Collapse of Late Permian chert factories in the equatorial Tethys and the nature of the Early Triassic chert gap

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Abstract:

Permian chert successions were geographically extensive, spanning from the palaeoequator to the northern high latitudes. Large-scale chert production was abruptly terminated in the latest Permian, resulting in a multi-million-year "chert gap" in the Early Triassic. In order to constrain the tempo of chert production changes and understand their nature, we combine proxy data with Si box model analyses and focus on the Talung Formation of South China—the most representative Upper Permian siliceous unit in the equatorial Tethys. Two deepwater sections from the northern margin of the Yangtze Platform were investigated, showing that bedded cherts had already become less common in the *Clarkina changxingensis* conodont zone. The waning of chert production coincided with water column deoxygenation and an increase in carbonate and siliciclastic components in the late Changhsingian. The final collapse of the chert factory in South China predated the negative $\delta^{13}C$ excursion and climate warming but coincided with a sharp decrease in primary productivity. Together with Si box model output, we suggest that warming-induced expansion of the oceanic dissolved silica inventory (and decrease in burial efficiency) alone cannot maintain a multi-million-year chert gap. Instead, a loss of siliceous biomass during the end-Permian crisis is the primary cause of the Early Triassic chert demise.

1. Introduction

The end-Permian mass extinction (~252 Ma) is the largest extinction in the Phanerozoic, eliminating over 90% of marine and 75% of terrestrial species (Erwin, 2006). The extinction was a complex event, possibly caused by interplays of multiple killing mechanisms, including climate warming (Joachimski et al., 2012; Sun et al., 2012), and ocean anoxia (Wignall and Hallam, 1992; Isozaki, 1997), initiated by eruptions of the Siberian Traps (Wignall, 2001; Burgess and Bowring, 2015). The aftermath of the end-Permian extinction was marked by long-term environmental instability, manifested by, e.g., large perturbations in the global carbon cycle, prolonged ocean anoxia, and an exceptional hothouse climate in the Early Triassic (Payne et al., 2004; Grasby et al., 2013; Sun et al., 2021).

Dramatic environmental changes across the Permian–Triassic (P-T) transition are archived in the sedimentary record (e.g., Wignall and Hallam, 1992; Pruss et al., 2006). These include, among others, the prevalence of anachronistic facies in shallow marine settings (e.g., microbialites and synsedimentary seafloor cements) and the extensive development of continental red beds in the Pangea interior (Sengupta, 1970; Pruss et al., 2006; Woods, 2014). Unusual climatic conditions following the end-Permian mass extinction are shown by the absence of coals on land and a lack of cherts in epicontinental seas (Retallack et al., 1996; Beauchamp and Baud, 2002). The coal gap was probably due to low plant mass following the end-Permian mass extinction and high remineralization rates in warm climates (Looy et al., 1999; Sun et al., 2012). However, the chert gap is much less understood.

Most bedded cherts in the Palaeozoic were deposited in relatively deep settings, possibly equivalent to the depth of radiolarian and diatom ooze deposition in modern oceans (Tucker, 2003). However, Permian cherts were not only extensively developed in much shallower settings, e.g., at continental margins and in intra-platform basins, but had a wide latitudinal distribution. Such a large-scale chert depositional event was initially constrained from the Kungurian to the Wordian in North America and termed the Permian Chert Event (PCE; Murchey and Jones, 1992). Subsequent research

71   suggests that the PCE lasted ~30 Myr, from the Artinskian to the late Changhsingian,

72   representing a major chert-accumulation event in the Phanerozoic (Beauchamp and

73   Baud, 2002).

74   The termination of the PCE occurred in the late Changhsingian (Beauchamp and

75   Baud, 2002; Sperling and Ingle, 2006). In the northern Panthalassic Ocean and at the

76   northwestern margins of Laurentia, a transition from bedded cherts to black, organic-

77   rich claystone, shales, and siltstones in the uppermost Permian is documented (Wignall

78   et al., 1998; Xia et al., 2004; Beauchamp et al., 2009). At the eastern Gondwana margin,

79   cherts and siliceous shales in the Late Permian are replaced by carbonates, mudstones,

80   and calcareous shales in the Early Triassic (Baud et al., 2012). In South China, the

81   demise of the Late Permian cherts is best seen in the transition between the Talung

82   Formation and overlying strata (e.g., Yan et al., 2013; Lyu et al., 2019). Intermittent

83   Early Triassic chert deposition is only known from a few accreted terranes from

84   southern Panthalassa that preserve oceanic successions (e.g., Isozaki, 1997; Grasby et

85   al., 2021).

86   Whether the collapse of Permian chert production was a facet of the end-Permian

87   mass extinction remains an open question. As most cherty units across the P-T transition

88   are not adequately dated, we first focus on the timing of changes in chert production

89   and redox evolution of two sections in South China to constrain the waning stage of the

90   PCE at equatorial latitudes. We document an increase in chert production in the earliest

91   Changhsingian. The shutdown of chert production occurred in the latest Changhsingian

92   and coincided with water column deoxygenation and the waning of primary

93   productivity. This is combined with a box model of the ocean Si cycle to show that the

94   final shutdown of chert factories is attributed to synergistic effects occurring during the

95   end-Permian mass extinction.

96

97   **2. Geological background**

98   During the Permian, South China was a large, isolated carbonate platform near the

99   equator in the eastern Palaeo-Tethys Ocean (Scotese, 2014; Fig. 1A). In the

Changhsingian, South China represents an epicontinental sea with developed barriers, including the Cathaysia Old Land to the east, the Yunkai Old Land to the south, and the Kangdian Old Land to the southwest (Feng et al., 1996). Siliceous facies are primarily developed along the northern margin of the Yangtze Platform and in the Hunan-Guizhou-Guangxi Basin (Fig. 1B).

The study sections at Chibi (29°45′5.33″N, 113°57′6.75″E) and Changtanhe (29°27′40″N, 111°04′04″E) were both located along the northern margin of the middle Yangtze Platform. The sections, though far apart, share a similar sedimentary history. Both show a deepening trend from a middle shelf setting in the Wuchiapingian to a basinal setting in the Changhsingian, with the deeper-water environment having persisted into the Early Triassic. Stratigraphically, both sections contain the Upper Permian Wuchiaping Formation and Talung Formation, as well as the Lower Triassic Daye Formation (Figs. 2, 3). The Talung Formation represents the main chert strata, consisting predominantly of thinly-bedded spicule and radiolarian cherts, siliceous mudstones, cherty carbonate, and shales (Li et al., 1989; Yan et al., 2013). The Daye Formation is characterised by dark-grey shales, mudstones, and thinly-bedded marls in deeper basins and finely laminated micritic mudstones and oolitic grainstones at platform margins during the Griesbachian (Mei and Gao, 2012; Lyu et al., 2019).

3. Methods

3.1 Sedimentary facies and conodont biostratigraphy

The study sections were logged in detail in the field. For litho- and microfacies analysis, 165 and 124 thin sections were prepared from the Chibi and Changtanhe sections, respectively. For conodont biostratigraphy, 68 and 20 samples weighing ~3–5 kg were collected. Conodont samples were crushed into small rock chips and firstly treated with 10 % acetic acid. While carbonate samples were entirely disintegrated, siliceous samples were further treated with 10 % HF. Undissolved residues were wet-sieved and air-dried. In total, 543 intact conodont specimens were recovered from 48

128   samples. Selected specimens were photographed using the Hitachi SU8010 scanning

129   electron microscope (SEM) at the State Key Laboratory of the China University of

130   Geosciences (Wuhan).

131

132   3.2 Pyrite framboid analysis

133   A total of 77 polished slabs of ~ 2 cm × 2 cm in size were prepared from both

134   sections and examined using the above-mentioned SEM. Pyrite framboid diameters

135   were measured at 2500× magnification under backscattered electron mode. The

136   Kolmogorov–Smirnov (K-S) test is used to determine distribution patterns of framboid

137   sizes in each sample. The Kruskal-Wallis (K-W) test is applied to examine whether

138   differences in framboid size distributions in a group of samples are statistically

139   significant (see the Supplementary Material for details).

140

141   3.3 Carbonate carbon isotope ($\delta^{13}C_{carb}$) analysis

142   A total of 188 samples were milled into fine powders (<100 mesh) and dried.

143   $\delta^{13}C_{carb}$ measurements were carried out in a Finnigan MAT 253 mass spectrometer

144   connected online to a Kiel III autosampler in the State Key Laboratory of Geological

145   Processes and Mineral Resources, China University of Geosciences (Wuhan). The

146   reproducibility, monitored by replicate analyses of two standards (GBW 04416,

147   GBW04417), was better than 0.1 ‰ (1 σ; n=21). All data were converted to δ notation

148   relative to V-PDB.

149

150   3.4 Bulk rock SiO_2 content

151   SiO_2 contents were determined on bulk rock powders. A total of 34 samples were

152   fused into glass discs using a 12 : 22 lithium metaborate: lithium tetraborate flux, with

153   a lithium nitrate oxidizing agent at the ALS Chemex (Guangzhou). The discs were

154   analysed using XRF spectroscopy with a reproducibility better than 0.1 wt% (1 σ).

155

156   3.5 Si box model

We use a simple two-box representation of the ocean silicon cycle to investigate the interplay between biosiliceous production and climate on the burial of biogenic silica in marine sediments (Fig. 4A). The model is based on the De La Rocha and Bickle (2005) framework with modifications from Frings et al. (2016) and Fontorbe et al. (2020). It does not aim to capture the complex dynamics of the P-T ocean, but rather serves as a framework to test different scenarios. For simplicity, radiolarian test burial is prescribed as the only biogenic silica sink, with siliceous sponges conceptually grouped into this sink.

In brief, radiolarian biosiliceous production occurs within a 100 m upper water column box, governed by a Michaelis-Menten dependence on dissolved silica (DSi) concentrations. Dissolution occurs in both the surface box and the deep box, as a function of DSi concentration, parameterised as a linear dependence on the degree of biogenic silica undersaturation. Fluxes of DSi into the ocean follow Frings et al. (2016), using a total of 9.55×10^{12} mol yr^{-1} as the baseline scenario. The model includes a non-radiolarian sink, the precipitation of which is proportional to ocean DSi concentrations above a threshold, though it is agnostic about the physical nature of this sink. The palaeotemperature reconstruction from Joachimski et al. (2012) is used to modify the solubility of biogenic silica, the rate constants associated with biogenic silica dissolution and non-radiolarian sink precipitation, and the flux Si into the ocean from continental weathering, following standard formulations in all cases. Beyond the baseline scenario in which only temperature changes, we also investigate a scenario in which radiolarian biosiliceous production is decimated by prescribing an instantaneous increase in radiolarian half-saturation constant and decrease in maximum uptake rate. Further details are given in the supplementary material.

4. Results

4.1. Sedimentary facies

184 The lower part of the Chibi section consists of medium to thick-bedded grey

185 packstones of the Wuchiaping Formation (~ 20 m) (Fig. 2A, B). The packstones are

186 highly bioturbated and contain diverse and abundant fossils, with echinoderms,

187 foraminifers, brachiopods, calcareous algae, ostracods, trilobites, gastropods, sponges,

188 conodonts, and bryozoans the most common (Fig. 3A). Chert nodules are common

189 within the Wuchiaping Formation. A volcanic ash layer marks the transition to the

190 overlying Talung Formation. The Talung Formation (~ 13.9 m) comprises bedded cherts,

191 siliceous wackestones, black shales, and thin marls (Fig. 2C, D). Black, thinly-bedded

192 cherts mostly appear at the basal part of the unit and become comparably less common

193 towards the top, while carbonate and siliciclastic components increase. In some parts,

194 black shales and marls are sandwiched between siliceous wackestones.

195 Fossil abundance declines sharply from the Wuchiaping Formation to the Talung

196 Formation, with a faunal shift from shallow-water bottom dwellers to a radiolarian and

197 siliceous sponge-dominated community (Fig. 3B, C). Siliceous fossil components are

198 more abundant in the lower and middle parts and decrease toward the top of the Talung

199 Formation.

200 The overlying Daye Formation consists of thinly bedded wackestone and marls

201 (Fig. 2F). Bioclastic components reflect a typical, monotonous post-extinction

202 assemblage consisting of echinoderms, ostracods, micro-gastropods, and ammonoids

203 (Fig. 2G and 3D).

204 At Changtanhe, the uppermost Wuchiaping Formation is characterised by ~ 6.2 m

205 thick grey, medium-bedded, and strongly bioturbated wackestones with chert nodules.

206 Bioclasts, typically composed of echinoderms, brachiopods, coral, ostracods, and

207 foraminifers, are abundant in thin sections (Fig. 3E, F). The overlying Talung Formation

208 is ~15.4 m thick and dominated by grey to black, siliceous wackestones and packstones

209 interbedded with bedded cherts and marls (Fig. 2H, I). Bedded cherts and marls occur

210 mostly in the lower part of the Talung Formation. There is a sharp decrease in benthic

211 calcareous fossil components from the Wuchiaping Formation to the Talung Formation.

212 Radiolarians and sponge spicules are common throughout the Talung Formation and

are most abundant in the middle part of this unit (Fig. 3G-J, L). Ostracods, brachiopods, and echinoderms occur sporadically, while gastropods only exist in the lower part of this unit (Fig. 3H, M). The lowermost Daye Formation is characterised by light brown, medium-bedded marls (Fig. 2J). These are overlain by grey, thinly bedded, micritic mudstones bearing detrital grains but lacking siliceous components. The transition from the Talung Formation to the Daye Formation coincides with a sharp decrease in fossil abundance, with almost no macrofossils appearing in the lower part of the Daye Formation (Fig. 3K).

4.2. Conodont Biostratigraphy

At Chibi, fifteen conodont species assigned to three genera were identified. Samples from the Wuchiaping and the Talung Formations predominantly yield *Clarkina* spp., while *Hindeodus* and *Isarcicella* occur only in the Lower Triassic Daye Formation (Fig. 5). These conodonts are assigned to nine biozones, in ascending order, the *C. guangyuanensis*, the *C. transcaucasica*, the *C. longicuspidata*, the *C. subcarinata,* the *C. changxingensis*, the *C. yini – H. praeparvus,* the *H. parvus*, the *I. lobata,* and the *I. isarcica* zones. The P-T boundary was placed 83 cm above the base of the Daye Formation according to the first occurrence (FO) of *H. parvus* (Fig. 6). Except for the lowermost *C. guangyuanensis* Zone, all conodont zones are established by the FO of the corresponding zonal taxon.

At Changtanhe, five species of *Clarkina* were obtained and assigned to four biozones (Fig. 5). The zones are, in ascending order, the *C. wangi*, the *C. subcarinata*, the *C. changxingensis*, and the *C. zhangi* zones. No conodonts were recovered from the Daye Formation (Fig. 7).

4.3 Framboid pyrite analysis

The occurrence and abundance of framboid pyrite vary significantly in the study sections. They are generally absent in wackestones and packstones of the Wuchiaping

241   Formation but become much more abundant in the Talung and Daye Formations (Figs.

242   6, 7). Thirty-four out of 35 samples have abundant framboids (n > 50). The K-S test

243   provides rigorous examinations on distribution patterns and shows that framboid sizes

244   in 22 out of 35 samples are normally distributed (see supplementary material).

245   At Chibi, mean framboid diameters range from 4.9 to 8.1 μm in the Talung

246   Formation (Fig. 6). Most framboids exhibit a narrow size distribution with a small

247   standard deviation (1 σ < 3 μm; Fig. 8). A noticeable decrease in mean diameter from

248   8.1 to 5.2 μm occurs in the top 2 metres of the Talung Formation. At Changtanhe, the

249   mean framboid diameter of most samples falls into the ~6–9 μm range, with a standard

250   deviation of ~2–5 μm (Fig. 8). The mean framboid diameter decreases from 8.7 to 4.9

251   μm towards the top of the Talung Formation (Fig. 7).

252   Framboids are absent in the lowermost Daye Formation (earliest Griesbachian) in

253   both study sections, but euhedral pyrites are present (Fig. 3K). Such absence of

254   framboids is facies independent, occurring both in carbonates and mud rocks. Framboid

255   becomes abundant in the lower and mid- Griesbachian, ranging from 5.6 to 7.2 μm.

256   Framboids show narrower size distributions in the Griesbachian than in the

257   Changhsingian, with standard deviations mostly < 2 μm.

258   K-W tests were carried out to test the statistical robustness of framboid size

259   distribution and the statistical significance of the conspicuous decrease in mean

260   framboid diameter in the latest Changhsingian. Firstly, samples are subdivided into

261   three groups according to their redox implications (mean diameters 4–6 μm, 6–8 μm,

262   and 8-10 μm, respectively). The results show the majority of samples within a group

263   show no (statistically) significant differences in size distribution. A second test was

264   carried out specifically for a group of samples from the top Talung Formation. Size

265   distributions of framboids in the group are statistically different, implying true redox

266   changes at the P-T boundary.

267

268   **4.4 Carbon isotope composition ($\delta^{13}C$)**

269   At Chibi, $\delta^{13}C$ values of carbonates from the Wuchiaping Formation vary between

270   ~3.0 % and 5.0 ‰. A prominent negative excursion of ~5.0 ‰ (from 4.0 to -1.1 ‰)

271   occurs in the uppermost Wuchiaping Formation. $\delta^{13}C$ values are largely stable (~1.0–

272   3.0 ‰) in the Talung Formation, showing a minor increasing trend from ~1.0 to 2.2 ‰

273   towards the top. The onset of a significant negative shift of ~3.0 ‰ (from 2.8 to 0 ‰)

274   occurs at the Talung–Daye transition and reaches a minimum value at the P-T boundary

275   (Fig. 6).

276   At Changtanhe, $\delta^{13}C$ values from the Talung Formation vary between -4.0 and

277   2.6 ‰. A positive shift from -2.6 to 2.0 ‰ occurs in the lower part of the Talung

278   Formation. A stepwise decrease in $\delta^{13}C$ from 2.2 to -4.5 ‰ occurs in the uppermost 4

279   m of the Talung Formation and reaches a minimum value in the basal Daye Formation,

280   above the P-T boundary (Fig. 7).

281

282   **4.5 SiO$_2$ contents**

283   Bulk rock SiO$_2$ contents range from 3.0 to 91.3 wt% and from 7.1 to 68.8 wt% at

284   Chibi and Changtanhe, respectively. At Chibi, SiO$_2$ contents are around ~50 wt% in the

285   lower part of the Talung Formation and increase to >75 wt% in the lower to middle

286   parts. SiO$_2$ contents show a two-step decrease from the uppermost Changhsingian to

287   the lower Griesbachian. The first decrease, from 91.3 to 13.9 wt%, occurs in the *C.*

288   *subcarinata* Zone and the second decrease, from 77.8 to 3.0 wt%, occurs across the P-

289   T boundary (*C. yini* Zone to *I. isarcica* Zone). SiO$_2$ contents remain consistently low

290   (<10 wt%) in the Daye Formation.

291   SiO$_2$ contents in the Changtanhe section are generally lower than those at Chibi,

292   with values in the ~25–50 wt % range in the lower and middle parts of the Talung

293   Formation. The first decrease in SiO$_2$ contents, from 44.6 to 7.0 wt %, occurs in the *C.*

294   *changxingensis* Zone. This decrease is less conspicuous, probably because of the low

295   sample density. A noticeable decrease in SiO$_2$ contents, from 68.8 to 11.0 wt%, occurs

296   across the P-T boundary interval. SiO$_2$ contents are low in the Daye Formation, as seen

297   at Chibi (Figs. 6, 7). But the uppermost marl sample contains 46.9 wt% SiO$_2$ that derives

298　mainly from detrital silicates.

299

300

5. Discussion

5.1 Conodont biostratigraphy and regional correlation

303　　The high-resolution conodont scheme for the upper Permian has been established
304　in the Meishan and Shangsi sections (Jiang et al., 2011; Yuan et al., 2014). Therefore,
305　the careful study of conodont biostratigraphy allows us to insert key events of Permian
306　chert production into the well-established P-T timeline. The depositional environment
307　at Shangsi was similar to that found at Chibi and Changtanhe, while the Meishan section
308　is probably slightly shallower. Therefore, the study sections can be easily correlated to
309　the two classic sections. The *C. wangi* and the *C. meishanensis* zones are absent at Chibi.
310　Thus, the *C. longicuspidata* Zone in the Chibi section correlates with the *C.*
311　*longicuspidata* and *C. wangi* zones in the Meishan section and the *C. orientalis* and *C.*
312　*wangi* zones in the Shangsi section. The *C. yini – H. praeparvus* Zone in the Chibi
313　section correlates with the *C. yini*, *C. meishanensis*, and *H. changxingensis – C.*
314　*zhejiangensis* zones at Meishan and the *C. yini* and *H. changsingensis* zones at Shangsi.
315　In the Changtanhe section, the *C. zhangi* Zone correlates with the lower part of the *C.*
316　*yini* Zone at Meishan and Shangsi.

317

5.2 Age constraints on the Talung Formation and the terminal PCE

319　　Bedded cherts were geographically very abundant in the Permian (e.g., Murchey
320　and Jones, 1992; Kakuwa, 1996; Meng et al., 2022), but they largely disappeared in the
321　latest Permian and were almost entirely absent in epicontinental seas during most of the
322　Early Triassic (e.g., Beauchamp and Baud, 2002; Sperling and Ingle, 2006). Although
323　rarely preserved, the chert gap also (but not always) occurs in abyssal floor successions
324　(e.g., Isozaki, 1997; Grasby et al., 2021; summarised in Fig. 9)

325   In the equatorial eastern Tethys, the Talung Formation represents the best-known

326 deepwater facies in the Late Permian. Our conodont biostratigraphy indicates that the

327 unit spans from the upper Wuchiapingian *C. longicuspidata* Zone to the latest

328 Changhsingian *C. yini – H. praeparvus* Zone at Chibi and from the lower

329 Changhsingian *C. subcarinata* Zone to the uppermost Changhsingian *C. zhangi* Zone

330 at Changtanhe, indicating the regionally diachronous nature of the Talung Formation.

331 A summary of conodont biostratigraphy from South China (Fig. 9) suggests a maximum

332 age range for the Talung Formation from the early Wuchiapingian *C. guangyuanensis*

333 Zone to the latest Changhsingian *H. changxingensis* Zone (Li et al., 1989; Yan et al.,

334 2013).

335   Investigations of the timing and lithological changes within the Talung Formation

336 provide valuable insights into the evolution of the PCE. In the northern margin of the

337 Yangtze Platform, extensive bedded cherts started to decrease in the *C. subcarinata*

338 Zone (e.g., at Chibi), somewhat earlier than most mid- and high latitude sites. However,

339 this varies regionally within the South China Block. At Bianyang (Nanpanjiang Basin),

340 the last bedded chert occurs at the basial *H. changxingensis* Zone (Yan et al., 2013).

341 Collectively, the termination of the PCE is marked by the top of the Talung Formation,

342 ranging from the latest Changhsingian *C. yini* Zone to the *H. changxingensis* Zone in

343 South China. The only known exception appears at Gaimao, Guizhou, where the Talung

344 Formation extends to the lowermost Triassic (Yang et al., 2012). This could imply that

345 regional oceanographic conditions also have played a role during the final shutdown of

346 the chert factories. At Nhi Tao in northwest Vietnam, the P-T succession represents an

347 extension of the Jinxi carbonate platform of the Nanpanjiang Basin. Cherty packstones

348 of the Dong Dang Formation are replaced by an oolitic grainstone layer in the latest

349 Permian (Algeo et al., 2007), suggesting the termination of the PCE coincided with

350 shallowing and/or a sudden increase in water energy.

351   Along the northwest Pangea margin, middle and upper Permian cherts were

352 equally extensively developed. This is best exemplified by the van Hauen Formation

353 of the Sverdrup Basin and the Kapp Starostin Formation in Spitsbergen (e.g.,

354   Beauchamp and Baud, 2002; Bond et al., 2018). Carbon isotope chemostratigraphy

355   indicates that bedded cherts of the uppermost Black Stripe Formation (top of the van

356   Hauen Formation) and the Kapp Starostin Formation lasted to the latest Changhsingian

357   (Wignall et al., 1998). In equatorial latitudes, bedded cherts became less common in the

358   late Changhsingian. This observation is consistent with our bulk rock SiO_2 data in the

359   Talung Formation, which show a conspicuous decrease towards the P-T boundary.

360   However, the precise timing of the termination of the PCE in mid- and high latitudes

361   remains a conundrum due to a lack of age-diagnostic conodonts, hindering a better

362   correlation with Tethyan sections (Fig. 9). Therefore, whether the termination of the

363   PCE in equatorial latitudes was exactly time-equivalent to mid-and high latitudes

364   remains unsolved.

365

366   **5.3 Redox evolution**

367   Pyrite framboid mean size is a reliable measure of redox conditions for ancient

368   marine rocks (e.g., Bond and Wignall, 2010). In general, rare or absence of framboids

369   points to locally oxygenated conditions, while framboid mean diameters in the 6–10

370   μm range suggest dysoxic conditions. Anoxic and euxinic conditions are indicated by

371   framboid diameters <6 μm (Bond and Wignall, 2010). Here, we combine framboid

372   pyrite proxy data with bioturbation and fossil occurrences to better differentiate dysoxic

373   conditions and to reconstruct a full spectrum of the redox evolution in the studied

374   sections.

375   Our data collectively suggest prolonged water column deoxygenation along the

376   northern Yangtze Platform margin across the Changhsingian. The Wuchiapingian saw

377   a fully oxygenated epicontinental margin with diverse faunas, intensive bioturbation,

378   and carbonate rocks devoid of pyrite framboids. The Talung Formation was deposited

379   mainly under dysoxic conditions, corroborated by large framboid mean sizes of ~5–10

380   μm and common occurrences of benthic fossils (e.g., sponge spicules, brachiopods, and

381   gastropods). These fossil assemblages are typically monotonous. Anoxic conditions,

382   indicated by the mean framboid size of ~4–6 μm, occurred intermittently in the lower

383   to mid- Changhsingian, but became more common in the latest Changhsingian *C. yini*

384   – *H. praeparvus* Zone. The establishment of anoxic conditions, evidenced by framboids

385   with mean diameters of ~5 μm, a loss of bioturbation, and an absence of benthic faunas,

386   occurred in the uppermost cherty beds, and coincided with the end-Permian mass

387   extinction at Chibi. The Changtanhe section shows overall less anoxic conditions,

388   evidenced by larger mean framboid sizes and more common occurrences of benthic

389   fossils, possibly due to a shallower setting.

390   Most redox proxies are insensitive to dysoxic conditions. Denitrification occurs in

391   dysoxic conditions and is enhanced in anoxic environments. Our interpretation of

392   dysoxic-anoxic had occurred in the Changhsingian is consistent with the $\delta^{15}N$ record in

393   the Meishan GSSP (Cao et al., 2009), which shows a denitrification signature

394   throughout the Changhsingian.

395   The redox conditions in the earliest Griesbachian are undetermined due to an

396   absence of pyrite framboids. However, the finely laminated and almost fossil-free facies

397   are probably not indicative of an oxygenated environment. The absence of framboidal

398   pyrite is not due to the modern weathering of the rocks, as euhedral pyrites are well-

399   preserved in framboid-free facies. Instead, it may reflect iron depletion in euxinic

400   environments or S^{2-} depletion under anoxic ferruginous conditions (e.g., Clarkson et al.,

401   2016). The notion of framboid-free ferruginous conditions in the crisis interval could

402   be tested by further study of iron geochemistry (e.g., Li et al., 2022).

403

404   **5.4 On the causes of the demise of Late Permian cherts**

405   Chert is a general term for sedimentary rocks composed primarily of SiO_2 group

406   minerals. Most bedded cherts lack internal sedimentary features but contain remnants

407   of siliceous organisms that were subject to diagenetic dissolution and recrystallization.

408   Bedded cherts without silica-secreting organisms were postulated to precipitate directly

409   from silica-saturated seawater, e.g., Precambrian cherts (Maliva et al., 2005). Bedded

410   cherts are subdivided into four general types: 1) non-skeletal cherts, 2) radiolarites, 3)

411 spiculites, and 4) diatomaceous cherts (Boggs, 2012). Most Permian cherts are
412 spiculites and radiolarites.

413   What promoted and terminated the PCE has been a matter of debate. Beauchamp
414 and Baud (2002) proposed that the circulation of nutrient-rich cold waters along the
415 northwest margin of Pangaea was a precondition for extensive chert development
416 during the PCE. In this scenario, the shutdown of silica factories resulted from the rapid
417 breakdown of this cold-water circulation and the establishment of much warmer
418 conditions, accompanied by sluggish circulation and perhaps a reduced input of DSi to
419 the ocean (Beauchamp and Baud, 2002). As the uptake of DSi by silica-secreting
420 organisms and the post-mortem dissolution of tests, frustules, or skeletons play
421 essential roles in controlling the oceanic silica budget, a nutrient-rich and well-
422 oxygenated Late Permian ocean should have favoured phytoplankton growth,
423 promoting the deposition of cherts. In contrast, the loss of radiolarian and siliceous
424 sponges during the end-Permian mass extinction could impair the biosilica sink,
425 hindering chert deposition (Isozaki, 1997; Sperling and Ingle, 2006).

426   The Early Triassic "chert gap" is denoted by the absence of bedded cherts and the
427 disappearance of diagenetic chert nodules in epicontinental sea settings (Beauchamp
428 and Baud, 2002). Such an absence could reflect a decrease in the supply of DSi to the
429 ocean, as suggested by e.g., Beauchamp and Baud (2002). Yet this hypothesis of
430 reduced input of DSi into the ocean in the Early Triassic despite climate warming is
431 inconsistent with all formulations of the silicate weathering feedback. It is also
432 inconsistent with empirical evidence for significantly enhanced continental weathering
433 (Algeo and Twitchett, 2010; Sun et al., 2018). Because DSi from terrestrial input is the
434 principal source of marine DSi, whereas volcanogenic and hydrothermal sources are
435 only secondary (Laschet, 1984; Frings et al., 2016), climate warming across the late
436 Permian and into the Early Triassic would have enhanced weathering and increased the
437 input of DSi to the oceans.

438   Alternative, non-exclusive hypotheses for the chert gap include i) a decrease in
439 biogenic silica export to the sediment; ii) a decrease in silica preservation efficiency (cf.

440 Westacott et al., 2021); iii) a transient expansion of the ocean Si pool; iv) a shift towards

441 a non-chert ocean silicon sink (cf. Isson et al., 2022) or v) a shift towards increased

442 depositions of cherts that are not preserved in the sediment record (i.e., in the abyssal

443 realm). Here, we combine our proxy data with existing evidence and use the box models

444 described in Section 3.5 to test the above-mentioned hypotheses. Panels B and C in Fig.

445 4 display the results of the box-modelling exercise for three illustrative scenarios: i) the

446 effect of temperature increases alone, ii) the effect of an instantaneous collapse in

447 biosiliceous production alone, and iii) a combination of the two. In scenario i) invoking

448 only an increase in temperature (of maximum 17 °C, from the lower *yini* Zone to the

449 *isarcica* Zone), radiolarian burial is essentially unchanged from the pre-event

450 conditions at ~7 ×10^{12} mol yr^{-1}, and the ocean DSi inventory increases ~1.3 times,

451 sufficient to increase preservation efficiency enough to offset the temperature-induced

452 increase in silica dissolution rate. Conversely, both scenarios ii) and iii) invoking a large

453 reduction in radiolarian biomass production lead to a significantly more sizeable

454 expansion in ocean DSi inventory (almost threefold) whereas the burial of biogenic

455 silica decreases drastically. The non-radiolarian sink correspondingly increases, and a

456 new steady-state is reached within ~300 kyr, such that inputs and outputs of Si to the

457 ocean balance over longer timescales.

458

5.4.1 Reduced biogenic production during the end-Permian crisis

460   Chert production was significantly impacted by the end-Permian mass extinction.

461 Late Permian chert builders were exclusively primary consumers, namely radiolarians

462 and siliceous sponges, although some could have developed photosymbiosis to

463 maintain certain degrees of self-sustainability (Casey, 1993). Along the northwestern

464 Pangean margin, the latest Permian chert builders were mainly siliceous sponges (e.g.,

465 Ezaki et al., 1994; Beauchamp et al., 2009). Radiolarites are also common. The loss of

466 siliceous sponges in this region correlates to the global marine extinction event and is

467 attributed to high loading rates of volcanic toxins and the development of ocean anoxia

468 (e.g., Grasby et al., 2015). However, whether volcanic toxins had impacted the global

469 oceans is debatable. In South China, siliceous sponge spicules decreased gradually

470 during the late Changhsingian, and 88–90% of types and 88–92% of forms eventually

471 disappeared at the extinction horizon (Liu et al., 2008). Radiolarians appeared to play

472 a more critical role in chert-building in the Tethys realm, but suffered significant losses

473 during the extinction (e.g., Feng et al., 2007). Radiolarians have a Mesozoic diversity

474 nadir in the Early Triassic and are very rare in lower Triassic rocks (O'Dogherty et al.,

475 2009).

476   The termination of chert building in South China coincides with a sharp decrease

477 in Ni concentrations in the water column. Vertical profiles of Ni in modern seawater

478 show a depletion in surface waters that is characteristic of nutrients, and such

479 distribution is not affected by redox cycling (Yang et al., 2021). There is a strong

480 correlation between Ni concentrations and total chlorins (the immediate degradation

481 products of chlorophyll pigments) in surface water, because Ni is associated with

482 photoautotrophic enzymes in primary producers (Böning et al., 2015). Thus, Ni_{excess}

483 (total sedimentary Ni minus terrigenous Ni) is used as a proxy for primary productivity

484 and its decrease at Chibi indicates a collapse in equatorial primary production (Fig. 10;

485 Müller et al., 2022). As primary consumers, chert-builders would have been profoundly

486 impacted by such changes (i.e., a decrease in food sources).

487   In the modern ocean, the removal of DSi is controlled by the biogenic silica

488 production, with ~20% accumulating on continental shelves and the rest in deep ocean

489 (e.g., Tréguer et al., 1995). If biogenic silica survives dissolution, it is ultimately either

490 diagenetically transformed into cherts or preserved as silica components in other

491 sedimentary rocks. Thus, the extinction of siliceous sponges and radiolarians at the end

492 of the Permian reduced the probability of chert formation in shallow marine settings.

493 As the onset of decreases in bulk rock SiO_2 content in the Talung Formation predates

494 the $\delta^{13}C$ negative excursion and climate warming (Figs. 6, 7, 10), we suggest at least

495 the initial stage of the chert demise was possibly due to a decrease in biogenic silica

496 sink rather than a deterioration in preservation potential. Our box-model scenarios that

497 include a reduction in biosiliceous production do indeed yield a decrease in biogenic

silica burial (and thus presumably biogenic chert occurrences). They also highlight that the decrease in biosiliceous burial is quickly compensated by a second silicon sink which is not defined in the model. Conceptually, this could reflect the partitioning of Si into authigenic clays, as recently suggested (Isson et al., 2022). It could alternatively reflect the partitioning of biosiliceous burial towards deep ocean settings that are less likely to be preserved in the sediment record. Interestingly and although rare, the P-T abyssal deepsea/seafloor sections do host abundant cherts, and the chert gap there is much shorter or possibly absent (e.g., at Arrow Rocks, summarised in Fig. 9).

The progressive deoxygenation in the Talung Formation coincided with the shutdown of low latitude chert production in the late Changhsingian. In epicontinental sea settings such as South China, a shift to oxygen-restricted conditions could have inhibited chert development by directly stressing silica-secreting groups, especially bottom-dwelling siliceous sponges. Surface-dwelling radiolarians were probably less affected by the development of dysoxic conditions. However, oxygen restriction alters bioturbation intensity in soft sediments and at the seawater-sediment boundary. On one side, bioturbation slows silica dissolution by accelerating the silica burial process, in which reactive, freshly produced biogenic silica is transported away from the seawater-sediment interface to deeper sediments where silica dissolution is thermodynamically and/or kinetically inhibited (Dale et al., 2021). A sharp decrease in bioturbation during the end-Permian crisis, evidenced by the extensive development of finely laminated sediments and a loss of trace fossils (Pruss et al., 2006; Luo et al., 2021), could be detrimental to chert formation. However, on the other side, bioturbation increases the rate of advection of DSi-depleted waters into sediment and alters concentration gradients at the surface of biogenic silica, decreasing the burial efficiency.

5.4.2 Silica dissolution and controlling factors

Chert production has been in a subtle balance between biogenic silica production and dissolution, in which silica dissolution has a significant role. In modern open oceans, DSi is depleted in surface water and only ~3% of biogenic silica tests can survive silica

527   dissolution, reaching the seafloor (Tréguer and De La Rocha, 2013). However, DSi

528   concentrations may have been much higher before the rise of diatoms (e.g., Conley et

529   al., 2017; Racki and Cordey, 2000), although recent work contests this idea (Ye et al.,

530   2021; Trower et al., 2021). Nevertheless, silica dissolution could have been less

531   intensive in pre-Jurassic oceans than in modern oceans. In contrast, as a minor

532   component of all sedimentary rocks, cherts are more abundant in post-Jurassic strata

533   (e.g., Hein and Parrish, 1987), implying the biogenic silica production influx largely

534   controls chert production.

535   In the seafloor succession in the southern Panthalassa, radiolarians persisted

536   intermittently into the Triassic, whereas in South China, simple siliceous sphaeroids

537   persisted into the *isarcica* Zone (Yang et al., 2012; Grasby et al., 2021). This leads to

538   the speculation that the chert gap was a preservation phenomenon in which only a few

539   small sphaeroid survived the end-Permian mass extinction. Several key factors govern

540   silica solubility, including pH, temperature, bacterial activity, and bioturbation

541   (Krauskopf, 1979; Van Cappellen and Qiu, 1997; Bidle and Azam, 1999; Dale et al.,

542   2021). Changes in all these factors have been archived in the turbulent time of the P-T

543   transition.

544   Silica solubility increases with pH, and such an effect becomes only prominent

545   when pH rises > 9 (e.g., Krauskopf, 1979). Such high alkalinity is beyond the normal

546   range of seawater (pH≈8.1) and could only occur in pore waters. A drop in seawater pH

547   (i.e., ocean acidification) during the P-T transition (Clarkson et al., 2015; Jurikova et

548   al., 2020), if it indeed occurred, would have slightly reduced silica solubility, promoting

549   precipitation of DSi, e.g., by means of chert deposition, from seawater. The shutdown

550   of Late Permian biogenic silica production is inconsistent with the development of

551   ocean acidification that should instead have promoted chert formation. Indeed,

552   abundant direct precipitation of authigenic carbonate on seafloor suggests instead an

553   increase in seawater alkalinity (e.g., Wood, 2014).

554   Climate warming enhances silica dissolution and lowers seawater DSi saturation.

555   Laboratory studies and field observations reveal that silica solubility increases

556   markedly with temperature (Van Cappellen and Qiu, 1997). The increase in tropical sea

557   surface temperatures from ~25 to 40°C in the latest Permian (Joachimski et al., 2012;

558   Sun et al., 2012) likely resulted in a 1.4 times increase in silica solubility (Van

559   Cappellen and Qiu, 1997) and affect the kinetic rate constants associated with silica

560   dissolution (e.g., Rickert et al., 2002; see also supplementary text). Increasing bottom

561   water temperature would also significantly enhance silica recycling in sediments

562   (Varkouhi and Wells, 2020), inhibiting the formation of diagenetic chert nodules.

563   Westacott et al. (2021) recently proposed that the low diatom abundance in early

564   Cenozoic sediments is, in fact, a diagenetic artefact driven by higher bottom water

565   temperatures that promote silica dissolution, implying a similar process could be at play

566   during the Early Triassic hothouse. Yet our box modelling results (Fig. 4) suggest that

567   temperature (through its influence on biogenic silica solubility, dissolution rate

568   constants, and weathering fluxes) has a muted impact on biogenic silica burial rates.

569   This occurs because any initial decrease in preservation efficiency is countered by an

570   increase in ocean DSi inventory that decreases the thermodynamic driving force for

571   dissolution. Importantly, the balance is (re)established on timescales equivalent to a

572   few residence times of Si in the ocean, which today is ~10 kyr (Frings et al., 2016) and

573   cannot be substantially longer than ~200 kyr (calculated as volume×saturation/input, or

574    $1.3×10^{21}$ l × $1500×10^{-6}$ mol l^{-1} / $10×10^{12}$ mol yr^{-1}). Thus, we reject the hypothesis that,

575   via a preservation-efficiency mechanism, climate warming alone is sufficient to explain

576   the Early Triassic chert gap. We can also rule out a transient increase in the ocean Si

577   inventory because an imbalance between inputs and outputs cannot be maintained for

578   the million-year timescales of the chert gap seen in shallow-marine sections.

579

6. Conclusions

581   Both sections studied here from the eastern Tethys document prominent shifts in

582   sedimentary facies corresponding to the waning and termination of Permian chert-

583   building in equatorial latitudes. Conodont biostratigraphy reveals the diachronous

nature of the chert-bearing Talung Formation, with a maximum range from the upper Wuchiapingian *C. guangyuanensis* Zone to the uppermost Changhsingian *H. changxingensis* Zone. The decrease in bulk rock SiO_2 contents in the Talung Formation predates the $\delta^{13}C$ negative excursion, climate warming, and enhanced weathering in the latest Changhsingian but coincided with a decline in primary productivity (Ni_{excess}) and progressive water column deoxygenation, hinting that the decrease in biogenic silica production may have been a response to the collapse of the aquatic food chain.

By combining palaeontological, sedimentological and geochemical evidence with box modelling results, we conclude that the collapse of the Permian chert factory and the Early Triassic chert gap were the consequence of a series of "unfortunate" coincidences, of which the loss of siliceous skeleton producers in shallow water during the end-Permian crisis was the primary cause. Warming-induced decreases in silica preservation efficiency and synergistic effects during water column deoxygenation, if not directly annihilating radiolarians and siliceous sponges, were only secondary triggers to the chert gap.

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Figure Captions

Fig. 1 A) Paleogeographic reconstruction of Pangea in the Late Permian (modified from Scotese, 2014). B) Paleogeographic reconstruction of the South China Block during the Changhsingian (modified from Feng et al., 1996).

Fig. 2 Field photographs showing the general characteristics of the Chibi (A-G) and Changtanhe (H-J) outcrops. A) The main outcrop of the Chibi section shows four lithological units. Yellow lines represent boundaries between adjacent formations. B) Medium-bedded and bioturbated limestone in the uppermost Wuchiaping Formation. C) Thinly-bedded limestones in the lowermost Talung Formation. D) Dark, thinly-bedded cherts, cherty limestones, and black shale in the middle part of the Talung Formation. E) Thinly- and medium bedded limestones with marls partings of the lowermost Daye Formation. The yellow dashed line represents the end-Permian mass extinction horizon (EH). Hammer (ca. 30 cm) for scale. F) Thinly-bedded limestones at the middle part of the Daye Formation. G) Ammonoid imprints in the lower part of the Daye Formation. Coin (30 mm) for scale. H) An overview of the P-T boundary in the upper part of the Changtanhe section. I) The Talung-Daye boundary transition at Changtanhe shows a shift in facies from dark, medium-bedded siliceous limestones to brown, thinly-bedded marls. Hammer (ca. 30 cm) for scale. J) Thinly-bedded marls in the lower part of the Daye Formation at Changtanhe. Hammer (ca. 30 cm) for scale.

Fig. 3 Photomicrographs of samples from the Chibi (A-D) and Changtanhe (E-M) sections. A) Crinoids (Cr) packstone with foraminifers (Fo) and brachiopods (Br) from the upper part of the Wuchiaping Formation. B) Spiculite from the top bed of the Talung Formation. C) Radiolarite from the middle part of the Talung Formation. D) Gastropod wackestone from the Daye Formation. E) Echinoderm wackestone with a high content of bioclasts from the upper part of the Wuchiaping Formation. F) Brachiopod (Br) wackestone with a small number of foraminifers (Fo) from the upper part of the

Wuchiaping Formation. G) Radiolarite from the middle part of the Talung Formation. H) Packstone with radiolarians and brachiopods (Br) from the upper part of the Talung Formation. I) A foraminifer from the lower part of the Talung Formation, showing a well-preserved intricate internal structure. J) Chert with foraminifers (Fo) and sponge spicules (Sp) from the lower part of the Talung Formation. K) Non-bioturbated marl from the Daye Formation. Black opaque grains are pyrite. L) A small foraminifer from the upper part of the Talung Formation. M) A microgastropod from the chert facies in the lower part of the Talung Formation.

Fig. 4 Box model of the oceanic Si cycle in the Permian-Triassic transition and modelling output. A) The two-box representation of the ocean silicon cycle, after Frings et al. (2016). Modelled response of B) ocean dissolved silica inventory and C) burial rates of radiolarian biogenic silica (solid lines) and a non-radiolarian Si sink (dashed lines) in response to an imposed temperature increase after Joachimski et al. (2012) (pink curves), an instantaneous and sustained decrease in radiolarian biogenic silica production (purple curves), or a combination of the two (blue curves).

Fig. 5 Scanning electron microscope images of conodonts (P_1 elements) from the study sections. Scale bar = 200 μm. 'a' for upper view, 'b' for lateral view. **1,** *C. yini*, from sample CB-49. **2, 3, 11,** *C. changxingensis*, 2, CB-50; 3, CB-49; 11, CTH-5. **4, 5, C.** *transcaucasica*, 4, CB-50; 5, CB-51. **6, 7,** *C. guangyuanensis*, CB-51. **8, C.** *longicuspidata*, CB-57. **9,** *C. subcarinata*, CB-55. **10,** *C. liangshanensis*, CB-58. **12,** *C. orientalis*, CB-46. **13, C. zhangi**, CHT-49. **14, 15,** *C. wangi*, CTH-1. **16, I. huckriedi**, CB-41. **17, 20, 21,** *H. parvus*, 17, CB-41; 20, 21, CB-38. **18, 19, 22, H. praeparvus**, 18, CB-41; 19, 22, CB-40. **23,** *I. isarcica*, CB-38. **24,** *I. inflata*, CB-39. **25, H.** *anterodentatus*, CB-36. **26-28,** *I. lobata*, 26, 27, CB-40; 28, CB-38. Conodont specimens 16–28 share the same scale bar.

Fig. 6 Log of the Chibi section with lithology, conodont ranges, and pyrite framboid box-and-whisker plots. Fm – formation, EH – extinction horizon, PTB – Permian-Triassic boundary. Redox conditions are defined by framboid sizes, with considerations of bioturbation intensity and fossil occurrences (see Section 5.3).

Fig. 7 Log of the Changtanhe section with lithology, conodont ranges, and pyrite framboid box-and-whisker plots. Fm – formation, EH – extinction horizon. Redox conditions are defined by framboid sizes, with considerations of bioturbation intensity and fossil occurrences (see Section 5.3).

Fig. 8 Mean diameter versus standard deviation of framboid size distributions for studied samples. The dashed line separates euxinic from suboxic–oxic conditions (cf. Wilkin et al., 1996).

Fig. 9 Sedimentary facies change in representative chert-bearing sections from the Late Permian to Early Triassic, showing a diachronous nature of the chert gap. Lithofacies and conodont zones are from Algeo et al. (2007), Baud et al. (2012), Beauchamp et al. (2009), Hao et al. (2021), Hendserson (1997), Li et al. (1989), Lyu et al. (2019), Sperling and Ingle (2006), Takahashi et al. (2021), Wang and Xia (2004), Wignall et al. (1998), Wignall and Newton (2003), Xia et al. (2004), Yan et al. (2013), Yamakita et al. (2007), Yang et al. (2012, 2019), Zhang et al. (2014).

Fig. 10 Summary of changes in $\delta^{13}C_{carb}$, Ni_{excess}, SiO_2 content, and redox conditions across the P-T boundary at Chibi and major chert building events in South China. $\delta^{15}N$ and palaeotemperature records are from the Meishan GSSP. Conodont zones: ① - *C. wangi*; ② - *C. subcarinata*; ③ - *C. changxingensis*; ④ - *C. yini*; ⑤ - *C. meishanensis*; ⑥ - *C. zhejiangensis–H. changxingensis*; ⑦ - *H. parvus*; ⑧ - *I. isarcica*. $\delta^{15}N$,

914 seawater temperature changes, and $Ni_{excess,}$ are from Cao et al. (2009), Joachimski et al.

915 (2012), Sun et al. (2012) and Müller et al. (2022).

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