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1	Title: Progressive development of ocean anoxia in the end-Permian pelagic Panthalassa
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18	Keywords: carbon isotope, iron speciation, redox-sensitive metals, mass extinction, ocean
19	anoxia, pelagic deep sea, Permian-Triassic boundary
20	Abstract
21	The end-Permian mass extinction (EPME) has been linked with the widespread
22	development of oxygen-poor oceanic conditions. However, information on the spatial extent
23	of anoxia in the Panthalassa super-ocean has been limited. This study reports oceanic redox
24	records from a deep-sea chert succession (the Waiheke 1 section, WHK 1, New Zealand) that
25	was located in southern mid-latitudes of Panthalassa. High-resolution carbon isotope ( $\delta^{13}$ C)
26	correlation between Waiheke and the Permian-Triassic boundary (PTB) type section indicates
27	that the EPME is recorded in a thin black claystone interbedded between siliceous mudstone
28	beds at WHK 1. Pyrite-dominated enrichment in highly reactive iron, coupled with elevated
29	U/Al and Mo/Al ratios, are prevalent through this black claystone bed and the overlying
30	Permo-Triassic transition strata, suggesting the development of euxinic water column
31	conditions. Similar redox variations across the EPME horizon have been reported from other
32	Panthalassic deep-sea PTB sections. Comparison with these PTB sections indicates that
33	euxinic conditions were widespread in low-latitude regions of the Panthalassan ocean, and

34 such conditions developed earlier than in mid-latitude settings, up to 100,000 years before the 35 EPME. This suggests there was a gradual expansion of ocean anoxia from low to middle-high 36 latitude regions during the Permo-Triassic transition. The extent of ocean anoxia resulted in a 37 decrease in the seawater inventory of redox sensitive trace metals (e.g., Mo), which is evident 38 in the earliest Triassic strata of the studied section and other PTB sections. Panthalassic anoxia during the EPME coincides with extreme climate warming and the associated effects 39 40 (e.g., changes in ocean circulation, marine eutrophication intensified by terrestrial 41 weathering) were likely critical triggers for ocean deoxygenation.

42

# 43 1. Introduction

44 The most significant biotic catastrophe of the Phanerozoic, the end-Permian mass extinction 45 event (EPME), was associated with the widespread development of oceanic anoxia (e.g., 46 Wignall and Twitchett, 1996; Isozaki, 1997). Previous research has demonstrated that many 47 shallow water and deep oceanic regions of Late Permian and Early Triassic age experienced 48 anoxic conditions (e.g., Wignall and Twitchett, 2002; Kaiho et al., 2016). Organic molecular 49 fossils (biomarkers) of anaerobic green sulphur bacteria have shown that euxinia (anoxic, sulphidic conditions) extended into the photic zone in the paleo-Tethys (e.g., Grice et al., 50 51 2005, locality 3 in Figure 1A) and Panthalassan oceans (Hays et al., 2007, locality 5 in Figure 1A). Enrichments in pyrite and redox-sensitive trace elements have also been reported from 52 53 PTB sections of paleo-Tethys (e.g., Lei et al., 2017, Xiang et al., 2020, Shen et al. 2016, 54 Clarkson et al., 2016), pelagic Panthalassa (locality 2 in Figure 1A; Algeo et al., 2011; 55 Takahashi et al., 2014; Onoue et al., 2021), and the North Pangean margin (e.g., locality 4 in 56 Figure 1A; Grasby et al., 2009; Schobben et al., 2020), indicating the widespread 57 development of anoxia/euxinia. The extent of oxygen-poor conditions may have caused a 58 decrease in both seawater sulphate concentrations (Song et al., 2014; Schobben et al., 2017) 59 and trace elements such as Mo (e.g., Takahashi et al., 2014; Xiang et al., 2020), due to 60 enhanced pyrite burial and trace metal drawdown (Takahashi et al., 2014; Schobben et al., 61 2015). The extent of ocean anoxia also changed the U isotope ratio of seawater, as recorded in marine carbonate ( $\delta^{238}$ U<sub>carbonate</sub>) (Brennecka et al., 2011, Lau et al., 2016; Zhang et al., 62 2018ab, 2020). 63 64 While anoxia was clearly widespread, there remains a significant absence of

65 environmental records from the Panthalassa (Fig. 1A). Since most of the sedimentary record

of Permian-Triassic Panthalassic seafloor has been subducted, limited material is available to

67 allow reconstruction of redox conditions, particularly in terms of revealing temporal and spatial variability in oceanic redox during the EMPE. Previous research has, however, 68 69 focussed on Panthalassic PTB sections from Japanese accretionary complexes. These formed 70 in low latitude central Panthalassa (locality 2 in Figure 1A), based on measured paleo-71 latitudes of Middle Triassic chert from the Mino Belt of central Japan (cf. paleomagnetic 72 studies by Ando et al., 2001 and Oda and Suzuki, 2000). It was at least one hundred million 73 years before these sediments were accreted in the Middle to Late Jurassic (Mastuda and 74 Isozaki, 1991; Takahashi et al., 2014). Since oceanic plates migrate at a rate of several cm/yr, 75 this indicates that the Japanese PTB sections were originally thousands of kilometres from 76 land.

77 According to reports from Japan (e.g., Isozaki, 2009, Muto et al., 2020), the EPME 78 horizon occurs at the transition from Permian radiolarian chert to siliceous claystone and 79 black claystone layers. Based on the concentrations of redox-sensitive trace elements (Mo, U 80 and V) and framboidal pyrite populations in the PTB sections, a shift to oxygen-poor 81 conditions during the EPME has been suggested, with the specific development of either 82 anoxic through to euxinic bottom waters, or an oxygen minimum zone setting (Wignall et al., 83 2010; Algeo et al., 2011; Takahashi et al., 2014; Onoue et al., 2021). 84 Southern Panthalassa PTB sections have also been documented in the accretionary 85 complex on the North Island of New Zealand (Spörli et al., 2007a; Hori et al., 2011; Grasby 86 et al., 2021), where data from Lower Triassic chert suggests a paleolatitude of ca. 34°S 87 (Kodama et al., 2007). The Permian-Triassic deposits accreted during the Late Triassic, 88 suggesting the original depositional location was close to Gondwana (Spörli et al, 2007b; 89 locality 1 in Figure 1A). Two sections from Arrow Rocks and Waiheke Island (Fig.1B) 90 indicate that black, bedded chert and claystone occur around the EPME, similar to their 91 occurrence in the Japanese sequences. Hori et al. (2007) measured trace element enrichments

92 (Mo and U) in the Griesbachian black chert layers of the Arrow Rocks (Unit 2) and identified

93 an anoxic water column event they termed "OAE  $\alpha$ " (they described an "OAE $\beta$ " in the

94 Dienerian). However, this PTB section has minor faults around the basal part of the black

95 chert layers, making the continuous redox history in relation to the EPME and PTB unclear.

96 The PTB section on Waiheke Island (Waiheke section) has a continuous succession across

97 the PTB, which has been dated using conodonts (Hori et al., 2011). Organic carbon isotope,

98 sulphide sulphur isotope, and trace element profiles through this section suggest the

99 development of anoxic-sulphidic water column conditions during the EPME (Hori et al.,

100 2007; Takahashi et al., 2013; Grasby et al., 2021). Here, we present new, high-resolution

101 paleoenvironmental records for the Waiheke section, incorporating multiple paleoredox

102 proxies, including iron speciation and redox-sensitive trace element systematics. We aim to

103 reveal how ocean anoxia developed prior to and after the EPME, as well as the associated

104 changes in seawater chemistry. In addition, we present a compilation of pelagic Panthalassic

105 PTB records to investigate the spatial and temporal development of redox conditions in the

106 Permian-Triassic Panthalassa.

107

#### 108 2. Geological setting

109 The Waiheke PTB section is an intertidal platform section in Island Bay, north-western 110 Waiheke Island, North Island, New Zealand (Fig. 1B). It belongs to the Kiripaka Formation 111 of the Waipapa composite terrain (Schofield, 1974, 1979), which is the accretionary complex 112 forming part of the basement of New Zealand. The sedimentary sequence comprising the Waiheke section is approximately 10 m thick and divided into six litho-units (Unit A to F; 113 114 Hori et al., 2011). This study focuses on the lowest part of these units (Unit A), in the Waiheke 1 section (abbreviated as "WHK 1" hereafter). It mainly consists of pale green 115 116 tuffaceous claystone and mudstone towards the base, followed by black and yellowish-black 117 chert with black claystone (Fig. 2).

The pale green siliceous and tuffaceous claystone and mudstone in the lower half of Unit A are composed of mm- to cm-scale alternations of siliceous microfossil enriched layers (radiolarians and sponges) and muddy layers (Fig. 3A). The black claystone consists of finegrained clay materials and organic matter (Fig. 3B). Although siliceous microfossils are observed in the black claystone, fossils are rare and generally small (up to several µm in diameter). Black and black-yellow cherts in the upper part of WHK 1 also show mm- to cm-

scale microfossil enriched layers and muddy layers (Figs 3C, 3D). The size of visible

microfossils are similar to those from the pale green beds in the lower part of the study

section. 88 single beds have been identified and labelled as Beds 1 to 88 (Hori et al., 2011;

127 Takahashi et al., 2013). The conodont occurrences indicate that the section ranges from the

128 uppermost Permian to the lowermost Triassic (Figs. 2 and 4; Hori et al., 2011). *Hindeodus* sp.

129 and *Neogondolella carinata* were obtained from Bed 29 of the black-yellow chert. Above this

130 horizon, Ng. carinata and Sweetospathodus cf. kummeli occur from Bed 40. These index

131 fossils indicate that Bed 29 is Induan, and Bed 40 extends into the lower to upper part of

132 Induan (uppermost Griesbachian or even the Dienerian). Ten previously published organic

133 carbon isotope ( $\delta^{13}C_{org}$ ) analyses demonstrate a negative excursion from Bed 14 to Bed 22,

134 indicating the uppermost Permian carbon isotopic signal corresponding to the end-Permian

135 mass extinction event (Hori et al., 2011). Based on this information, we place the Permian-

136 Triassic transitional zone at this level. Here, we provide further  $\delta^{13}C_{org}$  data and discuss the

137 timescale issue in more detail.

138 3. Methods

139 3.1. Organic carbon isotope analysis

140 We examined organic carbon isotope ratios of bulk chert and claystone samples from 28 141 horizons of WHK 1, using samples with no visible veinlets or staining. After washing with 142 Ellix® water, all samples were ground into fine powder using an agate mill. The powdered samples were decarbonated with 10% HCl. Organic carbon isotopic compositions and 143 144 organic carbon contents were measured using an elemental analyser (Flash EA 1112) coupled with a Thermo-Finnigan Delta plus Advantage isotope ratio mass spectrometer at the Center 145 146 for Advanced Marine Core Research, Kochi University, Japan. Isotopic measurements were 147 repeated up to four times for each horizon to check reproducibility. The carbon contents were 148 calculated using standard sulfanilamide, and the precision of organic carbon isotope ( $\delta^{13}C_{org}$ ) analyses was better than 0.1‰. Organic carbon isotope measurements were calibrated using 149 150 histidine and alanine obtained from Sugito Ltd. Lab. All isotopic results are reported in conventional delta ( $\delta$ ) notation, defined as per mil ( $\infty$ ) deviation from the Pee Dee belemnite 151 152 (PDB) standard value. Here we use the average values calculated from repeat (up to 4 times) 153 measurements of the same sample.

154

#### 155 *3.2. Major and trace element analysis*

156 Major and trace elements were measured by inductively coupled plasma atomic emission 157 spectrometry (ICP-AES; SPS3500, SII nanotechnology) and inductively coupled plasma mass spectrometry (ICP-MS; iCAPQc, Thermo scientific) at the Department of Earth and 158 159 Planetary Science, University of Tokyo. For these analyses, 0.5 g of sample powder was treated with 4 mL of HClO<sub>3</sub> + HNO<sub>3</sub> (1:1 mixture) in PTFE beakers for 45 min at 120°C, 160 161 followed by two treatments with 4 mL of HClO<sub>3</sub> + HF (1:1 mixture) for 30 min at 120°C. 162 The residues from these acid treatments were re-dissolved with 5 mL HNO<sub>3</sub> and diluted to 1:2000 using ultra pure water. Indium (In) and bismuth (Bi) were used as internal standards 163 164 for the ICP-MS analyses. Working standards were prepared from a series of SPEX Multi-Element Plasma Standards supplied by SPEX Industries (SPEX). Repeated analysis on the 165 166 reference material (GSJ-JR-1; rhyolite reference material supplied by Geological Survey of

167 Japan) confirms that values are reproducible to within 1.8% for Al, 0.8% for Fe, 12% for U,

and 9% for Mo, respectively (as relative standard deviation: RSD).

169

# 170 *3.3. Normalization*

To assess the enrichment or depletion of redox sensitive elements relative to typical
detrital material, enrichment factors (X<sub>EF</sub>) were calculated as follows (e.g., Tribovillard et al.,
2006):

174	$X/Al = X_{sample} (ppm) /Al_{sample} (wt \%)$	(1)
175	$X_{EF} = (X_{sample} / Al_{sample}) / (X_{PAAS} / Al_{PAAS})$	(2)

Here, X<sub>sample</sub>, Al<sub>sample</sub>, X<sub>PAAS</sub> and Al<sub>PAAS</sub> are the weight concentrations of element X or Al
in the sample or in PAAS (the post-Archean average shale; Tayler and McLennan, 1985). To
compare our geochemical data with other PTB sections, Fe/Al, U/Al and Mo/Al ratios were
also calculated and compared with literature data (Algeo et al., 2011; Takahashi et al., 2014).

180

#### 181 *3.4. Iron speciation*

182 A sequential extraction targeting different operationally defined Fe pools, including

183 carbonate (Fe<sub>carbonate</sub>), ferric (oxyhydr)oxides (Fe<sub>OX</sub>) and magnetite (Fe<sub>magnetite</sub>), was

184 performed on a split of 0.07–0.09 g of powdered sample (Poulton and Canfield, 2005;

185 Poulton, 2021). Fe<sub>carbonate</sub> was first extracted using Na-acetate at pH 4.5 and 50 °C for 48 h,

186 followed by Fe<sub>OX</sub> using Na-dithionite for 2 hours at room temperature, and finally Fe<sub>magnetite</sub>

187 was determined with an ammonium oxalate extraction for 6 h. Dissolved iron concentrations

188 (for Fe<sub>carbonate</sub>, Fe<sub>OX</sub> and Fe<sub>magnetite</sub> pools) were measured by atomic absorption spectrometry

189 (AAS; Thermo ice 3000 at the School of Earth and Environment, University of Leeds).

190 Replicate extractions of an international reference material (WHIT; Alcott et al., 2021) gave a

191 RSD of <5% for each Fe pool.

192 Pyrite iron (Fe<sub>pyrite</sub>) was determined stoichiometrically based on Ag<sub>2</sub>S precipitates formed

193after a boiling HCl and chromous chloride distillation (Canfield et al., 1986). All samples

194 were tested for the presence of acid volatile sulphide (AVS; predominantly FeS) via an initial

195 6 M HCl distillation, but in all cases AVS was below detection (<0.001 wt %). Replicate

196 pyrite extractions gave a RSD of <5%. The sum of these measured Fe pools defines the total

197 concentration of highly reactive Fe ( $Fe_{HR}$ ):

198  $Fe_{HR} = Fe_{carbonate} + Fe_{OX} + Fe_{magnetite} + Fe_{pyrite}$  (1)

A 1 h 0.5 N HCl extraction was also conducted on ~0.5 g splits of powdered samples to 200 201 assess for potential oxidation during weathering (see Matthews et al., 2017). This treatment 202 targets poorly crystalline ferric oxide minerals (Fe(III)<sub>HCl</sub>), such as ferrihydrite, in addition to 203 reduced Fe phases such as Fe<sub>AVS</sub> and potentially some ferrous carbonate/phosphate phases. 204 Since Fe<sub>AVS</sub> was not present in our samples (see above), this phase can be discounted. Thus, 205 this extraction targets the remaining non-sulphidized Fe(II) minerals (termed Fe(II)<sub>HCI</sub>), as 206 well as Fe(III)<sub>HCI</sub>. Poorly crystalline Fe(III)<sub>HCI</sub> minerals such as ferrihydrite are not stable on 207 geological timescales, and hence the Fe(III)<sub>HCI</sub> pool can be considered to dominantly result 208 from more recent weathering of reduced minerals (particularly pyrite). Thus, quantification of 209 this pool provides a maximum estimate of the extent of post-depositional pyrite oxidation 210 (e.g., Matthews et al., 2017). 211 The Fe(II)<sub>HCl</sub> pool was determined immediately by spectrophotometer using the ferrozine 212 assay (Stookey, 1970). The total amount of Fe dissolved by the 0.5 N HCl extraction was 213 determined following reduction of Fe(III) to Fe(II) using hydroxylamine hydrochloride, 214 followed by analysis by spectrophotometer using the ferrozine assay. Subtraction of Fe(II)<sub>HCl</sub> 215 from this Fe pool gives Fe(III)<sub>HCl</sub>. Corrected Fe pools were calculated as: 216 Corrected  $Fe_{carbonate}$  ( $Fe^*_{carbonate}$ ) =  $Fe_{carbonate} - Fe(III)_{HC1}$ (2) 217 Corrected  $Fe_{pyrite}$  ( $Fe_{pyrite}^*$ ) =  $Fe_{pyrite}$  +  $Fe(III)_{HCl}$ (3)

- 218
- 219 4. Results

All geochemical data are shown in Table S1 and Figure 2.

221 4.1. Organic carbon isotopes

Organic carbon isotope ratios in WHK1 vary between -32.8‰ and -25.4‰, but with

223 distinct trends up-section. Specifically,  $\delta^{13}C_{org}$  values in Beds 1-7 vary between -27.5‰ and

224 –25.4‰ (Fig. 2). Values then decrease to –28.6‰ in Bed 8, followed by an increase to-

225 26.1‰ in Bed 14. The most pronounced decrease in  $\delta^{13}C_{org}$  then occurs between beds 14 and

- 17, reaching the minimum value of -32.8 &. Low  $\delta^{13}C_{org}$  values persist up to Bed 28, before
- a gradually increasing trend, interrupted by a low value in Bed 48 (-29.2‰), is established up
- to bed 50. Above Bed 50,  $\delta^{13}C_{org}$  values are relatively stable around -26.9‰, with variability
- 229 within 0.6‰.
- 230

#### 231 4.2. Major and trace elements

Concentrations of Al and Fe range between 0.74–5.2 wt % and 0.26–6.4 wt %, respectively (Table S1). Beds 35 and 38 have low values of 0.74 and 0.75 wt % for Al, and 0.42 and 0.40 wt % for Fe, respectively. The Al content is relatively high in the tuffaceous claystone and mudstone (3.3-5.2 wt %) and the black claystone (1.7-4.2 wt %), but is low in chert beds (0.9-2.7 wt %). Iron is high in the black claystone (more than 4 wt %) and the black chert of Beds 29 (6.4 wt %).

Concentrations of U and Mo vary between 1.0-39.1 ppm and 0.8-194.3 ppm, respectively. Normalized U/Al ratios (Fig. 2) and  $U_{EF}$  (Table S1) values range between 0.84-13.5 and 2.7-43.6, respectively. Notably, high U/Al ratios (>5) occur in Beds 17-35 and Bed 44. Mo/Al (Fig. 2) and Mo<sub>EF</sub> (Table S1) vary between 0.3-61.1 and 2.4-611.0, respectively, with particularly high Mo/Al ratios (>5) occurring in Beds 17-24 and Bed 29.

243

# 244 *4.3. Iron speciation*

245 Fe speciation profiles are shown in Figure 2. Relatively high concentrations of Fe(III)<sub>HCl</sub> (more than 0.7 wt %) were detected in the black claystone samples of Beds 22, 24 and 48, as 246 247 well as the black chert of Beds 23 and 29, which for these samples has a significant effect on corrected Fecarbonate and Fepvrite concentrations. However, this correction for oxidative 248 249 weathering of pyrite brings the Fe speciation data more broadly in line with the trends evident in Mo/Al ratios (Fig. 2). Indeed, both Fe<sub>pyrite</sub>/Fe<sub>HR</sub> and Mo/Al reflect the availability of sulphide 250 251 in the water column and during early diagenesis, and as such, the general similarity in the 252 position of peaks in Fe\*<sub>pyrite</sub>/Fe<sub>HR</sub> and Mo/Al (Fig. 2) provides strong support that our approach 253 is robust.

254 We distinguish the Fe speciation results for Beds 31, 35 and 50 (open circles in Figure 2) 255 from the remainder of the data, as these samples contain less than 0.5 wt % total Fe, and as 256 such should be viewed with caution when interpreting Fe speciation data (Clarkson et al., 2016). 257 We thus do not discuss the Fe speciation characteristics of these samples further. For the 258 remaining samples, Fe<sub>HR</sub>/Fe<sub>total</sub> ratios range from 0.15 to 1.0. Fe<sub>HR</sub>/Fe<sub>total</sub> ratios are higher than 259 0.38, which represents the conventional boundary for distinguishing samples deposited from 260 an oxic or anoxic water column (Raiswell and Canfield, 1998; Poulton and Canfield, 2011), across most horizons, with the exception of Beds 46 and 58. Fe<sup>\*</sup><sub>pyrite</sub>/Fe<sub>HR</sub> ratios range from 261 262 0.11 to 0.88, with low values (less than 0.22) in the siliceous siltstone and claystone beds of 263 the lower part of the section (Beds 1, 6, 7, 8, and 13). Fe\*<sub>pyrite</sub>/Fe<sub>HR</sub> ratios exceed 0.6 in the

- black claystone and chert beds in the middle and upper parts of the section, except for Beds 20and 28 which show moderate values (0.48 and 0.42, respectively).
- 266

267 5. Discussion

268 5.1. Carbon isotope correlation

269 The Upper Permian strata of WHK1 exhibits a two-step decrease in  $\delta^{13}C_{org}$  values,

270 resulting in an overall decrease of ca. 8‰. The first decrease occurs in Beds 7-8, followed by

- a larger decrease in Beds 14-17 (Figs. 2 and 4). The minimum  $\delta^{13}C_{org}$  value occurs in the thin
- black claystone bed (Bed 17) sandwiched between siliceous claystone beds. Then,  $\delta^{13}C_{org}$
- 273 shows an increasing trend towards the overlying Lower Triassic black chert beds.

Inorganic carbonate carbon isotope ( $\delta^{13}C_{carb}$ ) values from low-latitude carbonate PTB 274 sections show similar trends. One of the best documented examples is from the Meishan 275 276 section, the type section for the Permian-Triassic boundary (Fig. 4; GSSP: Global strata-type section and point; Yin et al., 2001). The Meishan section also displays a two-step decrease in 277 278  $\delta^{13}C_{carb}$  in the uppermost Permian strata below the base of the Triassic (Beds 23-25 in Fig 4; Jin et al., 2000; Cao et al., 2002; Kaiho et al., 2009). We label these two decreases in  $\delta^{13}$ C as 279 280 "the first  $\delta^{13}$ C decrease" and "the second  $\delta^{13}$ C decrease", respectively (marked by green and 281 blue horizontal bars in Figure 4).

282 Based on U-Pb ages from zircon minerals in volcanic ash beds at the GSSP, these two isotopic steps are estimated to have occurred at  $251.999 \pm 0.039$  Ma and  $251.941 \pm 0.037$  Ma, 283 284 respectively (Burgess et al., 2014), suggesting a 58 kyr separation. The first and second decreases are correlated with the two negative drops in  $\delta^{13}C_{org}$  observed at WHK 1 (Fig. 4). 285 The second decrease in  $\delta^{13}C_{carb}$  at Meishan corresponds to the EPME horizon, and is 286 287 associated with the loss of many marine taxa (Jin et al., 2000; Song et al., 2012). The Meishan section also shows a gradually increasing trend in  $\delta^{13}C_{carb}$  above the EPME horizon 288 289 up to the Permian-Triassic boundary and into the overlying lowest Triassic strata, similar to 290 the increasing trend seen in the strata of Beds 17-28 below the first Triassic conodont fossil occurrence from Bed 29 in WHK 1(Figs. 2 and 4). This increasing  $\delta^{13}$ C trend above the 291 EPME horizon provides a further correlative interval between PTB sections (marked by the 292 293 pink horizontal bar in Figure 4). Therefore, based on this carbon isotope correlation within 294 the biostratigraphic framework for the Permian-Triassic transition, defined at the GSSP 295 Meishan section, we place the EPME horizon at the base of Bed 17 in WHK 1, which is a thin black claystone bed within the uppermost pale-green siliceous mudstone beds (Figs. 2 296

and 4). Another deep-sea PTB section from New Zealand (Arrow Rocks) also has a published

- 298  $\delta^{13}C_{org}$  profile across the PTB (Fig. 4; Hori et al., 2007). This PTB section also shows
- 299 decreasing trends in  $\delta^{13}C_{org}$  between a chert bed with the Changhsingian *Neogondolella*
- 300 *prechangxingensis* in the lower part of the section (at -7 m, not shown in the Figure 4) and a
- 301 Triassic black chert beds which yield conodonts of *Neogondolella carinata* and *Hindeodus*
- 302 sp. of Triassic affinity (Yamakita et al., 2007). As the number of  $\delta^{13}$ C data from the lower half
- 303 of the section are limited, the exact positions of the first and second  $\delta^{13}C$  decreases and their
- 304 minimum troughs are uncertain. However, the  $\delta^{13}C_{org}$  profile in the Permian chert and
- 305 siliceous mudstone beds shows a decrease at -0.6 to -0.3 m, and then a further decrease across
- 306 the fault dividing a siliceous claystone unit (Unit 2a; Hori et al., 2007) and overlying black
- 307 chert unit (Unit 2b; Hori et al., 2007). These  $\delta^{13}$ C trends are interpreted to correspond to the
- 308 first  $\delta^{13}$ C decrease and the negative trough above the second  $\delta^{13}$ C decrease observed in the
- 309 WHK 1 section (Fig. 4).

The two-step  $\delta^{13}C_{org}$  decrease during the Permian-Triassic transition, followed by a 310 311 gradual increase toward the PTB, are also observed in the low latitude, deep-sea PTB 312 sections of the Canadian Ursula Creek section (Wang et al., 1994), as well as the Japanese 313 Akkamori-2 (Takahashi et al., 2010; Fig. 4), Ubara (Kaiho et al., 2012, Fig. 4) and NF1212C 314 (Sano et al., 2012) sections. In the Japanese PTB sections, located in central Panthalassa, black claystone commonly occurs instead of siliceous claystone and bedded chert during the 315 second  $\delta^{13}$ C decrease. This lithologic change reflects a significant decrease in siliceous 316 317 microfossils (Takahashi et al., 2009). The black claystone facies in the Japanese PTB section 318 continues during the Olenekian period, over a million years later (Takahashi et al., 2009). By 319 contrast, WHK 1 has bedded chert beds just above the EPME horizon. The dominant black 320 claystone facies of WHK 1 appears above these chert beds, with a return to chert beds below the PTB. This discrepancy in the timing of bedded chert deposition indicates a relatively 321 322 short duration for the radiolarian chert gap in the southern mid-latitudes of Panthalassa.

323

324 5.2. Redox evaluation inferred from Fe speciation and trace elements in the Waiheke 1
325 section

326 5.2.1. Fe speciation systematics

Fe-speciation is a widely used proxy for reconstructing regional water column redox
 conditions (Poulton and Canfield, 2011; Poulton, 2021). Enrichments in Fe<sub>HR</sub> (Fe<sub>HR</sub>/Fe<sub>total</sub> >

329 0.38) commonly characterise deposition under anoxic water column conditions, and for

330 samples that show such enrichment, the extent of pyritization of the Fe<sub>HR</sub> pool provides an 331 indication of whether the water column was ferruginous ( $Fe_{pyrite}/Fe_{HR} < 0.6-0.8$ ) or euxinic 332 (Fe<sub>pyrite</sub>/Fe<sub>HR</sub> > 0.6-0.8). The samples that record a euxinic water column obtain syngenetic 333 pyrite from the water column, in addition to possible continued pyritization of Fe<sub>HR</sub> during 334 diagenesis. The threshold values for Fe<sub>HR</sub>/Fe<sub>total</sub> and Fe<sub>pvrite</sub>/Fe<sub>HR</sub> are not absolute, and may be 335 influenced by high sedimentation rates (particularly during turbidite deposition; e.g., Canfield 336 et al., 1996) or transfer of Fe<sub>HR</sub> to clay minerals (such as glauconite) during diagenesis, the 337 latter of which may be particularly prevalent in organic-rich, non-sulphidic sediments (e.g., 338 Poulton and Raiswell, 2002; Poulton et al., 2010). However, we found no evidence for 339 glauconite in the samples from WHK 1, based on thin section observations, which would be 340 consistent with the relatively high pyrite contents of many of the samples. Regarding 341 sedimentation rates, deep sea cherts in general have slow sedimentation rates (order of 342 mm/kyr; e.g., Mastuda and Isozaki, 1991). Indeed, the calculated sedimentation rate for WHK 1 (3.8 mm/kyr) roughly corresponds to 0.001 g cm<sup>-2</sup>/yr (= 0.38 cm/kyr × 2.7g/cm<sup>3</sup>), 343 344 based on dating for Beds 7 and 17 (see above), which would not be expected to impact Fe 345 speciation systematics. However, the tuffaceous sedimentary layers in this interval may 346 potentially have masked Fe<sub>HR</sub> enrichments due to rapid sedimentation (see Poulton et al., 2004). 347

348

#### 349 5.2.2. Uranium and molybdenum systematics

350 Uranium and Mo exist as soluble oxyanions in oxic seawater (e.g., Tribovillard et al., 351 2006), with a relatively homogenous distribution because of their longer residence times 352 relative to the mixing time of the ocean. Under reducing conditions, U transforms to 353 tetravalent U(IV), whereas in the presence of dissolved sulphide, Mo converts to 354 thiomolybdate. This results in enrichments in these elements, with Mo removal primarily 355 occurring under euxinic conditions (but a degree of drawdown can also occur in open system 356 sulphidic porewaters), whereas U uptake occurs within anoxic sediments (McManus et al., 357 2006). Based on observations from modern environments, Mo enrichments may begin to 358 occur when transformation to thiomolybdates occurs (>11µM H<sub>2</sub>S; Helz et al., 2011). Scott 359 and Lyons (2012) suggest that sediment Mo concentrations >25 ppm commonly indicate at 360 least intermittent water column euxinia, whereas concentrations >100 ppm likely indicate a persistent, strongly euxinic water column. Bennett and Canfield (2020) recommend using 361 362 U/Al and Mo/Al ratios as the most objective normalization approach for minimising

363 influence from detrital inputs. Furthermore, based on a compilation of modern settings,

364 Bennett and Canfield (2020) suggest that euxinic conditions are indicated when U/Al and

365 Mo/Al ratios exceed ~5 ( $\mu$ g/g), and oxygen-poor sea floor sediments ( $O_2 \ge 10 \mu$ M) are

366 indicated when U/Al ratios are >1 ( $\mu$ g/g).

367 Consistent with the emerging perspective that local baseline values for redox proxy thresholds should be assigned wherever possible (Algeo and Li, 2020; Poulton, 2021), we 368 369 apply different threshold values to the very different lithologies that comprise the upper 370 cherty (partly muddy) strata (Beds 19-88) and the lower tuffaceous strata (Beds 1-18) (see 371 Figure 2). For the upper cherty sediments, two samples (Beds 46 and 58) that give a clear oxic signal based on all of our applied redox proxies (with Fe<sub>HR</sub>/Fe<sub>total</sub> <0.22, low U/Al (0.90 372 373 and 0.84; average = 0.87) and low Mo/Al (0.93 and 0.77; average = 0.83), can be used to 374 define the oxic baseline for these parameters. By contrast, the tuffaceous strata in the lower 375 part of WHK 1 would have a different baseline value, due to dilution by tuffaceous materials with a very different chemical composition, as well as the potential for masking of 376 377 enrichments due to rapid sedimentation (see above). Minimum U/Al and Mo/Al ratios are 378 observed in Beds 1 and 6, respectively. We use these beds to define oxic baseline ratios of 379 0.84 for U/Al, and 0.30 for Mo/Al. Although the elemental composition of volcanic ash may 380 depend on multiple factors (including magma source and crystallization differentiation), U is 381 commonly enriched in tuff, whereas Mo is relatively depleted (Zielinski, 1983; Pichavant et 382 al., 1987). For example, the Macusani tuff in southeast Peru has a U/Al ratio of at least 0.79, 383 and a Mo/Al ratio of 0.03 (Pichavant et al., 1987). Furthermore, Bennet and Canfield (2020) 384 show that oxic marine sediments have U/Al ratios in the range of 0.2-1.0, while Mo/Al ratios are in the range of 0.08-0.4. Thus, our defined oxic baseline for U/Al is comparable to these 385 386 values, whereas our Mo/Al oxic baseline value is only slightly higher than these values. In addition, our approach to defining local redox thresholds provides a high level of consistency 387 388 when interpreting the different redox proxies we apply. Thus, taken together, these 389 observations provide strong support that our approach is robust. 390

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# 391 5.2.3. Redox evaluation of the Waiheke 1 section

The lower part of WHK 1 (Beds 1-15) shows slightly elevated Fe<sub>HR</sub>/Fe<sub>total</sub> and U/Al ratios, both of which show an overall progressive increase through the Upper Permian strata (Fig. 2). This consistent behaviour between two independent proxies suggests a progressive decline of bottom-water oxygen levels through this interval. Low Fe\*<sub>pyrite</sub>/Fe<sub>HR</sub> and Mo/Al

ratios indicate that the water column did not become euxinic at this time. However, during

- deposition of the thin black claystone bed at the EPME horizon (Bed 17), enrichments in
- 398 Fe<sub>HR</sub>/Fe<sub>total</sub> and U/Al, combined with high Fe\*<sub>pyrite</sub>/Fe<sub>HR</sub> and Mo/Al (Fig. 2), strongly support
- 399 the onset of euxinia. This redox state was dominant until deposition of the earliest Triassic
- 400 bedded cherts, which contain the first occurrence of Triassic conodont fossils (Bed 29),
- 401 although two intervals of low  $Fe_{pyrite}/Fe_{HR}$  and Mo/Al in Beds 19 and 28, combined with
- 402 elevated Fe<sub>HR</sub>/Fe<sub>total</sub> and U/Al, suggest intermittent development of ferruginous conditions
- 403 (Fig. 2).
- 404 Above these strata, up until around Bed 44, Fe<sub>HR</sub>/Fe<sub>total</sub> and U/Al ratios remain high
- 405 (although U/Al ratios are somewhat lower in this interval, relative to the underlying euxinic
- 406 sediments; Fig. 2), suggesting persistent anoxia (as discussed above, the low Fe<sub>total</sub> data
- 407 shown by open circles are not considered reliable). The Fe\*<sub>pvrite</sub>/Fe<sub>HR</sub> ratios are elevated,
- 408 suggesting water column euxinia, while Mo/Al ratios are also slightly elevated, but at a lower
- 409 level than in the underlying euxinic strata. On a local scale, a reduction in the extent of Mo
- 410 drawdown could simply be a consequence of less intense euxinia in the water column (Nägler
- 411 et al., 2011). However, since U also shows a reduction in the extent of drawdown, and since
- 412 U responds to anoxia rather than specifically euxinia, less intense euxinia does not appear to
- 413 provide a valid interpretation for the muted trace metal enrichments we observe.
- 414 Alternatively, however, if euxinia was widespread, then the muted enrichments we observe
- under euxinic conditions would more likely reflect a significant decrease in the seawater trace
  metal inventory (e.g., Algeo, 2004; Takahashi et al., 2014; Goldberg et al., 2016), which we
  consider in more detail below.
- Above Bed 44, the limited available data show evidence for fluctuating oxic and anoxic redox conditions, with the possible development of euxinic conditions in some horizons (e.g., Bed 71). When the redox state appears to have been euxinic (i.e., Bed 71), low trace metal drawdown (Fig. 2) may indicate prolonged seawater trace metal limitation through the earliest Triassic.
- 423
- 424 5.3. Temporal relationship of end-Permian oceanic anoxia in the low latitude and south mid425 latitude Panthalassa
- 426 To investigate the development of anoxia across the Panthalassic ocean, we have
- 427 compiled redox proxy records for deep-sea PTB sections across the Permian to Triassic
- 428 transition (Fig. 5). Available conodont-dated, Panthalassic deep-sea PTB sections carbon

429 isotope records and redox sensitive trace element data include Arrow Rocks in New Zealand (Hori et al., 2007), and the Akkamori 2 (Takahashi et al., 2014) and Ubara sections (Algeo et 430 431 al., 2011) in Japan. In Figure 5, U/Al and Mo/Al ratios for WHK 1 and these additional PTB sections are compared based on  $\delta^{13}$ C chemostratigraphic correlation (Fig. 4). 432 433 WHK 1 and Arrow Rocks, which were deposited in the south mid-latitude of the 434 Panthalassa Ocean, might be expected to have similar redox characteristics. During the first 435  $\delta^{13}$ C decrease in the late Changhsingian, WHK 1 consists of pale green-coloured tuffaceous sedimentary rocks. Arrow Rocks also consist of similar tuffaceous strata in the late 436 437 Changhsingian (Fig. 5). Given this lithologic similarity, we use the baseline values for U/Al and Mo/Al defined for WHK 1 to guide interpretation of the Arrow Rocks redox data. 438 439 However, U concentrations were below detection (<1.5 ppm) in the lower part of the Arrow 440 Rocks succession (Hori et al., 2007), preventing a direct redox interpretation. Furthermore, while Mo/Al ratios are relatively high, total sulphur concentrations are below detection (<1.8 441 442 ppm), and thus it is difficult to provide a robust redox interpretation for this part of the succession. However, in the overlying Permian-Triassic transitional section at Arrow Rocks, 443 444 enrichment of U/Al is evident, alongside very high peaks in Mo/Al (up to 670). This 445 coincides with U and Mo enrichment in WHK 1 (Fig. 5), supporting the notion of widespread 446 development of euxinic water column conditions in the south mid-latitude Panthalassa, at 447 least from the EPME to the PTB.

448 Geochemical records from low latitude Panthalassa, represented by the Akkamori 2 and 449 Ubara sections, provide further insight into temporal and spatial redox dynamics. To evaluate 450 the redox records for these PTB sections, we again use the minimum measured U/Al (Akkamori = 0.55, Ubara = 0.11) and Mo/Al (Akkamori = 1.13, Ubara = 1.01) ratios to 451 452 define oxic baseline values. Both sites show evidence for generally persistent anoxia (elevated U/Al) throughout the entire section, while elevated Mo/Al ratios suggest that the 453 454 water column may have become euxinic prior to the first  $\delta^{13}$ C decrease (Fig. 5). Furthermore, 455 while there was some fluctuation in the precise chemistry of the anoxic water column after the EPME, euxinia was a prevalent feature immediately after the EPME at the Akkamori site, 456 457 and potentially also at the Ubara site.

458 Our interpretation of the redox dynamics at the Ubara site based on Al-normalized values 459 of U and Mo contrast with those of Algeo et al. (2011), who considered suboxic conditions to 460 have been prevalent. In their study, the elevated bulk concentrations of U and Mo at Ubara 461 site are interpreted as being due to the slower sedimentation rate of Permian-Triassic black 462 claystone relative to the Permian chert beds resulting in enrichment. There thus remains some

463 uncertainty in the precise redox state of the Ubara site. However, we note that our

464 interpretation is more consistent with the redox conditions that are much more compellingly

465 demonstrated by highly elevated enrichments in Mo/Al at the Akkamori site. Thus, taken

466 together, it appears likely that the ocean oxygenation state of the Akkamori and Ubara sites in

the low latitude Panthalassa deteriorated earlier, relative to the Waiheke site in the south mid-

- 468 latitude Panthalassa.
- 469

470 5.4. Covariation between U and Mo, and Mo drawdown after the Permian-Triassic boundary 471 The bulk concentrations of Mo and U in the PTB sections are recast as enrichment factors 472 (Mo<sub>EF</sub> and U<sub>EF</sub>) and shown as a cross plot in Figure 6. Algeo and Tribovillard (2009) and 473 Tribovillard et al. (2011) provide a framework for utilizing Mo<sub>EF</sub> and U<sub>EF</sub> as a means to 474 identify three enrichment patterns. Firstly, co-increases in MoEF and UEF may occur following 475 a deterioration in redox conditions from suboxic to euxinic in open marine settings (Fig. 6). 476 The second case occurs where the  $Mo_{EF}$  is significantly elevated relative to the  $U_{EF}$ , which 477 may be a consequence of active Mo transportation from the water column to the sediment, for example via Fe-Mn (oxyhydr)oxide shuttling. The third pattern occurs when smaller and 478 479 relatively constant Mo<sub>EF</sub> are combined with high U<sub>EF</sub>. This scenario is considered to represent the case where extensive Mo-depleted seawater arises because of a persistent sulphidic deep 480 481 water mass, as may occur in a relatively restricted setting.

482 In the PTB sections of the low latitude Panthalassa during the Late Permian (Changhsingian), before the  $\delta^{13}$ C decrease, Mo<sub>EF</sub> values are high relative to U<sub>EF</sub> values (Fig. 483 484 6-1). This supports the redox observations based on U/Al and Mo/Al ratios (Fig. 5), and 485 suggests anoxic, non-sulphidic water column conditions across this interval, with elevated 486 Mo drawdown due to uptake and sequestration by Fe-Mn (oxyhydr)oxide minerals. At the WHK 1 site, the Mo<sub>EF</sub> and U<sub>EF</sub> data (Fig. 6-1) document the slower development of anoxia in 487 the south mid-latitude Panthalassa, with evidence for the very beginning of water column de-488 489 oxygenation, consistent with the Fe speciation, U/Al and Mo/Al (Fig. 2).

Between the two step decreases of  $\delta^{13}$ C, highly elevated Mo<sub>EF</sub>, and to a lesser extent U<sub>EF</sub>, are evident for the low latitude Panthalassa localities (Fig. 6-2). These values support the continued deterioration of water column redox conditions, with sporadic development of euxinic conditions (as documented in Figure 5) further enhancing trace metal drawdown (particularly Mo). In contrast, at the WHK 1 site in the south mid-latitude Panthalassa, U<sub>EF</sub> and Mo<sub>EF</sub> values document a later, progressive increase (Fig. 6-2). Across this interval, the

496 gradual co-increase in U<sub>EF</sub> and Mo<sub>EF</sub> values at the WHK 1 site suggests a classic redox

497 transition from suboxic, through anoxic, to euxinic water column conditions (Fig. 6; Algeo et

498 al., 2009; Tribovillard et al., 2012). This is generally consistent with the trends evident in the

499 Fe speciation data (Fig. 2), supporting a progressive deterioration in the redox state of the

500 water column and enhanced drawdown of U and Mo into the sediments.

501 During the interval from the EPME to the PTB, high U<sub>EF</sub> and Mo<sub>EF</sub> values are recorded in 502 both the south middle latitude and low latitude Panthalassa (Fig. 6-3). However, data from 503 the WHK 1 site plot closer to the typical trend for euxinic settings, which supports the 504 suggestion from trends in U/Al and Mo/Al (Figs. 2 and 5), that while euxinia was likely 505 widespread, this redox state may have become more prevalent and persistent in south middle 506 latitude regions, relative to the low latitude Panthalassa.

507 After the peaks across the EPME-PTB interval, U<sub>EF</sub> and Mo<sub>EF</sub> shift to generally lower 508 values during the early Triassic (Fig. 6-4). Indeed, enrichment patterns do not return to the 509 open-marine redox evolution trend. Instead, while the data show a wide range, Mo<sub>EF</sub> values 510 in particular are generally lower than during the EPME-PTB interval. Thus, we suggest that 511 the development of widespread anoxia, with the common occurrence of euxinia, during the 512 EPME-PTB interval subsequently resulted in limited Mo sequestration in the sediments due 513 to a significant decrease in the seawater Mo inventory caused by intense Mo-bearing sulphide 514 deposition (e.g., Algeo, 2004; Takahashi et al., 2014; Goldberg et al., 2016). Although euxinic 515 water condition enhances uptake of both Mo and U into the sediment, relatively stronger 516 accumulation of Mo results in significantly decreased residence time of Mo in the seawater 517 and depletion of Mo relative to U. Alternatively, such a signal could be due to lower sulphide 518 availability in the water column, which might result from seawater sulphate drawdown after 519 EPME anoxia (Song et al., 2014; Schobben et al., 2017). However, the fact that several intervals have Fe<sub>HR</sub>/Fe<sub>total</sub> and Fe\*<sub>pyrite</sub>/Fe<sub>HR</sub> ratios suggestive of euxinia, implies that Mo 520 521 depletion from the water column, rather than low sulphate availability, is a more likely 522 explanation for the relatively subdued Mo enrichments evident in the earliest Triassic. 523

## 524 5.5. Possible drivers of Panthalassic anoxia

525 This study indicates that the pelagic Panthalassa became anoxic, and was often euxinic, in 526 south middle latitude and low latitude regions during the EPME. However, the development 527 of anoxia occurred earlier at low latitudes. The progressive development of ocean anoxia 528 recorded by our data is in agreement with a decreasing trend in  $\delta^{238}$ U<sub>carbonate</sub> recorded in

529 multiple carbonate PTB sections (Fig. 7; Zhang et al., 2020). The  $\delta^{238}$ U<sub>carbonate</sub> signal begins to

530 decrease during the first  $\delta^{13}$ C decrease of the Changhsingian, which continues across the

531 EPME, resulting in a negative trough in the earliest Triassic. This  $\delta^{238}U_{carbonate}$  variability is

532 consistent with drawdown of U into Panthalassic anoxic deep-sea sediments through the Late

533 Permian and Early Triassic.

534 In Figure 7, data that can promote marine anoxia are compiled for the EPME. The 535 Siberian Traps were likely the main trigger for environmental change across the Permo-536 Triassic boundary (e.g., Wignall., 2001). A mercury (Hg) anomaly, taken as an indicator of 537 enhanced volcanic activity, has been detected in late Changhsingian horizons in the Akkamori 2 and Ubara sections in the low latitude Panthalassa (Fig. 7: Shen et al., 2019), and at WHK 1 538 539 (Grasby et al., 2021), demonstrating a coincidence of major volcanism with the onset of 540 euxinia. Identified Hg anomalies appear below the EPME horizon at the low latitude sites, 541 but just above the EPME horizon at the south mid-latitude WHK 1site (Fig. 7). One possible 542 reason for this discrepancy is the south mid-latitude location was too far from the Siberian 543 Traps to receive enough Hg before the EPME. The low sampling resolution across the WHK 544 1 section could be another possibility for this discrepancy. Grasby et al. (2021) did not 545 measure Hg in the thin black claystone bed at the EPME (Bed 17 of this study) and adjacent 546 layers.

547 The development of ocean anoxia prior to the EPME and persistence into the earliest 548 Triassic coincides with extreme climate warming (Fig. 7; Joachimski et al., 2012, 2019). This 549 warming has been linked to massive release of CO<sub>2</sub> from heated sediments and upper crusts 550 by Siberian Traps sills (Svensen et al., 2009). Subsequently, seawater warming would contribute to marine deoxygenation in these oceanic regions through the decreasing solubility 551 552 of dissolved O<sub>2</sub>. Furthermore, thermohaline circulation driven by subduction of warm saline surface water formed in mid and low latitudes would potentially contribute to the 553 554 development of a stratified ocean structure with anoxic deep waters (Kidder and Worsley, 555 2004).

556 The development of anoxia during the EPME coincides the cessation of radiolarian chert 557 deposition (Fig. 7). Our  $\delta^{13}$ C correlation of PTB sections reveals that this phenomenon 558 occurred in the south mid-latitude Panthalassa around ten kiloyears later than in the low 559 latitude Panthalassa (Fig. 7). This may be due to a decreased biogenic silica burial flux 560 (declining radiolarian population and/or degraded preservation of siliceous tests) and dilution 561 of biogenic silica by increased clastic material (Takahashi et al., 2009; Muto et al., 2018, 562 2020). The environmental conditions during the EPME, including ocean anoxia and seawater

563 warming may have decreased the siliceous faunal population and increased sedimentation of clay-rich material relative to biotic silica. If warming is a major factor limiting deposition of 564 565 biotic silica, then the different timing for the disappearance of radiolarian chert in the low 566 latitude and south mid-latitude ocean is noteworthy. For example, the higher latitude ocean 567 would warm more slowly, thus resulting in the observed delayed onset of both ocean anoxia and the decrease in biotic silica deposition. The subsequent return to lower temperatures 568 569 favourable for the radiolarian chert deposition would also arrive earlier in mid-latitude 570 regions.

571

# 572 6. Conclusions

573 This study provides new geochemical records across the end-Permian mass extinction 574 event in the south middle latitude pelagic Panthalassa. Fe-speciation and redox-sensitive elements (U and Mo) show the progressive development of ocean anoxia, with euxinia 575 occurring during the EPME. Comparison with previously reported paleo redox records from 576 577 the low latitude Panthalassa indicates that anoxia developed earlier in low latitude regions. 578 The pelagic Panthalassa PTB sections show Mo drawdown in the earliest Triassic, after the 579 EPME likely attributable to high Mo burial flux into anoxic marine sediments. The Late 580 Permian anoxia that occurred in the low latitude Panthalassa, and the progressive 581 development of anoxia during the run-up to the EPME in the south middle latitude Panthalassa, coincides with Siberian Traps volcanic activity and de-vegetation trends on land. 582 Furthermore, the persistent anoxia that developed in both latitudinal regions of Panthalassa 583 coincide with severe seawater warming. 584

585 The results of this study shed light on spatiotemporal changes in open ocean redox 586 conditions across the Permian-Triassic boundary and show that the redox history of this 587 super-ocean varied according to latitude. Conditions for radiolarians were persistent and 588 harsh in equatorial latitudes relative to the mid-latitude site discussed here, indicating that 589 high temperatures were a major factor controlling their absence. Environmental records for 590 mid-high latitudes and pelagic regions of the ocean remain highly limited, and this should be 591 a prime target for further investigation.

592

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## 854 Figure captions

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856 Figure 1. Location map of the studied Permian-Triassic section (Waiheke 1 section, New Zealand). (A) Paleo-geographical map of the Permian-Triassic showing the depositional 857 position of pelagic deep-sea Permian-Triassic boundary sections. Labeled numbers (1-7) 858 859 indicate the following localities: (1) pelagic sections from New Zealand accretionary 860 complexes, such as the Waiheke section (Spörli et al., 2007); (2) pelagic sections from 861 Japanese accretionary complexes; (3) shallow marine sections such as Meishan, South China; 862 (4) sections in Sverdrup Basin, arctic Canada (Grasby and Beauchamp, 2011); (5) sections in 863 Peace River Basin, western Canada (Havs et al., 2007). (B) Locality of the Waiheke-1 section 864 (WHK1) in the North Island of New Zealand. Distribution of the Triassic-Jurassic accretionary complex is based on Black (1994) and Begg and Johnson (2000). Locality of 865 866 Arrow Rocks is also shown.

867 Figure 2. Lithologic column of the Waiheke 1 section, including organic carbon isotopes

868 ( $\delta^{13}C_{org}$ ), iron speciation pools (Fe<sub>pools</sub>), highly reactive iron normalised to total iron

869 (Fe<sub>HR</sub>/Fe<sub>total</sub>), corrected pyrite iron as a function of highly reactive iron (Fe $*_{pyrite}$ /Fe<sub>HR</sub>), U,

870 U/Al and Mo/Al. The error ranges on the organic carbon isotope values ( $\delta^{13}C_{org}$ ) are based on

871 repetitions of carbon isotope measurements (Table S1). Open circles in the plots of Fe<sub>pools</sub>,

 $Fe_{HR}/Fe_{total}$  and  $Fe_{pyrite}/Fe_{HR}$  mean the samples with low Fe content (less than 0.5 wt %)

873 Fe<sub>total</sub>). We did not use these samples for paleoenvironmental reconstruction. Local

background values of U/Al and Mo/Al for tuffaceous strata (Beds 1-18) and cherty strata

875 (Beds 19-88) are shown as vertical dashed lines with "baseline" notation. The values are

based on the minimum values in the tuffaceous strata and the values in the cherty strata with

877 oxic  $Fe_{HR}/Fe_{total}$  signals.

Figure 3. Thin section photographs from the Waiheke 1 section. (A) tuffaceous siliceous

claystone of Bed 8; (B) black claystone of Bed 22; (C) bedded chert of Bed 50; (D) bedded

chert from around Bed 60.

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882 Figure 4. Stratigraphic correlation of the Permian-Triassic boundary sections of the Meishan section, Waiheke 1 section, Arrow Rocks section, Akkamori 2 section and Ubara section. 883 884 Compiled data of the Meishan section are based on Jin et al. (2000), Cao et al. (2002), Kaiho 885 et al. (2009) and Burgess et al. (2014). Data for Arrow Rocks, Akkamori and Ubara sections 886 are modified from Hori et al. (2007), Takahashi et al. (2010) and Kaiho et al. (2012), respectively. The horizontal bars indicate correlative stratigraphic zones around the Permian-887 888 Triassic boundary. Green: the first decrease in carbon isotope ratio ( $\delta^{13}$ C) in the latest Changhsingian, Blue: the second decrease in  $\delta^{13}$ C in the latest Changhsingian coinciding with 889 890 the EPME, Pink: the interval from the  $\delta^{13}$ C minimum during the EPME to the  $\delta^{13}$ C increase 891 toward the PTB.

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893 Figure 5. Vertical plots of U/Al and (Mo/Al) for the Waiheke 1 and other pelagic deep-sea

894 sections. The data for Arrow Rocks, Akkamori 2 and Ubara are modified from Hori et al.

(2007), Takahashi et al. (2014) and Algeo et al. (2011), respectively. The local background
value (baseline) for U/Al and Mo/Al are based on the WHK 1 baseline values for Arrow

- 897 Rocks, and are based on the minimum values for the Akkamori and Ubara sections.
- 898

899 Figure 6. Cross plots of molybdenum (Mo) and uranium (U) enrichment factors (Mo<sub>EF</sub> and 900 U<sub>EF</sub>, respectively) for Panthalassic PTB sections from Waiheke 1, Arrow Rocks, Akkamori 901 and Ubara. The data for Arrow Rocks, Akkamori 2 and Ubara are modified from Hori et al. 902 (2007), Takahashi et al. (2014) and Algeo et al. (2011), respectively. The data are plotted in 903 four different panels representing the time intervals based on the carbon isotope correlation demonstrated in Figures 4 and 5. 1: Late Permian (Changhsingian) before the  $\delta^{13}$ C decrease: 904 905 2: between the first and second steps decreases of  $\delta^{13}$ C in the latest Permian; 3: the interval from the  $\delta^{13}$ C minimum at the EPME to the  $\delta^{13}$ C increase toward the PTB; 4: Earliest 906 Triassic (Induan) after the PTB. Superimposed grey-coloured areas representing modern 907 908 oceanic sediments are from Algeo and Tribovillard (2009) and Tribovillard et al. (2012). The 909 U/Mosw is the weight ratio in modern seawater (SW), which ranges from 3.0 to 3.1 (modern 910 Pacific and Atlantic, respectively; Anderson, 1987; Bruland, 1983; Chen et al., 1986; Emerson and Huested, 1991). 911

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- 913 Figure 7. Compilation of oceanic environmental records from Panthalassa, seawater
- 914 temperature for the paleo-Tethys reconstructed by oxygen isotope ratios in conodont apatite
- 915 ( $\delta^{18}O_{apatite}$ ; Joachimski et al., 2009, 2019), global anoxic water extent referred from uranium
- 916 isotopes in carbonate ( $\delta^{238}$ U<sub>carbonate</sub>; Zhang et al., 2020). Time scale through Permian and
- 917 Triassic is from Burgess et al. (2014). Information on oceanic environmental records for
- 918 Panthalassa is based on litho- and chemo-stratigraphy by this study, Hori et al. (2007, 2011),
- 919 Algeo et al., (2011), Takahashi et al. (2014), Kaiho et al. (2016), Shen et al., (2019) and
- 920 Grasby et al., (2021). Thin lines indicate the range of each Permian-Triassic boundary
- 921 section. The bars coloured black, orange, purple and grey refer to Hg anomaly (Hg/TOC >
- 922 100), radiolarian chert occurrence, geochemical signals of euxinia (high Fe<sub>HR</sub>/Fe<sub>total</sub>,
- 923 Fe<sub>pyrite</sub>/Fe<sub>HR</sub> and/or Mo/Al and U/Al), and seawater Mo drawdown (lower Mo/Al and Mo<sub>EF</sub>
- 924 despite high Fe<sub>HR</sub>/Fe<sub>total</sub> and Fe<sub>pyrite</sub>/Fe<sub>HR</sub> and/or U/Al and U<sub>EF</sub>), respectively.