

1 **Was climatic cooling during the earliest Carboniferous driven**
2 **by expansion of seed plants?**

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31 Abstract

32 The expansion of land plants is considered to have played a key role in
33 triggering the Late Paleozoic Ice Age (LPIA), but evidence linking climatic
34 events to terrestrial floral changes is limited. Here, we generated bulk
35 carbonate $\delta^{13}\text{C}$ and conodont $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ profiles from the lowermost
36 Carboniferous of South China and Vietnam in order to investigate their
37 relationship to contemporaneous land plant evolution. Climatic cooling in the
38 mid-Tournaisian coincided with large perturbations to the global carbon
39 cycle and continental weathering regimes as well as with a major
40 diversification episode among seed plants. These relationships are consistent
41 with terrestrial floral changes triggering intensified weathering of basalts (i.e.,
42 lower $^{87}\text{Sr}/^{86}\text{Sr}$), enhanced marine productivity (i.e., higher $\delta^{13}\text{C}_{\text{carb}}$), and
43 reduced atmospheric $p\text{CO}_2$ and attendant global cooling (i.e., higher
44 conodont $\delta^{18}\text{O}$). The results of our study suggest that expansion of terrestrial
45 floras was a key driver of Early Carboniferous climate change.

46

47 *Keywords:* carbon cycle; strontium isotopes; oxygen isotopes; lignophyte; Late
48 Paleozoic Ice Age

49

50 1. Introduction

51 The earliest Carboniferous witnessed a critical climatic transition from a
52 middle Paleozoic 'greenhouse' to a Permo-Carboniferous 'icehouse'

53 (Buggisch et al., 2008; Mii et al., 1999; Qie et al., 2019). This transition was linked
54 to a globally pronounced positive carbonate carbon-isotope ($\delta^{13}\text{C}_{\text{carb}}$) shift in the
55 mid-Tournaisian (Saltzman, 2002) known as the TICE (‘mid-Tournaisian carbon
56 isotope excursion’, Yao et al., 2015). This shift has been interpreted as recording
57 a major organic carbon burial event (Saltzman et al., 2004) that triggered global
58 climatic cooling (Buggisch et al., 2008). Increased primary productivity (Liu et al.,
59 2019) and/or expanded marine anoxia (Cheng et al., 2020) are thought to have
60 played key roles in driving this organic carbon burial event, although the
61 mechanism(s) resulting in productivity and/or redox changes during the TICE are
62 still debated (e.g., Yao et al., 2015). One possibility is expansion of terrestrial floras
63 (Algeo et al., 1995), although the cause-and-effect linkage among specific bio-
64 evolutionary events and contemporaneous global climatic and environmental
65 changes remains unclear. Here, we present $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{apatite}}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ profiles
66 for the lowermost Carboniferous of South China and Vietnam that provide new
67 insight into how changes in global climate, carbon cycling, and seawater chemistry
68 were mechanistically linked to a mid-Tournaisian diversification episode among
69 arborescent lignophyte plants.

70

71 **2. Geological setting**

72 Whole-rock $\delta^{13}\text{C}_{\text{carb}}$ and conodont $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ records were generated
73 for five Tournaisian-age sections of the South China Craton, which was located
74 near the paleoequator in the eastern Paleotethys Ocean (Fig. 1). The Naqing

75 section (N 25° 14' 40", E 106° 29' 26"), which consists of thin-bedded lime
76 mudstones intercalated with intraclast-bearing bioclastic wackestones to
77 packstones deposited as turbidites and debris flows (Chen et al., 2018),
78 accumulated in a slope setting of the Qian-Gui carbonate platform. The
79 Malanbian section (N 27° 22' 47.4", E 111° 33' 56.8"), which consists of gray to
80 dark-gray, medium-to thick-bedded wackestones, packstones, and grainstones
81 with intercalated calcareous mudstone beds, was deposited in the interior of the
82 Yangtze carbonate platform (Yao et al., 2015). The Qilinzhai section (N 25° 49' 04",
83 E 107° 29' 26"), which consists of mixed carbonates and siliciclastics, was
84 deposited in a restricted or open mixed carbonate–siliciclastic platform setting of
85 the Qian-Gui Platform (Qie et al., 2016). The Wangyou section (N 25° 49' 1.58", E
86 106° 30' 21.90"), which consists of dolomite, marls, and nodular limestones
87 containing a pelagic fauna, represents a slope to deep water setting within
88 Youjiang Basin. The Cat Co 3 beach section (N 20° 42' 58.0", E 107° 02' 54.8"), on
89 Cat Ba Island, Hai Phong Province, Vietnam, consists of micritic limestones
90 interbedded with organic-rich, black, friable limestones (Komatsu et al., 2014). It
91 is one of the few sections on the South China Craton that records continuous
92 deposition across the Devonian–Carboniferous boundary (Komatsu et al., 2014).
93 Detailed biostratigraphic data, age calibrations, and tie-points for correlation of
94 the study sections are given in Figure 2 and the Supplementary file within an
95 absolute age framework based on Gradstein et al. (2020) and Waters et al. (2011).
96

97

98 **3. Methods**

99 **Bulk-rock carbonate isotopes**

100 Calcite powders were drilled from freshly cut rock slab surfaces for carbon
101 isotopes analysis. Powders were reacted with 100% phosphoric acid at 70°C and
102 analyzed for carbon isotopes using a Kiel IV device connected to a Finnigan MAT
103 253 mass spectrometer at the Nanjing Institute of Geology and Paleontology,
104 Chinese Academy of Sciences (NIGPAS). Reproducibility was better than $\pm 0.03\text{‰}$
105 (1 SD) for carbon isotopes. All analyses were calibrated to the Chinese National
106 Standard (GBW-04405), which is an Ordovician carbonate from a site near Beijing,
107 with a $\delta^{13}\text{C}$ value of $+0.57\text{‰}$ and $\delta^{18}\text{O}$ value of -8.49‰ . All data are reported in
108 per mille (‰) relative to the VPDB scale.

109

110 **Oxygen isotopes of conodont apatite**

111 About 0.5–1.0 mg of conodont apatite was weighed and chemically converted
112 to Ag_3PO_4 following the method of [Joachimski et al. \(2009\)](#). The obtained Ag_3PO_4
113 measured using a high-temperature elemental analyzer coupled online to a
114 Thermo Delta V Plus mass spectrometer at NIGPAS, all oxygen isotope values are
115 reported in ‰ relative to VSMOW. The average oxygen isotopic composition of
116 NBS120c was measured as $+21.7\text{‰}$ (VSMOW). Accuracy was monitored by
117 replicate analyses of NBS120c. Reproducibility was calculated based on triplicate
118 samples and standards analyses and was better than $\pm 0.25\text{‰}$ (1 SD).

119

120 **Strontium isotopes of conodont apatite**

121 For strontium isotope analyses, about 0.1-0.3 mg conodont were picked and
122 ultrasonically washed three times using Milli-Q water. Then the samples were
123 subsequently immersed in 0.5 M acetic acid for 8 hours to remove potential
124 surface contamination. The residues were dissolved in distilled 7 N HNO₃ for about
125 12 hours at 150 C°, followed by separation of Sr using 0.1 ml Eichrom Sr Spec
126 resin. For ⁸⁷Sr/⁸⁶Sr analysis, a subset of Naqing samples was measured using
127 Finnigan Triton Thermal Ionization Mass Spectrometer at the Universität
128 Erlangen-Nürnberg, Germany. The remaining Naqing and all Wangyou samples
129 were measured on a Nu Plasma HR (Nu032) multi-collector inductively coupled
130 plasma-mass spectrometer (MC-ICPMS) at the University of California-Davis
131 (USA). The Malanbian, Qilinzhai, and Cat Co samples were measured using a Nu
132 Plasma II MC-ICP-MS at Nanjing FocuMS Technology Co. Ltd. The measured
133 ⁸⁷Sr/⁸⁶Sr values were corrected for interference of ⁸⁷Rb and for instrumental mass
134 fractionation assuming an ⁸⁶Sr/⁸⁸Sr value of 0.1194. Repeated analysis of the NIST
135 987 standard alongside with the samples yield a mean value of 0.710272 (2SD =
136 0.000025, n = 15), 0.710240 (2SD = 0.000010, n = 17), and 0.710251 (2SD =
137 0.000026, n = 44), at Erlangen, Nanjing, Davis, respectively. All data were
138 normalized to a NIST 987 value of 0.710248 (McArthur et al., 2012), the corrected
139 EN-1 standard processed along with the samples analyzed in Erlangen yielded a
140 value of 0.709183, which is close to its reported value of 0.709174 (McArthur et
141 al., 2012).

142 **Seed plant diversity database**

143 The compilation is mainly based on data from Cascales-Miñana et al. (2016)
144 and the Paleobiology Database (PBDB), with lesser amounts of data from new
145 publications (see Supplementary file table 1 for details). In this database, seed

146 plant fossils are assigned to two groups: (1) fossil genera that can definitely be
147 diagnosed as seed plants; and (2) some foliage genera such as *Sphenopteris* and
148 *Adiantites* in which at least one species is assigned to seed plants according to
149 [Boyce \(2005\)](#) and [Taylor et al. \(2009\)](#). Owing to lack of greater precision in the age
150 designations for plant fossils in the original references, age control for most of the
151 fossil taxa is possible only to the stage level, and some fossil taxa with problematic
152 stratigraphic assignments (denoted by question marks in Supplementary file table
153 1) were excluded from our calculations.

154

155 4. Results

156 Geochemical results are presented in Figures 2 and 3 and Supplementary
157 Table 2. In the Naqing section, the $\delta^{13}\text{C}_{\text{carb}}$ profile shows values varying between
158 +1 and +2 ‰ (VPDB) in the uppermost Famennian, then increasing from +3 ‰
159 to +5 ‰ in the upper *Siphonodella crenulata*-*S. isosticha* zones, followed by a
160 gradual decrease to +2 ‰ in the upper *Gnathodus typicus* Zone, and finally rising
161 again to +4.5 ‰ in the *Scaliognathus anchoralis* Zone. The $\delta^{18}\text{O}_{\text{apatite}}$ record from
162 the Naqing section shows a 1.5 ‰ increase from +19 ‰ to +20.5 ‰ (VSMOW)
163 from the upper *S. crenulata*-*S. isosticha* zones to the lower *G. typicus* Zone,
164 followed by a further increase from +20.5 ‰ to +22 ‰ in the late Tournaisian *Sc.*
165 *anchoralis* Zone (Fig. 2). The $^{87}\text{Sr}/^{86}\text{Sr}$ profile exhibits a decrease from 0.7082 to
166 0.7080 starting in the Lower *S. crenulata* Zone, followed by relatively stable values
167 (0.7080) in the Lower *G. typicus* Zone, varying values (0.7080-0.7082) in the upper

168 *G. typicus* Zone, and a further decline to 0.7078 in the *S. anchoralis* Zone (Fig. 2).

169 In the Malanbian section, the $\delta^{13}\text{C}_{\text{carb}}$ profile exhibits an excursion from -0.6
170 to $+3.3$ ‰ in the upper Famennian, followed by a gradual decrease to ~ 0 ‰ in
171 the lower Upper *Si. crenulata*-*Si. isosticha* zones, an increase to $+6$ ‰ in the mid-
172 upper *Si. crenulata*-*Si. isosticha* zones, another decrease to $+1$ ‰ in the upper
173 Upper *Si. crenulata*-*Si. isosticha* zones, and finally relatively stable values around
174 $+1$ ‰ in the *Gnathodus typicus* Zone. The $\delta^{18}\text{O}_{\text{apatite}}$ profile exhibits values around
175 $+18$ ‰ at the top of the *Protognathodus kockeli*-Lower *Siphonodella crenulata*
176 zones, and two isolated data points in the *Si. crenulata*-*Si. isosticha* zones also
177 yield values of $\sim +18$ ‰. The Sr isotope profile shows values around 0.7082 in the
178 upper *Protognathodus kockeli*-Lower *Siphonodella crenulata* zones and the lower
179 *Si. crenulata*-*Si. isosticha* zones, followed by a decrease to 0.7079 in the
180 *Gnathodus typicus* Zone (Fig. 2).

181 In the Qilinzhai section, the $\delta^{13}\text{C}_{\text{carb}}$ profile exhibits relatively high values
182 around $+4$ ‰ in the upper Famennian *Palmatolepis gracilis expansa*-*Bispathodus*
183 *ultimus* zones, which contain the Hangenberg carbon isotope excursion (Qie et
184 al., 2016), followed by a gradual decrease to ~ 0 ‰ in the lower *Siphonodella*
185 *sinensis* Zone, a large increase to $\sim +5$ ‰ in the upper *Siphonodella sinensis* Zone,
186 and finally a decline to $\sim +3$ ‰ in the *Polygnathus communis porcatus* Zone. The
187 $^{87}\text{Sr}/^{86}\text{Sr}$ profile exhibits relatively stable values around 0.7082 from the
188 *Siphonodella homosimplex* Zone to the lower *Siphonodella eurylobata* Zone,
189 followed by varying values of 0.7081-0.7083 in the *Polygnathus communis*

190 *porcatus* Zone (Fig. 2).

191 In the Wangyou section, the $\delta^{13}\text{C}_{\text{carb}}$ profile exhibits a decrease from +2 ‰ in
192 the upper Famennian *Palmatolepis gracilis expansa*-*Bispathodus ultimus* zones to
193 -1 ‰ at the D-C Boundary, followed by a rise to +2 ‰ in the lower
194 *Protognathodus kockeli*-Lower *Siphonodella crenulata* zones. The $\delta^{18}\text{O}_{\text{apatite}}$ profile
195 shows values around +18 ‰ in the *Protognathodus kockeli*-lower *Siphonodella*
196 *crenulata* zones, whereas in the same interval, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exhibit a gradual
197 decrease from 0.7084 to 0.7082.

198 In the Cat Co 3 beach section, the $\delta^{13}\text{C}_{\text{carb}}$ profile exhibits varying values around
199 +2 ‰ across the D-C boundary. The Hangenberg carbon isotope excursion is not
200 well defined in this section, possibly owing to its condensed nature ([Paschall et al.,](#)
201 [2019](#)). The $^{87}\text{Sr}/^{86}\text{Sr}$ profile shows an increase from 0.7082 in the upper Famennian
202 *Palmatolepis gracilis expansa*-*Bispathodus ultimus* zones to 0.7082 in the lower
203 Tournaisian *Protognathodus kockeli*-Lower *Siphonodella crenulata* zones (Fig. 2).

204 The composite $\delta^{13}\text{C}_{\text{carb}}$ profile shows values of \sim +2 ‰ around the D-C
205 boundary (359.3 Ma), followed by a decrease to 0 ‰ at ca. 355 Ma, a rise to a
206 maximum of \sim +6 ‰ at 353.5 Ma, a decrease to \sim +2 ‰ at 351 Ma, and another
207 rise to \sim +4.5 ‰ at 347 Ma. The $\delta^{18}\text{O}_{\text{apatite}}$ profile is relatively stable around +18 ‰
208 from 359.3 Ma to ca. 355 Ma, followed by an increase to +20.5 ‰ at 350 Ma, with
209 values remaining relatively constant (\sim +20.5 ‰) from 350 to 348 Ma, and a
210 subsequent increase to +22.0 ‰ after 348 Ma (Fig. 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain
211 steady at 0.7082 from 359.3 to 355 Ma, followed by a decrease to 0.7080 at 353

212 Ma (Fig. 3), with ratios remaining relatively stable (0.7080) up to 351 Ma, with a
213 further decrease to 0.7078 after 351 Ma.

214 The seed plant diversity database compilation shows genus-level diversity of
215 seed plants increased from 37 taxa in the Famennian to 69 taxa in the Tournaisian
216 (or an increase from 31 to 62 taxa if limited to type 1) (Fig. 4). This increase may
217 represent a major diversification event in the early stages of seed plant evolution,
218 since seed plant diversity during the Visean and Serpukhovian did not increase
219 relative to that of the Tournaisian (Fig. 4). Furthermore, seed plants like those
220 reported from low-latitude areas (e.g., Laurussia) are first found in higher-latitude
221 areas (e.g., Argentina) during the Tournaisian (Fig. 4; [Prestianni et al., 2015](#)).

222

223 **5. Discussion**

224 **5.1 Evaluation of diagenetic influences**

225 The carbon isotope composition of bulk carbonate potentially can be
226 overprinted by interaction with diagenetic fluids, and this effect has to be
227 evaluated before interpreting $\delta^{13}\text{C}_{\text{carb}}$ data as a record of a primary seawater signal.
228 Carbon isotope results from the Naqing section show only minor scatter, which
229 may have resulted from limited diagenetic alteration during partial chertification.
230 Overall, the profile is inferred to preserve a near-primary marine $\delta^{13}\text{C}_{\text{carb}}$ record.
231 The Naqing section is a slope succession that does not show any sedimentological
232 evidence of subaerial exposure, and an early diagenetic overprint by meteoric
233 water is thus unlikely. This inference is supported by the lack of significant positive

234 covariation between C and O isotopes at Naqing ($r = +0.33$, $p(a) < 0.001$, $n =$
235 185) (Fig. x). Similarly, C and O isotopes at Malanbian also show only weak
236 covariation ($r = +0.18$, $p(a) < 0.05$, $n = 176$) (Fig. x), even though the section was
237 deposited in a shallow-marine setting and contains a number of organic-rich
238 calcareous mudstone layers (Yao et al., 2015) that have a higher potential for
239 resetting of $\delta^{13}\text{C}_{\text{carb}}$ by meteoric waters or secondary oxidation of organic matter.
240 Importantly, the $\delta^{13}\text{C}_{\text{carb}}$ profiles of both sections exhibit a mid-Tournaisian positive
241 excursion similar to that seen in coeval sections globally (Bruckschen et al., 1999;
242 Buggisch et al., 2008; Mii et al., 1999; Saltzman et al., 2004), indicating no major
243 overprints by local or regional diagenetic processes.

244 The oxygen isotopic composition of conodont apatite is known to be relatively
245 resistant to diagenetic alteration (Joachimski et al., 2009), although it can still
246 potentially be modified by microbiological activity mediated by enzymes (Zazzo
247 et al., 2004) or by diagenetic fluids at high temperatures (Puc at et al., 2004).
248 There is no robust method at present to identify post-depositional exchange of
249 oxygen isotopes in biogenic apatite (Buggisch et al., 2008; Joachimski et al., 2009),
250 but similar absolute $\delta^{18}\text{O}_{\text{apatite}}$ values and/or trends in coeval sections globally can
251 be considered as evidence of preservation of primary $\delta^{18}\text{O}$ signals (Joachimski et
252 al., 2009). The $\delta^{18}\text{O}_{\text{apatite}}$ values measured in the study sections are similar to values
253 reported from coeval North American and European sections (Buggisch et al.,
254 2008) (Fig. 5), suggesting that they retain a primary seawater oxygen isotope
255 signal.

256 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured from conodont apatite in this study are generally
257 in agreement with contemporaneous brachiopod calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported
258 from European and North American sections (Fig. 3), suggesting that these
259 samples largely preserve a primary seawater signal. However, a few samples from
260 the upper parts of the Naqing and Qinlinzhan sections yielded distinctly high
261 $^{87}\text{Sr}/^{86}\text{Sr}$ outliers. These relatively radiogenic values may reflect minor siliciclastic
262 contamination, since they are found within the intervals in which siliciclastic
263 sediments are dominant. This is comparable to the lower Tournaisian conodont
264 specimens analyzed by Kürschner et al. (1993), which yielded slightly elevated
265 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7084 vs 0.7082) due to minor contamination by radiogenic Sr (Fig.
266 4). In the present study, immersion of conodont specimens in 0.5 M acetic acid
267 for 8 hours was used to minimize this form of contamination.

268

269 **5.2 Was climatic cooling during the earliest Carboniferous driven by** 270 **expansion of seed plants?**

271 The globally recognized TICE (Saltzman et al., 2004) was one of the largest
272 perturbations to the global carbon cycle of the entire Phanerozoic (Saltzman,
273 2005), but the cause of this $\delta^{13}\text{C}_{\text{carb}}$ excursion remains uncertain. The leading
274 hypothesis is elevated marine productivity due to an increased nutrient supply,
275 possibly caused by intensified oceanic circulation and upwelling associated with
276 climatic cooling (Liu et al., 2019) or by increased subaerial silicate weathering (Yao
277 et al., 2015), with a concurrent expansion of global-ocean anoxia enhancing

278 organic matter burial (Cheng et al., 2020). However, climatic cooling (as indicated
279 by rising $\delta^{18}\text{O}_{\text{apatite}}$) coincided with the onset of the secular rise in $\delta^{13}\text{C}_{\text{carb}}$ (Buggisch
280 et al., 2008), suggesting that cooling was a consequence rather than a cause of
281 the carbon-cycle perturbation.

282 Changes in global continental weathering can be evaluated based on
283 seawater $^{87}\text{Sr}/^{86}\text{Sr}$ records. Whereas previous studies reported a gradual decrease
284 in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the earliest Tournaisian (359.3 Ma) (McArthur et al.,
285 2012), our new record shows an initial decline in the mid-Tournaisian (~355 Ma)
286 from an earliest Carboniferous baseline of 0.7082 to 0.7080 (Fig. 5). Lower
287 seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are commonly interpreted as due to either reduced
288 siliciclastic weathering (i.e., reduced flux and/or average isotopic composition of
289 continental Sr) or an increased flux of non-radiogenic Sr related to hydrothermal
290 circulation at mid-ocean ridges or weathering of mantle-derived mafic rocks. The
291 mid-Tournaisian decrease in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios was closely followed by a
292 significant positive shift in $\delta^{13}\text{C}_{\text{carb}}$ and a gradual decline in $\delta^{18}\text{O}_{\text{apatite}}$. These
293 relationships constrain the range of scenarios for contemporaneous global
294 changes. Lower continental weathering fluxes (e.g., due to waning of the Acadian
295 Orogeny (Bruckschen et al., 1999)) would normally imply a reduction in CO_2
296 consumption and nutrient supply to the oceans, but this is inconsistent with
297 increased organic carbon burial (i.e., higher $\delta^{13}\text{C}$) coupled with climatic cooling (i.e.,
298 higher $\delta^{18}\text{O}_{\text{apatite}}$) linked to falling $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 5). A mid-ocean ridge hydrothermal
299 mechanism is also less likely given the slow timescales of tectonic changes (>10

300 Myr) ([Bruckschen et al., 1999](#)). Rather, the gradual shift in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ to
301 lower values in the mid-Tournaisian (Fig. 5) may signal enhanced weathering of
302 ^{87}Sr -poor silicate rocks (e.g., young basalts). An increase in the total surface
303 exposure of young basalts available for weathering may have been triggered by
304 arc-continent collision or large igneous province emplacement during the mid-
305 Tournaisian ([Swanson-Hysell and Macdonald, 2017](#); [Young et al., 2009](#)). Increased
306 weathering of basalt would have enhanced the consumption of atmospheric CO_2
307 ([Dessert et al., 2003](#)) as well as increased riverine nutrient inputs to the oceans,
308 stimulating primary productivity and enhancing organic carbon burial, with
309 climatic cooling as a further consequence. Similar mechanisms have been
310 proposed for the onset of the Sturtian Ice Age (720 Ma) in the Neoproterozoic
311 ([Cox et al., 2016](#)) and the Late Ordovician Ice Age (465-455 Ma) ([Young et al.,](#)
312 [2009](#); [Swanson-Hysell and Macdonald, 2017](#)) as well as for a period of extremely
313 low $p\text{CO}_2$ during the first 10 Myr of the Early Permian, coincident with the apex of
314 LPIA glaciation ([Richey et al., 2020](#)). However, the mid-Tournaisian is not an
315 interval of known major arc-continent collision or volcanic activity ([Ernst and](#)
316 [Youbi, 2017](#); [Macdonald et al., 2019](#)).

317 An alternative hypothesis is that mid-Tournaisian global events were
318 triggered by an expansion of terrestrial floras (Fig. 5) (cf. [Algeo et al., 1995](#)). Plants
319 acquire essential nutrients for growth from their mineral substrate, causing
320 intensified chemical and physical weathering. For example, trees yield Ca
321 weathering fluxes $\sim 5\text{--}30\times$ higher than rootless non-vascular plants ([Quirk et al.,](#)

322 [2015](#)), and seed plants and their associated mycorrhizal fungi cause an even larger
323 weathering amplification of phosphorus compared to calcium ([Lenton et al., 2012](#);
324 [Lenton et al., 2016](#); [Quirk et al., 2015](#)) A major expansion of areal coverage of
325 seed-plant floras along with development of deeper root systems would have
326 considerably accelerated silicate weathering, especially of basaltic rocks ([Lenton
327 et al., 2012](#); [Lenton et al., 2016](#); [Quirk et al., 2015](#)), releasing large amounts of
328 nutrients such as phosphorus ([Berner, 2003](#); [Lenton et al., 2012](#)). This process
329 accelerated drawdown of atmosphere CO₂ via a combination of enhanced
330 pedogenic weathering of silicates, elevated marine primary productivity, and
331 sequestration of organic carbon in terrestrial plant biomass ([Berner, 2003](#)). These
332 effects ultimately triggered global climatic cooling as evidenced by increasing
333 $\delta^{18}\text{O}_{\text{apatite}}$ values and glacial sedimentary deposits in both low- and high-latitude
334 areas ([Caputo and dos Santos, 2019](#); [Kammer and Matchen, 2008](#)).

335 Although the terrestrial floral record is far from complete, our data
336 compilation shows that Tournaisian seed-plant floras underwent a major
337 diversification (from 37 genera in the Famennian to 69 genera in the Tournaisian)
338 along with an expansion of habitats into high-latitude areas (Fig. 4). These events
339 were accompanied by major evolutionary changes among arborescent
340 lignophytes, yielding higher seed plants with true leaves, larger sizes, and deeper
341 root systems that were capable of occupying drier areas ([Cascales-Miñana, 2016](#);
342 [Decombeix et al., 2011a](#))(Fig. 4). Arborescent lignophytes experienced a turnover
343 accompanied by an increase in taxonomic diversity during the mid-Tournaisian,

344 with new taxa having more distinctive phenotypes than the dominant late
345 Devonian tree genus, *Archaeopteris* (Decombeix et al., 2011a) (Fig. 4). This event,
346 which dates to the late Hastarian and Ivorian stages (355-347 Ma), may record a
347 major episode of diversification and expansion of seed plants into drier habitats
348 and high-latitude areas that were previously sparsely vegetated or completely
349 lacking in floral cover (Decombeix et al., 2011b; Fairon-Demaret, 2004; Prestianni
350 et al., 2010; Prestianni et al., 2015).

351 Although secular changes in terrestrial floral biomass are difficult to
352 reconstruct, taxonomic diversity is a reasonable proxy for plant abundance,
353 especially during the early stages of terrestrialization as land plants expanded into
354 previously unoccupied habitats (Decombeix et al., 2011b; Fairon-Demaret, 2004;
355 Prestianni et al., 2010; Prestianni et al., 2015). Although the relationship between
356 floral biomass and taxonomic diversity eventually broke down as land plants
357 achieved a global distribution, coupling between these records has been inferred
358 for the Devonian (Algeo et al., 1995) and is likely to have persisted into the Early
359 Carboniferous as seed plants expanded into upland areas of continents (Clea and
360 Thomas, 2005). Each episode of floral expansion triggered increases in CO₂
361 utilization and chemical weathering (Lenton, 2001; Van Cappellen and Ingall, 1996)
362 that terminated only when the area of floral cover and soil development stabilized
363 at a new equilibrium (Lenton, 2001). In the marine environment, intervals of
364 terrestrial stabilization were expressed as a return to lower $\delta^{13}\text{C}_{\text{carb}}$ (owing to
365 reduced riverine nutrient fluxes and marine primary productivity levels) and

366 invariant $\delta^{18}\text{O}_{\text{apatite}}$ (reflecting permanently cooler conditions) and seawater $^{87}\text{Sr}/^{86}\text{Sr}$
367 (reflecting the long residence time of Sr in seawater, ~2-5 Myr).

368

369 **6. Conclusions**

370 Multi-proxy geochemical analysis of Lower Carboniferous sections in South
371 China and Vietnam demonstrates decreases in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios followed
372 by large positive excursion in $\delta^{13}\text{C}_{\text{carb}}$ and an inflection in $\delta^{18}\text{O}_{\text{apatite}}$ during the mid-
373 Tournaisian. These events coincided with a turnover among and an increase in
374 diversity of arborescent lignophyte plants, suggesting that the latter were a
375 primary driver of contemporaneous global changes. A rapid expansion of seed
376 plants into drier (e.g., upland) habitats (1) accelerated silicate weathering,
377 especially of basaltic rocks (accounting for lower seawater $^{87}\text{Sr}/^{86}\text{Sr}$), (2) enhanced
378 nutrient fluxes to the ocean, promoting marine primary productivity and organic
379 carbon burial (accounting for higher $\delta^{13}\text{C}_{\text{carb}}$), and (3) triggered climatic cooling
380 (accounting for higher $\delta^{18}\text{O}_{\text{apatite}}$). Although the terrestrial floral record remains
381 incomplete and subject to re-interpretation, this study serves to highlight likely
382 important relationships between land plant evolution and marine biogeochemical
383 cycles at the onset of the Late Paleozoic Ice Age.

384

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407 [tectonics-in-deep-time-series/360-ma-moll_dev_gpt-min-2/](https://deeptimemaps.com/global-paleogeography-and-tectonics-in-deep-time-series/360-ma-moll_dev_gpt-min-2/)
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540

541 **Figure captions**

542

543 **Fig. 1.** Paleogeographic reconstruction showing locations of South China (A) (after
544 [Blakey, 2013](#)) and study sections in South China Craton (B) (after [Feng et al., 1998](#)).

545

546 **Fig. 2.** Biostratigraphic correlations, $\delta^{13}\text{C}_{\text{carb}}$ (blue circles), $\delta^{18}\text{O}_{\text{apatite}}$ (purple squares),
547 and $^{87}\text{Sr}/^{86}\text{Sr}$ (orange diamonds) for the study sections ($\delta^{13}\text{C}_{\text{carb}}$ for Qilinzhai and Cat
548 Co 3 from ([Paschall et al., 2019](#); [Qie et al., 2016](#)), respectively). Solid lines represent
549 locally weighted scatterplot smoothing (LOESS, 0.2 smoothing) regressions with
550 2.5 % and 97.5 % bootstrapped errors (dotted lines). Conodont biozonation based
551 on ([Becker et al., 2016](#); [Corradini et al., 2017](#); [Lane et al., 1980](#)).

552

553 **Fig. 3.** Integrated $\delta^{13}\text{C}_{\text{carb}}$ records of the study sections and conodont apatite
554 $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ data compared to correlative Euro-American sections for the
555 Tournaisian. Conodont biozonation (C. Z.) as in Fig. 2, D. = Devonian. W.E. =
556 Western Europe, Fam. = Famennian, Vi. = Viséan, Mo. = Moliniacian.

557

558 **Fig. 4.** Genus-level diversity (A) and geographic distribution (B) of seed plants
559 during the late Devonian and early Carboniferous. Paleogeographic map from
560 ([Blakey, 2013](#)).

561

562

563 **Fig. 5.** Integrated $\delta^{13}\text{C}_{\text{carb}}$ and conodont apatite $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}_{\text{apatite}}$ profiles for
564 the Tournaisian. Solid lines represent LOESS smoothing (0.2), with 2.5 % and 97.5 %
565 bootstrapped errors (gray shade). Also shown are changes in arborescent
566 lignophyte communities ([Decombeix et al., 2011a](#)). Conodont biozonation as in
567 Fig. 2, and abbreviations as in Fig. 3.

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