (1994) first emphasized its great magnitude. During the last decade, various unique geologic phenomena, in addition to the extinction, around the Guadalupian–Lopingian (Late Permian) boundary (G-LB) have been emphasized; i.e., the lowest sea-level in the entire Phanerozoic (Jin et al., 1994; Haq and Schutter, 2008), the eruption of the Emeishan flood basalt in South China

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(Chung and Jahn, 1995; Zhou et al., 2002), the onset of prolonged deep-sea oxygen-depletion (superanoxia; Isozaki, 1997), one of the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the Phanerozoic (Veizer et al., 1999), and the onset of frequent geomagnetic polarity changes (Illawarra Reversal; Irving and Parry, 1963). See Isozaki (2009) for more details of the uniqueness of the end-Guadalupian geologic phenomena. Nonetheless, the ultimate cause of the end-Guadalupian extinction is still in discussion (e.g., Isozaki, 2007, 2009; Bottjer et al., 2008; Clapham et al., 2009; Bond et al., 2010a,b).

Previous stratigraphic researches on the environmental changes around the G-LB mainly analyzed fossiliferous shallow-marine shelf carbonates in South China (e.g., Jin et al., 1998) and paleo-atoll limestones on ancient seamounts (e.g., Isozaki and Ota, 2001; Ota and Isozaki, 2006; Kasuya et al., 2012) and pelagic deep-sea cherts (e.g., Isozaki, 1997; Nishikane et al., 2011) in accretionary complex in Southwest Japan. The Middle–Upper Permian strata deposited in South China have exceptionally continuous stratigraphic records with diverse shallow-marine fossils (e.g., Zhao et al., 1981; Yang et al., 1987; Jin et al., 1998). For example, the best continuous Penglitan section in Guangxi is officially designated as the Global Stratotype Section and Point (GSSP) for the G-LB (e.g., Jin et al., 1998, 2006; Shen et al., 2007).

Nonetheless, more information from a relatively deep disphotic zone (usually deeper than 150 m), below a euphotic zone, is needed in order to identify the entire environmental changes in the oceans relevant to the end-Guadalupian extinction, particularly to understand the relationships between the shallow-sea extinction and the deep-sea oxygen-anomaly. Few previous studies, however, have focused on the disphotic zone in the Permian oceans. In fact, the late Guadalupian to early Lopingian carbonates of deep-water facies on the northwest margin of South China (e.g., Li et al., 1989; Zhu et al., 1999; Wang and Jin, 2000) recorded that an oxygen-depleted condition has emerged on the disphotic slope/basin in the Capitanian (Late Guadalupian) during a rapid sea-level rise slightly before the end-Guadalupian extinction (Isozaki et al., 2008; Saitoh et al., 2013; Fig. 1). The causal relationships between the oxygen-depletion in a deeper disphotic zone and the extinction in a shallower euphotic zone are, however, still unknown.

For analyzing the end-Guadalupian environmental changes, several chemostratigraphic studies of carbon isotope values of carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ) have been conducted. Wang et al. (2004) first analyzed C-isotope stratigraphy of the G-LB interval of the GSSP at Penglitan in Guangxi, and reported a negative  $\delta^{13}\text{C}_{\text{carb}}$  shift across the boundary. Isozaki et al. (2007a) confirmed the identical G-LB negative shift in paleo-atoll limestone deposited on an ancient seamount in mid-Panthalassa at Kamura in Southwest Japan. On the other hand, on the basis of the analyses of several sections in western South China, Bond et al. (2010a) pointed out that a large (over 5‰) negative excursion occurred not at the G-LB but in the earlier middle Capitanian. They also postulated the “end-Guadalupian extinction” was associated with their middle Capitanian large  $\delta^{13}\text{C}_{\text{carb}}$  excursion. Their propositions were later criticized by Chen et al. (2011) and by Saitoh et al. (2013), independently.

Under the circumstances, causal relationships between fluctuation of global carbon cycle and environmental changes relevant to the end-Guadalupian extinction are still controversial. We investigated the  $\delta^{13}\text{C}_{\text{carb}}$  values of the Guadalupian–Lopingian marine carbonates (ca. 65 m thick) at Chaotian in northern Sichuan, in order to examine the processes how the oxygen-depleted waters in a deeper disphotic zone previously recognized at Chaotian did affect the carbon cycle in a shallower euphotic zone around the G-LB. We analyzed exceptionally fresh and continuous drill core samples at Chaotian and clarified the unique and large carbon isotopic fluctuations across the G-LB in accordance with the emergence of disphotic oxygen-depletion. This article reports the new C-isotope chemostratigraphy across the G-LB at Chaotian. On the basis of

the new isotopic results, we discuss its geological significance with respect to the environmental changes around the G-LB in north-western South China.

## 2. Geologic setting and stratigraphy

During the Permian, the South China craton was located on the east of the Pangea around the equator (e.g., Scotese and Langford, 1995). Thick shallow-marine carbonates with diverse shallow-marine fossils were extensively deposited on continental shelves of South China (e.g., Zhao et al., 1981; Jin et al., 1998). In northern Sichuan, along the northwestern edge of South China, carbonates of relatively deep-water facies accumulated (Wang and Jin, 2000). We have analyzed one of such carbonates of deep-water facies at Chaotian ( $32^{\circ}37'\text{N}$ ,  $105^{\circ}51'\text{E}$ ), located 20 km to the north of Guangyuan (Isozaki et al., 2004; Fig. 1). The Chaotian section displays extensive exposures of continuous Middle Permian to Lower Triassic rocks along a gorge called Mingyuexia of the Jialingjiang River. Zhao et al. (1978) and Yang et al. (1987) originally described the overall biostratigraphy at Chaotian on the basis of fusulines, conodonts, and ammonoids. Several studies on litho- (Isozaki et al., 2004, 2007c, 2008; Lai et al., 2008; Saitoh et al., 2013), bio- (Xu, 2006; Ji et al., 2007; Kuwahara et al., 2007, 2008; Isozaki et al., 2008; Lai et al., 2008), chemo- (Lai et al., 2008), and chrono-stratigraphy (He et al., 2007) were subsequently performed at Chaotian.

The Permo-Triassic rocks at Chaotian consist of the Guadalupian Maokou Formation, the Lopingian Wujiaping and Dalong formations, and the lowermost Triassic Feixianguan Formation, in ascending order (Yang et al., 1987; Isozaki et al., 2004, 2007c, 2008; Ji et al., 2007; Saitoh et al., 2013; Fig. 1). This study analyzed in detail the upper Maokou and lower Wujiaping formations (ca. 65 m thick) for chemostratigraphic study. The analyzed carbonate rocks comprise three distinct stratigraphic units (Fig. 1); i.e., the Limestone Unit of the Maokou Formation, the Mudstone Unit of the Maokou Formation, and the lower part of the Wujiaping Formation, in ascending order. The Limestone Unit of the Maokou Formation, ca. 35 m thick, is mainly composed of dark gray massive bioclastic limestone and contains shallow-marine fossils such as algae and fusulines. This Unit was probably deposited on a euphotic shelf. This part largely corresponds to ‘the L3 subunit of the Limestone Unit’ of the Maokou Formation in Saitoh et al. (2013). The Mudstone Unit of the Maokou Formation, ca. 11 m thick, is mainly composed of thinly bedded black calcareous mudstone, black chert, and black siliceous mudstone and yields abundant radiolarians, conodonts, and ammonoids. This Mudstone Unit was deposited on a relatively deep disphotic slope/basin under oxygen-depleted condition, on the basis of litho- and bio-facies characteristics (Saitoh et al., 2013). This Unit comprises the lower M1 subunit (ca. 8 m thick) and the upper M2 subunit (ca. 3 m thick). The lower M1 subunit yields abundant brachiopods and conodonts, whereas the upper M2 subunit contains abundant radiolarians and ammonoids (Saitoh et al., 2013). The lower part of the Wujiaping Formation, ca. 20 m thick, is mainly composed of dark gray bioclastic limestone and contains calcareous algae and small fusulines. At the base of the Wujiaping Formation, a unique ca. 2 m thick volcanoclastic ‘Wangpo bed’ occurs. The lower Wujiaping Formation was deposited on a euphotic shelf.

Previously reported index fossils such as fusulines, conodonts, and ammonoids constrained the ages of these three stratigraphic units (Isozaki et al., 2008; Lai et al., 2008): The Limestone Unit of the Maokou Formation entirely belongs to the *Jinogondolella post-serrata* Zone of the early Capitanian (Upper Guadalupian). The M1 subunit of the Mudstone Unit of the Maokou Formation belongs to the *Jinogondolella shannoni* Zone of the early-middle

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