Devonian paleoclimate and its drivers: A reassessment based on a new conodont $\delta^{18}O$ record from South China

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Abstract

A new Devonian oxygen isotope record based on 180 measurements of conodont apatite is reported from South China. The comparison with published Devonian $\delta^{18}O_{apatite}$ data shows a considerable offset between records from different paleocontinents. This difference can be interpreted by regional variations in salinity, with the epicontinental seas having a distinctly lower salinity and $\delta^{18}O_{seawater}$ than the open ocean due to the influence of fresh-water runoff. Our findings suggest that the oxygen isotope record from open ocean settings is the preferred archive for reconstructing the history of ocean temperature and/or ice volume over the Phanerozoic

Despite regional differences, the South China and European records show similar long-term trends characterized by a pronounced cooling during the Pragian to Eifelian followed by significant warming over the Eifelian/Givetian to Frasnian, and a further cooling starting in the Famennian, accelerating in the earliest Carboniferous. The Early Devonian cooling coincided with early vascular plant root−soil interactions and a significant diversity increase in both spores and

megaplant fossils, suggesting that the rise of rooted vascular plants may have played a key role in triggering climate cooling. Subsequent climatic warming over the Middle to Late Devonian transition may have been linked to metamorphic CO_2 input from the Acadian Orogeny, while Famennian cooling occurred in a context of exposure and weathering of basalts and ophiolites and coincided with the advent of seed plants. We conclude that climate changes during the Devonian were likely driven by a combination of plant evolutionary advances and changes in tectonics.

We further test these interpretations by running the COPSE (Carbon, Oxygen, Phosphorus, Sulphur and Evolution) biogeochemical model. The model prediction is capable of reproducing the pCO$_2$ record under these scenarios, although the model is not capable of reproducing the degree of temperature variation, likely due to its simplicity.

Key words: Paleotemperatures; Vascular vegetation; Acadian Orogeny; Volcanism; Regional δ^{18}O difference

1 Introduction

The Devonian period was characterized by the radiation of vascular plants. The colonization of the terrestrial landscape by rooted vascular plants is considered to have been a key factor in driving changes in Devonian climate (Berner, 2003). The so-called "Devonian plant hypothesis" (Algeo et al., 1995; 2001) proposed that the appearance of trees with deep root systems and the establishment of forests in the Middle Devonian (Meyer-Berthaud et al., 2010; Stein et al., 2012; Giesen and Berry, 2013) may have accelerated silicate weathering and/or organic carbon burial (Sandberg et al. 1988; Joachimski et al., 2002; Joachimski and Buggisch, 2002), resulting in multiple oceanic anoxic events (Algeo et al., 2001), lower atmospheric CO_2 levels (Berner, 2003; Taylor et al. 2009), and global climatic cooling as documented in a brief glaciation in the Late Devonian-Carboniferous boundary (Caputo et al., 2008). However, the climatic consequences of Devonian plant expansion have not been well evaluated in the context of reliable paleoclimatic reconstructions. Atmospheric pCO$_2$ reconstructions are sparse for the Devonian (Royer et al., 2014; Foster et al., 2017), whereas modelling generally predicts a major drop in pCO_2 in the late Early Devonian (ca. 400 Ma late Emsian; Lenton et al., 2016, 2018). Reconstructions of seawater temperatures based on oxygen isotope ratios measured on marine calcitic or phosphatic fossils indicate long-term cooling through most of the Devonian with an interruption by a short but significant warming interval around the Middle to Late Devonian transition (Givetian to Frasnian) (van Geldern et al, 2006; Joachimski et al., 2009) which - according to the "Devonian plant hypothesis" (Algeo et al., 2001) - should be represented by significant climatic cooling. This detailed climate history points to a complex relationship between vascular plant colonization and Devonian climate. For example, in addition to plant evolution, the Devonian Period is characterized by multiple orogenies (Stewart and Ague, 2018) and LIP (large igneous province) volcanic episodes especially in the Late Devonian (Ernst et al, 2020; Racki, 2020). These geological processes could have exerted a significant influence on Devonian climate, but their effects have not been systematically evaluated.

In this contribution, we provide a new Devonian conodont apatite oxygen isotope record measured on samples from the South China Craton. The new data confirm the major oxygen isotope shifts demonstrated in previous studies in Europe, North America and Australia (Joachimski et al., 2004; 2009), thus excluding local climate conditions (e.g., evaporation/precipitation ratio) as an important driver of the observed secular variations. We therefore consider the Devonian oxygen isotope records to principally reflect global climatic changes and interpret the significant changes in the context of plant cover expansion, volcanism and orogenic activities. We test these interpretations by using the COPSE biogeochemical model.

2. Geological setting.

The study sections are located in the Guangxi Zhuang Autonomous Region, as well as in the Guizhou and Yunnan provinces in southwest China, where Devonian strata are well exposed and intensively studied. Paleogeographically, these sections were all located on the Yangtze Platform which, during the Devonian, was situated in low latitudes in the eastern Tethyan Ocean (Fig. 1). Except for the Qinfang Trough in southern Guangxi, the study area was uplifted during the Late Silurian as a consequence of the Guangxi (Caledonian) Orogeny. Marine sedimentation started again in the earliest Devonian in the areas north of the Qinfang Trough (Wu et al., 1987; Liu et al., 1993; Chen et al., 2002, Chen et al., 2014) (Fig. 1 b, c) and progressively expanded northwards during the Middle to Late Devonian. This transgression is well recorded across Guangxi and adjacent areas, with Lochkovian deposits dominated by terrigenous siliciclastic followed by Pragian and Emsian siliciclastics interbedded with carbonates and Middle to Late Devonian carbonates.

Pragian conodonts were collected from the Dashatian section situated in Nanning City (Fig. 1). The section is characterized by siltstones and mudstones alternating with few carbonate beds. The conodont assemblage identified in this section includes *Eognathodus irregularis, E. nagaolingensis, E. sulcatus* mu morph, *Masaraella pandora* indicating an early Pragian age (Wang et al., 2016). Emsian to Givetian conodonts were collected mainly from the Changputang, Sihongshan, Nayi as well as Caiziyan sections. The Changputang section is situated at Wenshan in Southeastern Yunnan province (Fig. 1) and is characterized by alternating deep-water siliceous rocks or cherty limestones and shales with shallow water bioclastic and micritic limestones (Jin et al., 2005), indicating significant relative sea level fluctuations. The Sihongshan section is located at Debao County, in southwestern Guangxi Zhuang Autonomous Region. The section is composed of pelagic and dolomitic limestones alternating with few siliceous horizons. A nearly complete conodont sequence from the Early Devonian *Polygnathus excavatus* Zone (Emsian) to Late Devonian *Palmatolepis crepida* Zone (Famennian) was identified in this section (Ziegler and Wang, 1985). The Caiziyan section is located approximately 30 km northeast of Guilin city in Guangxi. The conodont biostratigraphy of the exposed Givetian–Frasnian boundary interval is well studied in this section, with 10 standard conodont zones being identified (Li et al., 2009).

Frasnian-Famennian conodont samples were collected from the Dongcun and Huohua sections. The Dongcun section is located at about 20 km northwest of Yangsuo County in Guangxi and is mainly composed of limestones with few inter-bedded dolomites, representing marginal platform and slope facies with abundant pelagic faunas, especially conodonts (Wang, 1994). Conodont zones range from the Early Frasnian *Polygnathus transitans* to the early Famennian *P. crepida* Zone (Wang, 1994; Wang and Ziegler, 2002) with the Frasnian/Famennian boundary precisely identified in the upper part of the section (Wang and Ziegler, 2002). The Huohua Section is situated in Ziyun County in south Guizhou (Fig. 1) where carbonates yielding abundant conodonts have been deposited in marginal platform and slope settings during the Frasnian to the earliest Carboniferous. The stratigraphic range of the sampled intervals in the study sections is shown in Fig. 2.

3. Material and methods

3.1 Oxygen isotope analyses of conodont apatite

Conodonts were extracted by dissolving carbonate rocks in 10% acetic acid. Residues were separated using heavy liquid fractionation (lithium-polytungstate). Conodont elements were picked from the heavy fraction under a binocular microscope. 0.5 to 1.0 mg conodont apatite was weighed into a small polyethylene beaker, and 5 ml 2 M HNO_3 was added to completely dissolve conodont apatite. The clear solution was pipetted to a new beaker and chemically converted to Ag_3PO_4 following the method described by Joachimski et al. (2009). The obtained Ag_3PO_4 crystals were ultrasonically washed 5 times with distilled water, dried at 60 °C for 1 hour and ground to fine powder using an agate mortar. 0.2 to 0.3 mg Ag_3PO_4 powder was weighed into silver foil, which was transferred to the sample carousel of a TC-EA (high temperature elemental analyser) coupled online to a Thermo Fisher Delta Advanced IRMS. Sample and standard Ag_3PO_4 samples were combusted at 1450 °C by TC-EA and the generated CO gas was transferred in a helium stream via a Conflo IV interface to the mass spectrometer. All oxygen isotope values are reported in ‰ relative to VSMOW. The average oxygen isotopic composition of NBS 120c standard was measured as 21.7‰ VSMOW. Accuracy was monitored by replicate analyses of NBS120c. Reproducibility was calculated based on triplicate sample and standard analyses and was generally < ±0.3‰ (1 std. dev.).

Despite the oxygen isotopic composition of conodont apatite being relatively resistant to diagenetic alteration (Joachimski et al., 2009), a potential isotopic overprint by microbiological activity mediated by enzymes (Zazzo et al., 2004) or by diagenetic fluids at high temperatures (Pucéat et al., 2004) is possible. Unfortunately, there is no robust method at present to identify post-depositional exchange of oxygen isotopes in biogenic apatite (Buggisch et al., 2008; Joachimski et al., 2009). For example, REE and trace element patterns as well as cathodoluminescence characteristics, as usually used for evaluating the preservation of brachiopod calcite (e.g. Garbelli et al., 2017), are demonstrated to be invalid in identifying exchange of oxygen in the phosphate ion of biogenic apatite (Buggisch et al., 2008; Joachimski et al., 2009). The conodont color alteration index (CAI) is a proxy for the maximum thermal overprint of sediments (Rejebian et al., 1987), with a high thermal overprint potentially causing recrystallisation (aggrading neomorphism) of conodont apatite (Nöth, 1998). The varying CAI value is suspected as a potential reason for the symmetric $\delta^{18}O_{apatite}$ values discrepancy between coeval late Permian sections in South China (Chen et al., 2016, Shen et al., 2019). However, several studies have found no major difference in oxygen isotope ratios from time-equivalent conodont samples with CAI values ranging from 1 (corresponding to ~75 °C) to 7 (>300 °C) (Buggisch et al., 2008; Joachimski et al., 2009; Trotter et al., 2015), suggesting that intense heating does not necessarily result in oxygen isotope exchange in apatite phosphate. Similar $\delta^{18}O_{apatite}$ values and/or trends in coeval sections are considered to document the preservation of primary $\delta^{18}O$ signals (Joachimski et al., 2009; Huang et al., 2018).

In order to reconstruct long-term trends, the nonparametric locally weighted regression method 'Locfit' is utilized to calculate isotope trend lines (Loader, 1999). Locfit produces a smoothed curve retaining local minima and maxima and yields good results, even with unevenly spaced data points. All calculations were performed with the open source statistic software 'R' (version 3.3.1, Ihaka and Gentleman, 1996).

3.2 COPSE model

To explore drivers of Devonian climate change, we compare out dataset to the COPSE global biogeochemical model (Lenton et al., 2018). We plot the latest 'baseline' model run from Tostevin and Mills (2020) and consider some basic alterations which may enable the model to better fit the data. COPSE considers the cycling of carbon, oxygen, phosphorus and sulfur over geological timescales. The model equations are described in full in Tostevin and Mills (2020).

4. Results

A total of 180 conodont apatite oxygen measurements spanning the Devonian were performed (Fig. 3A). An additional 103 $\delta^{18}O_{apatite}$ values of Frasnian-Famennian conodonts from South China reported by Huang et al. (2018) were used to construct a $\delta^{18}O_{apatite}$ curve for South China. The new data from South China show a ~2‰ variance in $\delta^{18}O$ apatite from the given time intervals, which is in the range by previous reconstructions (e.g. Joachimski et al., 2009; Chen et al., 2013; 2016). Mean values calculated using Locfit are around ~17 ‰ during the Pragian followed by a pronounced rise to maximum value ~20.5 ‰ in the Eifelian. Mean $\delta^{18}O_{apatite}$ values decrease from approximately 20.5‰ to 18 ‰ in the Eifelian to early Frasnian and show a large variation with values between 16‰ and to 19‰ across the Frasnian-Famennian boundary. Latest Famennian conodonts from South China yield $\delta^{18}O_{apatite}$ values around 18‰ at the Devonian-Carboniferous boundary (Fig. 3A), followed by a pronounced rise in $\delta^{18}O_{apatite}$ in the earliest Carboniferous.

5. Discussion

5.1 Comparison of $\delta^{18}O_{apatite}$ records from South China and other parts of the World

Comparable absolute $\delta^{18}O_{apatite}$ values with systematic trends are observed in coeval Emsian samples from three different sections in South China (Shihongshan, Changputang and Nayi Sections, Fig. 3A). However, a systematic difference in $\delta^{18}O_{apatite}$ is observed for conodonts from two well-studied Frasnian-Famennian boundary sections (Huang et al. 2008), conodonts from the Yangdi section (17-19‰)

are on average 1‰ higher in $\delta^{18}O_{apatite}$ compared to conodonts from the Dongcun section (16-18‰). Nevertheless, both records exhibit similar positive shifts at the Lower and Upper Kellwasser levels. Both sections were situated in close neighborhood in an inter-platform basin formed by rifting activity, representing a tropical open-marine setting without significant continental siliciclastic influx (Fig. 1C; Chen et al. 2001a, b, 2002). Significant variations in seawater temperature and seawater $\delta^{18}O$ (due to salinity changes) are unlikely, however there may have been a slight difference in depositional water depth. For example, the Yangdi section was deposited in a lower slope or basinal setting (Huang et al., 2018; Huang and Gong, 2016). By contrast, the Dongcun section was deposited in a slightly shallower, possibly upper slope setting (Wang and Ziegler, 2001; Ma et al., 2008). The systematic ~1‰ difference could be interpreted as reflecting differences in water depth, with conodonts from shallower waters (Dongcun section) recording 4 °C warmer temperatures than conodonts from the relative deeper water Yangdi section. However, this implies that *Palmatolepis,* the dominating conodont taxon measured in the two sections may have lived in slightly deeper parts of the water column, contradicting previous suggestions that *Palmatolepis* was a surface dweller (Joachimski et al., 2009; Huang et al., 2018), but in line with the traditional conodont biofacies models (e.g. Sandberg et al., 1988) that considered *Palmatolepis* as a pelagic taxon which could have lived at variable water-depths.

The comparison of published $\delta^{18}O_{apatite}$ records with the South China record shows that Pragian $\delta^{18}O_{apatite}$ data from South China yield comparable values to those from Australia but lower $\delta^{18}O_{apatite}$ values than those from Europe (Fig. 3 A, B), The late Emsian to Eifelian $\delta^{18}O_{apatite}$ data from South China and Europe yield higher $\delta^{18}O_{apatite}$ values compared with those from Australia and USA (Fig. 4), with the regional differences in $\delta^{18}O$ becoming less obvious during the Late Devonian and Early Carboniferous. The $\delta^{18}O$ difference could be interpreted by regional effects such as salinity (e.g. via river discharge, upwelling, seasonal rainfall patterns). It is interesting that the discrepancy in $\delta^{18}O_{apatite}$ appears to be dependent on the ocean basins, with China and Europe located in the Palaeotethys ocean yielding higher $\delta^{18}O_{apatite}$ values, whereas western USA and Australia were situated in the Panthalassa ocean and have lower $\delta^{18}O_{apatite}$ values (Figs. 3 A, B). This observation may reflect freshwater runoff and thus lower salinities in the Panthalassa seas in southeastern Australia and the US Midcontinent (low $\delta^{18}O_{seawater}$ value), while $\delta^{18}O_{apatite}$ values from the shelf seas bordering the western (Europe) and eastern Palaeotethys (China) may represent an open-marine settings with higher salinities (high $\delta^{18}O_{seawater}$ values). A similar pattern is observed in the Pennsylvanian North American Midcontinent Sea, which was an extensive tropical epicontinental sea within the Laurentian Craton (Heckel, 1977; Algeo and Heckel, 2008) with increased continental runoff resulting in an obvious offshore-onshore decrease in surface water $\delta^{18}O$ (Joachimski and Lambert, 2015; Rosenau et al., 2014, Macarewich et al., 2021), and, resulting in considerably lower values (~3‰) of Pennsylvanian conodonts from the US Midcontinent compared to coeval conodonts from open ocean South China (Joachimski et al., 2006; Joachimski and Lambert, 2015; Chen et al., 2016). Using the $\delta^{18}O$-salinity relationship for modern tropical settings like the Gulf of Panama where a change of 0.25‰ in $\delta^{18}O$ corresponds to a 1 psu salinity change (Tao et al., 2013), the observed $\delta^{18}O$ difference of 1.5-2.0‰ between the Panthalassa and Palaeotethys sea would translate into ~6-8 psu salinity variation. Assuming that the Palaeotethys had normal marine salinities like the modern ocean (~35 psu salinity), the Panthalassa sea would have salinities of 27-29 psu salinity.

Continental runoff lowering seawater $\delta^{18}O$ may also explain why comparably low $\delta^{18}O_{apatite}$ values are measured in South China and Australia in the Pragian. The Pragian was a time when marine sediment initially occurred after the Guangxi Orogeny, and all Pragian data from South China are from the Dashatian section, which is dominated by terrigenous siliciclastics interbedded with few carbonate beds, representing a near coastal setting (Wang et al., 2016; Qiao et al., 2021). Thus, this section likely was influenced by enhanced freshwater input, resulting in lower seawater $\delta^{18}O$ and $\delta^{18}O_{apatite}$ values. Accordingly, the data from this section were not considered for palaeotemperature reconstruction. All Late Devonian and Early Carboniferous $\delta^{18}O_{apatite}$ data are from the Palaeotethys ocean. Thus, it is not surprising that regional differences in $\delta^{18}O_{apatite}$ are less obvious (Fig. 3A, B; Fig. 4).

The above observations indicate that Devonian oceans may have been characterized by significant differences in $\delta^{18}O_{seawater}$, with epicontinental seas having distinctly lower $\delta^{18}O_{seawater}$ than the open ocean as consequence of the input of freshwater. An average $\delta^{18}O_{seawater}$ value of −1‰ is usually assumed for time intervals without major ice caps in high latitudes. However, this assumption is an oversimplification (Judd et al. 2020) as documented in the variability of seawater $\delta^{18}O$ in the modern oceans (Schmidt et al., 1999). Thus, reconstruction of deep time ocean temperatures and/or ice volume should preferentially be based on oxygen isotope data from open ocean settings.

Despite regional differences in $\delta^{18}O_{apatite}$ between palaeocontinents (Fig. 3A, B) or even between sections from one paleocontinent (e.g. Girard et al., 2020) (Fig. 3A, B), the Devonian $\delta^{18}O_{apatite}$ records from South China and Europe generally show similar secular trends characterized by a pronounced increase in $\delta^{18}O_{apatite}$ during the Pragian to early Emsian to Eifelian followed by significant decrease during the late Eifelian/Givetian to Frasnian, and a further rise starting in the early Famennian, accelerating in the earliest Carboniferous (Fig. 3A, B). Interestingly, similar long-term oxygen isotope trends are also seen in the $\delta^{18}O$ record of well-preserved brachiopod calcite measured from multiple low latitude continents (Fig. 3C, van Geldern et al., 2006). These parallel trends measured on brachiopod calcite and conodont apatite deriving from various low latitude locations (Fig. 3) can serve as evidence supporting the inference that the primary oxygen isotope signals are well preserved in most of the South China samples and the observed changes in $\delta^{18}O$ mainly record global climatic changes. Since the regional differences in seawater $\delta^{18}O$ complicate absolute temperature estimation, we only compare the temperature records from two low latitudinal regions (0-15 °S) within Palaeotethys (South China and Europe).

Applying the temperature equation of Lécuyer et al. (2013) and assuming a $\delta^{18}O$ value for Devonian seawater of -1 ‰ VSMOW, the $\delta^{18}O_{apatite}$ records suggest cooling of tropical seawater by ~8 to 10 ℃ (Fig. 4) during the Pragian to Emsian/Eifelian followed by 8 to 10 ℃ (Fig. 4) warming during the Eifelian/Givetian to Frasnian. The

European record shows a moderate ~5 ºC temperature decrease during the Famennian. Unfortunately, coeval data from South China are sparse, hindering a direct comparison between the two regions. However, both records suggest further cooling during the earliest Carboniferous (Chen et al., 2021; Fig. 4). The parallel palaeotemperature trends suggest that the Devonian climate variations occurred globally.

5.2 Potential drivers of Devonian climate change

It is generally assumed that variations in atmospheric CO_2 concentration played a key role in controlling changes in Earth's climate over the Phanerozoic Eon (Royer et al., 2004; Came et al., 2017; Mills et al., 2019). Primary carbon sources to the atmosphere are CO_2 emitted by tectonic and volcanic processes and oxidative weathering of organic carbon, while CO_2 sinks are silicate weathering and burial of organic carbon. CO_2 emission is linked to the intensity of tectonic or volcanic activities which are generally represented over long timescales by the rate of material generation and subduction, based on ridge production rate and lengths of arcs (Van Der Meer et al., 2014; Mills et al., 2017; Cao et al., 2017). Silicate weathering depends on multiple factors including runoff, temperature, and physical erosion rates (Royer, 2014; Goddéris et al., 2014), which in turn would be influenced by changes in topography, paleogeography, climate, and terrestrial plant coverage.

Enhanced silicate weathering due to the advent of terrestrial vascular plants (Algeo et al., 1995, 2001; Algeo and Scheckler, 1998; Lenton et al., 2018) has been considered as major trigger of the pCO_2 decrease during the Devonian, which resulted in the transition from the Early Paleozoic "greenhouse" to Late Paleozoic "icehouse"(Qie et al., 2019). However, the exact timing of events is uncertain. Proxy pCO_2 data and modelling studies have suggested that cooling started in the Emsian at ca. 400 Ma or even earlier (Royer et al., 2014; Foster et al., 2017; Lenton et al., 2018), while other authors suggested a later onset in the Middle (Givetian) to Late Devonian following the advent of forests and deeper root systems (Stein et al., 2012; Giesen and Berry, 2013). The oxygen isotope based palaeotemperature reconstructions indicate that the first Devonian climatic cooling took place in Pragian to Emsian times, followed by climatic warming during the Givetian and Frasnian interval, and further cooling occurring again in the Famennian (Fig. 4). In the following sections, the Devonian climate evolution and the potential driving mechanism(s) will be discussed.

5.2.1 Was Early Devonian cooling triggered by the radiation of early rooted plants?

The South China and European palaeotemperature records (Fig. 4) suggest that cooling occurred in the Early Devonian, with a more stable climate dominating the late Emsian to Eifelian which is generally in agreement with modeling based pCO_2 predictions (Fig. 5). Long-term climatic cooling is usually interpreted as resulting either from increased CO_2 consumption via silicate weathering or reduced CO_2 degassing from tectonic and volcanic activities. In particular, low-latitude arc-continent collisions or emplacement of larger igneous provinces would significantly promote exhumation and erosion of mafic and ultramafic rocks (Cox et al., 2016; Macdonald et al., 2019), which are effective at consuming CO_2 via chemical weathering (McKenzie et al., 2016; Hartmann et al., 2014; Schopka et al., 2011). Fresh exposure of ophiolites following arc-continent collisions or of basalt after LIP emplacement may significantly accelerate silicate weathering and carbon sequestration (Cox et al., 2016; Macdonald et al., 2019), especially if occurring in tropical latitudes. However, the low active suture length and LIP area reconstructed for the Pragian-Emsian (Macdonald et al., 2019; Fig. 5) suggest that silicate weathering from both was likely ineffective in removing CO_2 from the atmosphere. In addition, although reconstructions suggest an overall decrease in the CO_2 outgassing rate from mid ocean ridges or continental arc activity from the Ordovician to Carboniferous (Mckenzie et al., 2016; Cao et al., 2017; Mills et al., 2017, 2019), short-term outgassing rates are extremely difficult to calculate, so a reduced tectonic degassing flux cannot be clearly implicated in Pragian-Emsian cooling.

We suggest that Early Devonian cooling may be a consequence of accelerating silicate weathering initiated by the occurrence of the early rooted vascular plants. According to Algeo et al. (1995, 2001), early vascular plants prior to the Middle Devonian were mainly herbaceous, relatively small in stature (<1 m) and ecologically restricted to specific habitats. Roots or rhizomes of these early plants are rarely found and/or incompletely preserved (Morris et al., 2015). However, the impact of these early plants on soil production and continental silicate weathering could be substantial (Algeo, et al., 2001; Xue et al., 2016). For example, recent paleobotanical studies document a complex rhizome system for the lycopsid *Drepanophycus* (Xue et al., 2016) and rooting systems for lycophytes (Matsunaga and Tomescu, 2016) almost simultaneously occurring in South China and North America in the Pragian (Fig. 5). Similar rhizomes or rooting structures were also observed in Lochkovian to Emsian sediments of Southern Britain (Hillier et al., 2008) and Bathurst Island/Arctic Canada (Gensel et al., 2001). Larger and deeper root systems capable of penetrating downward into the substrate by ~1 m are reported from Emsian strata in Canada, although the parent plant is unclear (Elick et al., 1998).

These findings suggest that rhizomes or rooting systems having the capability of producing rooted paleosols (Xue et al., 2016) may have been well established since the Pragian. This further suggests that relatively complex plant−soil interactions already existed prior to the advent of forests and deep root systems (Algeo, et al., 2001; Xue et al., 2016; Matsunaga and Tomescu, 2016). Additionally, advanced root systems in the Pragian were coincident with a significant increase in spore and mega plant fossil diversities (Fig. 5, Wang et al., 2000, Cascales-Minana, 2016, Xue et al., 2018, Shen et al., 2020), as well as a significant expansion of global vegetation cover, estimated to be from 10 to 30% of modern coverage (Fig. 5; Simon et al., 2007). Furthermore, a pronounced increase in plant biomass and terrestrial organic carbon burial is evidenced by the development of coal-like accumulations in multiple localities (Wehrmann et al., 2005, Kennedy et al., 2013, Morris et al., 2011; Nelsen et al., 2016) and high $\delta^{13}C_{carb}$ values in coeval marine carbonates (Fig. 6, Buggisch and Joachimski, 2006).

An increased influence of Early Devonian vegetation and its root systems on continental weathering can also be inferred from multiple lines of indirect evidence, for example significant changes in river systems characterized by a shift from braided to meandering streams (Davies and Gibling, 2010; Gibling and Davies, 2012), and a prominent increase in mud deposition in alluvial plain system allowing more complete weathering of primary minerals (McMahon and Davies, 2018) under a context of higher weathering intensity in response to the expansion of land plants (Lipp et al., 2021). Mo isotope and I/Ca data from South China and North American sections, as well as isotope mass balance models for global sedimentary $\delta^{13}C$, indicate that a major oxygenation pulse took place in the Early-Middle Devonian (ca. 400 Ma) (Dahl et al., 2010; Krause et al., 2018; He et al., 2019, Lu et al., 2018) with excess O_2 likely produced by enhanced burial of terrestrial biomass due to the higher C/P ratio of early land plants, coupled with a plant-driven P weathering increase promoted the burial of marine organic carbon (Lenton et al., 2016).

These ideas suggest that terrestrial as well as marine productivity and biomass may have substantially increased since the Pragian. In conjunction with the advent of root systems and the co-evolution of symbiotic mycorrhizal fungi (Remy et al., 1994; Strullu-Derrien et al., 2014; Mills et al., 2018), the Early Devonian vegetation may have considerably enhanced silicate weathering and organic carbon burial, promoting sequestration of atmospheric CO_2, culminating in climatic cooling. The COPSE model as shown in Figure 5 (Tostevin and Mills, 2020) incorporates the essentials of the plant root hypothesis but assumes that the significant radiation of rooted terrestrial vegetation occurred between ~400 and ~380 Ma (Lenton et al., 2018). The model predictions therefore indicate that Early Devonian cooling started at 400 Ma. Alternatively, assuming an earlier onset of the radiation of rooted vegetation at ~410 Ma, the COPSE model predicts a more comparable pCO_2 and oxygen isotopic based temperature record (Fig. 5).

5.2.2 Givetian–Frasnian warming triggered by metamorphic CO_2 degassing?

Climate warming during the late Givetian to Frasnian is unexpected, since the Middle Devonian is generally considered as a time interval with the earliest forests with deep root systems and a complex floral community (Stein et al., 2007; 2012). However, a significant climatic warming episode has been identified from both conodont apatite and brachiopod calcite $\delta^{18}O$ records (Fig. 5; Joachimski et al., 2009; van Geldern et al. 2006). In addition, the broader latitudinal distribution of tropical floras and miospores, indicating a weak latitudinal temperature gradient is considered as a biosphere response to this warming (Streel et al., 2000). Van Geldern et al. (2006) suggested that intensified CO_2 outgassing from midocean ridges as inferred from the high sea-level (Johnson et al., 1985) and/or island arc volcanism, was a potential reason for this warming event. However, long-term reconstructions of CO_2 outgassing from mid-ocean ridges or continental arc activity tend to show a decreasing or flat trend during the Middle-Late Devonian transition (Mckenzie et al., 2016; Cao et al., 2017; Mills et al., 2017). The abrupt rise in tropical active suture length and LIP area (Macdonald et al., 2019; Fig. 5) further suggest that a reduction in mafic and ultramafic rock weathering was unlikely to be the cause of this warming.

Stewart and Ague (2018) proposed that metamorphic CO_2 degassing derived from fluid infiltration-driven decarbonation during the Acadian Orogeny (Fig. 5 ca. 390-375 Ma) may have injected a total flux of 0.7~2.5 $\times 10^{19}$mol CO_2 to the atmosphere, resulting in significant global warming and the "Taghanic bio-crisis". The proposed CO_2 injection is thought to have started at 390 Ma coinciding with climate warming as suggested by the $\delta^{18}O_{apatite}$ records. Interestingly, this climate warming coincides with a significant sea level rise observed in both South China and North America (Fig. 6, Johnson et al., 1985; Ma et al., 2017). The rising sea level could be interpreted to indicate the melting of ice masses (Elrick et al., 2009), however no direct glacial deposits have been observed at this time. To assess the likelihood of Acadian degassing driving this warming, we incorporated enhanced CO_2 degassing into the COPSE model run. We increased the model degassing rate by 33% over a 10 Myr period corresponding to the Acadian orogenesis, which gives an additional CO_2 input at the upper end of the estimates of Stuart and Ague (2018). pCO_2 proxy data are highly scattered but do broadly confirm a minor increase over the degassing interval, as predicted by the COPSE model. However, the model does not reproduce the degree of warming that is indicated by the $\delta^{18}O$ records.

5.2.3 Famennian cooling: the advent of seed plants or Arc-continent collisions?

The $\delta^{18}O_{apatite}$ record indicates two abrupt and transient cooling events across the Frasnian-Famennian boundary, which have been reported in multiple low latitude-sections (Joachimski and Buggisch, 2002; Balter et al., 2008; for summary see Huang et al. 2018) and are attributed to a transient increase of organic carbon burial (Joachimski and Buggisch, 2002). However, these short-term changes are not well defined in the long-term records (Fig. 4). The long-term $\delta^{18}O_{apatite}$ record indicates cooling starting in the early Famennian and accelerating into the earliest Carboniferous (Fig. 4).

The Famennian cooling coincided with the origin and diversification of seed plants (Fig. 5; Algeo et al., 1995), alongside the occurrence of more complex vascular systems (Meyer-Berthaud et al., 1999; Hilton et al., 2003; Rowe and Speck, 2005; Wang and Liu, 2015), diversification in leaf morphologies (Boyce and Knoll, 2002; Xue et al., 2015) as well as a significant increase in plant height (Mosbrugger, 1990; Dilcher et al., 2004; Meyer-Berthaud et al., 2010). The advent and diversification of seed plants (Prestianni and Gerrienne, 2010) was of particular importance, since the reproduction of seed plants is fully independent of water, enabling them to colonize drier uplands (Algeo and Scheckler, 1998; Fairon-Demaret and Hartkopf-Fröder, 2004, Taylor et al., 2009). Consequently, vegetation coverage dramatically increased during the Famennian (Simon et al., 2007, Algeo and Scheckler, 2010). The taller, leafier plants had to develop more advanced rooting systems and hosted more symbionts in order to obtain more water and nutrients (Raven and Edwards, 2001). As a result, the root systems of Famennian plants became larger (10 to 15 cm in diameter, up to 1.5 m in deep), more complicated in morphology (Driese and Mora, 2001), with the total root mass, a parameter regarded as a reliable proxy for pedogenic weathering intensity, dramatically raising to near ~50% of modern levels (Algeo and Scheckler, 2010). These significant innovations in vegetation may have resulted again in a significant promotion of terrestrial weathering.

It is interesting to note that reconstructions of active suture length in the tropics indicate an abrupt increase to ~3,000 kilometers in the latest Frasnian and Famennian (Macdonald et al., 2019). Basalt weathering following the emplacement of LIPs in the tropics has a similar climatic effect as low-latitude arc-continent collisions (Macdonald et al., 2019; Park et al., 2021). The emplacement of the Viluy and Kola-Dnieper LIPs are dated as Middle to Late Devonian (Kusznir et al., 1996; Wilson and Lyashkevich, 1996, Courtillot et al., 2010, Kravchinsky et al., 2012), with the estimated LIP exposed area increasing substantially over 385-380 Ma (Fig. 5), ranking this period as a peak interval of basalt exposure (Macdonald et al., 2019). Weathering of freshly exposed basalts or ophiolites may have provided a mechanism to drive climatic cooling (Dessert et al., 2003). However, the increase in active suture length and basalt areas started in the Givetian (380 Ma) and late Frasnian (375 Ma), respectively, during warming climatic conditions and 12 and 7 Ma before the onset of Famennian cooling (Fig. 5). This suggests that weathering of basalts or ophiolites did not immediately result in climatic cooling. However, the relatively large basalt and ophiolite exposure areas alongside with declining tectonic CO_2 degassing imply that these factors may still possibly make a considerable contribution to the Famennian cooling, which culminated in a short glaciation in the late Famennian (Caputo, 1985; Caputo et al., 2008).

In summary, enhanced silicate weathering in association with the advent of seed plants and their deeper and complicated root systems could have played a leading role in driving the Famennian cooling, which was further reinforced by weathering of ophiolites and basalts. The combined effect of these events would have significantly accelerated removal of CO_2 from the atmosphere (Berner et al., 2003), ultimately leading to the global climate transition from the Early Paleozoic Greenhouse to the Late Paleozoic Icehouse. The continued expansion of land plants and the weathering of volcanic terranes were already included in the COPSE model run (in a basic form), and it is capable of generating a CO_2 record that is consistent with the proxy data and predicts cooling over the Famennian. However, as above, the model does not recreate the large changes in tropical temperatures that are reconstructed from the $\delta^{18}O$ record. Given that the COPSE model is a simple nondimensional box model, the tropical temperature change is calculated from the global average temperature assuming a constant poleward heat transport by multiplying the global temperature change by a constant factor of $\frac{2}{3}$ (see Mills et al., 2019). This is an oversimplification as the polar amplification factor itself appears to be dynamic (Valdez et al., 2021), which could change the assumed model 'tropical' temperatures by several degrees.

6. Conclusions

Multiple Devonian oxygen isotope records from different low latitude areas illustrate a Devonian climate characterized by cooling during the Pragian to Emsian, significant warming during the Givetian to Frasnian, and cooling starting in the Famennian and accelerating in the earliest Carboniferous. A close comparison of the climatic variations and vegetation innovation events suggests that the Pragian to Emsian and Famennian cooling corresponded to the first establishment of vascular plant root-soil interactions, and later to the advent of seed plants in conjunction with the development of deep and morphological complex root systems. These dynamic Devonian climatic changes add complexity to a more generally assumed gradual decrease in atmospheric CO_2 resulting from the rise of the Devonian vegetation. In addition, tectonic and volcanic activities are suggested to have played an important role in driving the Devonian climate, with weathering of freshly exposed ophiolites and basalts consuming CO_2 and thus driving climatic cooling in the Late Devonian, whereas contact metamorphism produced by orogenic activities likely contributed to a CO_2 rise and climatic warming in the Middle Devonian.

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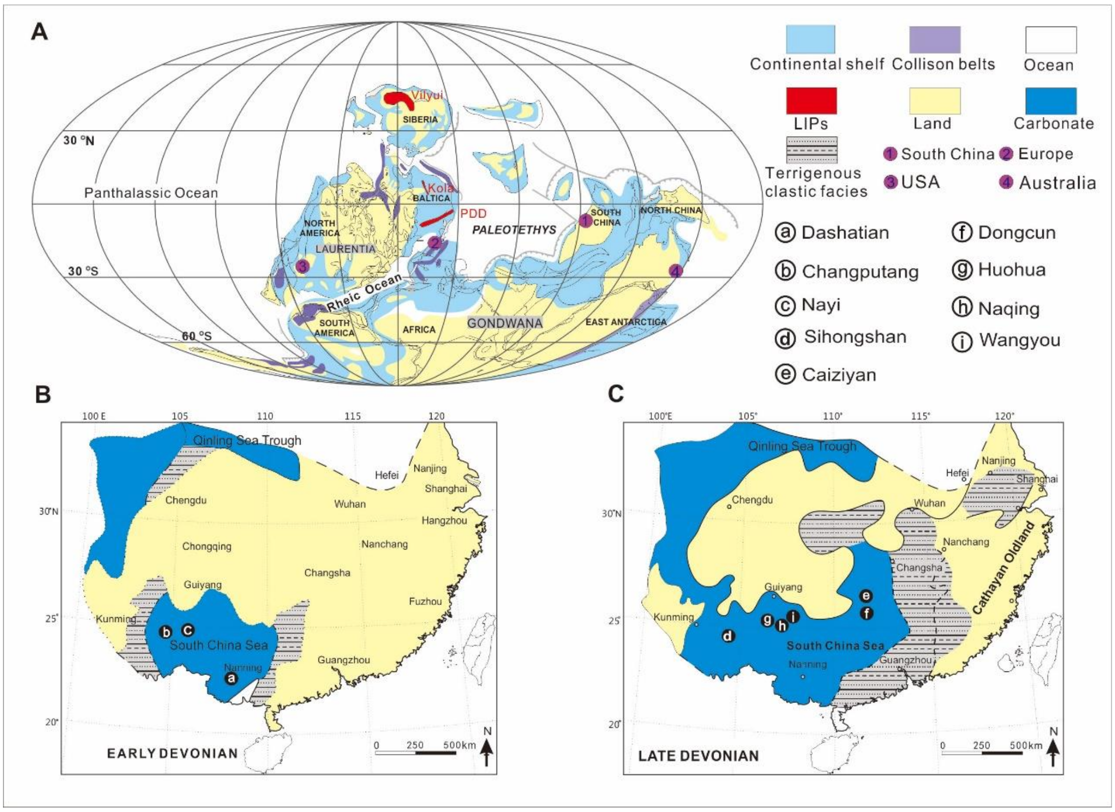

Fig. 1. A: Global palaeogeographic reconstruction for the Middle/Late Devonian (revised from Golonka, 2000). B and C: Early and Late Devonian palaeogeographic reconstructions for South China and location of study sections (revised from Ma et al., 2009).

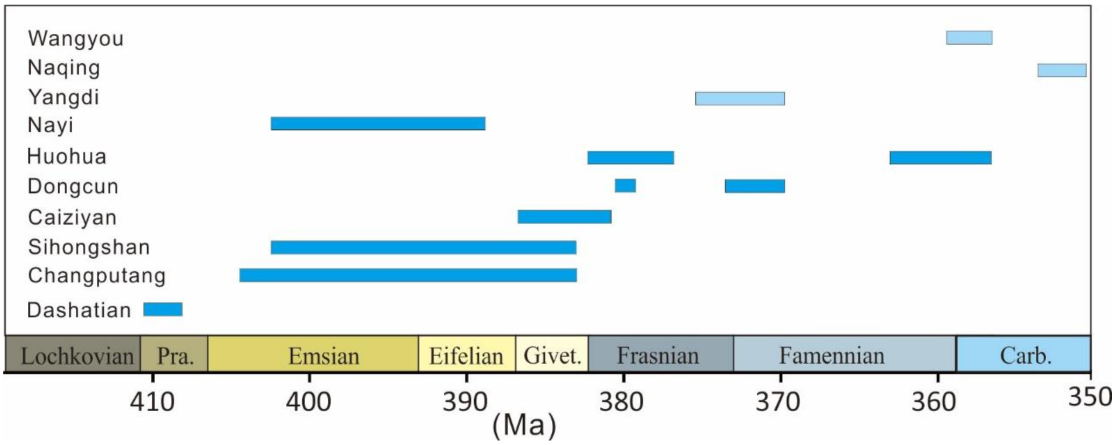

Fig. 2. Stratigraphic range of sections studied in South China. Absolute ages after Geological Timescale 2012 (Gradstein et al., 2012). Light blue box represents sections reported in Huang et al., 2018 and Chen et al., 2021. Pra. = Pragian, Givet. = Givetian, Carb. = Carboniferous

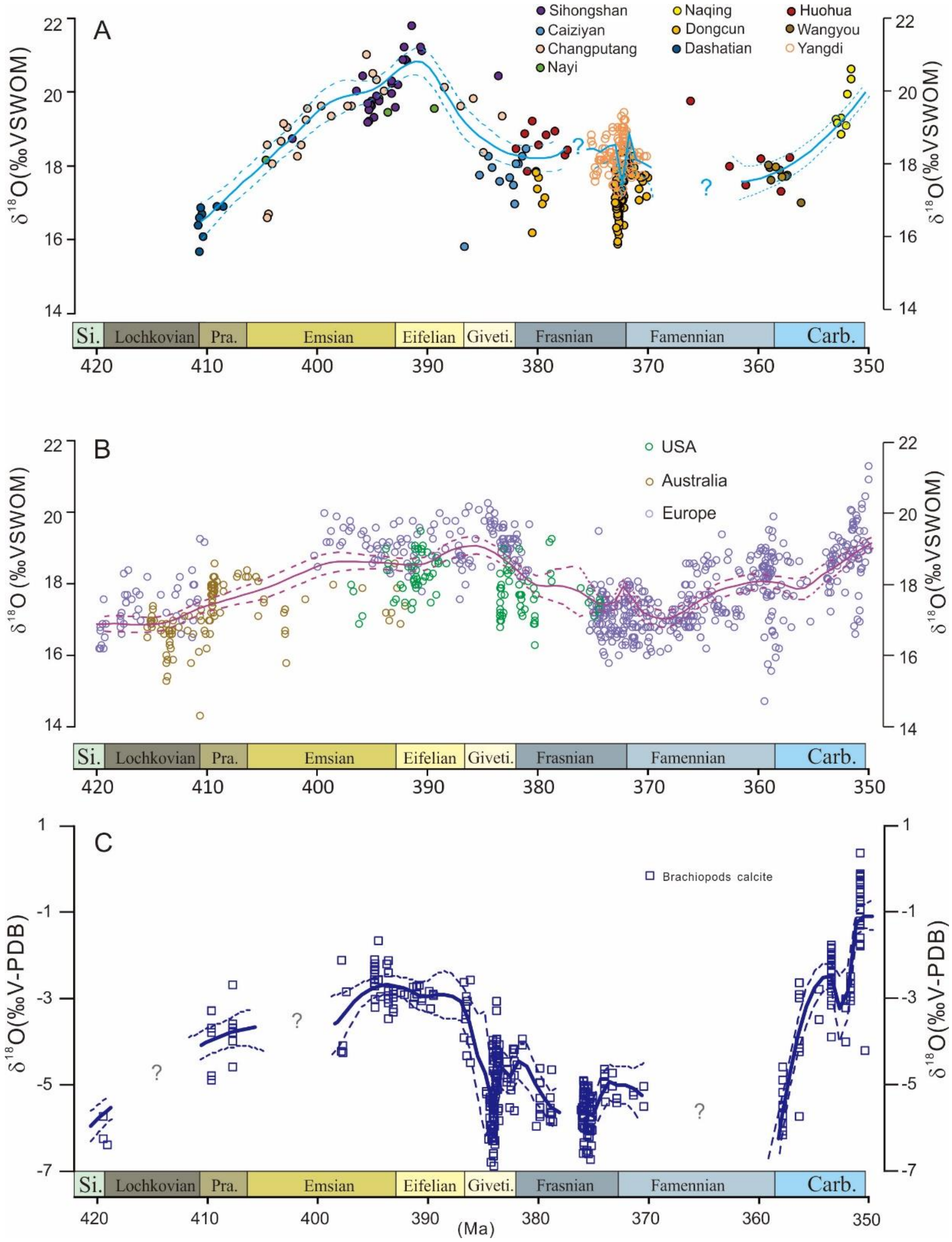

Fig. 3. South China conodont apatite $\delta^{18}O$ record (A) compared with published $\delta^{18}O_{apatite}$ (B) (Joachimski et al., 2009; Elrick et al., 2009; Girard et al., 2020) and brachiopod $\delta^{18}O_{calcite}$ records (C) (van Geldern et al., 2006). Solid lines represent Locfit regression, dotted lines give 95% confidence interval. All published data are recalibrated to Geological Timescale 2012 (Gradstein et al., 2012). Si = Silurian, Pra. = Pragian, Givet. = Givetian, Carb. = Carboniferous

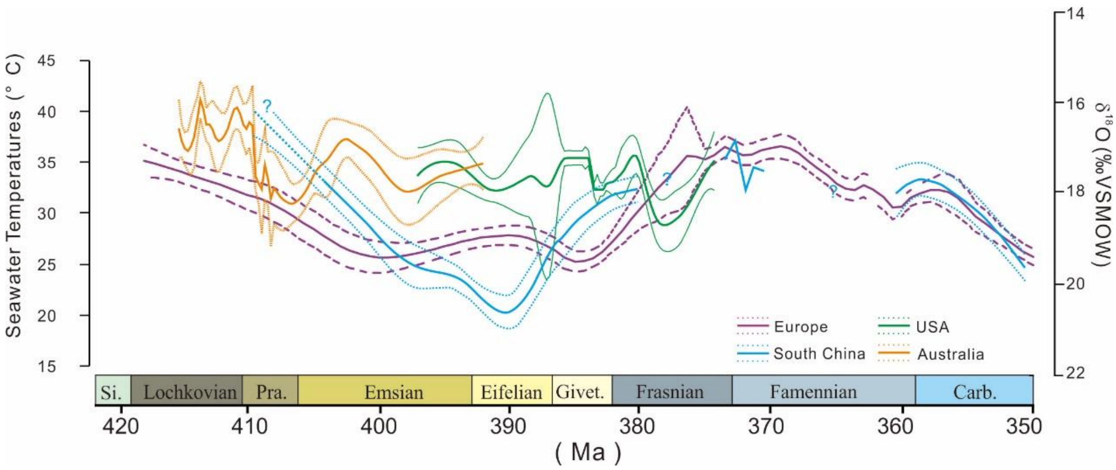

Fig. 4. Comparison of Devonian temperature records from different paleocontinents. Solid lines give Locfit regressions for samples from South China (data from the Dashatian section is excluded since δ^{18}O likely influenced by freshwater input), Europe, USA and Australia; dotted lines give 95% confidence interval. Temperature calculated using temperature equations given by Lécuyer et al. (2013) assuming an average oxygen isotope value for Devonian oceans of −1‰ VSMOW. Abbreviations as Fig. 3

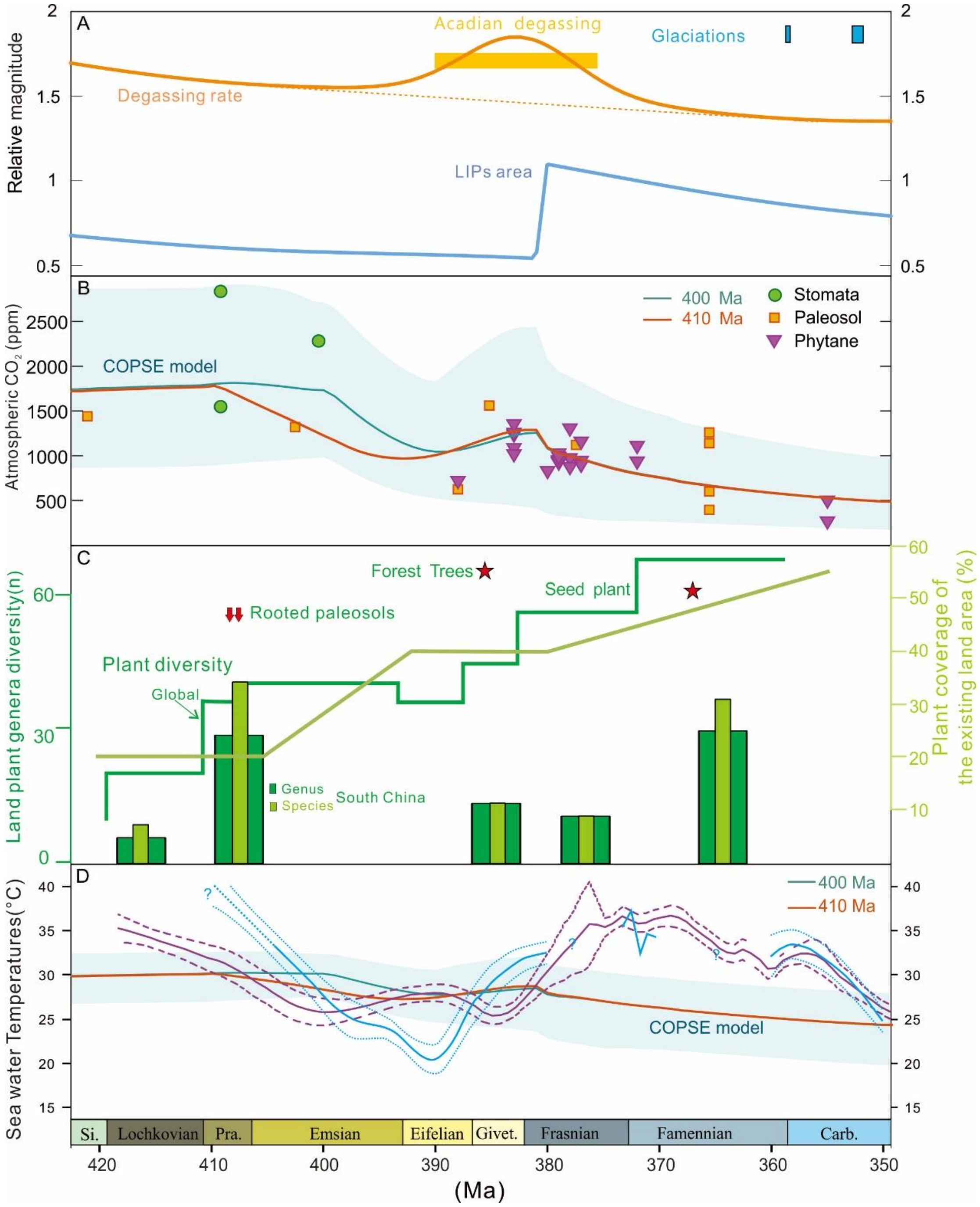

Fig. 5. Comparison of Devonian temperature records with significant events in terrestrial vascular plants, pCO_2, volcanism and glaciation records. (A) Global LIPs (and other mafic rock) area and tectonic CO_2 degassing rate (magnitude normalized to the present) used to compute the COPSE model (Mills et al., 2017; 2019), including degassing pulse due to Acadian orogenic activity (Stewart and Ague, 2018), and glaciation record (Caputo et al., 2008). (B) Proxy (Royer et al., 2014; Foster et al., 2017) and modelling (Lenton et al., 2018; Tostevin and Mills, 2020) reconstructions of atmospheric pCO_2 by assuming significant radiation of rooted terrestrial vegetation

started at ~410 or ~400 Ma. (C) Significant plants innovation events (Red Arrow and Pentacle, Stein et al., 2012; Matsunaga and Tomescu, 2016; Xue et al., 2016), mega plant fossil diversities (Green line, Global Plant fossil diversity, Cascales-Minana, 2016; and Histogram, Genus and Species level fossil diversity from South China, Xue et al., 2018) and terrestrial plant coverage in the existing land (Light green line, Simon et al., 2006) (D) Devonian low latitude temperature records (as Fig. 3) compared to low latitude temperatures modelled by COPSE. Abbreviations as Fig. 3.

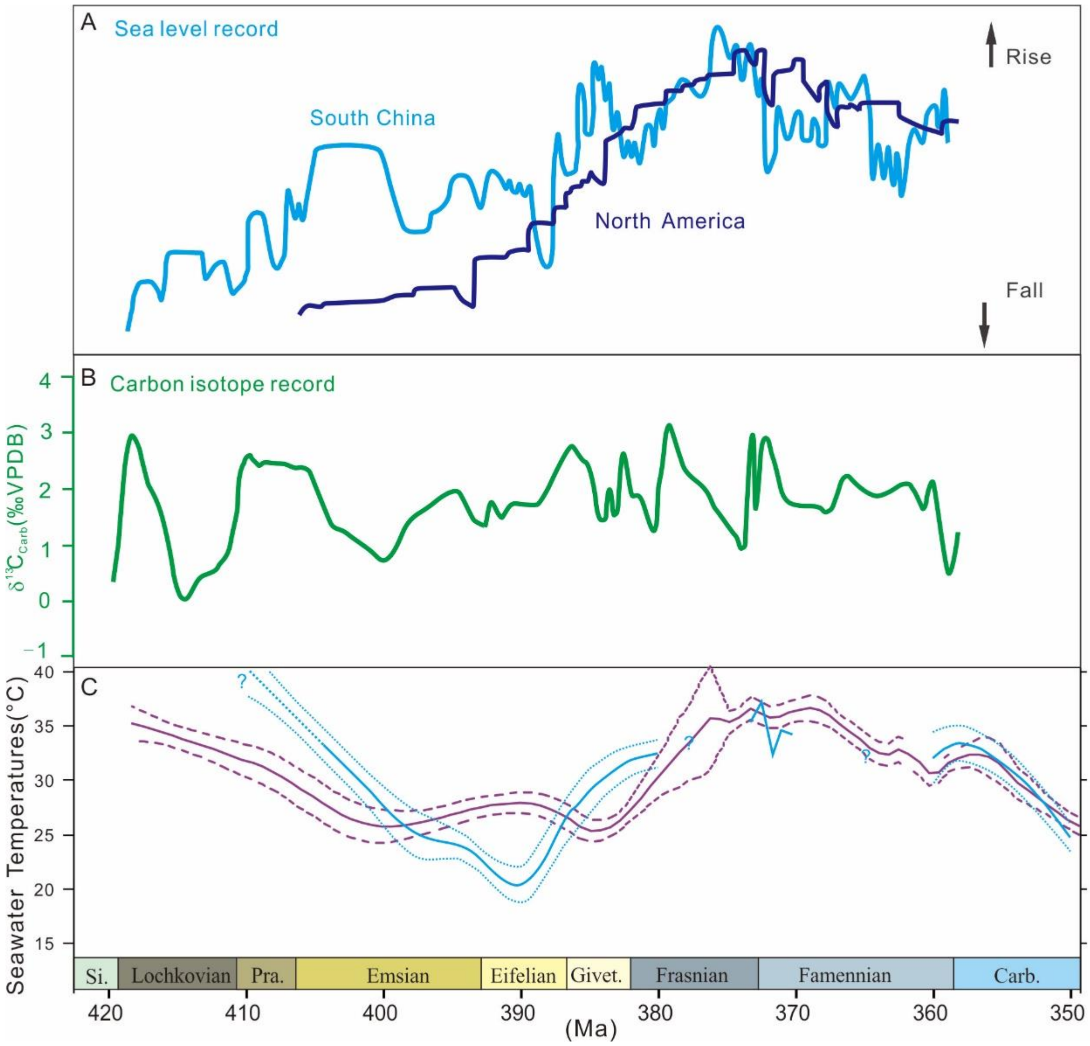

Fig. 6. Comparison of Devonian temperature records with sea level changes and carbonate $\delta^{13}C_{carb}$ record. (A). North America (Johnson et al., 1985) and South China (Ma et al., 2009) relative sea level change curves (B) $\delta^{13}C_{carb}$ record from whole rock carbonate (Buggisch and Joachimski, 2006), (C) Devonian temperature records (this study). Abbreviations as Fig. 3.