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1 Latest Permian to Middle Triassic redox condition variations in
2 ramp settings, South China: pyrite framboid evidence

3
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13
14 **ABSTRACT**

15 **A detailed, 10 Myr redox history of the Changhsingian to Anisian (latest**
16 **Permian to Middle Triassic) oceans in ramp settings is reconstructed based on**
17 **framboidal pyrite analysis from South China. The result shows that the**
18 **well-established phenomenon of intense ocean euxinia-anoxia is faithfully recorded**
19 **in pyrite framboid data. Three major euxinia-anoxia episodes, namely the**
20 **end-Changhsingian to end-Smithian, middle to late Spathian, and early to middle**
21 **Anisian, have been recognized from the ramp facies successions. The first reducing**
22 **episode is subdivided into four sub-episodes: Permian–Triassic boundary (PTB),**
23 **Griesbachian-Dienerian boundary, earliest Smithian, and end-Smithian intervals.**
24 **Redox variations broadly track other oceanographic proxies. Euxinia-anoxia**
25 **coincide with positive excursions of conodont ΩCe anomalies, negative shifting**
26 **excursions of $\delta^{34}\text{S}_{\text{cas}}$, increases in sea surface temperature (SST), and negative**
27 **excursions of $\delta^{13}\text{C}$ in most cases. However, euxinia-anoxia near the**
28 **Dienerian-Smithian boundary coincided with positive excursions of $\delta^{13}\text{C}$ and a**
29 **general cooling period. This exception might be result of locally distributed of**
30 **reduced water columns. The PTB interval witnessed two ephemeral euxinia-anoxia**

31 **phases separated by a dysoxic to oxic period. The former, together with a rapid**
32 **increase in SST (up to 8°C), may be responsible for biodiversity crisis, while the**
33 **latter reducing event destroyed ecosystem trophic structures. Except for the PTB**
34 **euxinia-anoxia that spread over habitats in all oceans, the Spathian and Anisian**
35 **reduction events also prevailed in global oceans. Variation of the oxygen minimum**
36 **zone is suggested as the driving mechanism facilitating the move of reduced water**
37 **columns in various paleogeographic settings over this critical period.**

38

39 Key word: redox history, euxinia-anoxia, oxygen minimum zone, end-Permian mass
40 extinction, Early Triassic

41

42 **INTRODUCTION**

43

44 Marine ecosystems suffered severe degradation in the latest Permian mass extinction,
45 over 90% of marine species being wiped out (Erwin, 2006). It has been suggested that the
46 ecosystem did not fully recover until the early Middle Triassic, ~8–9 Myr after the crisis
47 (Chen and Benton, 2012; Wignall, 2015). Such a long, protracted biotic recovery process
48 is believed to have resulted, in part, from the effects of repeated environmental stresses
49 during the Early Triassic (Hallam, 1991; Payne and Clapham, 2012; Sun et al., 2012;
50 Romano et al., 2013; Song, H.J. et al., 2014). In particular, recurring oceanic anoxia has
51 been proposed as a key element responsible for the prolonged delay of marine recovery
52 (Hallam and Wignall 1997; Knoll et al., 2007; Algeo et al., 2011; Grasby et al., 2013;
53 Song, H.J. et al., 2014).

54 A range of geochemical and paleoecologic proxies have been employed to reconstruct
55 the marine redox history, such as authigenic uranium concentrations, iron concentrations,
56 cerium anomalies, Mo isotopes, U isotopes, sulfur isotopes, carbon isotopes, framboidal
57 pyrite morphology, and biomarkers (e.g. Wignall and Twitchett, 1996, 2002; Isozaki,
58 1997; Wignall and Newton, 2003; Newton et al., 2004; Grice et al., 2005; Kaiho et al.,
59 2006, 2012; Riccardi et al., 2006, 2007; Algeo et al., 2007, 2008; Gorjan et al., 2007; Xie
60 et al., 2007; Brenneka et al., 2011; Shen et al., 2007, 2011, 2015; Takahashi et al., 2009,
61 2013, 2014, 2015; Proemse et al., 2013; Dustira et al., 2013; Zhou et al., 2013; Song, H.Y.

62 et al., 2013, 2014; Chen et al., 2015; Schoepfer et al., 2015). These authors, however,
63 focus mostly on the P–Tr transition, although some papers have addressed marine redox
64 history through the entire Early Triassic (Wignall et al., 2010; Grasby et al., 2013; Song
65 et al., 2012; Song, H.Y. et al., 2013, 2014; Tian, L. et al., 2014) and fewer still have
66 looked at the Middle Triassic (Song et al., 2012).

67 Diverse geochemical proxies are powerful in reconstructing redox history, but many
68 are easily affected by diagenesis, and thus require fresh, unaltered samples. In contrast,
69 even when affected by later diagenetic overgrowths, the original framboidal morphology
70 can still be distinguished. After overgrowth, pyrite framboids become sunflower-like
71 pyrite aggregates, and the boundary between original framboidal pyrite and the
72 overgrowth rim is very distinct (Supplementary Fig. S1). Furthermore, surface
73 weathering, a major issue in most geochemical studies, does not affect framboid analysis
74 because the pyrite is converted to iron oxyhydroxides, whilst preserving the original
75 morphology (Lüning et al., 2003; Bond and Wignall, 2005). Such data have been
76 successfully employed to reconstruct redox conditions in both modern and ancient
77 sediments (Bond and Wignall, 2010), and work well in both carbonate and
78 mudstone/shale facies sediments (Tian, L. et al., 2014).

79 In order to build a detailed redox history (mainly based on conodont zones) during
80 biotic mass extinction and subsequent recovery process, we assessed both size
81 distributions and morphologies of framboidal pyrites from four sections, namely Meishan,
82 West Pingdingshan, South Majiashan, and Qingyan (Fig. 1), spanning the interval from
83 latest Permian to Anisian (early Middle Triassic) in South China. Reconstruction of a
84 high-resolution redox history allows us to investigate the temporal link between oceanic
85 anoxia and biotic and environmental extremes through this critical period of biotic
86 evolution.

87

88 **GEOLOGICAL AND STRATIGRAPHIC SETTINGS**

89

90 During the Permian–Triassic (P–Tr) transition, the South China Block was located
91 near the equator in the eastern Paleotethys Ocean (Fig. 1A), in which two positive blocks,
92 namely the Kongdian and Cathaysia landmasses, were situated at its western and

93 southeastern parts. Between these two areas the Nanpanjiang Basin and South China
94 northern marginal basin were separated by the extensive Yangtze Platform during Early
95 to Middle Triassic times (Fig. 1B). There were a broad and a narrow ramps situated at the
96 northern and southern margins of the Yangtze Platform, respectively. The nearshore and
97 siliciclastic shallow seas were distributed between these two land areas and carbonate
98 platforms or basins (Feng et al., 1997; Fig. 1B). The selected four study sites were all
99 situated in ramp settings during the Early to Middle Triassic (Fig. 1B). The marine P–Tr
100 boundary beds and Lower Triassic successions are both complete and extensive in the
101 South China block. South China therefore is one of the best regions for studying biotic,
102 environmental and climatic variations during the turnover across the P–Tr transition
103 (Chen and Benton, 2012; Benton et al., 2013).

104 Size distributions and morphologies of pyrite framboids are here documented and
105 analyzed from the uppermost Permian to lower Middle Triassic of four ramp facies
106 sections, namely Meishan, West Pingdingshan, South Majiashan, and Qingyan in South
107 China (Fig. 1).

108

109 **Meishan (MS) section**

110 The pyrite framboid samples across the P–Tr boundary were collected from the
111 intensively studied Meishan section, which crops out in the Changxing county, ~300 km
112 west of Shanghai City, eastern China (Fig. 1B). This section is not only the Global
113 Stratotype Section and Point (GSSP) for the P–Tr boundary, which is placed in the
114 middle of Bed 27 (Yin et al., 2001), but also has the best documented record of extinction
115 losses and environmental conditions (e.g. Chen et al., 2015). The uppermost Permian
116 succession comprises thin-bedded limestone of the upper Changxing Formation, while
117 the lowest Triassic sediments are dominated by alternations of thin-bedded marlstone and
118 mudstone with numerous clay ash layers of the Yinkeng Formation. Integration of
119 lithofacies and paleoecologic features show that the P–Tr succession represents a
120 deepening cycle up sections and depositional settings vary from upper ramp to lower
121 ramp/or offshore shelf (Chen et al., 2007, 2015; Tian, S. et al., 2014).

122 More recently, Chen et al. (2015) updated conodont zonation from the uppermost
123 Changxing and Yinkeng Formation in Meishan. The new conodont zones (with their

124 lithostratigraphic ranges in brackets) include *Clarkina changxingensis* Zone (Beds
125 22–23), *C. yini* Zone (Bed 24), *C. meishanensis* Zone (Bed 25), *Hindeodus*
126 *changxingensis* Zone (Bed 26), *C. taylorae* Zone (Bed 27a–b), *H. parvus* Zone (Bed
127 27c–d), *Isarcicella staeschei* Zone (Beds 28–29a), *I. isarcica* Zone (Bed 29b), *C. planata*
128 Zone (Beds 30–54), and *Neoclarkina discreta* Zone (Bed 35 and above). Establishment of
129 these eight conodont zones from the P–Tr boundary beds enables high-resolution
130 correlations with sections throughout China (Jiang et al., 2007; Zhang et al., 2007, 2014;
131 Chen et al., 2015).

132

133 **West Pingdingshan (WPDS) section**

134 Both the West Pingdingshan (WPDS) and South Majiashan (SMJS) sections are
135 situated in a southeastern suburb of Chaohu city, Anhui Province, South China. The
136 Chaohu area was part of the Lower Yangtze platform ramp during the Early Triassic
137 (Feng et al., 1997; Fig. 1B), and records a wide range of relatively deep-water settings
138 from epicontinental basin to inner and outer ramp (Chen et al., 2011; Li, M. et al., 2016).
139 The P–Tr boundary beds and the lower part of the Lower Triassic succession are well
140 exposed at the western slope of the Pingdingshan Hill, while the upper Lower Triassic
141 succession is better exposed 2 km away on the southern slope of the Majiashan Hill. The
142 WPDS section (Fig. 1C) records one of the most complete and best known
143 Induan–Olenekian boundary successions in China (Zhao et al., 2007).

144 The Lower Triassic strata exposed at WPDS comprises the Yinkeng and Helongshan
145 Formations and the basal Nanlinghu Formation. The Yinkeng Formation consists of
146 greenish/black shale interbedded with marlstone (Beds 3–37), while the Helongshan
147 Formation is characterized by thin-bedded dolomitic limestone interbedded with
148 calcareous mudstone (Beds 38–53). The lower Nanlinghu Formation is composed of
149 medium-bedded limestone interbedded with few thin mudstone layers (Beds 54–58).
150 Conodont zones and ammonoid assemblages are well established in this section (Fig. 2).
151 The Griesbachian to early Spathian successions yield conodonts *Hindeodus typicalis*,
152 *Neoclarkina krystyni*, *Sweetospathodus kummeli*, *Neospathodus dieneri*, *Novispathodus*
153 *waageni eowaageni*, *Nv. waageni waageni*, *Nv. pingdingshanensis*, and *Triassospathodus*
154 *homeri* Zones, ammonoids *Ophiceras-Lytophicears*, *Prionolobus-Gyronites*,

155 *Flemingites-Euflemingites*, *Anasibirites*, and *Columbites-Tirolites* Assemblages, and
156 bivalves *Claraia stachei*-*C. aurita* and *Eumorphotis inaequicostata*-*E. huancangensis*
157 Assemblages (Tong et al., 2003, 2004; Zhao et al., 2007, 2008).

158

159 **South Majiashan (SMJS) section**

160 The Spathian succession of the Nanlinghu Formation is well seen in the SMJS
161 section (Fig. 1C). The lower Nanlinghu Formation is composed of medium- to
162 thick-bedded limestone showing large ripples and wavy cross-bedding. The middle
163 Nanlinghu Formation is characterized by thin- to medium-bedded limestone with
164 *Gyrochorte* and *Thalassinoides*, and marine reptile and fish assemblages (Chen et al.,
165 2011; Motani et al., 2014, 2015; Jiang et al., 2014). The upper Nanlinghu Formation
166 comprises medium- to thick-bedded muddy limestone and dolomite, with laminar
167 microbial mats being well developed in the uppermost portion of the Formation (Zhao et
168 al., 2007; Chen et al., 2011; Li, M. et al., 2016). Conodonts of the *Nv. pingdingshanensis*,
169 *Tr. homeri*, and *Ns. anhuiensis* zones, ammonoids of the *Columbites-Tirolites* and
170 *Subcolumbites* assemblages, and bivalves *Guichiella angulata* and *Periclararaia circularis*
171 assemblages are present in the Nanlinghu Formation. Conodont zones established from
172 the lower part of the section correlate well with the same biozones recognized from the
173 uppermost part of the WPDS section (Zhao et al., 2007, 2008).

174

175 **Qingyan (QY) section**

176 The Middle Triassic samples were collected from the Qingyan (QY) section, which
177 is located in the Huaxi District, 30 km south of Guiyang, capital city of Guizhou Province,
178 South China. During the Early to Middle Triassic, the Qingyan area was situated on a
179 ramp between the Yangtze Platform in the north and the Nanpanjiang Basin in the south
180 (Feng et al., 1997; Fig. 1B). This ramp zone was ~400 km long and 25–70 km wide, and
181 lay as an S-shaped belt from northeast to southwest, separating a shallow carbonate
182 platform from a deep basin of mixed carbonate and clastic facies in southern Guizhou
183 areas (Feng et al., 1997). The uppermost Permian to Middle Triassic succession is
184 exposed continuously in Qingyan (Chen, J. et al., 2010a).

185 The uppermost Spathian to upper Anisian succession in QY was sampled (Fig. 1C).

186 The uppermost Spathian rocks are assigned to the upper Anshun Formation. The lower
187 part of the exposed succession is dominated by vermicular limestone (a micritic
188 limestone with densely-packed, small *Planolites* that give the rock a “wormlike”
189 appearance), while the upper part consists of dolomitic limestone. Conodonts from these
190 two units indicate the *Tr. homeri* Zone (Ji et al., 2011). In addition, bivalves
191 (*Eumorphotis* cf. *inaequicostata*, *Pteria* cf. *murchisoni*, *Entolium discites*, *Mysidiopteria*
192 cf. *striosus*, *Claraia* sp., *Entolium* sp., and *Leptochondria* sp.), ammonoids (*Tirolites* sp.
193 and *Prophychitoides* sp.), and brachiopods (?*Crurithyris* sp. and ?*Septaliphoria* sp.) are
194 also abundant and corroborate the Spathian age assignment (Chen, J. et al., 2010b).

195 The Anisian Qingyan Formation is subdivided into five members: the Xiaoshan,
196 Mafengpo, Yingshangpo, Leidapo, and Yuqing Members (Chen, J. et al., 2010b). Of
197 these, the Xiaoshan Member is dominated by grey, medium-bedded micrite, calcareous
198 mudstone and bioclastic limestone, yielding conodonts of the *Chiosella timorensis* Zone
199 and diverse ammonoids, bivalves, brachiopods and gastropods, all of which indicate an
200 earliest Anisian age (Yao et al., 2004; Chen, J. et al., 2010b; Ji et al., 2011; Yan et al.,
201 2015). The Mafengpo Member is characterized by dark mudstone interbedded with
202 numerous limestone layers, while the Yingshangpo Member consists of thin- to
203 medium-bedded bioclastic limestone interbedded with yellowish mudstone. These two
204 members yield abundant conodonts, ammonoids, bivalves, brachiopods, gastropods, and
205 echinoids (Chen, J. et al., 2010b; Ji et al., 2011). Of these, conodonts are assignable to the
206 *Neogondolella* cf. *bulgarica* Zone of early to middle Anisian age (Ji et al., 2011).

207 The Leidapo Member is composed of yellow mudstone interbedded with thin-bedded
208 limestone with brachiopod-bearing concretions increasing in abundance up section. The
209 uppermost Leidapo Member is well exposed at the so-called Fossil Hill and is dominated
210 by marly and sometimes silty mudstones (Chen, J. et al., 2010b). This member is
211 abundantly fossiliferous and contains calcareous algae, ammonoids, annelids, bivalves,
212 brachiopods, bryozoans, cnidarians, conodonts, corals, crinoids, echinoids, foraminifers,
213 gastropods, nautiloids, ostracods, scaphopods, and sponges (Chen, Z.Q. et al., 2010; Chen,
214 J. et al., 2010a, b). Of these, age-diagnostic ammonoid genera (*Bulogites*,
215 *Acrochordiceras*, *Proarcestes*, *Rieppelites*, *Judicarites*, *Ptychites*, and *Gosauites*)
216 constrain the Leidapo Member to the middle-late Anisian (Stiller and Bucher, 2008,

217 2011). The overlying Yuqing Member comprises dolomitic limestone and yields
218 ammonoids of late Anisian age (Stiller and Bucher, 2008, 2011).

219

220 **MATERIALS AND METHODS**

221

222 We studied 48, 55, and 86 sedimentary rock samples from the West Pingdingshan,
223 South Majiashan, and Qingyan sections, respectively. In addition, the analytical results of
224 pyrite framboids obtained recently from the Meishan section (Chen et al., 2015; Li, G. et
225 al., 2016) are also included here to reconstruct oceanic redox variation history through
226 the latest Permian to Middle Triassic times. A polished surface ($\sim 1 \times 1$ cm) of each
227 sample was examined for its pyrite content using the SEM (Hitachi SU8000) at the State
228 Key Laboratory of Biogeology and Environmental Geology in Wuhan, China. The
229 framboid size distributions were measured where this morphology was present, and
230 where possible, a minimum of 100 pyrite framboid sizes were measured for each sample.
231 Measurement bias may come from overlooking smaller framboids, possibly shifting the
232 spectrum toward larger sizes, but such shifts are compensated for, as framboid diameters
233 tend to be underestimated, because spheres are unusually not exactly broken in half
234 (Hethke et al., 2013). Furthermore, the same analytical approach was used for each
235 sample.

236 Framboidal iron monosulfides are authigenic mineral forms found in abundance at
237 the redox interface between the oxic and sulfidic zones in modern environments that
238 convert to pyrite during burial (Wilkin et al., 1996). In euxinic settings, framboids rarely
239 reach 5–6 μ m diameter before the dense particles sink to the seabed and accumulate as
240 small-size populations with a narrow size distribution (Wilkin et al., 1996). In dysoxic
241 environment seafloor conditions are weakly oxygenated and framboids form within the
242 surface sediments where their size is governed by the local availability of reactants, with
243 the result that they are more variable and generally larger in size (Wilkin et al., 1996).
244 Criteria based on size distribution and morphology of framboids to distinguishing five
245 redox states follow mainly Bond and Wignall (2010). In general, when framboids are
246 small (mean diameters: 3–5 μ m), abundant, with a narrow size range, and form the
247 dominant pyrite fraction, they indicate euxinia (a persistently sulfidic lower water

248 column). If framboids are small (mean diameters: 4–6 μm), abundant, with a few, larger
249 forms, and dominate the pyrite fraction, then they indicate anoxic condition (without
250 oxygen in bottom waters for long periods). When framboids have mean diameters of
251 6–10 μm and are moderately common, with a few, larger framboids together with
252 crystalline pyrite, then such populations are encountered in lower dysoxic condition (with
253 weakly oxygenated bottom waters). In upper dysoxic environments (with partial oxygen
254 restriction in bottom waters) framboids are usually still present, (although crystalline
255 pyrite is more abundant) and have a broad range of sizes with only a small proportion of
256 framboids < 5 μm . In oxic condition (without oxygen restriction), no framboids are
257 present, and pyrite crystals occur rarely.

258 Cross plots of mean framboid size (M) versus standard deviation (SD) (Tian, L. et al.,
259 2014) can also be employed to interpret redox conditions. On the cross-plot diagram the
260 boundary separating euxinic from oxic-dysoxic facies was determined by a means of
261 equation: $M = -3.3 \cdot SD + 14$ (Tian, L. et al., 2014). Here, M is mean diameter of
262 framboids, while SD represents the standard deviation. If M falls in the euxinic facies
263 area, the sampled framboids indicate a euxinic condition. Similarly, M values in the
264 oxic-dysoxic facies area point to an oxic-dysoxic condition (Tian, L. et al., 2014). Both
265 Bond and Wignall's (2010) criteria and M-SD crossplot diagram (Tian, L. et al., 2014)
266 are utilized here to assess the redox history of the ramp settings in South China through
267 the latest Permian to Middle Triassic.

268

269 **RESULTS AND INTERPRETATION OF REDOX HISTORY**

270

271

272 **MS and WPDS section**

273 The redox history in the Meishan section during the P–Tr transition has been well
274 studied based on morphology and size variation of pyrite framboids (Shen et al., 2007;
275 Chen et al., 2015; Li, G. et al., 2016). Here we focus on the layers which have not been
276 sampled before, mainly from Beds 30–56 (*C. planata* zone) (online supplementary Table
277 1). However, most of the samples yielded rare or no pyrite framboids, and only one
278 sample from Bed 30-2 yielded a few pyrite framboids of 5.43 μm mean diameter,

279 suggesting anoxia at this level..

280 In WPDS, the framboid distribution is highly variable, 20 of 48 samples yielded a
281 few or abundant pyrite framboids; the rest of the samples had few or no pyrite framboids
282 (online supplementary Table 1). The relationship between framboid abundance and
283 lithology is unclear because framboids are found in a range of lithologies but also
284 inconsistently present in samples of the same lithology (Fig. 2). Most framboids in the
285 productive samples have small mean diameters (3–6 μm ; Fig. 2), and similarly small
286 standard deviation with the result that they plot in the euxinic-anoxic spectrum (Fig. 3).
287 The exception is a series of samples from the mid Yinkeng Formation that have much
288 larger maximum framboid size (up to 33.22 μm), which fall into the dysoxic field on the
289 mean/standard deviation plot (Fig. 3).

290 Ten samples were collected from Griesbachian strata and three of them yielded
291 framboids. The earliest Griesbachian sample with pyrite framboids had populations that
292 are mostly < 5 μm in diameter, indicating euxinic-anoxic condition. A higher sample
293 from (upper *C. krystyni* Zone, late Griesbachian) is also dominated by tiny framboids but
294 with rarer larger examples, up to 13.5 μm , suggesting an overall lower dysoxic redox
295 regime. Dienerian samples (*Sw. kummeli* to the *Nv. waageni eowaageni* zones) also have
296 tiny, euxinic framboids, but three samples from the Dienerian–Smithian boundary (DSB)
297 have a much broader framboid size range (> 15 μm in diameter) that fall in the dysoxic
298 field of the M-SD plot (Fig. 3). Euxinic conditions are then inferred to return in the early
299 Smithian where tiny framboids with a narrow size range reappear.

300 Above this, in the lower part of *Nv. w. waageni* Zone most samples contain no or few
301 large framboids indicating well oxygenated conditions. Redox condition abruptly
302 returned to euxinia in the middle part of *Nv. w. waageni* Zone where abundant framboids
303 are mostly < 5 μm in diameter. Samples from across the Smithian–Spathian boundary
304 (SSB) (defined by the upper *Nv. w. waageni* Zone and lower *Nv. pingdingshanensis*
305 zones) also yield abundant tiny framboids. Immediately above the SSB framboids
306 become very large and a few pyrite crystals appear: a dysoxic facies. Only two samples
307 from the upper *Nv. pingdingshanensis* Zone and lower *Tr. homeri* Zone yielded abundant
308 tiny framboids (< 5 μm in diameter) but with a “tail” of larger examples, indicating that
309 the early Spathian waters were likely in a lower dysoxic state.

310 To sum up, the general picture from the WPDS section shows that redox conditions
311 fluctuated frequently in the Early Triassic, including three relatively long euxinic periods,
312 corresponding to the early Griesbachian, Griesbachian–Dienerian boundary, early
313 Smithian, and latest Smithian (Fig. 2).

314

315 **SMJS section**

316 Pyrite framboids are relatively common in the Spathian SMJS section (Fig. 4): 32
317 of 43 samples yielded examples (Online supplementary Table 1). The M-SD plot (Fig. 5)
318 shows that only two samples fall within the dysoxic field with the remainder in the
319 euxinic-anoxic field. However, the overall picture (Fig. 4) is one of frequent oscillation of
320 redox conditions, from framboid-free oxic beds to small framboid-rich euxinic beds, in
321 the early Spathian followed by more persistent euxinia in the later Spathian
322 (corresponding to the middle to upper *Ns. anhuiensis* Zone). Finally, in the highest beds
323 in this section, belonging to the uppermost *Ns. anhuiensis* Zone, framboids are absent
324 implying oxic conditions. Several of the beds that lack framboids are burrowed. Pelagic
325 fauna (marine reptiles and fish) appear in beds that record a range of redox conditions
326 although they are most common in euxinic facies where preservational conditions were
327 optimal (Fig. 4; Motani et al., 2014, 2015; Jiang et al., 2014).

328

329 **QY section**

330 A total 37 of 88 samples from the uppermost Spathian to uppermost Anisian
331 section at QY yielded pyrite framboids (Fig. 6) with sizes that record a spectrum of redox
332 conditions (Fig. 7). The late Spathian saw a relatively long anoxic-euxinic phase
333 terminated by a short dysoxic period and then a relatively long oxic period during the
334 Spathian–Anisian transition (Fig. 6). This is a similar redox history to that recorded in the
335 SMJS (Fig. 4). Noteworthy euxinic episodes in the Anisian are recorded in the Mafengpo
336 Member and the lower Yingshanpo Member (Fig. 7). Interestingly, the lower
337 euxinic-anoxic interval in the latter unit coincides with the presence of microgastropod
338 shell beds, microbialites and sea-floor carbonate precipitates (Chen, Z.Q. et al., 2010) – a
339 range of attributes typical of Early Triassic times. In contrast, the redox conditions in the
340 Xiaoshan and Mafengpo Members (early Anisian) were generally well oxygenated and

341 such conditions are also common in the uppermost Leidapo Member. However, the pyrite
342 assemblages from the upper part of this suggest a return to dysoxic bottom waters (Fig.
343 6).

344

345 **DISCUSSION**

346

347 **Ten million year oceanic redox history from latest Permian to early Middle Triassic** 348 **in South China**

349

350 Pyrite framboid morphologies and size variations allow recognition of three major
351 euxinic-anoxic episodes from the uppermost Permian to lower Middle Triassic succession
352 in South China: end-Changhsingian to end-Smithian (Episode 1), middle to late Spathian
353 (Episode 2), and early to middle Anisian (Fig. 8). The end-Changhsingian to
354 end-Smithian reducing episode is subdivided into four sub-episodes: P–Tr boundary
355 (Sub-episode 1-a), Griesbachian-Dienerian boundary (Sub-episode 1-b), earliest Smithian
356 (Sub-episode 1-c), and end-Smithian (Sub-episode 1-d) intervals (Fig. 8).

357

358 **P–Tr boundary sub-episode**

359 Both sulfur isotopic excursions and biomarker analysis suggested that short periods
360 of euxinic water columns have developed at Meishan during the *C. yini* Zone (Grice et al.,
361 2005; Shen et al., 2011). Similarly, pyrite framboids also indicate dysoxic conditions due
362 to their large sizes (> 6 µm in diameter) with only one very short interval of
363 euxinic-anoxic conditions (Li, G. et al., 2016; Fig. 9). Anoxia then developed in the *C.*
364 *meishanensis* Zone (Bed 25, Shen et al., 2007) and a euxinic peak occurred in the *H.*
365 *changxingensis* Zone (Bed 26) and succeeding *C. taylorae* Zone (Bed 27b) (Chen et al.,
366 2015; this study). No pyrite framboids occur in Bed 27c–d, and large pyrite framboids
367 (8.7 µm in mean diameter) are found in Bed 28, indicating dysoxic to oxic conditions in
368 the *H. parvus* Zone and lower *I. staeschei* Zone (Bond and Wignall, 2010; this study).
369 Abundant tiny framboids return in Bed 29a–b implying anoxic conditions in the upper *I.*
370 *staeschei* Zone and *I. isarcica* Zone, that persisted, with short interruptions, into the early
371 to middle Griesbachian (Fig. 9; Chen et al., 2015; Li, G. et al., 2016).

372 The two euxinic-anoxic phases in Bed 26–27a and Bed 29a–b, coincide closely with
373 metazoan extinction, which occurs at the top of Beds 25 and 28 (Song, H.J. et al., 2013).
374 These two euxinic-anoxic peaks coincide with the two microbial blooms bracketed to
375 Beds 26–27a and Bed 29, respectively in Meishan (Xie et al., 2005). They also
376 correspond to two negative excursions of carbon isotope (Xie et al., 2007) and sulfur
377 isotope values (Song, H.Y. et al., 2013) as well as TOC concentration peaks from the
378 same section (Yin et al., 2012) (Fig. 8). The first reducing phase coincided with a rapid,
379 dramatic 8°C increase in seawater surface temperature (SST) from Bed 24e to Bed 27a
380 (Sun et al., 2012). The SST remained high (up to 35°–39°C), during the second
381 euxinic-anoxic phase. Accordingly, the first reduced water column event may have
382 resulted from the rapid increase in SST, and both factors may have directly killed marine
383 life in the first phase of the P–Tr extinction (Song et al. 2014). The early to middle
384 Griesbachian redox conditions (*I. isarcica* Zone to upper *C. planata* Zone) fluctuated
385 frequently (Fig. 9), indicating high frequency chemocline fluctuations at this time too.

386

387 **Griesbachian–Dienerian (G–D) boundary sub-episode**

388 The presence of small framboids indicates the presence of a G–D boundary
389 euxinic-anoxic interval (Fig. 8). This reducing event is also recorded as a distinct positive
390 conodont Ce anomaly (Song et al., 2012), and corresponds to a pronounced negative
391 excursion of $\delta^{34}\text{S}_{\text{cas}}$ isotopes and $\delta^{13}\text{C}_{\text{carb}}$ isotopes (Fig. 8). This euxinia-anoxia was also
392 associated with a peak of SST (Sun et al., 2012). The G–D transition also saw a dramatic
393 decline in diversity amongst conodonts and ammonoids (Orchard, 2007; Brayard et al.,
394 2009; Stanley, 2009). Thus, the prevailing euxinic-anoxic water columns over the G–D
395 transition may be linked with the extinction of pelagic clades such as conodonts and
396 ammonoids that had survived with reasonable success during P–Tr mass extinction.

397

398 **Earliest Smithian sub-episode**

399 Following the establishment of generally well-oxygenated conditions in the
400 Dienerian, dysoxia was established at the end of the Dienerian (upper *Ns. dieneri* Zone at
401 WPDS). The anoxia then intensified to give a pronounced euxinic-anoxic period in the
402 *Nv. waageni eowaageni* Zone. Conodont oxygen isotopes also reveal the onset of a

403 warming trend at this time (Sun et al. 2012). The coeval conodont ΩCe record shows a
404 negative excursion (Fig. 9) that also indicates increasing dysoxia (Song et al., 2012).
405 However, the $\delta^{34}\text{S}_{\text{cas}}$ isotope record exhibits a turnover from positive to negative
406 excursions, suggesting a global decrease in the amount of pyrite accumulating – an
407 unexpected trend if global anoxia has increased (Fig. 9). It is possible that this brief
408 earliest Smithian anoxic event has not been sampled in the $\delta^{34}\text{S}_{\text{cas}}$ record or the event may
409 be a regional event that is only manifest in South China.

410

411 **End-Smithian sub-episode**

412 Pyrite framboid evidence suggests euxinic condition developed at the end of the
413 Smithian (*Nv. waageni waageni* Zone) followed by a slight improvement to dysoxic
414 conditions in the earliest Spathian *Nv. pingdingshanensis* Zone. This redox trend shows
415 close parallels in the sea-surface temperature trend, which reached a peak of warmth
416 around the Smithian–Spathian boundary (SSB) before cooling (Sun et al., 2012). Other
417 indicators of anoxia (conodont ΩCe anomaly and Th/U ratios) also reveal a short-lived
418 but intense anoxic event at this time (Song et al. 2012). The SSB was also marked by a
419 major crisis amongst conodonts and ammonoids (Orchard, 2007; Stanley, 2009; Brayard
420 et al., 2009). Both $\delta^{34}\text{S}_{\text{cas}}$ and $\delta^{13}\text{C}_{\text{carb}}$ isotopes experienced a sharp transition from a
421 negative to positive excursion across the SSB (Song, H.Y. et al., 2014; Zhang et al.,
422 2015).

423

424 **Middle to late Spathian episode**

425 This long euxinic-anoxic interval corresponds to the upper *Ns. anhuiensis* Zone
426 (also equivalent to the upper part of the regional conodont *Tr. homeri* Zone in South
427 China (Zhao et al., 2013)) and the upper *Subcolumbites* ammonoid assemblage zone in
428 SMJS (Fig. 5). The upper part of this interval was also detected in upper *Tr. homeri* Zone
429 of the QY section (Ji et al., 2011). The euxinia is also revealed by a contemporaneous,
430 positive conodont ΩCe excursion (Song et al., 2012). This long-period euxinic-anoxic
431 event predates the purported end-Spathian anoxia recognized based on biomarker
432 analysis from the same section (Saito et al., 2015). However, this latter event is neither
433 recorded in our data nor in the data of Song et al. (2012), suggesting biomarker evidence

434 alone does not provide a strong criterion for ocean anoxia.

435

436 **Early to middle Anisian episode**

437 Oxygenation levels fluctuated during the entire Anisian with most frequent euxinic
438 conditions occurring during the Bithynian substage (early–middle Anisian) when three
439 distinct cycles can be recognized (Fig. 8). Each redox cycle is featured by two reducing
440 phases interrupted by an abrupt, short oxic phase. Oxygen deficiency overall became less
441 intense up section (Fig. 8). The coeval conodont Ce anomaly data also show dysoxic
442 conditions at this time (Song et al., 2012).

443

444 **Paleoceanic redox variations in various paleogeographic settings and global** 445 **correlations from the latest Permian to Middle Triassic**

446

447 Several other studies have attempted to reconstruct the Early and Middle Triassic
448 redox history in other regions allowing consideration of the global redox changes (Fig.
449 10b). Thus, Song et al. (2012) reconstructed the Triassic redox history of a shallow
450 platform margin section in South China based on the ΩCe anomaly record (Fig. 10A).
451 Grasby et al. (2013) reconstructed the Late Permian to Early Triassic redox history of the
452 north-west Pangean Sverdrup Basin, in the Canadian High Arctic, based on pyrite
453 framboid analysis and $\delta^{13}\text{C}_{\text{org}}$ isotope data obtained from five sections (Fig. 10A). Finally,
454 Wignall et al. (2010) reconstructed the Permian to Jurassic redox history of the
455 Panthalassa Ocean also based on pyrite framboid analysis from several sections in the
456 Mino-Tamba Terrane, Japan (Fig. 10A). In addition to this spatial coverage, variations in
457 redox values with water depth have also been interpreted as movement of chemocline
458 (Riccardi et al., 2007) or oxygen minimum zone (OMZ) (Algeo et al., 2011) (Fig. 10C).

459 Prior to the latest Permian mass extinction in *C. yini* Zone, dysoxic water columns
460 prevailed in both platform margin and ramp settings, although other evidence showed
461 that brief anoxic phases may have invaded the shallow photic zones (Wignall and
462 Twitchett, 1996; Grice et al., 2005; Shen et al., 2011; Li et al., 2015). Coeval euxinia was
463 also observed in pelagic basins of the Panthalassic Ocean based on framboid, organic
464 carbon isotope, trace element compositions, and sulfur isotope (Fig. 10C-1) evidence

465 (Wignall et al., 2010; Takahashi, et al., 2010, 2013, 2014), although Algeo et al. (2010,
466 2011) suggested that the expansion of low-oxygen conditions within the Panthalassic
467 Ocean was focused within the OMZ rather than at the deepest seafloor. Coeval
468 euxinia/anoxia was also observed in the deepwater Sverdrup basin (Algeo et al., 2012;
469 Grasby et al., 2013; Proemse et al., 2013). Knies et al. (2013) further emphasized that the
470 Late Permian euxinic/anoxic seawater of the Sverdrup basin may have originated from
471 the OMZ rather than the deep basin floor.

472 In the main phase of the latest Permian mass extinction and its aftermath, which are
473 bracketed by the *C. meishanensis* and *C. taylorae* Zones, euxinic-anoxic conditions were
474 recognized in all sections from pelagic basin, to deep shelf basin, ramp to platform
475 margins (Fig. 10C-2). This event therefore swept across the whole ocean from shallow to
476 deep water, implying a huge expansion of the OMZ coincident with biotic extinction at
477 that time.

478 During the *H. parvus* Zone, euxinic-anoxic conditions were pronounced in the
479 relatively shallow platform margin (e.g. Guandao section), however in some northwest
480 Pangea shallow marine sections yield unusually diverse Early Triassic ichnofossil
481 assemblages indicating some well-oxygenated refuges (Beatty et al., 2008). This region
482 of Pangea also witnessed major oscillations of seafloor oxygenation from oxic to euxinic
483 conditions (Wignall et al., 2016). But the assignment of euxinic-anoxic conditions to the
484 P–Tr boundary beds of those deep and pelagic basin facies successions is rather tentative.
485 The OMZ was confined to relatively deep basins and platform margin settings (Fig.
486 10C-3). In the second phase of the P–Tr mass extinction and its aftermath, equivalent to
487 the *I. staeschei* and *I. isarcica* Zones, euxinic-anoxic water columns were pronounced in
488 these settings and basins (Fig. 10C-4).

489 During the Griesbachian–Dienerian transition euxinic-anoxic conditions were
490 detected in the relatively deep Sverdrup basin, and both shallow platform margin and
491 ramp settings, although samples from the Panthalassa Ocean suggest more dysoxic
492 conditions at this time (Fig. 10B; Wignall et al., 2010). Thus deep-ocean anoxia
493 weakened at this time whilst remaining intense in shallower settings (Fig. 10C-5).

494 During the earliest Smithian, euxinic-anoxic water columns can be recognized in
495 ramp settings whereas dysoxia-oxia prevailed in basins (Fig. 10B). This level has not

496 been sampled in Panthalassan sections and so the redox values during the early Smithian
497 are unknown.

498 Euxinic-anoxic conditions expanded dramatically in the late Smithian although once
499 again the redox values in the deep ocean have yet to be studied (Fig. 10B). Anoxia
500 expanded into shallow water photic zone (platform margin settings) and into ramps and
501 deep-water shelf basins (Fig. 10C-7). Widespread and intense euxinia recurred in the
502 middle-late Spathian but did not coincide with major biotic and climatic changes. This
503 environmental event is widely recognized in all settings and basins (Fig. 10B, 10C-8). In
504 addition, end-Spathian euxinia-anoxia is recognized by biomarker analysis reported from
505 the Panthalassian sections in Japan (Takahashi et al., 2009, 2015), although this extreme
506 reducing condition was not indicated by pyrite framboids in the studied sections. Besides,
507 the end-Spathian is poorly defined as the last conodont zone of Early Triassic ranges the
508 middle to late Spathian in many regions (Zhao et al., 2007). Thus, the precise correlation
509 between the Panthalassian and South Chinese sections still remains uncertain. The
510 possibility that the Panthalassian end-Spathian strata are equivalent to the middle to late
511 Spathian of South China cannot be excluded.

512 During the Anisian, oceans were generally much better oxygenated. However,
513 oxygen-poor conditions became widespread in the middle part of the stage especially in
514 ramp settings, suggesting strong OMZ development (Fig. 10B). However, this interval
515 coincided with the rapid recovery of marine biotas (Chen and Benton, 2012), suggesting
516 that after frequently and long time oxygen-poor events in early Triassic, the survived
517 Middle Triassic animals got the ability to tolerate the oxygen-poor environment to some
518 extent. This general amelioration of conditions coincided with the rapid recovery of
519 marine biotas (Chen and Benton, 2012).

520

521 **CONCLUSIONS**

522

523 Detailed sampling of pyrite framboid size and morphologies has revealed episodic
524 and frequent development of euxinia-anoxia within ramp settings in South China during
525 the latest Permian to Middle Triassic. Three major euxinia-anoxia episodes were
526 recognized in these locations. The longest phase of reducing conditions occurred in the

527 middle to late Spathian in ramp settings. Redox history broadly tracks covariations with
528 positive shifting excursions of conodont ΩCe anomalies, negative excursions of $\delta^{13}\text{C}$,
529 negative shifting excursions of $\delta^{34}\text{S}_{\text{cas}}$, and with peaks in tropical SST. The P–Tr
530 boundary reducing sub-episode is resolved in ramp settings into two euxinia-anoxia
531 phases separated by a dysoxic to oxic period. These two euxinic-anoxic episodes coincide
532 with two phases of mass extinction on either side of the P–Tr boundary. Global
533 correlations of redox history in different environmental settings and oceanic basins show
534 that three euxinia-anoxia phases (P–Tr boundary, middle to late Spathian and early to
535 middle Anisian) are widespread and probably global. Further study in other regions is
536 required to see if the other three anoxic phases were global phenomena.

537

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539

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548

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912 **Figure and Table captions**

913

914 Figure 1. (A) Early Triassic global paleogeographic configuration (base map courtesy of
915 R. Blakey: <http://www2.nau.edu/rcb7/240moll.jpg>). (B) Location map of China. (C)
916 Early Triassic paleogeographic map of South China showing the study sites (base map
917 modified from Feng et al., 1997). (D) Simplified chrono- and litho-stratigraphic
918 framework through the latest Permian to Middle Triassic of the four studied sections.
919 Abbreviations of the studied sections: MS = Meishan, WPDS = West Pingdingshan,
920 SMJS = Southern Majiashan, QY = Qingyan. 1 = *C. meishanensis* Zone, 2 = *H.*
921 *changxingensis* Zone.

922

923 Figure 2. Griesbachian to early Spathian (Early Triassic) paleoredox condition changes
924 from the West Pingdingshan (WPDS) section. Carbon isotope data are after Tong et al.
925 (2007), trace fossil data after Chen et al. (2011), conodont zonation after Zhao et al.
926 (2007), ammonoid and bivalve assemblages after Tong et al. (2003, 2004). Seri. = Series,
927 Subs. = Substage, Fm. = Formation, Lith. = Lithology, SH = Sample horizon, FAP =
928 Frequency of authigenic pyrite, FFP = Frequency of framboid pyrite, ii = ichnofabric
929 index, CA = Conodont zonation, AA = Ammonoid assemblage, BA = Bivalve assemblage,

930 Lop. = Lopingian, Dal. = Dalong Formation, MISS = microbially induced sedimentary
931 structure.

932

933 Figure 3. Crossplot diagram shows mean diameter (M) versus standard deviation (SD) of
934 pyrite framboid sizes from the WPDS section. The determination of the dash line
935 separating euxinic/anoxic facies from dysoxic facies sees text (after Tian-L. et al., 2014).
936 Note all samples, other than both CPW24-5 (end-Dienerian) and CPW-53-1 (early
937 Spathian) that fall into the dysoxic condition field, fall into anoxic/euxinic condition area.

938

939 Figure 4. Spathian paleoredox condition variations from the South Majiashan (SMJS)
940 section. Reptile and fish data sourced from Motani et al. (2014, 2015) and Jiang et al.
941 (2014). All isotopic and paleontologic datum sources, abbreviations, and legends see
942 Figure 2.

943

944 Figure 5. Crossplot diagram shows mean diameter (M) versus standard deviation (SD) of
945 pyrite framboid sizes from the South Majiashan (SMJS) section. Noted that four samples
946 (CMS-87, CMS-83-8, CMS-86, CMS-61) are plotted in euxinic-anoxic field but with
947 mean diameter > 6 μ m.

948

949 Figure 6. Latest Spathian to late Anisian paleoredox variations from the Qingyan (QY)
950 section. Conodont zonation is after Ji et al. (2011) and Yao et al. (2004), ammonoid
951 assemblage after Stiller and Bucher (2011, 2008), bivalve assemblage after Chen, J. et al.
952 (2010b). AS = Anshun Formation, other abbreviations and legends see Figure 2.

953

954 Figure 7. Crossplot diagram shows mean diameter (M) versus standard deviation (SD) of
955 pyrite framboid sizes from the Qingyan (QY) section.

956

957 Figure 8. Covariations between pyrite framboid sizes, redox conditions, conodont Ω Ce
958 values, sulfur and carbon isotopic excursions, and surface seawater temperatures (SST)
959 through the latest Permian to late Anisian (Middle Triassic) from South China. Datum
960 sources include conodont Ω Ce (Song et al., 2012), $\delta^{34}\text{S}_{\text{cas}}$ data (Song, H.Y. et al., 2013),

961 SST (Sun et al., 2012), Carbon isotopes (Payne et al., 2004; Tong et al., 2007).
962 Conodont zones: 1 = *C. yini* Zone, 2 = *C. meishanensis* Zone, 3 = *H. changxingensis*
963 Zone, 4 = *C. taylorae* Zone, 5 = *H. parvus* Zone, 6 = *I. staeschei* Zone, 7 = *I. isarcica*
964 Zone, 8 = *Nv. Pingdingshanensis* zone; Ammonoid zones/assemblages: 9 = *Otoceras*
965 *fissisellatum* Zone, 10 = *Otoceras woodwardi* Zone, 11 = *Ophiceras tibeticum* Zone, 12
966 = “*Pleurogyronites*” *planidorsatus-Discophiceras* Zone, 13 = *Rohillites rohilla* Zone,
967 14 = *Flemingites flemingianus* zone, 15 = *Anawasa tardus* Zone, 16 = *Columbites*
968 *parisianus* zone, 17 = *Prohungarites-Subcolumbites* zone, 18 = *Nicomedites osmani*
969 zone. MD = Mean diameter.

970

971 Figure 9. Pyrite framboid size and redox variations through the P–Tr boundary transition
972 spanning from conodonts *C. yini* Zone to *Nc. discreta* Zone. MD = Mean diameter.
973 Conodont zones are after Chen et al. (2015), pyrite framboid size data after Shen et al.
974 (2007), Chen et al. (2015), Li et al. (2015) and this study.

975

976 Figure 10. (A) Paleogeographic settings of selected sections studied herein during the
977 latest Permian to Middle Triassic. (B) Global correlations of Early–Middle Triassic redox
978 histories in shallow platform margin and ramp settings of South China, the Sverdrup
979 Basin of Canada, and Mino-Tamba Terrane, Japan. (C) Evolution of oceanic oxygen
980 minimum zone (OMZ, cf. Algeo et al., 2011) through the entire latest Permian to Middle
981 Triassic. Datum sources: Panthalassan ocean of Mino-Tamba Terrane, Japan (Wignall et
982 al., 2010) and Momotaro Jinja section, Central Japan (Takahashi et al., 2009, 2015),
983 platform margins of South China (Song et al., 2012), Sverdrup Basin of Canada (Grasby
984 et al., 2013), ramp settings of South China (This study).

985

986 Supplemental Files

987 Table 1. Presence/absence, morphologic and size data of pyrites from all observed
988 samples and their corresponding redox conditions.

989

990 Figure S1. Overgrowth sunflower-like pyrite aggregates.