

1 Climate warming, euxinia and carbon isotope perturbations
2 during the Carnian (Triassic) Crisis in South China

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21 **Abstract**

22 The Carnian Humid Episode (CHE), also known as the Carnian Pluvial Event, and associated
23 biotic changes are major enigmas of the Mesozoic record in western Tethys. We show that the
24 CHE also occurred in eastern Tethys (South China), suggestive of a much more widespread and
25 probably global climate perturbation. Oxygen isotope records from conodont apatite indicate a
26 double-pulse warming event. The CHE coincided precisely with an initial warming of 4°C. This
27 was followed by a transient cooling period and then a prolonged ~7°C warming in the later Carnian
28 (Tuvalian 2). Carbon isotope perturbations associated with the CHE of western Tethys occurred
29 contemporaneously in South China, and mark the start of a prolonged period of carbon cycle
30 instability that persisted until the late Carnian. The dry-wet transition during the CHE coincides
31 precisely with the negative carbon isotope excursion and the temperature rise, pointing to an
32 intensification of hydrologic cycle activities due to climatic warming. While carbonate platform
33 shutdown in western Tethys is associated with an influx of siliciclastic sediment, the eastern
34 Tethyan carbonate platforms are overlain by deep-water anoxic facies. The transition from
35 oxygenated to euxinic facies was via a condensed, manganiferous carbonate (MnO content up to
36 15.1 wt%), that records an intense Mn shuttle operating in the basin. Significant siliciclastic influx
37 in South China only occurred after the CHE climatic changes and was probably due to foreland
38 basin development at the onset of the Indosinian Orogeny. The mid-Carnian biotic crisis thus
39 coincided with several phenomena associated with major extinction events: a carbonate production
40 crisis, climate warming, $\delta^{13}\text{C}$ oscillations, marine anoxia, biotic turnover and flood basalt eruptions
41 (of the Wrangellia Province).

42 **Key words:** Carnian Humid Episode, carbon isotopes, marine anoxia, climate warming,
43 Wrangellia flood basalt, large igneous provinces

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45 **1. Introduction**

46 Environmental and biotic changes during the Carnian Stage (~237-227 Ma) of the Triassic
47 are amongst the most enigmatic of the geological record (Simms and Ruffell, 1989; Ogg, 2015).
48 Prominent amongst these was the Carnian Humid Episode (CHE, after Ruffel et al., 2015, but also
49 known as Carnian Pluvial Event or Carnian Pluvial Phase), a short-lived phase (<1 Myr, Zhang et
50 al., 2015) of increased rainfall. The CHE has been attributed to an intensification of a mega-
51 monsoonal climate (Parrish, 1993; Kozur and Bachmann, 2010), although climate change driven
52 by voluminous volcanism and greenhouse gas exhalation has also been suggested (Dal Corso et
53 al., 2012). A contemporaneous major increase in siliciclastic influx to marine areas has been
54 implicated in the shutdown of carbonate platforms and the demise of reef ecosystems in western
55 Tethys and the peri-Gondwana margin (e.g., Hornung et al., 2007a). The CHE also coincided with
56 extinctions amongst crinoids and scallops, while nekton such as ammonoids and conodonts also
57 suffered losses (Simms and Ruffell, 1989; Rigo et al., 2007), suggesting a broad-reaching marine
58 crisis. Terrestrial floras record a shift towards hygrophytic forms in the late Julian substage (early
59 Carnian, ~237-233 Ma) before returning to xerophytic associations by the early Tuvanian substage
60 (late Carnian, ~233-227 Ma) (Roghi et al., 2010, Mueller et al., 2016); a change that may have
61 been responsible for elevated extinction rates reported amongst herbivorous tetrapods (Benton,
62 1986).

63 Despite the magnitude of the changes, the majority of evidence for the Carnian Crisis has
64 come from western Europe (Fig. 1) and major questions remain as to the global significance and
65 cause(s) of this event. We evaluate the global extent of the CHE and associated environmental
66 changes by investigating palaeotemperature, $\delta^{13}\text{C}$, sedimentary facies and redox changes in South
67 China, a region far removed (~13,000 km distant) from the better-studied western Tethyan

68 locations. Our results indicate that the environmental changes in the Carnian were truly global and
69 associated with a carbonate production crisis, double-pulse climate warming, intense oceanic
70 anoxia and large $\delta^{13}\text{C}$ oscillations associated with flood basalt eruptions.

71 **2. Geological setting**

72 The studied section at Long Chang (25°26.565'N, 105°28.791'E) outcrops in a road cut ~2
73 km south of the town of Long Chang (Figs. 2 and 3). In comparison to the well-known section of
74 Enos et al. (1998) in the nearby area (Fig. 2C), our section is more condensed and has been chosen
75 for its excellent outcrop situation and ease of access. The Long Chang area was located in a
76 transitional zone between the Yangtze Platform and Nanpanjiang Basin in eastern Tethys at ~15°N
77 during the Carnian (Enos et al., 1998; Golonka, 2007). The deep-waters of the Nanpanjiang Basin
78 opened to the east into the Panthalassa Ocean (Fig. 1). This platform-and-basin topography later
79 evolved into a foreland basin in the latest Carnian due to collision between the North and South
80 China blocks that saw carbonate platforms swamped by siliciclastic input (Enos et al., 1998).
81 Therefore, while in western Tethys, the mid-Carnian is marked by a transition from carbonate to
82 siliciclastic deposition, and a re-establishment of carbonate production in the aftermath of the CHE
83 (e.g., Hornung et al., 2007b), in South China renewed carbonate deposition was short-lived
84 because foreland basin siliciclastics were soon established. Our interpretation of climatic and
85 environmental history of this region during the Carnian must therefore be viewed in the context of
86 an on-going, and as yet poorly understood major tectonic change.

87 **3. Methods**

88 The 50 m-thick Long Chang section was logged and sampled at ~20 cm intervals yielding
89 190 samples for thin sections, conodont biostratigraphy, pyrite framboid and geochemical
90 analyses. Conodont samples were crushed to small chips and dissolved by using 6%-10% acetic

91 acid. The acid solution was buffered with tricalcium phosphate and exchanged every 48 hours until
92 the samples were fully dissolved. Residuals were wet sieved, dried at 50°C and separated for heavy
93 fractions using sodium polytungstate. Conodont elements were picked under a binocular
94 microscope. For carbonate carbon isotope analyses ($\delta^{13}\text{C}_{\text{carb}}$), sample powders were reacted with
95 100% phosphoric acid at 70°C in a Gasbench II gas preparation and introduction system connected
96 online to a Thermo Delta Plus mass spectrometer. Reproducibility, monitored by replicate analyses
97 of laboratory standards calibrated to NBS 19 and LSVEC, was $\pm 0.09\text{‰}$ (1σ). Carbon isotopes were
98 determined from total organic carbon ($\delta^{13}\text{C}_{\text{org}}$) using decarbonated samples in an elemental
99 analyzer (CE 1110) connected online to a Thermo Delta Plus mass spectrometer. Reproducibility,
100 monitored by replicate analyses of the standard USGS 40, was $\pm 0.06\text{‰}$ (1σ). All carbon isotope
101 values are given in per mille relative to VPDB. Oxygen isotopes were measured on conodont
102 apatite ($\delta^{18}\text{O}_{\text{PO}_4}$) following the method described in Joachimski et al. (2009) and are given in per
103 mille relative to VSMOW. Analyses were performed using a TC-EA coupled online to a Thermo
104 Delta Plus mass spectrometer. Reproducibility, monitored by replicate analyses of the standard
105 NBS 120c (21.7‰), was $\pm 0.14\text{‰}$ (1σ). Pyrite framboid analysis was performed on 30 samples in
106 the form of small polished chips that were examined at 2500x magnification using a Zeiss scanning
107 electron microscope under backscattered electron mode. The minimum, maximum and mean
108 diameter of framboids in each sample, and their standard deviation were calculated. Where
109 possible, >100 individual framboids were measured in each sample. Mo, Mn, U, Th and Al
110 contents were measured on powdered samples digested in a 2:2:1:1 acid solution of H₂O-HF-
111 HClO₄-HNO₃. Solutions were analyzed using a PerkinElmer ICP-MS with a reproducibility better
112 than $\pm 2\%$ (2σ). XRF analyses on high-Mn samples were further performed on an AMETEK
113 Spectro XEPOS XRF analyzer for cross comparisons. Data were calibrated to the limestone

114 standard JLS-1. Ten major element contents (CaO, P₂O₅, SiO₂, Al₂O₃, MgO, Fe₂O₃, Na₂O, K₂O,
115 MnO and TiO₂) were quantitatively determined. Reproducibility was better than ±0.06 wt% (1σ).
116 Mn concentrations were calculated from the MnO content by multiplication with a coefficient
117 0.775 (=molecular weight [Mn]/ molecular weight [MnO]).

118 **4. Results**

119 **4.1 Biostratigraphy**

120 The global Carnian conodont biostratigraphy is complex, and no consensus has been
121 reached on a single biostratigraphic scheme (e.g., Kozur, 2003; Orchard, 2010). Here we present
122 the first detailed attempt at an approach combining conodont zonation, bivalve and ammonoid
123 biostratigraphy to define Carnian substage boundaries in South China. The Zhuganpo and Wayao
124 Formations (Fm.) are likely regionally diachronous lithological units that require site-specific age
125 diagnosis, and we have studied a part of the Zhuganpo Fm. that is time-equivalent to only the upper
126 part of Enos et al.'s (1998) Zhuganpo Fm. Since most Late Triassic conodont species are long-
127 ranging, we use assemblage zones for a better age constraint. The strata are biostratigraphically
128 dated to the Julian 1 to Tuvanian 2 and record continuous sedimentation through most of the
129 Carnian Stage (Fig. 4). The Long Chang conodont fauna is dominated by the genus *Quadralella*
130 (*Q.*) with less abundant *Paragondolella* (*P.*), *Norigondolella* and exceptionally rare
131 *Gladigondolella*. Three conodont zones are recognized. They are, in ascending order, the *P.*
132 *foliata-Q. polygnathiformis* assemblage zone, *Q. polygnathiformis noah* zone and *Q. carpathica*
133 assemblage zone. These zones can be correlated with the western Tethys zonation (e.g., Hornung
134 et al., 2007b; Kozur, 2003; Fig. 5).

135 Conodonts from Long Chang display some features endemic to the region (Fig. 6). In
136 comparison to western Tethyan and North American faunas, the South China conodonts generally

137 have more elongated and less up-turned platforms. Adult specimens are locally rather rare in the
138 Tuvalian strata. Some diagnostic features such as the presence of a bifurcated keel are less
139 developed in the *Q. carpathica* group.

140 A few ammonoid and bivalve body fossils were collected from the uppermost Zhuganpo
141 Fm. and overlying Wayao Fm. (Fig. 7). The ammonoid *Austrotrachyceras* ex gr. *A. austriacum* at
142 ~26 m level (sample LC 34) indicates basal Julian 2 (i.e., Julian 2/I a sensu Gallet et al., 1994).
143 The bivalve *Halobia* cf. *zitteli* at ~30 m level (sample LC 41) is suggestive of a Julian age.

144 Collectively, the Julian 1-Julian 2 boundary is assigned below sample LC 34. The Julian-
145 Tuvalian boundary is tentatively assigned above sample LC 41 in which the youngest age-
146 diagnostic Julian fossil is last seen. The Tuvalian 1-Tuvalian 2 boundary is defined at sample LC
147 53 (~38 m level) where *Q. ex. gr. carpathica* occurs.

148 **4.2 Sedimentology**

149 The Long Chang section records major facies changes. The basal 13 m lie within the early
150 Carnian Zhuganpo Fm. (Julian 1) and consist of bioclastic wackestones. Thin-shelled bivalves
151 (filaments) and holothurian sclerites are abundant; calcispheres are locally common while
152 *Tubiphytes*, ostracods and benthic foraminifers are rare. The succeeding 8 m consist of intraclastic
153 limestones in which the matrix, of filamentous limestone, surrounds clasts of darker better-
154 cemented patches of the matrix lithology (Fig. 3F). The clasts are generally well rounded and often
155 rotated so that the alignment of the bivalve filaments is at an angle to the filaments in the matrix.
156 The topmost metre of the Zhuganpo Fm. (Julian 2) sees the development of two distinct
157 manganese-rich limestone beds: a lower bed consisting of nodular limestone with abundant
158 ammonoids and an upper bed consisting of thinly bedded mudstones with calcispheres.

159 The overlying Wayao Fm. (Julian 2-Tuvalian 2) consists mostly of black shales with
160 interbeds of filamentous packstones composed of valves of the bivalve *Halobia* (Fig. 3E). The
161 *Halobia* packstones range from 2 - 30 cm thick, although a metre-thick example is found around
162 45 m above the base of the section (Fig. 4). Ammonoids, crinoids and radiolarians are common,
163 together with calcispheres (Fig. 3G-I). At one level, 28 m above the base of the section,
164 calcispheres ranging in size from 20 - 200 μm , dominate in thin section. Towards the top of the
165 section (beginning at 45.5 m above the base of the section) thin interbeds of sharp-based, laminated
166 calcisiltites appear.

167 The Wayao Fm. is overlain by a thick development of amalgamated sandstone turbidite
168 beds belonging to the Laishike Fm. (possibly Tuvalian 3) that marks the start of flysch-style
169 sedimentation (Enos et al., 1998), but note that black shale facies persist into the lowermost metres
170 of the Laishike Fm. The boundary between Wayao Fm. and Laishike Fm. is defined regionally by
171 the first occurrence of a fine-grained sandstone/mudstone (normally yellow-brownish in colour).

172 **4.3 Redox Proxies**

173 Pyrite framboid analysis is a widely used petrographic palaeoredox proxy (Wilkin et al.,
174 1996). In general, populations of tiny framboids (mean 3-6 μm in diameter) indicate anoxic-
175 euxinic conditions, and populations of larger framboids (mean 6-10 μm in diameter, and typically
176 a larger standard deviation) indicate dysoxic conditions (Bond and Wignall, 2010). Pyrite crystals
177 are absent from much of the Zhuganpo Fm. Only in the topmost metre does euhedral pyrite become
178 common, although there are no framboids at this level. In contrast, tiny pyrite framboids are
179 prolifically abundant throughout the Wayao Fm. Average diameters are small (mean ~ 4 μm , with
180 maximum framboid diameter [MFD] ~ 8 μm) in the lower part of the Wayao Fm., and somewhat
181 larger in the upper part, where MFD increase to ~ 20 μm (Fig. 4).

182 Trace metals provide additional information on depositional conditions since many trace
183 metals are insoluble in reducing environments and consequently adsorbed to sediments under an
184 anoxic water column. Redox-controlled trace metal concentrations (Mn, Mo, U) show marked
185 fluctuations at Long Chang. Manganese values are low (~200-2,500 ppm) through most of the
186 section, but increase notably by two orders of magnitude to values ranging from ~0.8 to 11.2 wt%
187 (8,000-112,000 ppm) in a 2 m interval at the Zhuganpo-Wayao transition (Julian 2) (Table 1; Fig.
188 3C; Fig. 4). Mo/Al ratios show a different trend. Mo/Al is ≤ 1.0 throughout the Zhuganpo Fm.,
189 before the ratio rises sharply at the base of the Wayao Fm. from where it remains between ~3 and
190 ~10 up-section. U/Th ratios are ≤ 1.0 throughout most of the Zhuganpo Fm., and rise to ~2 in the
191 uppermost Zhuganpo Fm. from where they remain between 1 and 2 up-section.

192 **4.4 Stable isotopes**

193 The $\delta^{13}\text{C}_{\text{carb}}$ values are stable at ~-2.6‰ through the lower part of the section, then show an
194 abrupt ~-4.5‰ negative excursion starting at the latest Julian 1 (Fig. 4). A low point of -2‰ is
195 reached at the Julian-Tuvalian boundary before values rise again to ~-1.5‰ in the middle of the
196 Tuvalian 1. A second, short-lived negative shift of ~-2‰ is seen in the upper Tuvalian 1, before
197 values stabilize up-section at ~-2.5‰. $\delta^{13}\text{C}_{\text{org}}$ data show good covariance with $\delta^{13}\text{C}_{\text{carb}}$. Thus,
198 $\delta^{13}\text{C}_{\text{org}}$ values decrease from ~-26‰ in the Julian 1 to ~-29‰ at the Julian-Tuvalian boundary,
199 before stabilizing at pre-excursion values in the Tuvalian 2. However, the double negative spike
200 observed in the $\delta^{13}\text{C}_{\text{carb}}$ record is not well developed in the $\delta^{13}\text{C}_{\text{org}}$ record, although there is a small
201 increase in $\delta^{13}\text{C}_{\text{org}}$ values between the two negative shifts (Fig. 4).

202 The $\delta^{18}\text{O}_{\text{PO}_4}$ record contains two negative excursions. A ~-1‰ negative shift occurs in the
203 Julian 2 when $\delta^{18}\text{O}_{\text{PO}_4}$ decreased from ~20.0 to ~19.0‰. This was followed by a positive shift to

204 pre-excursion $\delta^{18}\text{O}_{\text{PO}_4}$ values. A second, more gradual $\sim 1.5\%$ negative shift occurs throughout
205 Tuvalian 2, when $\delta^{18}\text{O}_{\text{PO}_4}$ decreased from ~ 20.0 to $\sim 18.5\text{‰}$ (Fig. 4).

206 **5. Discussion**

207 The Long Chang section records many of the attributes of the Carnian Crisis and CHE that
208 have been reported from far removed sections of western Tethys, indicating that those changes
209 were manifest over a large (global?) geographical area (Fig. 1B). Significantly, the $\delta^{13}\text{C}_{\text{org}}$ trends
210 known from western Tethys (e.g., Dal Corso et al., 2015) are replicated eastern Tethys where they
211 also occur in the $\delta^{13}\text{C}_{\text{carb}}$ record. The $\delta^{18}\text{O}_{\text{PO}_4}$ record reveals that the Carnian Crisis was associated
212 with two phases of warming that correlate with the dry-wet climatic transition.

213 **5.1 Towards an age model**

214 Establishing the timing of the Carnian Crisis and the CHE in South China and elsewhere
215 is a crucial step in the evaluation of various causal mechanisms that have been postulated for the
216 inferred environmental changes. However, the age of Late Triassic strata in Guizhou is a subject
217 of intense debate. Unfortunately, many age-diagnostic taxa exhibit regional differences both in
218 terms of individual morphologies and in terms of temporal range during the Carnian (Fig. 5) and
219 so thorough dating of individual sections is essential when developing a regional biostratigraphy
220 for South China. Our approach combines conodont interval and assemblage zones (based on a
221 combination of conodont species) with ammonoid/bivalve ranges to define the biostratigraphic
222 scheme, therefore excluding problems caused by regional differences in the first and last
223 occurrences of individual conodont species. Our biostratigraphy supports conclusions of a recent
224 ammonoid study (Zou et al., 2015) that assigned the upper part of Zhuganpo Fm. (studied in this
225 paper) and the overlying Wayao Fm. to the Carnian. However, our biostratigraphic age assignment
226 for the Long Chang sequence differs from that inferred by magnetostratigraphy and

227 cyclostratigraphy performed on similar lithological units (Zhang et al., 2015). Zhang et al. (2015)
228 place the Zhuganpo, Wayao, Laishike and Bana formations entirely within the Carnian, thus
229 constraining the older formations to the early part of the Carnian. It is possible that the discrepancy
230 between bio- and magneto- and cyclostratigraphy is due to the diachronous nature of these rather
231 loosely defined local lithological units. Thus, while other interpretations might be valid, our
232 detailed ammonoid, bivalve and conodont sampling provides the first detailed biostratigraphy for
233 the area, and it is independently verified by our carbon isotope chemostratigraphy that is
234 correlatable to well-dated western Tethyan sections (Fig. 8).

235 **5.2 A carbonate production crisis**

236 A decrease in carbonate productivity is indicated by the facies changes at Long Chang. The
237 basal bivalve-holothurian wackestones of the Zhuganpo Fm. represent a rather unusual variety of
238 platform carbonate that probably formed in deeper waters (compared to the underlying Yangliujing
239 cyclic limestones and dolostones, Fig. 2C). The lack (or rarity) of typical shallow-water Carnian
240 components such as calcareous algae, *Tubiphytes* and crinoids is probably due to the location of
241 Long Chang at the transition between the Yangtze platform and an adjacent basin. The overlying
242 intraclastic limestones show a high degree of early cementation followed by re-orientation of the
243 clasts. Enos et al. (1998) argued that the intraclasts did not undergo significant transport because
244 they are of the same lithology as the matrix. While this observation is pertinent we note that
245 frequent re-orientation of the clasts suggests some degree of movement, perhaps during debris
246 flow emplacement. Carbonate productivity declined at the Julian 1-Julian 2 transition when a
247 manganese-rich, ammonoid wackestone developed—a facies typical of deep-water, condensed
248 limestones such as the Jurassic Ammonitico Rosso (Jenkyns, 1991). This was followed by
249 deposition of deep-water black shales and *Halobia* packstones of the Wayao Fm., indicating

250 further base-level deepening. The *Halobia* packstones consist of horizontally laminated, densely
251 packed thin valves, probably formed under sediment-starved conditions (Fig. 3G). This facies
252 persists up to 42 m above the base of the studied section, suggesting that the sedimentation rates
253 were probably locally still low in the early Tuvalian 2 substage.

254 The drowning of the carbonate platform did not result in a complete shutdown of carbonate
255 productivity because 1) though carbonates were relatively rare, *Halobia* packstones occur at
256 several levels in the Wayao Fm. (Fig. 3D, G); 2) in the adjacent Guanling area ~60 km away from
257 Long Chang, carbonate production (though briefly punctuated by black shale deposition)
258 continued well into the Tuvalian 3 substage (Wang et al., 2008); and 3) further afield, on the
259 northwestern Yangtze Platform, carbonate platforms were replaced by ramp deposits and sponge
260 reefs in Tuvalian and carbonate production persisted until the early Norian in Sichuan Province at
261 which time they were inundated by flysch sediments (Wu, 1989; Li et al., 2014). The transition
262 from an extensional platform-and-basin setting to a foreland basin setting in South China probably
263 occurred between the latest Carnian (~Tuvalian 3 at Long Chang) and earliest Norian (in NW
264 Sichuan). In this scenario the loss of carbonate production late in the Julian cannot be the result of
265 foreland basin development because it slightly predates this tectonic change. At Long Chang, it
266 seems that sedimentation rates were still rather low during the Julian 2 (uppermost Zhuganpo Fm.)
267 and the Tuvalian 1-2 substages (lower-middle Wayao Fm.) as suggested by the occurrence of
268 nodular ammonoid wackestones and *Halobia* packstones. Indications of foreland basin
269 development such as a substantial increase in sedimentation rates and occurrence of basin infill
270 only occurred in the Laishike Fm. (probably Tuvalian 3 and later).

271 **5.3 Marine anoxia**

272 The inferred increase in water depth at the top of the Zhuganpo Fm. at Long Chang saw
273 the establishment of intense euxinia, although only after the development of Mn-rich limestones
274 (MnO content is generally >1.0 wt%, up to 15.1 wt%). The U/Th ratio increases at the same level,
275 suggesting that redox is one of the main controls on Mn scavenging. The increase in the U/Th ratio
276 slightly predates the increases of Mo/Al, probably a function of the greater enrichment of U in
277 dysoxic waters relative to Mo, which only enriches in intensely anoxic sulfidic water (Algeo and
278 Tribovillard, 2009). Unlike most metal sulfides, manganese sulfide is soluble in anoxic waters, but
279 in oxygenated waters Mn is rapidly precipitated in a carbonate form or as particulate oxides
280 (Brewer and Spencer, 1974). In many euxinic basins Mn is shuttled from sulfidic, deeper basinal
281 waters to the redox boundary where manganese-rich carbonates form a “bath-tub ring” (Frakes
282 and Bolton, 1984). Manganese-rich deposits in effect herald the arrival of upward-expanding
283 euxinic waters (Jenkyns et al., 1991). Thus, the Mn enrichment in the uppermost Zhuganpo Fm.
284 suggests deeper water euxinia had already developed prior to the appearance of euxinic facies at
285 Long Chang.

286 Pyrite framboids in the Wayao Fm. are even smaller than those raining to the seafloor in
287 the modern euxinic Black Sea (Wilkin et al., 1996), indicating intense water column stratification
288 (Bond and Wignall, 2010) developing later in the Julian 2 interval. This conclusion is supported
289 by the exceptionally high Mo/Al values and low biodiversity in the Wayao Fm., which lacks
290 benthos, and is dominated by the bivalve *Halobia* and the pseudoplanktonic crinoid
291 *Traumatocrinus* which attached itself to driftwood. The ecology of *Halobia* has been debated –
292 some regard it as pelagic while others suggest it is a low-oxygen specialist able to survive during
293 short periods of elevated benthic oxygen levels (Allison et al., 1995). Thus occurrences of *Halobia*
294 coquinas in the Wayao Fm. indicate recurring dysoxic conditions in an overall anoxic environment.

295 Our pyrite framboid data, which show a clear trend from no pyrite to euhedral pyrite and then
296 abundant small framboids up-section, help to exclude the possibility that the enrichment of redox
297 sensitive elements in the uppermost Zhuganpo Fm. reflects a post-depositional exchange with the
298 overlying anoxic Wayao black shales because although trace metals can migrate after deposition,
299 pyrite crystals cannot – they record a primary signal of oxygen depletion.

300 An alternative interpretation of the low biodiversity of the Wayao Fm. lies in the poisoning
301 of benthos due to the excessive supply of terrestrial nutrients in the local basin. However, the lack
302 of apparent faunal changes, the lack of evidence for increase in bioerosion towards the termination
303 of platform, and the lack of phosphate enrichment in the pelagic and condensed intervals at Long
304 Chang and adjacent areas (Enos et al., 1998) do not support a substantial increase of nutrient level.
305 Instead, contemporaneous oxygen depletion recorded in the Italian Alps, North Africa, Sicily, and
306 South China provides compelling evidence for a supra-regional anoxic event (Bellanca et al., 1995;
307 Keim et al., 2006; Hornung et al., 2007b; Soua, 2014; Minzoni et al., 2015).

308 **5.4 Carbon isotope and sea-surface temperature (SST) trends**

309 The late Julian 1 negative $\delta^{13}\text{C}$ excursion at Long Chang matches that seen in the western
310 Tethyan marine and terrestrial organic carbon isotope records (Dal Corso et al., 2012, 2015)
311 indicating that it is a Tethys-wide, and probably global signal. The Long Chang $\delta^{13}\text{C}_{\text{carb}}$ profile
312 reveals several further negative shifts, which are not yet known from elsewhere. This probably
313 reflects a lack of detailed sampling at this level – the Tuvalian has received much less attention
314 than the Julian (Fig. 1B; Fig. 8). In contrast, the $\delta^{13}\text{C}_{\text{org}}$ profile in South China suggests a single,
315 prolonged negative excursion between the Julian 2 and Tuvalian 2 substages (Fig. 2). Despite this
316 minor discrepancy between the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ records, there was clearly a prolonged
317 perturbation of the carbon cycle in the later Carnian, coincident with several contemporaneous

318 volcanic eruptions (Walderhaug et al., 2005; Maury et al., 2008; Greene et al., 2010; summarized
319 in Fig. 1C). The Wayao Fm. is known for the excellent preservation of large pieces of driftwood
320 that were encrusted with crinoids (Wang et al., 2008). It is possible that the negative excursion
321 seen in the $\delta^{13}\text{C}_{\text{org}}$ record is an artefact of such terrestrial organic carbon input. However, this is
322 unlikely because in general, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ co-vary at Long Chang, and terrestrial organic
323 carbon input cannot account for the scale of changes seen in the $\delta^{13}\text{C}_{\text{carb}}$ record. However, $\delta^{13}\text{C}_{\text{org}}$
324 records from Long Chang and Lutz basin (Mueller et al., 2016) as well as within Northern
325 Calcareous Alps (Dal Corso et al., 2015 v.s. Mueller et al., 2016) show different variation patterns
326 in the Julian 2 (Fig. 8). Such differences likely suggest a major disturbance and compositional
327 variation in regional organic carbon pools. The $\delta^{13}\text{C}_{\text{org}}$ signal may reflect local effects (e.g.,
328 terrestrial/marine organic carbon mixing) and (potentially) the unreliability of measuring $\delta^{13}\text{C}_{\text{org}}$
329 on a very small amounts of carbon (e.g., on sandstone, claystone etc.).

330 Calculating absolute seawater temperatures from $\delta^{18}\text{O}_{\text{PO}_4}$ using Pucéat et al.'s (2010)
331 equation and assuming an ice-free world in the Late Triassic ($\delta^{18}\text{O}_{\text{seawater}}=-1\text{‰}$), yields warm
332 subtropical SSTs ($\sim 26^\circ\text{C}$ - 33°C). These temperatures correspond to modern equatorial SSTs and
333 are similar to temperatures calculated for the Middle Triassic of the same region (Sun et al., 2012).
334 The two negative $\delta^{18}\text{O}_{\text{PO}_4}$ excursions indicate increased warmth with temperatures increasing by
335 4°C from $\sim 27^\circ\text{C}$ to $\sim 31^\circ\text{C}$ in the Julian 2 substage, followed by a short-lived cooling and then a
336 second rise of $\sim 7^\circ\text{C}$ from ~ 26 to $\sim 33^\circ\text{C}$, beginning in the Tuvallian 1 substage and persisting until
337 the later Carnian. Despite differences in analytical methods, sampling resolution and regional
338 $\delta^{18}\text{O}_{\text{seawater}}$, a comparable warming trend of ~ 6 - 8°C from the Julian to the late Tuvallian is also
339 reported from contemporaneous sections in the Northern Calcareous Alps and Southern Alps

340 (Hornung et al., 2007b; Trotter et al., 2015), suggesting that this is a true, global signature (Fig.
341 9).

342 **5.5 Precipitation changes during the CHE**

343 One of the most intriguing features of the CHE is that the prevailing Late Triassic dry
344 climate was interrupted by a transient interval of enhanced rainfall (e.g., Simms and Ruffell, 1990).
345 In western Tethys this caused the sudden shutdown of carbonate platforms by enhanced terrestrial
346 siliciclastic input (sands and muds, etc.) due to elevated run-off rates (e.g., Kozur and Bachmann,
347 2010). High run-off is also invoked in North America where mid-Carnian sandstone occasionally
348 contains kaolinite, suggesting a humid climate (Simms and Ruffell, 1990). The arid-humid
349 transition in the Carnian is best constrained by palynological studies — the Carnian in general was
350 very arid, but a humid pulse began at the Julian 1- Julian 2 boundary and ended in the early
351 Tuvalian (Roghi et al., 2010; Mueller et al., 2016).

352 The ultimate cause(s) for the mid-Carnian climate change is a matter of intense debate.
353 Enhanced precipitation is has long been postulated the result of mega-monsoon activities due to
354 the palaeogeographic configuration of Pangea (e.g., Parrish, 1993). However, climate changes
355 triggered by tectonic movements are generally gradual and long-lasting, in contrast to the sudden
356 and transient nature of the CHE. The global climate change from arid to humid conditions in the
357 Julian 2 (Mueller et al., 2016) coincided with the negative carbon isotope excursion and
358 temperature rise seen at Long Chang and elsewhere (Fig. 4; Hornung et al., 2007b), which suggests
359 instead a warm-climate-driven model.

360 Volcanic activity, both silicic and basaltic, was geographically widespread and intense
361 during the Carnian (e.g., Walderhaug et al., 2005; Maury et al., 2008; Greene et al., 2010; Moix et
362 al., 2013). The Wrangellia Large Igneous Province (LIP) and contemporaneous volcanic activity

363 elsewhere (Fig. 1) likely injected copious light carbon to the atmosphere and initiated the first
364 warming event seen in the Julian 2 substage. An intensification of the hydrologic cycle and an
365 increase in precipitation is a predictable consequence of climate warming. Thus, widely-distributed
366 wind-blown dust found in the Carnian Panthalassa Ocean points to strong atmospheric convection
367 (Nakada et al., 2014).

368 Our combined biostratigraphy and carbon isotope records provide a temporal framework
369 for the succession of intra-Carnian events, facilitating the detailed reconstruction of the sequence
370 of environmental changes. The late Julian was marked by carbonate platform drowning (possibly
371 correlating to sea level rise) and the development of intense basin anoxia. This coincided with the
372 onset of a negative carbon isotope excursion and a warming trend that is correlative with the CHE
373 and similar $\delta^{13}\text{C}$ trends in western Tethys. Platform drowning may have been related in part to the
374 development of deep-water euxinia, which could have “poisoned” carbonate production leading
375 initially to the development of condensed, manganiferous carbonates and ultimately to the loss of
376 all but filamentous limestone production as the area of black shale deposition expanded. High
377 Mn^{2+} concentrations in euxinic waters may have been another contributing (if not the key) factor
378 to rarity of carbonates in the Wayao Fm. because Mn^{2+} inhibits carbonate precipitation (Dromgoole
379 and Walter, 1990).

380 Once established, black shale and filamentous limestone deposition persisted into the
381 Tuvalian when $\delta^{13}\text{C}$ and $\delta^{18}\text{O}_{\text{PO}_4}$ fluctuations reveal substantial further perturbations to both the
382 carbon cycle and SSTs: at least one more prolonged, warm episode and two further negative $\delta^{13}\text{C}$
383 excursions. These phenomena have not been reported from western Tethys, probably due to the
384 less intense study of the post-CHE interval there (Fig. 1B). Coincident with the Wrangellia LIP

385 and other coeval substantial volcanic activity, the CHE likely represents another case of
386 volcanism-induced global climatic changes.

387 **6. Conclusions**

388 Major Carnian climatic and environmental changes were widespread throughout the
389 Tethyan ocean region: they have the hallmarks of many mass extinction events including warming,
390 carbon isotope oscillations, transgression and the spread of deep-water anoxic facies. The
391 coincidence with the Wrangellia LIP and several Tethyan volcanism strengthens the similarity of
392 the Carnian Crisis to major Permian and Triassic extinctions, and suggests the Carnian event could
393 rank alongside those in terms of environmental perturbations.

394 The dry-wet transition occurred during the CHE and coincided with a -4‰ negative carbon
395 isotope excursion and a 4°C warming, arguing for a volcanism-induced, warm-climate-driven
396 intensification of hydrologic cycle activities.

397 A decrease in carbonate productivity during the CHE is likely a global phenomenon
398 triggered by different mechanisms. The complete shutdown of carbonate production by siliciclastic
399 influx seen in western Europe only occurred at a regional scale. Though inhibited, carbonate
400 precipitation persisted until at least the end of the Julian 2 in many deeper water localities (e.g.,
401 Lukeneder et al., 2012; Soua, 2014; this study). The carbonate production decrease in South China
402 (Julian 2) predated foreland basin development (latest Tuvalian 2 to Tuvalian 3) at the onset of the
403 Indosinian Orogeny and was probably the result of platform drowning, euxinia and high Mn^{2+}
404 concentrations.

405 Though more studies on other regions will provide a better understanding of this intriguing
406 interval in Earth history, our work in South China supports a scenario in which environmental
407 changes were both geographically and temporally widespread during the Carnian. The most

408 harmful interval for marine life is likely to have occurred during the early Julian, coincident with
409 the CHE, when a warming trend, increasing precipitation and intense marine anoxia were
410 established, resulting in widespread, but as yet poorly constrained, faunal losses.

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564

565 **FIGURE CAPTIONS**

566 **Figure 1.** A) Palaeogeographic reconstruction of the Carnian world (revised after Golonka, 2007);
567 B) summary of previous studies on the Carnian Humid Episode. Gray shading represents the short-
568 lived CHE interval; C) (inset) biostratigraphic and radiometric ages of contemporaneous volcanic
569 activity (Walderhaug et al., 2005; Maury et al., 2008; Greene et al., 2010; Moix et al., 2013).

570 **Figure 2.** Maps of the study area and summary of local Triassic stratigraphy (simplified from Enos
571 et al., 1998). A) Palaeogeographic reconstruction of South China during the Triassic period; B)
572 Geological map of the Long Chang area showing the location of the study section approximately
573 2 km southwest of Long Chang town; C) Summary of the Middle-Late Triassic strata in the study
574 area. Formation abbreviations: YLJ., Yangliujing; ZGP., Zhuganpo; WY., Wayao; LSK.,
575 Laishike; BN., Banna; HBC., Huobachong.

576 **Figure 3.** Field photographs of the Long Chang section (A-E) and photomicrographs of samples
577 (F-I). A) The middle and upper part of the Long Chang section, showing three lithological units.
578 Yellow pentagons indicate carbonate beds within the black shale-dominated Wayao Fm.
579 Motorcycle and passengers for scale (approximately 1.5 m high); B) The thickly bedded lower
580 Zhuganpo Fm., C.B. Yan (~1.8 m high) for scale; C) The uppermost Zhuganpo Fm., showing a
581 transition from thickly bedded limestone to ammonoid-bearing nodular limestone to Mn-enriched
582 thin-bedded limestone. Manganese concentration increased by two orders of magnitude through
583 the interval marked by the white arrow. Yellow field notebook (~15 cm long) for scale; D) Highly
584 condensed *Halobia* limestone intercalated in the middle part of the Wayao Fm. Ruler for scale; E)

585 crinoid *Traumatocrinus* stems (white arrows) at the Zhuganpo-Wayao transition (~27 m above the
586 base of the section); F) Intraclast wackestone from the upper Zhuganpo Fm. (sample LC 24, 21 m
587 above base of section), showing dark, better cemented intraclasts surrounded by a filamentous
588 matrix. The clasts are generally well rounded and often rotated so that the alignment of the bivalve
589 filaments is at an angle to the filaments in the matrix; G) *Halobia* filamentous floatstone from the
590 Wayao Fm. (sample LC 53, ~38.5 m above base of section). *Halobia* valves are densely packed,
591 and this facies probably formed under sediment starved conditions. A crinoid (Cr) is also visible
592 in this sample; H) Ammonoid wackestone from the Zhuganpo Fm. (sample LC 18, ~18 m above
593 base of section), showing an ammonoid surrounded by aligned filaments in the matrix; I)
594 Calciphere (Ca) and radiolarian (R) packstone from the Wayao Fm. (sample LC 46, ~33 m above
595 base of section).

596 **Figure 4.** Log of Long Chang section with pyrite framboid box-and-whisker plots (the ‘box’
597 depicts the 25th and 75th percentile of framboid distributions, the ‘whiskers’ depict the minimum
598 and maximum framboid diameters, and the central line depicts the median), inferred precipitation
599 changes, conodont oxygen and carbon isotopes records and trace metal variations. Precipitation
600 conditions are based on palynological studies (Roghi et al., 2010; Kozur and Bachmann, 2010;
601 Mueller et al., 2016), and reflect a general (and potentially global) trend observed in the western
602 Tethys. Mo/Al and Mn are plotted using a log scale. The black ammonoid symbol represents a
603 level yielding Julian 2 ammonoid *Austrotrachyceras* ex gr. *A. austriacum* (Mojsisovics). The
604 bivalve symbol represents the youngest occurrence of age-diagnostic Julian fossil *Halobia* cf.
605 *zitteli* Lindstroem. The crinoid symbols represent levels yielding abundant pseudoplanktonic
606 crinoid *Traumatocrinus*. A. Z., assemblage zone. CPE (Carnian Pluvial Event) here follows the

607 definition of Mueller et al. (2016) as a sudden sedimentary turnover from carbonates to
608 siliciclastics.

609 **Figure 5.** Correlation of ammonoid and conodont zonations of western Tethys, North America
610 and South China. Data are collated from Kozur (2003), Hornung et al. (2007b), Balini et al. (2010),
611 Orchard (2010) and this study.

612 **Figure 6.** Scanning electron microscope images of conodonts from the Long Chang section. Scale
613 bars are 100 μm long. 'a' = upper view, 'b' = lateral view, and 'c' = back view. **1, 8,**
614 *Paragondolella foliata* Budurov, 1, from sample LC30_02; 8, LC31_04. **2, Paragondolella**
615 *inclinata* Orchard, LC19_01. **3, Metapolynathus tadpole** (Hayashi) LC19_03. **4, 6, 9, Quadralella**
616 *polygnathiformis* (Budurov & Stefanov), 4, LC7.5_04; 6, LC34_02; 9, LC48_04. **5, 7, 14,**
617 *Quadralella* sp. 5, LC2_02; 7, LC40_04; 14, LC42_01. **10, Quadralella cf. carpathica** (Mock,
618 1979), LC53_19. **11, Quadralella carpathica** (Mock, 1979), LC53_21. **12, 13, Quadralella**
619 *polygnathiformis noah* Hayashi, 12, LC46_04; 13, LC46_06.

620 **Figure 7.** Ammonoids (A and B) and bivalves (C and D) recovered from the studied section. The
621 ammonoids *Austrotrachyceras* ex gr. *A. austriacum* (Mojsisovics) were from the nodular
622 limestone of the uppermost Zhuganpo Fm (sample LC 34 at ~26 m level shown in Fig. 2C),
623 indicating the basal Julian 2 (i.e., Julian 2/I a). Suture lines of respective specimens are included
624 in the right side of the photos. Well-preserved thin-shelled *Halobia* cf. *zitteli* Lindstroem in the
625 lower Wayao Fm. (sample LC 41, ~30 m above the base of section) indicates a Julian age.

626 **Figure 8.** Comparison of carbon isotope records from South China (this study) and western
627 Tethyan sections from Europe (Dal Corso et al., 2012, 2015; Mueller et al., 2016). Note the
628 regional difference in organic carbon records in the Julian 2 may reflect compositional variations
629 in regional organic carbon pools. NCA, Northern Calcareous Alps.

630 **Figure 9.** Summary of intra-Carnian palaeotemperature variations in South China (this study) and
631 the Lagonegro Basin (Trotter et al., 2015) and Northern Calcareous Alps (Hornung et al., 2007b).
632 Data are derived from conodont oxygen isotope thermometry. Pink shades indicate warming
633 intervals. Despite differences in analytical methods, sampling resolution and regional $\delta^{18}\text{O}$ of
634 seawater, all three studies show a long term temperature rise of 6-8°C from the Julian to the late
635 Tuvalian.

636 **Table 1.** XRF data of major element variations in the manganiferous limestone from the uppermost
637 Zhuganpo Fm. and lowermost Wayao Fm., showing unusually high MnO contents. Mn
638 concentrations can be calculated from the MnO contents by multiplying with a coefficient 0.775
639 (molecular weight [Mn]/ molecular weight [MnO]). LOI, loss on ignition. Numbers are in wt%.