RESEARCH ARTICLE

Glacio-eustasy and $\delta^{13}C$ across the Mississippian–Pennsylvanian boundary in the eastern Paleo-Tethys Ocean (South China): Implications for mid-Carboniferous major glaciation

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A positive carbonate $\delta^{13}C$ excursion (by $\sim$1.5–3.0‰) has been reported across the Mississippian–Pennsylvanian boundary (MPB) from Euramerican epicontinental seas, implying a coeval atmospheric $pCO_2$ decrease and Gondwanan glaciation at that time. This excursion was mainly observed in carbonate platforms which experienced repeated subaerial exposure. The South China Block was located in the middle of the Paleo-Tethys Ocean and the Panthalassic Ocean during the Carboniferous and contains well-preserved carbonate slope strata across the MPB. Four lithofacies were defined in the studied Naqing, Narao, and Dianzishang sections, including thin-bedded lime mudstones, laminated wackestones to packstones, normally-graded packstones, and slumped limestones. Immediately above the MPB, a bed of normally-graded packstones or slump masses occurs in the studied sections, which together with coeval subaerial-exposure features in shallow-water carbonate platform of South China, suggests a significant sea-level fall across the MPB. Carbonate $\delta^{13}C$ records show a consistent value of $\sim$3.0‰ below the MPB in the Naqing and Narao sections, and both sections show an obvious rise in $\delta^{13}C$ across the MPB (by $\sim$0.5–1.0‰). The relatively small-magnitude rise in $\delta^{13}C$ would have resulted from well-mixed seawater induced by intensified upwelling in the eastern Paleo-Tethys Ocean during the glacial peak. Hence, the carbonate $\delta^{13}C$ values recorded in the South China Block may represent a mean $\delta^{13}C$ of the dissolved inorganic carbon in global ocean water at that time. Correlation between carbonate $\delta^{13}C$ and previously published conodont $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ records suggests that the MPB glaciation was mainly driven by enhanced continental weathering, rather than increased organic carbon burial, although further quantitative simulation is required to better understand the interlinked processes during the Earth's penultimate icehouse.

KEYWORDS
carbon cycle, carbonate slope, Gondwana glaciation, late Palaeozoic ice age, mid-Carboniferous boundary, Paleo-Tethys Ocean

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1 | INTRODUCTION

The late Palaeozoic ice age (LPIA) started in the latest Devonian and ended in the middle Permian, when global palaeogeography (closure of Rheic Ocean and formation of supercontinent Pangaea) and land ecosystems (radiation and evolution of the oldest rainforests) experienced major changes (Chen, Montañez, Qi, Shen, & Wang, 2018; DiMichele, Cecil, & Montañez, 2014; Isbell et al., 2012; Montañez, 2016; Montañez & Poulsen, 2013; Veevers, 2013). Sedimentological and geochemical studies suggest that major continental glaciation on Gondwana was most likely initiated in the late Visean (e.g., Barham, Murray, Joachimski, & Williams, 2012; Fielding & Frank, 2015; Chen, Sheng, et al., 2018; Smith & Read, 2000; Wright & Vanstone, 2001) and reached the first peak in the Mississippian–Pennsylvanian boundary (MPB) interval (B. Chen et al., 2016; Montañez & Poulsen, 2013). The MPB glaciation was recorded both in high-latitude Gondwana as glacial deposits (Fielding et al., 2008; Henry, Isbell, & Limarino, 2008; Henry, Isbell, Limarino, McHenry, & Fraiser, 2010; Isbell, Cole, & Catuneanu, 2008; Krainer & Vachard, 2003; Mory, Redfern, & Martin, 2008) and in low-latitude successions as a depositional hiatus (Bishop, Montañez, Gulbranson, & Brenchle, 2009; Blake & Beuthin, 2008; Pareyn, Conrad, Conrad, & Lemosquet, 1971; Remack-Petitot, 1960; Rygel, Fielding, Frank, & Birgenheier, 2008; Saunders & Ramsbottom, 1986). Coeval with the MPB glaciation, a severe biodiversity crisis event occurred in global marine ecosystems (McGhee, Sheehan, Bottjer, & Droser, 2012; Stanley & Powell, 2003; Wang et al., 2013), which may be attributed to global cooling and loss of habitat diversity related to Gondwanan glaciation.

Global carbon perturbation and atmospheric pCO2 decrease have been hypothesized as the driver of the LPIA (e.g., Algeo, Berner, Maynard, & Scheckler, 1995; Chen, Montañez, et al., 2018; Goddéris et al., 2011; Montañez, 2016). The δ13C values of global ocean dissolved inorganic carbon (DIC) recorded in marine carbonates can be used as a proxy for organic carbon burial and global carbon perturbations (e.g., Kump & Arthur, 1999; Saltzman, 2003). A positive carbonate δ13C excursion across the MPB has long been reported from Euramerican (Laurussian) epicontinental seas (Brand, 1989; Bruckschen, Oesmann, & Veizer, 1999; Dyer, Maloof, & Higgins, 2015; Grossman et al., 2008; Grossman, Mii, & Yancey, 1993; Mii, Grossman, & Yancey, 1999; Mii, Grossman, Yancey, Chuwashov, & Egorov, 2001; Popp, Anderson, & Sandberg, 1986; Saltzman, 2003; Veizer et al., 1999), although there is an obvious difference in magnitude between North America (~1.5‰) and Russia (~3.0‰). The positive shift in δ13C (by ~3.0‰) was interpreted as a result of increased organic carbon burial which drew down pCO2 and caused the MPB glaciation (e.g., Mii et al., 2001). The regional variations (western Paleo-Tethys Ocean vs. eastern Panthalassic Ocean) in magnitude of the δ13C shift were hypothesized to have resulted from ocean circulation and enhanced upwelling on the epicontinental seas of North America, associated with the closure of the palaeo-equatorial seaway (the Rheic Ocean) between the Laurussia and Gondwana continents (Grossman et al., 1993; Mii et al., 2001).

Investigations on glacio-eustasy and carbonate δ13C across the MPB came mostly from Euramerica, and the studied MPB successions were all deposited in epeiric carbonate platforms that were punctuated by either development of palaeokarsts, palaeosols, and incised valleys, or input of siliclastics (Barnett & Wright, 2008; Bishop et al., 2009; Blake & Beuthin, 2008; Brand & Bruckschen, 2002; Cecil & Englund, 1989; Davydov & Puchkov, 2009; Dvorjanin et al., 1996; Kabanov, Alekseev, Gibshman, Gabdullin, & Bershov, 2016). Furthermore, the carbonate δ13C recorded in shallow epeiric carbonate platforms was either readily altered by meteoric diagrasis given the repeated subaerial exposures (e.g., Algeo, Wilkinson, & Lohmann, 1992; Bruckschen et al., 1999; Saltzman, 2003) or decoupled from the ocean water values due to local processes on platforms (e.g., Brand, Tazawa, Sano, Azmy, & Lee, 2009; Immenhauser, Dela, Porta, Kenter, & Bahamonde, 2003; Panchuk, Holmden, & Kump, 2005; Patterson & Walter, 1994). Thus, the δ13C profiles reported from these MPB successions are most likely incomplete and not representing the δ13C of global ocean DIC.

The South China Block was located in the eastern Paleo-Tethys Ocean near the palaeo-equator during the late Palaeozoic, containing well-preserved, near-continuously deposited, carbonate slope successions across the MPB, which provides an opportunity to explore the continuous and pristine MPB δ13C records. The bulk carbonate δ13C values were previously reported from one of the South China slope successions (Buggisch, Wang, Alekseev, & Joachimski, 2011), showing nearly consistent values of ~3.0‰ across the MPB, in sharp contrast with the positive excursion recorded in Euramerica. In order to test the δ13C values from South China carbonate slope successions as a reliable record for the global ocean water δ13C values, here we present detailed sedimentary facies analysis and high-resolution, microdrilled δ13C time series of carbonate samples from three carbonate slope sections (Naqing, Narao, and Dianzishang).

2 | GENERAL GEOLOGY

2.1 | Geological settings

The South China Block was located in an equatorial or subequatorial position during the Carboniferous (Figure 1) and formed as a result of collision between the Yangtze Block and the Cathaysia Block during the Neoproterozoic. Many intraplatform sedimentary basins formed by extension of continental crust during the early Devonian, developing a “platform–basin–platform” palaeogeographic framework (Mei & Li, 2004; Wang et al., 2013). The South China Block consists of several subunits, including the Upper Yangtze Landmass, Cathaysia Landmass, Dian-Qian-Gui-Xiang Platform, Jiangnan Basin, and Qian-Gui Basin during the Carboniferous. The Qian-Gui Basin was an open marginal sea basin between the Jinshajiang-Honghe-Majang suture zone and the Yangtze Block (Huang et al., 2013; Liu, Jarochowska, Du, Vachard, & Munnecke, 2015; Qie & Wang, 2012). Near-continuous slope carbonate deposits accumulated in the Qian-Gui Basin that belongs to
2.2 | Conodont biostratigraphy

Three conodont zones, the latest Mississippian *Gnathodus postbilineatus* Zone and the Pennsylvanian *Declinognathodus noduliferus* s. l. and *Idiognathoides sinuatus* zones, can be recognized in the MPB interval of the Naqing section (Figure 2; Hu, Qi, & Nemyrovska, 2019; Wang & Qi, 2003; Wang et al., 2019). The *G. postbilineatus* Zone represents the uppermost part of the Mississippian. The *D. noduliferus* s. l. Zone is marked by the entry of *D. noduliferus* s. l. but is dominated by elements characterizing the preceding *Gnathodus postbilineatus* Zone. The *I. sinuatus* Zone, marked by the appearance of *I. sinuatus*, is typified by the diversity of *Declinognathodus* and *Idiognathoides* and the disappearance of *Gnathodus* and *Lochriea*. Three conodont zones, the Mississippian *Lochriae ziegleri* Zone and the Pennsylvanian *Declinognathodus noduliferus* s. l. and *Neognathodus symmetricus* zones, can be recognized in the MPB interval of the Dianzishang section (Qi, Hu, Wang, & Lin, 2014). In the Narao section, only the earliest Bashkirian *D. noduliferus* s. l. Zone was defined; the Serpukhovian conodont zones have been identified but not published yet (Y. Qi, pers. communication). The MPB boundary of the studied sections coincides with the base of the *D. noduliferus* s. l. Zone (Hu et al., 2019; Qi et al., 2014; Figure 2).

3 | METHODS

We carried out bed-by-bed sedimentologic logging and description for the MPB successions in the three sections (Naqing, Narao, and Dianzishang; Figure 3). In total, 391 hand specimens were collected, slabbed, and thin-sectioned to observe detailed sedimentary and diagenetic features using microscopes. Fine-grained, micritic sediment (50–150 μg) without obvious calcite veins and recrystallization was drilled from the freshly cut surfaces of samples using a dental drill with stainless-steel bits for bulk carbonate analysis. Eighty-six bulk carbonate samples from the Narao and Dianzishang sections were analysed on a MAT 253 mass spectrometer coupled with a Kiel IV carbonate device in the State Key Laboratory of Palaeobiology and Stratigraphy at Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences. The carbon isotope values are reported relative to the standard PDB.
GBW-04405 laboratory standard (δ^{13}C_{carb}: 0.57‰, δ^{18}O_{carb}: -8.49‰); analytical precision for δ^{13}C_{carb} and δ^{18}O_{carb} is better than 0.04‰ and 0.08‰, respectively.

In order to evaluate the reliability of δ^{13}C values from bulk carbonates, 50 thin sections (70–100 μm thick) from the Naqing section were stained with Alizarin Red-S and Potassium Ferricyanide (Dickson, 1965). Target areas for microsampling and analysis (i.e., well-preserved micrite) were identified using transmitted and cathodoluminescent microscopy. Pink-staining (i.e., low [Fe^{2+}]), non/dully luminescent micrite was microdrilled from thick sections using a fully automated Merchantek microdrilling system with ~20μm spatial resolution at the University of California, Davis. Powders (50–100 μg) were collected and roasted for 30 min at 375°C in vacuo in order to remove organic volatiles and analysed using a Fisons Optima isotope ratio mass spectrometer with a 90°C Isocarb common acid bath autobody system in the Stan Margolis Stable Isotope Laboratory,

FIGURE 3 Sedimentary facies and δ^{13}C time series of the Mississippian–Pennsylvanian boundary interval in studied sections. Blue circles indicate data from this study; other data are from Buggisch et al. (2011; blue squares) and J. Chen et al. (2016; blue triangles). Trend lines in δ^{13}C profiles are locally weighted scatterplot smoothing (LOESS, 0.2 smoothing) regressions with 2.5% and 97.5% bootstrapped errors, and arrows indicate distinct inflections (for discussion, see text). For facies code, see Table 1 [Colour figure can be viewed at wileyonlinelibrary.com]
University of California, Davis. All isotope values are reported relative to Pee Dee Belemnite (PDB) using standard delta notation; analytical precision for both δ^{13}C and δ^{18}O is better than ±0.1‰.

4 | SEDIMENTARY FACIES AND SEA-LEVEL CHANGE ACROSS THE MPB

4.1 | Facies description

Four lithofacies were defined in the MPB successions from the studied sections based mainly on lithology, grain size, and sedimentary structures (Table 1 and Figure 3), including thin-bedded lime mudstones (LMtb), laminated wackestones to packstones (W-Pi), normally-graded packstones (Png), and slumped limestones (Ls). Thin-bedded lime mudstones (Figure 4a,d) are the dominant lithofacies of studied successions, which are often intercalated with laminated wackestones to packstones (Figure 4b,e) and normally-graded packstones (Figure 4c,f).

The lime mudstones are generally homogeneous and lack of current- or wave-induced sedimentary structures (i.e., ripples, dunes, or and cross-laminations) and trace fossils. Laminated wackestones to packstones consist of weak laminated characterized by alternation of darker micrite and lighter bioclastic calcisilts. Normally-graded, bioclastic packstone beds consist of coarse-grained packstones with intraclasts in the lower part gradually changing upward into fine-grained, weakly laminated wackestones to packstones. Slumped limestone beds comprise of folded limestone beds and poorly sorted carbonate breccias of lime mudstone to packstone, with sharp, irregular lower or upper boundaries. Chert nodules with round, irregular, or elongate shapes occur in all the facies, roughly parallel to bedding planes, throughout the entire studied interval in all the sections.

| TABLE 1 | Description and interpretation of lithofacies in the carbonate slope MPB successions in South China |
|---|---|---|
| Lithofacies | Description | Interpretation |
| Thin-bedded lime mudstones (LMtb) | Mostly homogeneous or weakly laminated, nodular, conglomeratic; scarce burrows; dominantly micritic with dispersed fossil fragments (foraminifers and crinoids). | Lack of current/wave-induced structures and scarce burrows suggesting low-energy conditions below the stormwave-base and photic zone. |
| Laminated wacke- to packstones (W-Pi) | Weakly planar to cross-laminated or massive, composed of alternating dark-grey micrite and light-grey bioclastic calcisilt laminae. | Moderate-energy conditions, partly reworked by currents; distal storm or turbidite deposits. |
| Normally-graded packstones (Png) | Normal grading from intraclast-bearing, coarse packstones to fine-grained, weakly laminated wacke-packstones. | Turbidity currents with intraclasts and fossil fragments, A-C portions of the Bouma turbidite sequence. |
| Slumped limestones (Ls) | Irregular boundary with the lower and upper strata, composed of coarse-grained fossil fragments and poorly sorted, polymictic breccias. | Typically forming on slopes as a result of sediment failure triggered by factors such as rapid sea-level change or seismic activity. |

4.2 | Facies distribution

All the above-mentioned facies are present in the studied three sections, and in particular, the Naqing and Narao sections show roughly similar vertical facies patterns (Figure 3). The lowermost part (70–74.5 m in Naqing and 70–76.3 m in Narao) is dominated by thin-bedded lime mudstones, intercalated with few wackestone to packstone beds. The middle part of the Serpukhovian (74.5–84.9 m in Naqing and 76.3–85.6 m in Narao) is characterized by more massive or normally-graded packstones, with one slump bed in the Narao section, intercalated with lime mudstone beds. The uppermost part of the Serpukhovian (84.9–91.4 m in Naqing and 85.6–90.0 m in Narao) is again dominated by thin-bedded lime mudstones. The Dianzishang section has a much shorter Serpukhovian succession with one slump bed containing the base of the Serpukhovian in the lowermost part and chertified thin-bedded lime mudstones in the upper part (Figure 3; J. Chen et al., 2016; Qi et al., 2014).

Immediately above the MPB, a bed (~75 cm thick) of normally-graded packstones occurs in the Naqing section (Figure 4g), whereas a bed of slumped limestone mass occurs in the Narao (~2 m thick) and Dianzishang (~5 m thick; Figure 4h,i). The Bashkirian successions in the studied sections show a similar vertical facies pattern, i.e., with gradually increasing amount of thin-bedded lime mudstones upward (Figure 3).

4.3 | Facies interpretation and sea-level change

Thin-bedded lime mudstones were deposited in low-energy, deep-water conditions (most likely below the storm wave-base and photic zone), suggested by lack of current- or wave-induced structures and trace fossils (J. Chen et al., 2016). Laminated wackestones to packstones are interpreted as distal turbidites deposited in moderate- to low-energy conditions. Normally-graded beds were deposited from turbidity currents, interpreted as A-C portions of the Bouma sequence (Korn, 2008; Reijmer, Palmieri, & Groen, 2012). Slump beds formed by slumping and deformation of sedimentary strata, which are often triggered by earthquakes and relatively sea-level changes (Altsop & Marco, 2011; Hilbrecht, 1989). The chert nodules or irregular beds formed most likely by replacement of preceding calcite by silica during diagenesis given that they show nodular or irregular shapes (primary chert beds are mostly thin- and flat-beded) and that they occur in all facies and some of the partially chertified bioclastic wackestones to packstones still remain the bioclastic features with unchertified fossil fragments such as crinoids ossicles.
Development of palaeosol and palaeokarst or occurrence of siliciclastics and dolomite across the MPB in carbonate platform successions of South China indicates a sea-level fall across the MPB (e.g., Chen, Sheng, et al., 2018; Mei et al., 2005; Wang et al., 2013). Integrating these coeval subaerial exposure features in the inner platform of South China, the normally-graded packstones or slump masses that occur immediately above the MPB in the studied sections most likely indicate a significant sea-level fall. The other slump bed in the wackestone-packstone-dominated interval in the middle part of the studied Serpukhovian succession in the Narao section might also have been triggered by a relative sea-level fall, assuming that they can be correlated with the normally-graded packstone beds of the similar stratigraphic height in the Naqing section (Figure 3; e.g., Martin, Montañez, & Bishop, 2012; Yose & Heller, 1989). Rapid relative sea-level fall could cause increased pore-water pressure that eventually overcomes the shear strength of sediments and triggers sediment failure on a slope setting of various degrees (e.g., Chen, Chough, Han, & Lee, 2011; Hilbrecht, 1989; Spence & Tucker, 1997). Slumping could potentially erode the substrate sediment in the Dianzishang upper slope setting, resulting in a submarine hiatus, suggested by missing of the upper Serpukhovian conodont zones (Figure 3; Qi et al., 2014).

The MPB sea-level fall and hiatus are widely recorded in the Euramerican carbonate platform successions. For instance, the GSSP (Global Stratotype Section and Point) section for the MPB in Arrow Canyon, Nevada, is punctuated by several subaerial hiatuses represented by palaeosol or palaeokarst, defining several fourth-order glacio-eustatic cycles (Barnett & Wright, 2008; Lane, Brenckle, Baesemann, & Richards, 1999). In the nearby Marble Canyon, the mid-Carboniferous lowstand in sea level was recognized as parasequence boundaries with local exposure features in the outermost platform to upper slope settings (Martin et al., 2012). In the Appalachian Basin, several levels of palaeo-valleys developed across the MPB (Blake & Beuthin, 2008; Cecil & Englund, 1989). In the southeastern Moscow Basin, the Serpukhovian shallow-marine carbonates (e.g., the Protva and Pestovo formations) were heavily karstified, overlain directly by Moscovian carbonates (Kabanov et al., 2016). Deep palaeokarsts also occurred in the Algerian Béchar Basin during the MPB interval (Pareyn et al., 1971; Remack-Petitot, 1960).

In summary, carbonate platform successions in both Euramerica and South China record a significant sea-level fall across the MPB, which resulted in discontinuity in deposition. Rygel et al. (2008) reported a sea-level drop of up to ~150 m based on depth of the palaeo-valley in North America. The studied carbonate slope successions in South China were most likely deposited below the photic zone (>200 m deep) given the lack of biogenic and wave activities. Although there was rapid glacio-eustatic fall across the MPB, the carbonate slopes in South China were not subaerially exposed and thus most likely recorded a near-continuous MPB succession. Detailed conodont
studies also reveal a complete evolutionary lineage in Naqing section, suggesting near-continuous sedimentary records (Hu et al., 2019).

5  CARBONATE $\delta^{13}$C ACROSS THE MPB

The $\delta^{13}$C values of the slope carbonates from the three sections in South China range largely from 0.5‰ to 3.9‰, with an average value of 2.6‰ (Figure 3). The $\delta^{13}$C values from the Naqing section range from 1.8‰ to 3.9‰, with an average value of 3.2‰, and those from the Narao section vary from 1.5‰ to 3.7‰, with an average value of 3.0‰. The $\delta^{13}$C values from these two sections are similar in range and average. The $\delta^{13}$C values from the Dianzishang section range from 0.5‰ to 3.4‰, with an average value of 2.3‰, which is slightly lower than those from the Naqing and Narao sections.

The upper Serpukhovian interval (70–87.8 m) in the Naqing section is characterized by consistent $\delta^{13}$C value of ~3.0‰, followed by a distinct rise to ~3.9‰ from 87.8 to 95.5 m across the MPB. The $\delta^{13}$C values slightly decrease to ~3.5‰ upward and keep largely invariant throughout the rest of the section. The Narao section shows a similar $\delta^{13}$C profile: a slightly fluctuating $\delta^{13}$C values of 2.0–3.0‰ in the upper Serpukhovian interval (70–83 m), followed by a distinct, long-term rise to ~3.8‰ from 83 to 103 m, and a subsequent fall back to ~3.3‰ upward. The $\delta^{13}$C values in the Serpukhovian of the Dianzishang section show a slight fall from 2.7‰ to 2.2‰ upward from 48 to 57.5 m. A long-term, relatively small-magnitude positive excursion (from ~2.2‰ to 2.9‰) across the MPB from 57.5 to 66.5 m is followed by a relatively large-amplitude negative excursion (from 2.9‰ to 1.6‰) with the lowest values at ~69.5 m. The $\delta^{13}$C values increase back to ~2.5‰ at 72 m. Overall, there is a distinct increase in $\delta^{13}$C values across the MPB in the three carbonate slope sections although the magnitude of the positive excursion is small (<1.0‰), compared to those recorded in Euramerica. The variable thickness from the inflection point in the $\delta^{13}$C profiles to the MPB in the three sections is likely due to the potentially different sedimentation rate among sections.

6  DISCUSSION

6.1  Diagenetic evaluation of carbonate $\delta^{13}$C

Carbon isotopic composition ($\delta^{13}$C) recorded in marine carbonates is influenced by both global and local carbon cycling as well as diagenetic alteration (e.g., J. Chen et al., 2016; Immenhauser et al., 2003; Panchuk et al., 2005; Patterson & Walter, 1994; Saltzman & Thomas, 2012; Swart, 2015). Before use as a proxy for $\delta^{13}$C of depositional seawater and as a tool for stratigraphic correlation, carbonate $\delta^{13}$C should first be evaluated with respect to early and late diagenetic alteration.

We utilized petrographically screened, microdrilled samples ($n = 50$) from the Naqing section in order to evaluate the reliability of bulk carbonate $\delta^{13}$C values as being representative of $\delta^{13}$C values of the depositional sea water. The results reveal that the microdrilled samples and bulk carbonates have overlapping $\delta^{13}$C values (Figure 3). On the other hand, the studied slope carbonates lack subaerial exposure features (e.g., palaeokarst, palaeosol, and mud cracks), which suggest that the carbonates were barely influenced by meteoric diagenesis. Covariation between the $\delta^{13}$C and $\delta^{18}$O values is often used to evaluate alteration by either meteoric water diagenesis (Knauth & Kennedy, 2009) or burial diagenesis (Derry, 2010). Lack of the $\delta^{13}$C and $\delta^{18}$O covariation in the three carbonate slope sections (Figure 5) indicates carbon isotopic compositions of depositional seawater. The relatively high $\delta^{18}$O values (ranging from ~7.7‰ to 9.0‰, average of ~2.7‰) also suggest minimal diageneric alteration (e.g., Kaufman & Knoll, 1995).

Degradation of organic matter below the sediment-water interface could shift the carbonate $\delta^{13}$C values more negative due to incorporation of light carbon during early diagenesis, especially in stagnant water masses (e.g., Patterson & Walter, 1994). The Carboniferous slope carbonate $\delta^{13}$C values from South China were most likely not influenced by such processes given that the ocean water was most likely well mixed during the MPB maximum glacial interval because vertical ventilation is commonly stronger during glacial period than during the warmer period (e.g., Saltzman, 2005). Furthermore, the fact that the Carboniferous $\delta^{13}$C values from the Naqing section in South China largely represent the mean of the Euramerican brachiopod data (Chen, Montañez, et al., 2018) suggests that the South China data were overall not specifically influenced by organic degradation.

6.2  Global spatial variation in carbonate $\delta^{13}$C across the MPB

Carbonate $\delta^{13}$C values are influenced by various local to regional factors and thus do not simply reflect the average $\delta^{13}$C values of global ocean DIC. The spatial variation in carbonate $\delta^{13}$C is obvious across...
the MPB, documented in the North American midcontinent and Great Basin, Russian Platform, and South China. Unfortunately, most of, if not all, the published geochemical records across the MPB in Euramerica either lacked the data across the MPB or likely were altered during meteoric diagenesis when epeiric carbonate platforms were subaerially exposed.

The studied sections (except the Dianzishang section) in South China were deposited near continuously in a carbonate slope setting, which warrants high-resolution carbonate δ13C time series across the MPB (Figure 3). The slope carbonates were unaltered by meteoric diagenesis (Buggisch et al., 2011; J. Chen et al., 2016; Chen, Sheng, et al., 2018) and most likely preserved original seawater δ13C values across the MPB. Nevertheless, the carbonate δ13C values across the MPB in South China sections only record a minor but distinct increase by −0.5 to −1.0‰, which is significantly smaller in magnitude than that in Europe (−3.0‰) and North America (−1.5‰). What would have caused this large spatial variation in carbonate δ13C in low-latitude regions across the globe? The carbonate δ13C of which region would more closely represent that of the global ocean DIC?

Upwelling is one type of ocean currents with deep-water swelling upward due to the influence of seaward winds (Parrish, 1987; Tolmacheva, Danelian, & Popov, 2001; Yu & Wei, 2015). The deep water is relatively 13C depleted (nutrient enriched), which could lower the δ13C value of carbonates deposited around the upwelling region. Upwelling usually occurs on the eastern side of the ocean realm (e.g., Peruvian upwelling that occurs on the eastern side of the Pacific Ocean at the present day) owing to the stable trade winds and Coriolis Effect (Bakun, 1990; Smith, 1981). Heckel (1977, 1999) proposed that widespread phosphatic black shale facies were evidence of upwelling in North America (located in eastern Panthalassic Ocean) during the Carboniferous, especially after closing of the Rheic seaway.

During the Carboniferous, the South China Block was located at the eastern side of the Paleo-Tethys Ocean near the palaeo-equator (Figure 1), where the upwelling was highly possible (Liu et al., 2015; Figure 6). The South China Block can be regarded as a small terrain or a big island surrounded by Panthalassic Ocean to the east and Paleo-Tethys Ocean to the west. Based on the current palaeogeographic reconstructions, the Qian-Gui Basin where the studied sections were located, was an intraplatform basin on the Yangtze Platform but most likely connected to the Qinfang Basin to the southeast which was interpreted as a deep-ocean basin (Feng, Yang, Bao, & Jin, 1998; Jiao, Ma, Deng, Meng, & Li, 2003). Thus, the water mass on the Yangtze Platform could have exchanged freely with open-ocean water. Furthermore, Carboniferous slope carbonates were all originated from the platforms as calcareous plankton had not yet evolved at that time (Riding, 1993), so they could preserve δ13C values affected by upwelling and mixing of ocean water but not influenced by meteoric diagenesis.

In summary, the MPB δ13C recorded in slope carbonates in South China would have represented the mean δ13C of the global ocean DIC at that time, because the ocean water was well-mixed in the eastern Paleo-Tethys Ocean due to upwelling. The δ13C values recorded in North America were also influenced by upwelling processes (e.g., Mii et al., 2001) and the MPB δ13C is probably unrelated to regional processes.

### 6.3 Implication for MPB glaciation

The MPB glaciation is recognized by extensive occurrence of glacial deposits on Gondwana, a worldwide glacio-eustatic drawdown, and a distinct positive shift in δ18O recorded in brachiopod calcite (Mii et al., 2001) and conodont apatite across the MPB (Buggisch, Joachimski, Sevastopulo, & Morrow, 2008; B. Chen et al., 2016).

Significant atmospheric pCO2 fall was hypothesized to account for the MPB glaciation, which in turn, was attributed to increased organic carbon burial implied by previously documented large increase (by −3.0‰) in carbonate δ13C (e.g., Mii et al., 2001; Popp et al., 1986). The hypothesis seems largely consistent with radiation of palaeotropical rainforests (Cleal & Thomas, 2005; Montañez, 2016) and increased occurrence of coal deposits in Euramerica (Ferm & Joachimski, 2008; Phillips & Peppers, 1984) but lacks support from precise age control for the correlation of these two aspects. Furthermore, the carbonate δ13C recorded in Euramerica actually lacks the data immediately across the MPB or might have been altered during meteoric diagenesis (Figure 7). If, however, the carbonate δ13C recorded in slope carbonates in South China represents the δ13C of
global ocean DIC, the relatively small-amplitude (by ~0.5–1.0‰) increase in δ¹³C would need less amount of organic carbon burial than previously assumed. Consequently, the atmospheric pCO₂ would not have been lowered enough (due solely to organic carbon burial) to trigger the MPB glaciation, although quantitative modelling is required in further studies.

Alternatively, continental weathering also plays an important role in regulating atmospheric pCO₂, especially on timescales of more than 10⁵ years (Kump & Arthur, 1999). Strontium isotopes (⁸⁷Sr/⁸⁶Sr) are one of the important geochemical proxies for continental weathering, and when combined with carbon isotopes, they can provide better constraints on palaeoclimate changes (e.g., Chen, Montañez, et al., 2018; Goddéris et al., 2017). Chen, Montañez, et al. (2018) presented a high-resolution seawater (conodont apatite) ⁸⁷Sr/⁸⁶Sr record of the late Mississippian to early Permian, which delineates a rapid increase during the MPB interval from 0.70792 at ~326 Ma to 0.70823 at ~317 Ma (Figure 7). The rapid increase in seawater ⁸⁷Sr/⁸⁶Sr indicates enhanced continental weathering that resulted mainly from increased Hercynian orogenic uplift during formation of the supercontinent Pangaea by collision between Gondwana and Euramerica (e.g., Chen, Montañez, et al., 2018; Goddéris et al., 2017). In addition, rapidly expanded palaeo-tropical rainforests during the late Mississippian to the early and middle Pennsylvania (Cleal & Thomas, 2005; DiMichele et al., 2014) would also have enhanced continental weathering through the complex root systems.

Detailed correlation between conodont apatite ⁸⁷Sr/⁸⁶Sr (Chen, Montañez, et al., 2018) and δ¹⁸O (B. Chen et al., 2016) from the same carbonate slope succession (the Naqing section) reveals that the distinct shift in ⁸⁷Sr/⁸⁶Sr from near consistent value (~0.70791) to rapid monotonic rising at ~326 Ma is slightly earlier than that in δ¹³C from ~22.1‰ to rapid rising during ~325.4 Ma, when carbonate δ¹³C from the Naqing section (as well as from Euramerica) is nearly invariant (~3.0‰; Figure 7). The correlation suggests that the significant cooling across the MPB (or increasing in ice volume proxied by rapid increase in conodont δ¹⁸O) as a result of decreased pCO₂ was probably caused by enhanced continental weathering (rapid increase in ⁸⁷Sr/⁸⁶Sr) rather than increased organic carbon burial (invariant δ¹³C).

### 7 CONCLUSIONS

1. The Mississippian–Pennsylvanian boundary (MPB) is well recorded in near-continuously deposited carbonate slope successions in Guizhou Province, South China. Detailed sedimentary facies

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**FIGURE 7** Carbonate δ¹³C and conodont apatite δ¹⁸O and ⁸⁷Sr/⁸⁶Sr records across the Mississippian–Pennsylvanian boundary interval in the Naqing section, South China. Trend lines in δ¹⁸O and ⁸⁷Sr/⁸⁶Sr profiles are locally weighted scatterplot smoothing (LOESS, 0.2 smoothing) regressions with 2.5% and 97.5% bootstrapped errors, and arrows indicate distinct inflections (for discussion, see text). Grey box indicates the studied interval (Figure 3). Con. Zones, conodont zones; A, Lochriae ziegleri; B, Gnathodus bollandensis; C, Gnathodus postbilineatus; D, Declinognathodus noduliferus s. l.; E, Idiognathoides sinuatus; F, Neognathodus symmetricus; G, Idiognathodus primulus; H, "Streptognathodus" expansus M1 [Colour figure can be viewed at wileyonlinelibrary.com]
analysis of the MPB successions (the Naqing, Nara, and Dianzishang sections) suggests a carbonate slope setting likely below the photic zone. Immediately above the MPB, a bed of either normally graded packstones or slump deposits occurs in the studied sections, which, when integrated with coeval subaerial exposure signals on shallow-water platform of South China, indicates a distinct sea-level fall likely as a result of the Gondwanan glacial expansion at this time.

2. Carbonate δ13C records show a consistent value of ~−3.0‰ below the MPB in the Naqing and Nara and ~−2.5‰ in the Dianzishang; all three sections show a rise in δ13C by ~−0.5~1.0‰ across the MPB. The relatively small-magnitude rise in δ13C compared to the coeval records in Euramerica was likely due to upwelling in the eastern Paleo-Tethys Ocean. The well-preserved slope carbonates (free of meteoric diagenesis) and well-mixed ocean water by upwelling of deep-ocean water onto shallow-platform seawater would represent an average δ13C value of the global ocean DIC during the Carboniferous and thus can be used as a proxy for global biogeochemical cycling.

3. The rapid increase in 87Sr/86Sr, in contrast to the small-magnitude increase in Δ13C (by ~−0.5~1.0‰), suggests that the decreasing pCO2 and glaciation during the MPB interval were mainly attributed to enhanced continental weathering rather than increased organic carbon burial. The hypothesis is consistent with the Hercynian orogenic uplift and radiated palaeo-tropical rainforests; both of which would have enhanced continental weathering. Further quantitative modelling of the evolution of the late Palaeozoic carbon cycle is required for better understanding of primary driver of pCO2 during the Earth's penultimate icehouse.

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CONFLICT OF INTEREST

There is no conflict of interest.

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