1 # A nutrient control on marine anoxia during the end-Permian

2 # mass extinction

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6   Oxygen deprivation and sulfide toxicity is considered a potent kill mechanism during the

7   mass extinction just before the Permian–Triassic boundary (~251.9 million years ago).

8   However, the mechanism that drove vast stretches of the ocean to an anoxic state is

9   unclear. Here, we present paleoredox and phosphorus speciation data for a marine

10   bathymetric transect from Svalbard. This shows that, prior to the extinction, enhanced

11   weathering driven by Siberian Traps volcanism increased the influx of phosphorus, thus

12   enhancing marine primary productivity and oxygen depletion in proximal shelf settings.

13   However, this non-sulfidic state efficiently sequestered phosphorus in the sediment in

14   association with iron minerals, thus restricting the intensity and spatial extent of oxygen-

15   depleted waters. The collapse of vegetation on land immediately prior to the marine

16   extinction changed the relative weathering influx of iron and sulfate. The resulting

17   transition to euxinic (sulfidic) conditions led to enhanced remobilization of bioavailable

18   phosphorus, initiating a feedback that caused the spread of anoxic waters across large

19   portions of the shelf. This reconciles a lag of >0.3 My between the onset of enhanced

20   weathering and the development of widespread, but geographically variable, ocean anoxia,

21   with major implications for extinction selectivity.

22   The Permian–Triassic (P–Tr) boundary (~251.9 million years ago[1]) record contains

23   multiple signals suggestive of widespread marine anoxia, a kill mechanism widely implicated in

24   the end-Permian mass extinction[2–7]. This crisis was the most dramatic turning-point in the

25   evolution of post-Cambrian life, with a loss of up to 81% of marine species[8]. Mechanisms for the

26   development of oxygen-depleted oceans on timescales compatible with the duration of the

27   extinction (~60 ky[1]), include changes in ocean circulation[9], decreased O_2 solubility under

28   globally rising temperatures[10], and enhanced eutrophication[10–13]. In the latter case, recent studies

29   have postulated that changes in the marine inventory of phosphorus (P)—the ultimate limiting

30   nutrient for marine productivity on geological timescales[14]—was the main driver for

31   eutrophication-induced oxygen depletion and ultimately the development of euxinic conditions

32   in extensive regions of the global ocean[10,11,13].

33   During Siberian Traps volcanism, an increase in bioavailable phosphorus would be an

34   expected consequence of increased continental weathering via the dissolution of exposed rock

35   (driven by CO_2-induced warming, and SO_2-induced acid rain), and the disintegration of rock by

36   an invigorated hydrological cycle[11,12,15,16]. Indeed, a coeval change in both lithium (Li)

37   concentrations and Li isotope ratios has been interpreted to reflect an increase in weathering[16].

38   Subsequently, a change in eruption style to intrusive basalt emplacement has been linked to

39   halocarbon remobilization and exhalations leading to ozone layer depletion and consequent

40   terrestrial plant extirpations by UV-B irradiance[17,18]. The effects of this intrusive volcanic phase

41   on land-plant communities have therefore been related to reduced soil stability[12,15,19]. Combined

42   with continued greenhouse-induced global warming, and associated changes in the hydrological

43   cycle, this situation likely led to increased soil erosion and physical weathering, thereby loading

44   near-shore environments with a higher sediment influx and terrestrial organics[4,7,12,15]

45   Certain aspects of this scenario are problematic, as Siberian Traps activity spans >1 My,

46   with 2/3 of the volume of lava deposited ~0.3 My before the main extinction pulse[18].

47   Furthermore, localized regions of dysoxia/anoxia occur prior to the mass extinction[3,4,6], but a

48   major expansion in the areal extent of these conditions occured at the extinction horizon[5,7]. The

49   role of these precursor environmental changes in pre-stressed communities is underexplored[20],

50   and requires knowledge of the mechanisms that drove the initiation of localized oxygen

51   depletion and the ensuing expansion of anoxic regions.

52   While an increase in the oceanic influx of bioavailable phosphorus may have occurred in

53   association with Siberian Traps activity[11,16], the catalytic effect of local redox conditions on

54   benthic phosphorus remobilization has often been overlooked in scenarios of eutrophication-

55   induced marine anoxia. Phosphorus is delivered to sediments in the form of organic matter and

56   skeletal remains (biogenic apatite), as well as in association with Fe (oxyhydr)oxides and

57   recalcitrant detrital minerals[21–24]. Organically bound-P (P_{org}) may be preferentially released to

58   sediment porewaters upon microbial remineralisation, resulting in increased C_{org}/P_{org} ratios in

59   deposited sediments[21,22]. In addition, the reductive dissolution of Fe (oxyhydr)oxides releases

60   adsorbed P to solution[21–23], while biogenic apatite tends to be highly soluble[24].

61   The dissolved P generated by these processes may undergo 'sink-switching', whereby

62   dependent on the precise conditions, dissolved P may precipitate as either carbonate-fluorapatite

63   (CFA)[25] or Fe phosphates (e.g., vivianite)[26], or may be readsorbed to Fe (oxyhydr)oxides where

64   such minerals persist[23]. However, under sulfidic conditions in particular, a significant proportion

65   of the dissolved P generated during early diagenesis may be recycled back to the water column,

66   thus promoting a positive productivity feedback[27]. By contrast, organic-rich oxic, dysoxic and

67   ferruginous (anoxic Fe(II)-rich) settings are potential loci of high P deposition. These features of

68 phosphorus cycling thus place important constraints on the bio-availability of P, and hence may

69 ultimately control both the spread of anoxia and the generation of toxic dissolved sulfide[11,27,28].

70   Previous attempts to reconstruct phosphorus availability[13] across the P–Tr transition have

71 lacked a precise reconstruction of ocean redox conditions, and detailed consideration of the

72 phase partitioning of P, which are essential to evaluate the role of the P recycling feedback. To

73 address this we apply novel sedimentary P records combined with independent redox proxies to a

74 bathymetric transect across the P–Tr boundary.

Geological setting and materials

76   We investigated the Festningen and Deltadalen sequences (Svalbard; Fig. 1), that were

77 deposited on a shallow, open-marine shelf at the northern margin of Pangaea, facing the Boreal

78 Sea and the Panthalassa Ocean beyond (Supplementary Fig. 1 and Sections 1–4). The Kapp

79 Starostin Formation consists of dark, massive to bedded spiculitic chert (with minor shale) at

80 Festningen[6,29], and glauconitic, fine-grained sandstone with chert nodules and beds at Deltadalen,

81 where the latter is interpreted to be a comparatively more proximal facies[6,30,31]. The Kapp

82 Starostin Formation is overlain by the shale-dominated Vardebukta Formation at Festningen,

83 and, the Vikinghøgda Formation at Deltadalen.

84   The end-Permian mass extinction has been defined by a loss of intense bioturbation

85 dominated by *Zoophycos*[4,6]. However, shallow bioturbation, dominated by small *Planolites*,

86 persists for ~3 m above the formational contact at Festningen, before disappearing[2]. The P–Tr

87 boundary is defined by the aid of the $\delta^{13}C_{org}$ record (Fig. 2 and Supplementary Fig. 2) and the

88 conodont marker species *Hindeodus parvus*[31].

89

Local redox chemistry

90

91   We combined iron speciation analyses with redox-sensitive trace element concentrations

92   (Methods) to differentiate oxic, dysoxic, anoxic ferruginous, and euxinic water column

93   conditions[32,33]. The Fe speciation method relies on the quantification of operationally-defined Fe

94   fractions that are considered highly reactive (Fe_{HR}) towards dissolved sulfide on early diagenetic

95   timescales[34,35]. The proportion of Fe_{HR} relative to total iron (Fe_{tot}) has been extensively calibrated

96   in modern and ancient settings, such that Fe_{HR}/Fe_{tot} >0.38 suggest an anoxic water column,

97   values below 0.22 indicate oxic depositional conditions, and values of 0.22–0.38 are considered

98   equivocal[36]. The extent of pyritisation of Fe_{HR} is used to differentiate euxinic (Fe_{py}/Fe_{HR} >0.7–

99   0.8) from ferruginous water column conditions (Fe_{py}/Fe_{HR} <0.7)[36].

100   Non-sulfidized Fe_{HR} has the potential to be converted to less reactive sheet silicate

101   minerals (termed poorly reactive sheet silicate Fe; Fe_{PRS}) during early diagenesis and deeper

102   burial[35,37,38]. Depletion of Fe_{HR} by this mechanism is clearly observed in some of the studied

103   samples, and is marked by the co-occurrence of glauconite at both localities. Glauconite occurs

104   as fibroradiated precipitates covering quartz grains and shell fragments, suggesting an authigenic

105   precipitate rather than a late diagenetic replacement product or detrital source, and thus Fe_{HR}

106   minerals would have been the primary source. To compensate for this transfer of Fe_{HR} to

107   glauconite, we apply a correction to samples that show clear enrichment in Fe_{PRS} over

108   background values, yielding estimates (Fe_{HR}/Fe_{tot}*, Fe_{py}/Fe_{HR}*) of initial depositional ratios[39]

109   (Fig. 2, Supplementary Figs. 3 and 6, and Section 7.2).

110   The distinctive geochemical behaviour of molybdenum (Mo), uranium (U) and rhenium

111   (Re) provides further insight into water column redox conditions. High sediment Mo

112 accumulation tends to occur when water column concentrations of sulfide are high, and likely

113 relates to the formation of particle-reactive thiomolybdates[33]. By contrast, U may be fixed in the

114 sediment under anoxic porewater conditions, without the requirement for free H_2S, and Re may

115 be sequestered under dysoxic conditions in the water column and sediments, where O_2 penetrates

116 <1 cm below the sediment–water interface[33,40]. Therefore, high Re/Mo ratios tend to indicate

117 dysoxic water column conditions[40], whereas enhanced Mo/U ratios suggest a euxinic water

118 column[33].

119   The pre-extinction sandstone of the proximal Deltadalen locality is conspicuous for its

120 authigenic glauconite content. Glauconite formation is favoured by elevated concentrations of

121 Fe_{HR}, silica and potassium under dysoxic conditions[41,42]. High Re/Mo ratios across this interval

122 (Fig. 2)[40] coupled with the ichnoassemblage and the impoverished shelly faunal record, which

123 consists of the inarticulate brachiopod *Lingularia freboldi*[43,44] (Supplementary Figs. 4 and 5; and

124 Section 7.1), are consistent with prevailing dysoxic seafloor conditions. Thus, the elevated

125 Fe_{HR}/Fe_{tot}* values of the Kapp Starostin Formation (Fig. 2) likely reflect the influx of a high

126 proportion of Fe (oxyhydr)oxides produced during enhanced weathering[35], rather than anoxic

127 water column conditions.

128   Enrichments in Re begin to decrease below the extinction interval at Deltadalen,

129 coincident with increasing Mo/U ratios (Fig. 2). These high ratios coincide with enhanced

130 fixation of Fe_{HR} as pyrite (Fig. 2), Mo_{EF}–U_{EF} that approach those observed in modern euxinic

131 settings (Fig. 3), and the disappearance of burrows (Supplementary Fig. 2), suggesting the

132 development of dominantly euxinic conditions in the water column in proximal settings at the

133 extinction boundary and into the Early Triassic[33,36]

134   The sponge spiculite chert of the Kapp Starostin Formation at Festningen (distal) is

135   marked by Fe_{HR}/Fe_{tot}* values in the equivocal zone, as well as low Mo/U and generally low

136   Re/Mo (Fig. 2). These vast sponge meadows are consistent with a well-oxygenated water

137   column[30], whereas infrequent peaks in Re/Mo may indicate occasional dysoxic conditions. A

138   pronounced peak in non-sulfidized iron, coincident with enrichments in Fe_{HR}, the precipitation of

139   glauconite, muted Re/Mo enrichments and bioturbation intensity (Supplementary Fig. 2), occurs

140   at the extinction horizon in the basal Vardebukta Formation (Fig. 2), suggesting the development

141   of dysoxic and/or ferruginous conditions in the water column. Enrichments in Fe_{HR} persist across

142   the P–Tr boundary at ~5 m above the base of the Vardebukta Formation, with elevated

143   Fe_{py}/Fe_{HR}*, moderate enrichments in Mo relative to U (Fig. 2), the cessation of bioturbation

144   (Supplementary Fig. 2), and Mo_{EF}–U_{EF} that are comparable to normal oxic marine settings (Fig.

145   3). Together, this implies the probable development of water column euxinia, but relatively low

146   levels of Mo drawdown imply either intermittent or weakly sulfidic conditions in this more distal

147   setting[46].

148   The spatio-temporal variability in water column redox implies the existence of dysoxic

149   conditions on the shallow shelf prior to the extinction (Fig. 2). Subsequently, at the extinction

150   horizon, euxinic conditions developed at the shallowest location (Deltadalen), and dysoxic to

151   ferruginous conditions expanded into more distal shelf settings (Festningen). This was followed

152   by the expansion of anoxia across the shelf, with euxinic conditions becoming more widespread

153   in the post-extinction Early Triassic. The S isotope composition of pyrite provides additional

154   support for this redox reconstruction. Generally low and quite variable pyrite δ^{34}S values (-32.7

155   ± 9.9‰) prior to the extinction horizon at the more distal locality (Fig. 2) are consistent with

156   microbial sulfate reduction in sediments deposited beneath an oxic water column[47]. By contrast,

157　high $\delta^{34}S_{py}$ where glauconite is prevalent, both in the lower section of the more proximal locality

158　(-16.7 ± 12.1‰) and just above the extinction horizon at the more distal locality (-16.8 ±

159　15.1‰), suggests more complete consumption of sulfate, possibly linked to temporal and spatial

160　variability in sulfate concentrations across the transect. Particularly in the case of the distal

161　glauconite-rich horizon, relatively high $\delta^{34}S_{py}$ may be due to significant drawdown of the

162　continental sulfate flux under euxinic conditions on the more proximal shelf. However, under

163　euxinic conditions at both sites, $\delta^{34}S_{py}$ values cluster around a narrow range (-27.8 ± 5.4‰),

164　which is consistent with the narrow range commonly found in modern and ancient euxinic

165　settings[47,48].

166　　　　We use our phosphorus data to test two scenarios that are compatible with redox change

167　at the extinction horizon. Firstly, the Fe_{HR} flux from the continent may have dropped (Fig. 2)

168　proportional to the sulfate influx with the switch to deforestation, soil erosion and increased

169　physical weathering[12,15,16,19]. Alternatively, an increase in organic carbon (C_{org}) availability (Fig.

170　4) under eutrophic conditions on the shelf may have increased the production of H_2S, thus

171　overwhelming the continental supply of Fe_{HR}. Both of these scenarios would initially promote

172　enhanced production of sulfide on the more proximal continental shelf.

Phosphorus recycling and the spread of anoxia

174　　　　To assess the potential role of phosphorus in driving our proposed redox structure we

175　quantified different phosphorus-bearing phases (Methods), specifically Fe (oxyhydr)oxide-bound

176　P (P_{Fe}), biogenic and authigenic apatite (P_{aut}), organic-P (P_{org}), and crystalline detrital phases

177　(P_{det})[25]. While detrital P is generally considered unreactive in the water column and during early

178　diagenesis, the remaining phases comprise a 'reactive' P pool (P_{reac}). However, Fe(III)-rich sheet

179 silicates (e.g. glauconite) can also effectively trap phosphate[49], which is extracted as part of the

180 P_{det} pool (Supplementary Fig. 7 and Section 7.3).

181   Prior to the extinction at Deltadalen (proximal), P_{tot}/Al is considerably enriched relative

182 to average marine shale (Fig. 4). This suggests an effective drawdown mechanism from a water

183 column that was rich in phosphate. Furthermore, although preferential release from organic

184 matter occurred during diagenesis (C_{org}/P_{org} > the molar Redfield ratio of 106/1), low C_{org}/P_{reac}

185 ratios (<< 106/1) combined with high P_{tot}/Al, suggest effective sequestration of P in the

186 sediment, with no evidence for extensive recycling. To explain these observations we invoke a

187 high initial weathering influx of phosphate to the proximal shelf associated with initial

188 emplacement of the Siberian Traps prior to the extinction[18], which enhanced productivity and

189 C_{org} remineralisation in the water column, leading to the development of dysoxic conditions (Fig.

190 5). However, the extent and intensity of deoxygenation was limited by effective drawdown of P

191 to the sediments in association with both C_{org} and the high weathering influx of Fe

192 (oxyhydr)oxide minerals, and with long-term retention in CFA and glauconite (Supplementary

193 Fig. 7).

194   These factors then controlled the geochemistry prior to the extinction at Festningen

195 (distal), where P_{tot}/Al ratios are close to average shale, C_{org}/P_{org} ratios are elevated relative to the

196 Redfield ratio, and C_{org}/P_{reac} ratios scatter close to the Redfield ratio (Fig. 4). This suggests that

197 the high initial weathering influx of P was efficiently sequestered in more proximal settings, thus

198 limiting the spatial extent of dysoxic conditions. Furthermore, while P was released from organic

199 matter during microbial respiration (C_{org}/P_{org} > 106/1), there is little evidence for a high sustained

200 flux back to the water column ($C_{org}/P_{reac} \approx 106$), consistent with the expected behaviour of P in

201 sediments deposited beneath an oxic water column[27,28].

202   At the extinction horizon, P_{tot}/Al ratios decrease to average shale values at Deltadalen

203   (proximal), and both C_{org}/P_{org} and C_{org}/P_{reac} ratios increase considerably to values that exceed the

204   Redfield ratio (Fig. 4).This suggests that the development of euxinia fuelled efficient release of P

205   from both C_{org} and Fe (oxyhydr)oxides, and a positive productivity feedback was promoted via

206   enhanced P recycling. The initial driver of euxinia is more difficult to ascertain, but was likely

207   related to the change to a chemical weathering-limited denudation regime[19] (Fig. 2), thereby

208   decreasing the land-derived influx of Fe_{HR}. This led to a tipping point whereby a relative excess

209   of dissolved sulfate over Fe_{HR} promoted the development of euxinia[36]. As discussed above, an

210   increase in eutrophication driven by an enhanced nutrient influx may also have promoted sulfide

211   production. However, this seems a less likely explanation for the initial driver of euxinia given

212   the already high input of P (Fig. 4).

213   In glauconite-rich sediments immediately above the extinction horizon at Festningen

214   (distal), there is an initial peak in P_{tot}/Al in association with the development of dysoxic and/or

215   ferruginous conditions. Here, our detailed P speciation analyses suggest that, as with the

216   glauconite-rich horizon in the proximal locality, P was trapped in the sediment in association

217   with CFA and glauconite (Supplementary Fig. 7). The high P content of this horizon likely

218   occurred due to drawdown of P that was recycled under euxinic conditions in more proximal

219   settings, suggesting the operation of a redox-controlled nutrient shuttle across the shelf. This

220   nutrient shuttle then drove the development of marine euxinia to its maximum extent in the

221   aftermath of the mass extinction (Fig. 5), where wind/density-driven water circulation on the

222   shelf would support upward transport of recycled P, and thus sustained deoxygenation[11]. At

223   Festningen, however, the development of only weak or intermittent euxinia after the P–Tr

224 boundary restricted the extent of P recycling to the water column ($C_{org}/P_{reac} \approx 106/1$; Fig. 4),

225 which effectively constrained the maximum spatial extent of euxinia.

226 **Implications for extinction selectivity**

227 This P-driven biogeochemical cascade is synchronous with independent proxy records for

228 the global-scale spread of anoxic water masses[5,7], and it was this that initiated the main marine

229 extinction pulse. The P-driven control on the extent of initial deoxygenation and subsequent

230 euxinia promoted life-viable environments in the deep marine realm, thereby shaping the

231 ecosystems of the surviving biota. Based on the benthos that survived the end-Permian mass

232 extinction at Deltadalen, a planktotrophic larval stage[50] (Supplementary Section 7.1) and a high-

233 tolerance to low-oxygen conditions are important traits. These benthic species could rapidly

234 disperse over large distances, thus increasing the chance of survival in habitable locations.

235 In accordance with theoretical ecological models[51], environmental deterioration of the

236 marine realm began before the extinction pulse. The initial development of dysoxic/anoxic water

237 masses, which were preferentially situated in shallow marine environments in the Boreal

238 region[20], may thus be regarded as a prelude to the impending mass extinction. Our redox model

239 also resolves the apparent conflict between the timing of magmatic activity[18], enhanced

240 weathering[16], and the main extinction pulse. The sum of these changes in marine redox

241 conditions across large stretches of the shelf, which harboured the majority of the Palaeozoic

242 biodiversity[2], appears to have been detrimental to many life forms at the end of the Permian.

243

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365 of Festningen and Deltadalen, respectively.

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Author contributions

The study was designed by MS, RJN, PBW and SWP. Samples were collected by VZ, ARNS, HS, SP, PBW, and DPGB. Palaeontological data acquisition was performed by WJF, MS, PBW, and DPGB. Geochemical analyses were performed by MS, FM and RJN. MS and SWP interpreted data. MS led the writing of the manuscript with contributions from all co-authors.

Competing interests

The authors declare no competing interests.

Figure captions

Figure 1: Geographical setting of the Festningen section (1) and Deltadalen core (2). Late Permian lithofacies of Spitsbergen after ref 29 and Supplementary Section 2; the tentative location of a northern source area (possibly on the Nordfjorden High) demarcated with a

386   question mark; and the Sørkapp-Hornsund High encircled with a dotted line. The red dots mark

387   the exact locations of the sites. Base map from GADM database (https://gadm.org/)

388

389   **Figure 2: Stratigraphic plot of $\delta^{13}C_{org}$, Fe speciation, Mo/U, Re/Mo and $\delta^{34}S_{py}$ for the**

390   **Festningen outcrop and Deltadalen core.** The boundaries (vertical dotted lines) for oxic,

391   anoxic, ferruginous (Fe(II)-rich) and euxinic (H_2S-rich) water column conditions were calibrated

392   in modern and ancient aquatic environments (see text for sources). Iron speciation (Fe_{py}/Fe_{HR}*,

393   Fe_{HR}/Fe_{tot}*) corrected for excess Fe_{PRS} (excess Fe_{PRS} = [measured Fe_{PRS}/Fe_{tot} - baseline

394   Fe_{PRS}/Fe_{tot}] $\times$ Fe_{tot}) is shown as black circles; uncorrected values are shown as open circles (See

395   Supplementary Section 7.2). Subscripts of isotope ratios; org = total organic matter and py =

396   pyrite. Fe_{py} = iron pyrite; Fe_{HR} = highly reactive iron (Fe_{carb} [iron bound to carbonate] + Fe_{ox}

397   [iron bound to Fe oxy(hydr)oxides] + Fe_{mag} [iron bound as magnetite] + Fe_{py}); Fe_{tot} = total iron;

398   Fe_{PRS} = poorly reactive sheet silicate iron. Reproducibility for Fe_{py} and Fe_{HR} is better than 5%

399   and 9% relative standard deviations (RSD), better than 8% RSD for total elemental

400   concentrations, and better than 0.1‰ and 0.9‰ SD for $\delta^{13}C_{org}$ and $\delta^{34}S_{py}$. Horizontal dashed

401   grey line: extinction event; solid grey line: Permian–Triassic boundary. Details on lithology and

402   stratigraphy in Supplementary Fig. 2 and Sections 2 and 3.

403

404   **Figure 3: Crossplots of Mo–U covariation.** Mo and U are given as enrichment factors (EF =

405   [element/Al]$_{sample}$/[element/Al]$_{AV}$, where AV represents average shale[45]) on a $\log_{10}$-scale. The

406   black dashed lines represent seawater (sw) Mo–U mass ratios for modern environments; high

407   (sulfidic Cariaco Basin), moderate (non-sulfidic open marine), and low (restricted, sulfidic Black

408   Sea)[33]. The panels present the data of: a) Deltadalen, b) Festningen, and c) a conceptual model to

409   explain the enrichment patterns and changes in sedimentary Mo_{EF} and U_{EF} at both sites in

410   relation to hydrographic and redox conditions[33], The solid red lines denoted by "particulate

411   shuttle" show systematics underlain by a fluctuating chemocline, whereas "redox variation"

412   pertains to the evolution of water mass chemistry. Note, that the red dashed line sketches the

413   trajectory of the open marine conditions of Deltadalen from dysoxic (low Mo–high U) to euxinic

414   (high Mo–low U). Fe_{py} = pyrite iron and Fe_{HR} = highly reactive iron.

415

416   **Figure 4: Stratigraphic distribution of P_{tot}/Al, C_{org}, C_{org}/P_{org}, and C_{org}/P_{reac} ratios.** The

417   threshold of P_{tot}/Al (mass ratio of 0.008; vertical red line) is the average shale reference value[45],

418   whereas the C/P molar ratio of 106/1 denotes the Redfield ratio (vertical blue line), and the red

419   circle represents an outlier (P_{tot}/Al > 2.0). C_{org} = total organic matter; P_{org} = organic-bound

420   phosphorus; P_{reac} = reactive phosphorus (P_{org} + P_{aut} [apatite P] + P_{Fe} [Fe (oxyhydr)oxide-bound

421   P]), and P_{tot} = total phosphorus. External reproducibility for total P and Al is better than 8%

422   RSD, better than 10% RSD for Corg, and better than 23% RSD for the different P phases.

423   Horizontal dashed grey line: extinction event; solid grey line: Permian–Triassic boundary.

424   Details on lithology and stratigraphy in Supplementary Fig. 2 and Sections 2 and 3.

425

426   **Figure 5: Conceptual model of the development of water column redox conditions.** In the

427   Late Permian, the inner shelf was dysoxic (demarcated with <[O_2]) and large amounts of reactive

428   P accumulated, whereas the outer shelf harboured a thriving ecosystem (here depicted as crinoids

429   and molluscs, but which are not representative of the actual fossil assemblages). During the end-

430   Permian mass extinction euxinia (demarcated with [H_2S]) developed on the inner shelf, whereas

431   the outer shelf environment became dysoxic/ferruginous (demarcated with [Fe(II)]). Under these

432   conditions, P was remobilized as dissolved P (demarcated with H_3PO_4) from the inner shelf,

433   invigorating productivity (and thus oxygen depletion), and dissolved P was recycled to the outer

434   shelf and initially deposited through uptake by Fe (oxyhydr)oxide particles settling on the

435   seabed. After the extinction, euxinic conditions became more prevalent across the shelf, which

436   was initiated and maintained by recycling of P. Fe_{HR} represents highly reactive iron.

Methods

438   **Organic carbon content and carbon isotopes.** Carbonate was removed by treating the

439   sample with 2 M HCl. The residues were repeatedly washed with MilliQ water^{TM} and dried at

440   40 °C. The de-carbonated samples were analyzed for total organic carbon (TOC = C_{org}) content

441   and associated carbon isotopic composition using an Elementar Pyrocube elemental analyser

442   linked to an Isoprime mass spectrometer following a standard protocol. Details regarding the

443   reproducibility of the carbon isotope measurements and an extended protocol are included in the

444   Supplementary Section 6.2.

445   **Bulk element content.** Whole rock major- (Fe, P, Al) and minor (Mo, U, Re) elements

446   where obtained by dissolving ashed samples (550 °C over night) with HNO_3–HF–$HClO_4$

447   followed by inductively coupled plasma optical emission spectrometry (ICP-OES). The precision

448   of elemental analysis was monitored by analyzing certified standards, and repeated measurement

449   yielded RSDs that are better than 8 % for all elements (Supplementary Section 6.1 and Table 1).

450   **Sequential Fe and P extractions.** A standard sequential Fe extraction was followed[32]. A

451   sodium acetate solution at pH 4.5 for 48 h at 50 °C was used to extract Fe_{carb}, followed by a 2 h,

452   room temperature extraction with sodium dithionite solution at pH 4.8 to obtain Fe_{ox}. An

453 extraction with ammonium oxalate for 6 h at room temperature was then applied to yield Fe_{mag}.

454 Iron from poorly reactive sheet silicates (Fe_{PRS}) was dissolved using concentrated, boiling HCl

455 for 1 min[32]. Iron concentrations in the extraction solutions were measured via atomic absorption

456 spectrometry (AAS). Phosphorus phases were extracted via a revised SEDEX scheme for ancient

457 rocks[25,52]. P_{Fe1} (poorly crystalline Fe (oxyhydr)oxides) was extracted with a sodium dithionite

458 solution (buffered with bicarbonate to pH of 7.6) for 8 h at room temperature; P_{aut} was extracted

459 with a sodium acetate solution at pH 4 for 6 h at room temperature; P_{det} was extracted with a

460 10 % HCl solution for 16 h at room temperature; P_{mag} was extracted with an ammonium oxalate

461 solution for 6 h at room temperature; P_{Fe2} (more crystalline Fe (oxyhydr)oxides) was extracted

462 with a sodium dithionite solution (buffered with citrate to a pH of 4.8) for 8 h at room

463 temperature, and, finally the residue was ashed (550 °C for 2 h) and reacted with 10 % HCl

464 solution for 16 h at room temperature to liberate P_{org}. The sum of $P_{Fe1} + P_{Fe2} + P_{mag}$ gives P_{Fe}.

465 The P content of the various extracts was determined either via the molybdate blue method[25] or

466 ICP-OES (in the case of P_{Fe1}, P_{Fe2} and P_{mag}). The precision of the various Fe and P phase

467 measurements as well as the extended protocols are reported in Supplementary Section 6.1 and

468 Tables 2 and 3.

469 **Pyrite content and sulfur isotopes.** Pyrite S was measured via the chromium reduction

470 method[53]. This method liberates H_2S, which is subsequently trapped as silver-sulfide (Ag_2S).

471 Pyrite iron was determined stochiometrically from the weight of the Ag_2S recovered. The Ag_2S

472 was analysed for S isotope composition using an Elementar Pyrocube linked to an Isoprime mass

473 spectrometer (see Supplementary Section 6.2 for reproducibility of S isotope measurements and

474 an extended protocol).

Data Availability

The raw and processed geochemical data that support the findings of this study are available under Zenodo: https://doi.org/10.5281/zenodo.3878094

Code Availability

The R Markdown files to reproduce the data analysis as well as generating the accompanying data figures and the main and supplementary information texts can be found under Zenodo: https://doi.org/10.5281/zenodo.3878094

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