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Title: Oceanic anoxia in Panthalassa during the Early Triassic Smithian–Spathian transition

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Research highlights:

- Smithian and Spathian deep-sea sequences in the Japanese accretionary complex

- Ferruginous anoxia in the middle to late Smithian Panthalassa
- Organic-rich black clay deposition and euxinia occurred in the latest Smithian Panthalassa
- Enhanced sulphate reduction under increased surface productivity across the Smithian–Spathian boundary

Keywords: Carbon isotopes, Iron speciation, Pyrite framboids, Redox-sensitive elements, Smithian–Spathian boundary

Abstract

The Smithian–Spathian transition during the Early Triassic was associated with significant environmental change, including global warming and oceanic anoxia. However, understanding ocean redox conditions in the pelagic Panthalassa during this period has been challenging due to a lack of well-dated sedimentary sections. Here, we provide new geochemical data for a Smithian–Spathian succession from an accretionary complex of central Japan (Inuyama, Aichi Prefecture), which was deposited in a low-latitude abyssal location. Conodont index fossils and carbon isotope stratigraphy reveal that the studied sections span the middle Smithian to lowermost Spathian (Momotaro-Jinja lower section), and the middle part of the Spathian (Momotaro-Jinja upper section). The Smithian–Spathian boundary is placed within a thick (~40 cm), organic-rich, black claystone layer in the lower part of the section. We reconstruct water column redox conditions using pyrite framboid size ranges, Fe speciation and redox sensitive trace elements. During the middle to late Smithian, we find that the water column changed from oxic to ferruginous anoxic, with a transition to euxinic during the latest Smithian to earliest Spathian. During the middle Spathian, the water column fluctuated between oxic and euxinic conditions. We suggest that late Smithian seawater warming contributed to deoxygenation of Panthalassa whilst surface productivity and organic matter fluxes were low, leading to non-sulfidic ferruginous anoxia. Productivity then increased during the latest Smithian to earliest Spathian, thereby stimulating microbial sulphate reduction and inducing widespread ocean euxinia.

1. Introduction

The Permian–Triassic boundary (PTB) is marked by a significant loss of biodiversity, especially of benthos and planktonic animals, which was followed by a muted recovery (e.g., Song et al., 2018). By the Olenekian stage which consists of Smithian and following Spathian substages, diversity was still low amongst many marine benthic groups, although nektonic conodonts and ammonoids had radiated significantly by the Smithian (Orchard,1998; Stanley, 2009). Other significant environmental perturbations, including changes in seawater temperature and ocean redox conditions, occurred around the Smithian–Spathian boundary (SSB), and nektonic fauna experienced an extinction event (Stanley 2009; Zhang L. et al., 2019). Oxygen isotopes in conodont apatite ($\delta^{18}O_{apatite}$) indicate that surface seawater may have reached ~43°C in the late Smithian (Sun et al., 2012; Romano et al., 2012; Fig. 1). Seawater temperatures subsequently decreased by more than 4°C after the SSB, but relatively warm conditions continued until the late Spathian. These climate warming and cooling trends coincide with negative and positive carbon isotope ($\delta^{13}C$) excursions, respectively termed N3 in the Smithian and P3 in the early Spathian (Song et al., 2014; Li et al., 2023; Fig. 1). Following these excursions, a warm period in the mid Spathian coincided with another negative $\delta^{13}C$ excursion, termed N4 (Fig. 1).

After widespread oceanic anoxia during the PTB event, anoxic and dysoxic oceanic conditions persisted and became especially widespread in both the Smithian and Spathian of Olenekian (Takahashi et al., 2009a, 2015; Wignall et al., 2010; Grasby et al., 2013; Huang et al., 2017, Shen et al., 2019; Li H.X. et al. 2023). This regional development of anoxic water masses broadly coincides with negative troughs in uranium isotope values in carbonate ($\delta^{238}U_{carbonate}$), which likely record increases in the depositional flux of U in anoxic basins (Zhang F. et al., 2019; Zhao et al. 2020). After the Early Triassic, oceanic environments returned to oxic conditions (e.g., Chen and Benton, 2012). Subsequently, oceanic anoxic events reoccurred in the Late Triassic, i.e., in the middle of Carnian (Carnian Pluvial event; Tomimastu et al. (2023) and references therein), across the Norian-Rhaetian boundary (e.g., Rigo et al., 2024), and at the end of Rhaetian (Triassic-Jurassic boundary; Somlyay et al., 2023). These events are also associated with $\delta^{13}C$ excursions and climate change (Trotter et al., 2015).

The Panthalassa Ocean (or paleo-Pacific) dominated a large area of the Permian–Triassic world. Paleoenvironmental records for this oceanic region are therefore crucial to understand global environmental conditions during this time interval. Sediments accumulated in Panthalassa are now preserved in the circum-Pacific accretional complex, including Japan, Canada and New Zealand, but continuous stratigraphic sections straddling the Permo-Triassic boundary and the stage and substage boundaries of Permian and Triassic are rare in the world (e.g., Matsuda and Isozaki, 1991; Wang et al., 1994; Spörli et al., 2007). Among these, the Panthalassic sedimentary sequence in Japanese accretionary complexes have been investigated. Previous studies have revealed that the Smithian to Spathian interval in the Japanese accretionary complex consists of siliceous claystone beds with interbeds of thin black carbonaceous claystone and dark-coloured chert beds (e.g., Kakuwa, 2008). Some of these strata have signals of anoxic or oxygen-poor conditions, as determined via pyrite framboid systematics, sulphur-bearing organic molecules, and elevated redox-sensitive elemental concentrations (Isozaki, 1997; Kakuwa, 2008; Wignall et al., 2010; Takahashi et al., 2009a, 2015; Muto, 2021). However, the precise timing of these redox changes, and the intensity and mechanisms involved, are uncertain, due to the lack of well-dated Smithian to earliest Spathian sections (Muto, 2021).

One of the best localities for studying the Panthalassic Lower Triassic is the Momotaro-Jinja section in central Japan (hereafter called the Mj section). The advantage of this locality is that the outcrops are extensive and well dated due to previous studies of index fossils and chemostratigraphy. However, under the accumulation of research, important assignments on age and stratigraphy have remained unresolved. The age of the Mj section has been determined by radiolarian and conodont biostratigraphy (Yao and Kuwahara, 1997; Takahashi et al., 2009a). Initially, it was considered that this section covers the Indian-Olenekian boundary (IOB) to the Olenekian-Anisian boundary (OAB). Several studies on the Mj section have been based on this timescale (e.g., Wignall et al., 2010; Sakuma et al., 2012; Takahashi et al., 2009a, 2015). However, it is now plausible to consider the Mj section as separate lower and upper Olenekian (Smithian and Spathian) stratigraphic sequences across a fault, with the IOB and OAB not present in the Mj section (Muto et al. 2019). This is due to the occurrence of lower Olenekian (Smithian) conodonts from the strata previously attributed to the Induan (Yamakita et al., 2010, 2016), and the absence of the Anisian conodonts (only the presence of the upper Olenekian (Spathian) conodonts) at the previously proposed OAB horizon determined by radiolarian zonation. Sakuma et al. (2012) erroneously reversed the stratigraphic position of the conodont ages given by Yamakita et al. (2010) and showed a columnar section of the Smithian siliceous claystone beds, with a black claystone bed with no fossil age at the bottom as the Induan. Our corrections to Sakuma et al. (2012) are shown in the supplementary material, while we also provide the first illustrative evidence for a Smithian age based on conodonts.

Several studies of paleoenvironmental conditions during deposition of the Mj section have been reported. Takahashi et al. (2009) reported evidence of an “anoxic” oceanic environment based on sulphur-containing organic molecules (dibenzothiophene) in the Spathian part of the section. This was later interpreted as a record of suboxic bottom water, based on the relatively low enrichment of redox-sensitive trace elements (such as U) in the sedimentary rocks (Takahashi et al., 2015). Wignall et al. (2010) examined the pyrite morphology of five samples from the Mj section and suggested water column euxinia. However, these samples were placed tentatively in the upper Induan (Dienerian), but without empirical age evidence, which as discussed above, needs to be reconsidered. In the context of this previous research, the Mj section would benefit from a comprehensive paleoenvironmental analysis based on the latest stratigraphic understanding.

The goal of this study is to decode the environmental history of the Smithian and Spathian from the Mj section, based on the correct stratigraphy and associating time scale. Here, we present a detailed litho-, bio- and chemostratigraphic study, combined with an analysis of water column redox conditions, for a Smithian-Spathian pelagic sedimentary sequence exposed at the Mj section. This reveals the evolution of local oceanic redox conditions in the central Panthalassa, which we then consider in terms of the spatial extent of oceanic environmental change during the Smithian-Spathian transition and their potential mechanism.

2. Geologic setting

2.1. Momotaro-Jinja section (Mj section)

The Mj section is located in the Inuyama area (Yao and Kuwahara, 1997), at the border of the Aichi and Gifu prefectures, central Japan. It belongs to the Jurassic accretionary complex of the Mino–Tamba–Ashio Belt of Southwest Japan. The Jurassic accretionary complex in the Inuyama area is composed of stacked thrust sheets of chert–clastic sequences, typical of accretionary complexes (Fig. 2), and the Sakahogi Syncline subsequently folded this thrust-sheet complex (Mizutani, 1964). The chert–clastic sequence comprises Lower Triassic pelagic siliceous claystone, Middle Triassic to Lower Jurassic pelagic bedded chert, Middle Jurassic hemipelagic siliceous mudstone, and Upper Jurassic trench-fill mudstone and sandstone (Kimura and Hori, 1993). Study of the red cherts of the Middle Triassic indicates a paleolatitude of approximately ± 6° either side of the equator (Ando et al., 2001). The Mj section belongs to the lowermost portion of one of the thrust sheets in the south limb (Fig. 2).

We divide the Mj section into two parts, namely the Momotaro-Jinja lower section (MjL), located in the southern part of the study region, and the Momotaro-Jinja upper section (MjU), located in the northern part (Fig. 3). Both the MjL and MjU sections have previously been studied (e.g., Yao and Kuwahara, 1997; Takahashi et al., 2009a; Wignall et al., 2010; Sakuma et al., 2012), but as described above, reports on the lithostratigraphy and biostratigraphy, especially of the MjL section, appear to be incorrect (see Supplementary Material).

2.2. Lithofacies at the Momotaro-Jinja section

The deep-sea sedimentary rocks of the Mj section comprise siliceous claystone, cherty claystone, dolostone, black claystone, chert and muddy chert. Siliceous and cherty claystone are composed of fine-grained siliciclastic material and siliceous bioclasts (Figs. 4a and 4b), with cherty claystone being relatively harder at outcrop. Organic matter and pyrite crystals (several to tens of micrometres in size) were observed in most beds of these lithologies. A dolostone layer appears as an interbed in the cherty claystone of the MjL section (Figs. 3 and 5), comprising authigenic dolomite rhombs (Fig 4c).

The black claystone beds contain fine-grained clay minerals and organic matter (Fig. 4d and 4e). Three different forms are present at outcrop. The first is thin (several mm to 1 cm-thick) black claystone beds interbedded with siliceous and cherty claystone beds (Figs. 1 and 6). These beds are often accompanied by a few mm to 1 cm thick chert bed at the top. This chert bed grades laterally into siliceous or cherty claystone in many cases. The second is thick layers (more than 30 cm thick) that occur in the topmost part of the MjL section (Figs. 1, 3, 5 and 6). The third occurrence is as a dozen cm-thick beds interbedded in a black chert bed (Figs. 1, 3 and 6). Under the microscope, pyrite (framboids and euhedral forms) and siliceous bioclasts occur in these black claystone layers. The siliceous bioclasts are generally circular-shaped in thin section, and are probably radiolarians (Fig. 4d). Abundant siliceous microfossils frequently appear in the black claystone interbeds within siliceous and cherty claystone beds (Fig. 4d). These microfossils are several hundred micrometres in diameter. Siliceous microfossils are also observed in thin sections from the thick black claystone layer in the uppermost part of the MjL section. Their diameter is up to 50 μm, and are hence smaller than those described above. The abundance of these fossils is not as high, and layers of abundant siliceous microfossils are not evident in these particular black claystone beds.

Chert and muddy chert are the dominant lithologies in the MjU section (Figs. 1 and 3). Based on thin section observations, the chert is composed of siliceous bioclasts, fine-grained siliciclastic material, and fine-grained clay minerals (Fig. 4f). Muddy chert also has similar components, but is particularly rich in fine-grained clay minerals and siliciclastic material (Fig. 4g and 4h).

2.3. Momotaro-Jinja lower section

The strata of the MjL section strike E–W and dip at high angles (Fig. 3). Multiple isoclinal synclines, anticlines and faults deform the strata, with fold axes parallel to bedding planes, while fault planes cut bedding at low angles and have high dips (Fig. 3 and Fig. 4). Five subsections were logged: MjL-1, MjL-2, MjL-3, MjL-4 and MjL-5 (Figs. 3 and 6). For each subsection, independent bed numbers are assigned from bottom to top. Subsection MjL-2 covers the entire stratigraphic interval corresponding to the composite of the five subsections (Figs. 6 and 7). The composite stratigraphy is composed of 0.7 m of grey siliceous claystone, 3.2 m of grey cherty claystone, and 0.5 m of black claystone in ascending order, giving a total thickness of ~4.4 m (Figs. 3 and 6).

The lowest grey siliceous claystone is exposed in the southern part of the MjL section (Fig. 3), with the total thickness estimated to be at least 0.8 m, although its base is hidden. The top of this claystone is conformably overlain by grey cherty claystone (~3 m in thickness) and overlying black claystone (0.3–0.5 m in thickness). The lithologic transition from cherty claystone to black claystone appears twice due to an anticlinal folding in the northern part of the outcrop (Fig. 3). A dolostone layer is interbedded within the middle part of the cherty claystone (Bed 3 of MjL-1, Bed 24 of MjL-2, Bed 25 of MjL-3, and Bed 13 of MjL-5; Figs. 3 and 6). The other dolostone layer is only observed in the MiL-1 section and overlies the cherty claystone (Bed 9 of Mj-1; Figs. 3 and 6).

The age of the MjL sections has previously been discussed based on radiolarian (Yao and Kuwahara, 1997) and conodont occurrences (Yamakita et al., 2010, 2016), in addition to carbon isotope profiles (Sakuma et al., 2012). Here we present a revised age assignment based on a more complete investigation of conodont biostratigraphy integrated with carbon isotope stratigraphy.

2.4. Momotaro-Jinja upper section

The MjU section is located north of the MjL section (Fig. 3), and has been described by Yao and Kuwahara (1997), Takahashi et al. (2009a; 2015) and Sakuma et al. (2012). Yao and Kuwahara (1997) and Takahashi et al. (2009a; 2015) considered that the MjU section includes the Lower Triassic–Middle Triassic boundary (i.e., the Olenekian–Anisian boundary). However, Muto et al. (2019) revised the age of radiolarian biozones and suggested that the section is entirely of Spathian age and does not reach the Anisian, which appears to be correct.

The 7.5-m-thick MjU sequence is composed of 1.5-m-thick grey siliceous claystone, 1.5-m-thick red siliceous claystone (cut by a small fault 0.25 m from the base), 1.25-m-thick grey siliceous claystone interbedded with two chert beds (0.16- and 0.24-m-thick black chert), and 1.5-m-thick alternating grey chert and siliceous claystone (Takahashi et al., 2009a). This study focuses on the upper 3.3-m interval of the MjU section (Figs. 1, 3 and 8), which is composed of dark greenish grey siliceous claystone beds (1.1 m thick; Beds 1–17), a thick black chert bed intercalated with black claystone (Bed 19), grey siliceous claystone beds (Bed 21–24), and grey siliceous claystone, muddy chert and chert beds (Beds 25–52), in ascending order (Fig. 8). This is the same interval studied by Takahashi et al. (2015) using trace metal analyses and pyrite observations.

3. Methods

3.1. Conodonts

Samples were collected for conodonts from MjL-2, MjL-3 and MjL-5. Conodonts were found by the "chip method" (Takemura et al., 2001; Muto et al., 2018, 2019), in which sample rocks are cleaved parallel to the bedding plane into small "chips'' and observed under a binocular microscope. This method is suitable for finding conodonts in deep-sea sedimentary rocks, which are frequently cracked or preserved as moulds and impossible to extract from the host rock. Some of the samples and recovered conodont specimens were briefly referred to in Yamakita et al. (2010, 2016).

3.2. Preparation of rock samples

Samples for geochemical analysis were collected from MjL-2. As it has the least disruption to the stratigraphic sequence by faults and folds, this subsection is the most stratigraphically complete and covers the entire stratigraphy of the MjL section. Weathered samples and samples covered in vegetation were avoided. Samples were cut and polished on cut surfaces for observation. For chemical analyses, fresh pieces of rock ~3 mm thick were cut from hand specimens. During this procedure, visible veinlets and stains due to weathering were carefully removed. The pieces were then polished on the cut surfaces to remove metal contamination from the blade, washed in deionized water, and dried. Samples for carbon (C) analyses were crushed using a mortar and pestle made of stainless steel. Samples for major and trace metal measurements were wrapped several times in polyvinyl chloride sheets and hammered into small pieces (~2 mm in diameter). Crushed fragments of all samples were finally pulverized using an agate planetary mill. The powdered samples of the MjU section used for geochemical analysis are splits from the samples analysed by Takahashi et al. (2015).

3.3. Carbon analyses

To remove all carbonates and other acid-soluble minerals, about 1 g of powder was treated with 50 mL of 20 wt% hydrochloric (HCl) acid for over 12 h. The residue was rinsed with deionized water until the pH was ~7, and dried. Around 1–30 mg of powder was sealed in tinfoil. Samples were analysed by an elemental analyser (Thermo Flash 2000; Thermo Scientific) at Tohoku University, Japan. Quantified C contents (wt%) were normalized by the ratio of weight loss of each sample after HCl treatment, to calculate total organic C (TOC). Reproducibility of these analyses was better than 0.01 wt%, as determined by repeat analysis of the internal reference material (BBOT standard; 2,5-Bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene; Thermo # 33835210).

Organic carbon isotopes were analysed on the pre-treated samples using a Finnegan MAT 253 mass spectrometer attached to an elemental analyser (Flash 2000) through an interface system (ConFlo IV) at Tohoku University. Isotopic values are reported relative to the Vienna Pee Dee belemnite (VPDB) standard. BBOT (Thermo Scientific) and L-Alanine (M8A0384) of SI Science Co., Ltd. ($\delta^{13}C = -18.5‰$ VPDB) were used as internal laboratory standards. The overall uncertainty of the measured values was ±0.2‰.

3.4. Pyrite observations

Thin sections of samples from MjL-2 were polished with diamond paste (1 μm in diameter). The thin sections were observed under a microscope with transmitted and reflected light to verify the mode of occurrence of pyrite.

3.5. Iron speciation

A sequential extraction targeting different operationally defined Fe pools, including carbonate (Fe_{carb}), ferric (oxyhydr)oxides (Fe_{ox}) and magnetite (Fe_{mag}), was performed on a split of 0.07–0.09 g of powdered sample following Poulton and Canfield (2005) and Poulton

(2021). Fe_{carb} was first extracted using Na-acetate at pH 4.5 and 50°C for 48 h, followed by Fe_{ox} using Na-dithionite for 2 h at room temperature. Fe_{mag} was then determined with an ammonium oxalate extraction for 6 h. Dissolved iron concentrations (for Fe_{carb}, Fe_{ox} and Fe_{mag} pools) were measured by atomic absorption spectrometry (AAS; Thermo ice 3000 at the University of Leeds, UK). Replicate extractions of international reference material (WHIT; Alcott et al., 2021) gave a RSD of <5% for each Fe pool.

Pyrite iron (Fe_{py}) was determined stoichiometrically based on Ag_2S precipitates formed after a boiling HCl and chromous chloride distillation (Canfield et al., 1986). All samples were tested for the presence of acid-volatile sulphide (AVS; predominantly FeS) via an initial 6 M HCl distillation, but in all cases, AVS was below detection (<0.001 wt%). Replicate pyrite extractions gave a RSD of <5%. The sum of these measured Fe pools defines the total concentration of highly reactive Fe (Fe_{HR}):

$$Fe_{HR} = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py} \qquad (1)$$

A 0.5 N HCl extraction was also conducted on ~0.5 g splits of powdered samples for 1 h to assess for potential oxidation during weathering (see Matthews et al., 2017). This treatment targets poorly crystalline ferric oxide minerals ($Fe(III)_{HCl}$), such as ferrihydrite, in addition to reduced Fe phases such as Fe_{AVS} and potentially some ferrous carbonate/phosphate phases. Since Fe_{AVS} was not present in our samples (see above), this phase can be discounted. Thus, this extraction targets the remaining non-sulphidized Fe(II) minerals (termed $Fe(II)_{HCl}$), as well as $Fe(III)_{HCl}$. Poorly crystalline $Fe(III)_{HCl}$ minerals such as ferrihydrite are not stable on geological timescales. Hence, the $Fe(III)_{HCl}$ pool can be considered to dominantly result from more recent weathering of reduced minerals (mainly pyrite). Thus, quantification of this pool provides a maximum estimate of the extent of post-depositional pyrite oxidation (e.g., Matthews et al., 2017).

The $Fe(II)_{HCl}$ pool was determined immediately by spectrophotometer using the ferrozine assay (Stookey, 1970). The total amount of Fe dissolved by the 0.5 N HCl extraction was determined following the reduction of Fe(III) to Fe(II) using hydroxylamine hydrochloride, followed by analysis by spectrophotometer using the ferrozine assay. Subtraction of $Fe(II)_{HCl}$ from this Fe pool gives $Fe(III)_{HCl}$. Corrected Fe pools were calculated as:

$$\text{Corrected } Fe_{carb}\ (Fe_{carb}^{*}) = Fe_{carb} - Fe(III)_{HCl} \qquad (2)$$

$$\text{Corrected } Fe_{py}\ (Fe_{py}^{*}) = Fe_{py} + Fe(III)_{HCl} \qquad (3)$$

3.6. Major and trace elements

Concentrations of total Al and Fe (Fe_T) were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; SPS3500, SII nanotechnology), and trace element (Mo, U) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS; iCAPQc, Thermo Scientific) at the University of Tokyo. For these analyses, the samples were treated by acid dissolution techniques established by Matsunami et al. (2010). First, 0.1–0.5 g of pulverized sample was treated with 4 mL of $HClO_4$ + HNO_3 (1:1 mixture) for 45 min at 120°C to decompose organic matter. This was followed by a double treatment with 4 mL of $HClO_3$ + HF (1:1 mixture) for 30 min at 120°C in a polytetrafluoroethylene (PTFE) beaker on a heated block (DigiPREP MS, SCP Science) to remove silicate minerals. After these two acid treatments, the solutions were heated at 175°C for 45 min. The residue was then dissolved in 25 mL of HNO_3 + ultra-pure water (1:4 mixture) by boiling gently at 100°C for 3–4 h, after which the solution was diluted by adding ultra-pure water to a volume of 100 mL. Finally, 1 mL of the solution was diluted to 1:10 by adding 5 mL of HNO_3 and ultra-pure water. Indium (In) was used as an internal standard for the ICP-MS analysis. Working standards were prepared from a series of SPEX Multi-Element Plasma Standards supplied by SPEX Industries. Reproducibility, based on replicate analyses of reference material (GSJ-JR-1; rhyolite reference material supplied by the Geological Survey of Japan), was better than ±3% for Al, ±1% for Fe, and ±3% for Mo and U.

Major-element concentrations of SiO_2, Al_2O_3, NaO_2, CaO and K_2O were determined using an energy-dispersive X-ray fluorescence spectrometer (EDXRF; PANanalytical Epsilon 5) at the Graduate School of Environmental Studies, Tohoku University. For this analysis, the sample powders were pressed into pellets using a hydraulic press (Specac Ltd). The instrument was calibrated using standard reference materials (listed in Matsunami et al. (2010) and Yamasaki et al. (2011)). Root square error based on repeated measurements of the reference materials was 0.30 wt% for N_2O, 1.28 wt% for Al_2O_3, 0.12 wt% for CaO, and 0.15 wt% for K_2O.

3.7. Enrichment factors (X_{EF})

To assess the enrichment or depletion of redox sensitive elements (U and Mo) relative to typical detrital material, enrichment factors (X_{EF}) were calculated as follows (e.g., Tribovillard et al., 2006):

$$X_{EF} = (X_{sample} / Al_{sample}) / (X_{PAAS}/Al_{PAAS}) \quad (4)$$

Here, X_{sample}, Al_{sample}, X_{PAAS} and Al_{PAAS} are the weight concentrations of element X or Al in the sample or in PAAS (post-Archean average shale; Taylor and McLennan, 1985).

3.8. Excess fraction of barium (Ba_{excess})

Barium (Ba) in sedimentary rocks is present as detrital and authigenic fractions (e.g., Tribovillard et al., 2006 and references therein). To determine the authigenic Ba contribution in the sedimentary rock, we estimated the amount of Ba in the detrital fraction and subtracted this value from the total Ba concentration (Ba_{total}) as follows. We refer to this result as the non-detrital excess fraction of Ba (Ba_{excess}) because it is actually the sum of authigenic Ba and Ba adsorbed to other minerals (e.g., Eagle et al., 2003).

$$Ba_{excess} = Ba_{total} - Al_{sample} \times (Ba/Al)_{detr} \qquad (5)$$

Al_{sample} reflects variability in the detrital fraction. $(Ba/Al)_{detr}$ represents the detrital Ba/Al ratio for the study section. This ratio was estimated from Ba-Al cross plots for the MjL and MjU sections, respectively, because $(Ba/Al)_{detr}$ is known to be able to vary spatially (Reiz et al., 2004; Shen et al., 2012). In the Ba-Al cross plots, minimum Ba/Al ratios were identified as 69 and 50, respectively (See Figure 9). We used these values as estimates of $(Ba/Al)_{det}$ for each section.

3.9. Biotic fraction of silica oxide ($SiO_{2(bio)}$)

Pelagic sedimentary rocks are, in general, composed of biogenic and terrigenous clastic silicate materials (e.g., Onoue, 2019). Therefore, biogenic silica content can be determined by subtracting the terrestrial source silica contents from total rock silica oxide content. Following Onoue et al. (2016) and Onoue (2018), biogenic silica oxide ($SiO_{2(bio)}$) was calculated as follows:

$$SiO_{2(bio)} = SiO_{2(total)} - [SiO_{2(AUCC)} \times (Al_2O_{3(sample)} / Al_2O_{3(AUCC)})] \qquad (6)$$

$SiO_{2(total)}$ and $Al_2O_{3(sample)}$ represent the total amount of SiO_2 and Al_2O_3 in the sample, respectively. $SiO_{2(AUCC)}$ and $Al_2O_{3(AUCC)}$ are the SiO_2 and Al_2O_3 concentrations of average upper continental crust (AUCC; McLennan, 2001), respectively.

3.10. Chemical index of alternation (CIA)

The chemical index of alteration (CIA) proposed by Nesbitt and Young (1982) is an indicator of the degree of chemical weathering of the detrital silicate fraction of sediments.

$$CIA = Al_2O_3 / [Al_2O_3 + CaO^* + Na_2O + K_2O] \times 100 \quad (7)$$

CaO^* represents the CaO content of the silicate fraction, which is used in place of total CaO in order to avoid contributions from the carbonate and phosphate fractions, including conodont apatite in our study section. We calculated CaO^* following McLennan (1993), by determining the CaO/Na_2O molar ratio of the bulk sediment and comparing it with an assumed CaO/Na_2O molar ratio (1.0) for the detrital silicate fraction. Based on this assumption, modified CIA (CIA^*) was calculated as follows:

$$CIA^* = Al_2O_3 / [Al_2O_3 + 2\times Na_2O + K_2O] \times 100 \quad (8)$$

4. Results

4.1. Conodont data

Conodonts from the MjL section and their occurrence range chart are shown in Figs. 6 and 10, and Figs. S3-S11. *Conservatella conservativa* (Müller, 1956) and *Conservatella* sp. occurred in Beds 1 and 8a in MjL-2, respectively. *Neospathodus waageni* Sweet, 1970b occurred in Bed 8a of MjL-2. *Guangxidella bransoni* (Müller, 1956) was observed in Bed 3 of MjL-2 and Bed 6 of MjL-3. *Parachirognathus* sp. and *Parachirognathus* aff. *ethingtoni* Clark, 1959 (in Koike 1982) occurred in Bed 8a of MjL-2 and Bed 9 of MjL-3, respectively. Elements of the *Ellisonia triassica* (Müller, 1956) apparatus (Koike, 1996; 2004; 2016), including its S0, S3 ("*Neohindeodella*" *nevadensis* (Müller, 1956) in form taxonomy) and S4 elements ("*Neohindeodella*" *raridenticulata* (Müller, 1956) in form taxonomy) were found in Beds 3, 8a, 15, 27–28, 32, 33, 34 and 35 of MjL-2, Beds 11 and 20 of MjL-3, and Bed 2 of MjL-5. *Chirodella breviramulis* (Tatge, 1956; P1 element) occurred in Beds 8a and 32 of MjL-2. "*Neohindeodella*" *triassica* (Müller, 1956) (form species) was obtained from Beds 3, 8a, 15, 32 and 35 of MjL-2, and Bed 20 of MjL-3. "*Neohindeodella*" *kobayashii* (Igo et al., 1965) occurred in Beds 8a and 32 of MjL-2. *Chirodella*? *igoi* (Koike, 1996) occurred in Beds 27–28 of MjL-2. *Spathicupsus spathi* (Sweet, 1970b) was recognized in Bed 30 of MjL-2. In addition, *Neospathodus dieneri* Sweet, 1970a and *Scythogondolella milleri* (Müller, 1956) occurred in Bed 2 of MjL-5.

4.2. Total organic carbon (TOC)

Concentrations of TOC in samples from MjL-2 are listed in Table S1 and shown in Figure 7. TOC varies between 0.06–2.3 wt%. High TOC (more than 1 wt%) samples occur in the siliceous claystone of Beds 1 and 4a, the black claystone interbeds of Beds 7b, 9b, 10b and 12b, the cherty claystones of Beds 23 and 34, and the black claystone of Bed 36.

4.3. Organic carbon isotopes

Organic carbon isotope ratios ($\delta^{13}C_{org}$) in MjL-2 vary between −31.2‰ and −27.4‰. In more detail, $\delta^{13}C_{org}$ values in Beds 1-19 range between −30.2‰ and −27.4‰ (Figs. 1 and 7, Table S1). The compositions frequently swing between high and low values by up to 2.5‰, but the 3-point moving average is relatively stable at around −29‰ in this interval (Fig. 7). Values then decrease to −30.9‰ in Bed 20, followed by an increase to −25.2‰ in Bed 25. The most pronounced decrease in $\delta^{13}C_{org}$ then occurs between Bed 30 and the basal part of Bed 36, reaching a minimum value of −31.2‰. The $\delta^{13}C_{org}$ values then show an increasing upward trend within Bed 36.

4.4. Pyrite observations

Pyrite petrographic observations are shown in Fig. 7, and Tables S3 and S4. Pyrite was observed in all of the selected samples. The pyrite can be divided into five types based on morphology: pyrite framboids, aggregated pyrite microcrystals, irregular-shaped pyrite, and euhedral pyrite (Fig. 4 i-l). Pyrite framboids occurred in Beds 1, 9b, 12b, 13a, 14b and 36 (0.02% to 1.0% in cross-section; Fig. 7). Aggregated pyrite microcrystals comprise clusters forming irregular shapes, such as filling spaces within sediments and/or tracing precursors such as organic matter (Fig. 4j). This form occurs in Beds 13b, 14b, 27 and 36 (Fig. 7). Irregular-shaped pyrite does not show a specific morphology, but microcrystals are not seen (Fig. 4k). This form occurs in Beds 1, 11a, 13a, 13b, 14b, 25, 27, 28, 33 and 36 (Fig. 7). Euhedral pyrite has a polygonal shape (Fig. 4l), and occurs abundantly in most of the investigated horizons, occupying 0.2% to 1.2% of the area of each cross-section (Fig. 7).

Size distributions of pyrite framboids are plotted in Fig. 7, for those samples with pyrite framboids (Beds 1, 9b, 13a, 13b, 14b and 36). In most samples, the minimum diameter of pyrite framboids in cross-section is 2–3 μm. The maximum diameter varies among samples, reaching 20 μm in Bed 36. The average diameter ranges from 5.6–7.1 μm (Fig. 7).

4.5. Iron speciation systematics

Iron speciation profiles are shown in Figs. 7 and 8 (with additional details in Figs. S1 and S2). $Fe(III)_{HCl}$ (up to 0.3 wt%) which likely derives from oxidized pyrite, was detected in samples throughout the section. However, the concentrations were low, and the applied corrections do not result in a significant difference between Fe_{py}/Fe_{HR} and Fe_{py}^{*}/Fe_{HR} ratios. Hence, the redox interpretations are unaffected (Figs. 7 and 8).

In the MjL section (MjL-2), Fe_{HR}/Fe_{T} ratios range from 0.2 to 0.9. The dolostone of Bed 24 has been excluded from redox interpretations, because the dominance of dolomite-rhombs suggests a strong diagenetic overprint (see Section 2.2). Above Bed 9a, Fe_{HR}/Fe_{T} ratios are persistently higher than 0.38, which is the conventional boundary for distinguishing oxic and anoxic water column conditions (Raiswell and Canfield, 1998; Poulton and Canfield, 2011). Fe_{py}^{*}/Fe_{HR} ratios range from 0.15 to 0.9, with a large degree of variability (from 0.15 to 0.75) in the siliceous and cherty claystone beds in the lower part of the MjL-2 section (Beds 3–15). However, with the exception of Bed 28, Fe_{py}^{*}/Fe_{HR} ratios are consistently high (exceeding 0.6) in the cherty claystone and black claystone beds of the upper part of the section (Beds 16–36).

In the MjU section, Fe_{HR}/Fe_{T} ratios range from 0.1 to 1.0. Takahashi et al. (2015) reported that carbonaceous veins coincided with high concentrations of Mn, Fe and Ca in Beds 4, 20 and 53, which were likely to be due to post-depositional effects and so we exclude these samples from the following discussion. Fe_{HR}/Fe_{T} ratios for most of the MjU samples are lower than 0.38 (Fig. 8). However, high Fe_{HR}/Fe_{T} ratios (>0.38) occur in the lowest part (Bed 1), the middle part (Beds 9–19), and in three discrete layers in the upper part (Beds 26 and 40). Fe_{py}^{*}/Fe_{HR} ratios range from 0.16 to 0.86, but in most cases the values are <0.6. An exception occurs in the middle part of the section (Beds 12–15 and 17), consisting of chert and siliceous claystone with black laminae, where samples have higher values of up to 1.0.

4.6. Major and trace elements

Major and trace element results are shown in Tables S1 and S2. In the MjL section, Al and Fe_{T} vary considerably, between 0.9–6.3 wt% and 1.1–3.2 wt%, respectively. The trace metals U and Mo also show a high degree of variability, from 0.2–5.3 ppm and 0.07–34.8 ppm, respectively (Fig. 7; Table S1). The normalized U/Al and Mo/Al ranges are 0.05–1.62 and 0.01–6.1, respectively (Fig. 7). Calculated Ba_{excess}, $SiO_{2(bio)}$ and CIA in the MjL section range between 0 to 358.5 ppm, 14.1-77.2 wt% and 60.6-72.3, respectively (Fig. 13). The results from the dolostone sample of Bed 24 were excluded because of possible diagenetic effects.

In the MjU section, Al and Fe_{T} concentrations range between 1.7–7.5 wt% and 0.8–4.5 wt%, respectively, while U and Mo concentrations vary between 1.0–9.5 ppm and 0.12–42.6

ppm, respectively (Fig. 8; Table S2). U/Al and Mo/Al ratios range between 0.7–10.3 and 0.04–13.7, respectively (Fig. 8). Ba_{excess}, $SiO_{2(bio)}$ and CIA* in the MjU section range between 0 to 280 ppm, 14.1-77.2 wt% and 69-73, respectively (Fig. 13). The results from Beds 4, 20 and 53 were not included because of likely contributions from carbonate veins (Takahashi et al., 2015).

5. Discussion

5.1. Age of the MjL section

5.1.1. Conodont dating

Conodonts are not sufficiently common in the MjL section to establish biozones. Therefore, we assign the age of this section by referring to the conodont biostratigraphy of Lower Triassic seamount carbonate deposited in the same pelagic Panthalassic region, which is calibrated to stage and substage boundaries based on worldwide correlations (Maekawa et al., 2018). Of the conodonts obtained in the present study, *Conservatella conservativa*, *Guangxidella bransoni* and *Scythogondolella milleri* are widely regarded as important age indicators (Maekawa et al., 2018 and references therein). The former two have an overlapping range and are middle Smithian species. *Scythogondolella milleri*, which occurs in the upper part of the MjL section (Fig. 6), is a conodont from the upper Smithian. This species is known to appear above the last occurrence of *G. bransoni*, according to data from the east Paleo-Tethys (Vietnam), and central and eastern Panthalassa (Japan and North America) (Maekawa and Igo, 2014; Orchard and Zonneveld, 2009; Maekawa and Jenks, 2021). The MjL section of the pelagic deep-sea Panthalassa also supports this occurrence pattern. *Ellisonia triassica*, a species that became extinct at the end of the Smithian (Koike, 2016), occurs up to the basal part of the black claystone at the top of the section (Fig. 6). Therefore, the upper part of the MjL section is considered upper Smithian in age. On the other hand, *Chirodella*? *igoi*, *Spathicuspus spathi* and *Neostrachanognathus tahoensis*, are species that appeared in the Spathian (Koike, 1996, 1998; Orchard, 2007), and these are found slightly below the black claystone. Therefore, we infer that the basal part of the black claystone is latest Smithian in age, and the occurrence of the conodonts with a Spathian affinity indicates a stratigraphic position close to the SSB. This interpretation is supported by the carbon isotope profile discussed below.

Other conodont occurrences in the MjL section are consistent with our age assignment.

Neospathodus waageni (from Bed 8a of MjL-2) is a typical Smithian conodont (e.g., Orchard, 2007; Zhao et al., 2007). *Neospathodus dieneri* (from Bed 2 of MjL-5) ranges from the Dienerian to Smithian (e.g., Orchard, 2007), and *Parachirognathus* (from Bed 8a of MjL-2 and Bed 9 of MjL-3) is characteristic of the Smithian.

Previous studies by Wignall et al. (2010) and Sakuma et al. (2012) also described the lithostratigraphy in the same outcrop as the MjL section. However, the columnar sections they drew are stratigraphically upside down for the following reasons. They considered that the black claystone bed corresponding to the uppermost part of this study is the bottom of the section and belongs to the Induan, because similar black claystone beds have been reported from basal Triassic deep-sea sections (e.g., Akkamori section; Takahashi et al., 2009b). However, black claystone in Lower Triassic pelagic deep-sea strata of Panthalassa is not restricted to the Induan (Muto, 2021). In fact, as we show, the conodonts indicate that the MjL section ranges through the middle and upper parts of the Smithian, and the thick black claystone layer (such as Bed 36 of MjL-2) is close to the SSB and should be at the stratigraphic top. Sakuma et al. (2012) also argued that sedimentary microstructures support their placement of the black claystone at the bottom, but we argue that there are no clear stratigraphic 'way up' indicators (see Supplementary Material). Note also that Sakuma et al. (2012) and subsequent studies citing this work (Ikeda and Tada, 2014; Zhang L. et al., 2019) plotted the occurrence of two important age-diagnostic conodonts, *G. bransoni* and *S. milleri*, the other way round on the lithological column, resulting in an erroneous age indication (see Supplementary Material).

5.1.2. Carbon isotope ($\delta^{13}C$) correlations

Song et al. (2013; 2014) identified negative and positive excursions in $\delta^{13}C$ from the Lower Triassic marine carbonate record, labelled as N1 to N4 and P1 to P4, respectively (Fig. 1). According to the low $\delta^{13}C_{org}$ values (ranging from -30 to -31‰) and the occurrence of middle to late Smithian conodonts, it can be inferred that $\delta^{13}C_{org}$ values in the lower to upper parts of the section (Bed 1 to the basal part of Bed 36 in MjL-2) are correlative to the N3 negative excursion reported from other Smithian sections (Fig. 1). Short-lived peaks in $\delta^{13}C_{org}$ values (approximately -28 to -27‰) are observed within the MjL section. Similar increases in $\delta^{13}C_{carb}$ values are also evident during the N3 excursion in the Paleo-Tethys section (Fig.1). The following increasing trend in $\delta^{13}C_{org}$ in Bed 36 (by 3‰ in MjL-2) correlates to the previously reported positive carbon isotopic excursion from N3 to P4 that encompasses the SSB. Because a fault cuts the upper limit of the black claystone bed in the MjL section, it is uncertain where this $\delta^{13}C_{org}$ positive excursion peaks. Therefore, it is difficult to further constrain the precise position of the SSB using $\delta^{13}C_{org}$ values.

Takahashi et al. (2015) reported a high-resolution $\delta^{13}C_{org}$ curve for the MjU section. This shows lower values (~−31‰) in the lower half of the section and higher values (~−25‰) in the upper half (Fig. 1). The reported conodont age of the MjU section suggests that this section is from the middle part of the Spathian (Muto et al., 2019). Hence, the increasing trend in $\delta^{13}C_{org}$ in the MjU section correlates with the N4 negative $\delta^{13}C$ trough.

5.2. Redox records in the Mj sections

5.2.1. Pyrite morphology

The size distribution of pyrite framboids can provide useful information on redox conditions in the overlying water column (Wilkin et al., 1996; Bond and Wignall, 2010). In MjL-2, euhedral pyrite is common in most observed horizons (Fig. 7), suggesting formation under anoxic conditions during diagenesis. Pyrite framboids were detected from the bottom (Bed 1), middle (Beds 9b, 13a, 13b and 14b), and uppermost parts of MjL-2 (Bed 36) (Fig. 7; >0.1% area in the thin section). The pyrite framboids from the bottom and uppermost parts of MjL-2 have small average diameters of less than 6.5 μm (5.3–6.5μm), except for the sample from Bed 9b (Figs. 7 and 11; Table S4). This suggests a euxinic water column at the time of deposition. The average framboid diameter for samples from Bed 13a in the middle part of the section is 7.0 μm. Although this value is slightly larger than 6.5 μm, the standard deviation for this sample is low (1.7 μm), indicating that these pyrite framboids also likely formed in a euxinic water column (Fig. 11). On the other hand, the black claystone of Bed 9b has a relatively higher standard deviation (2.2 μm) with pyrite framboids as large as 40 μm. These framboids fall close to the suboxic–dysoxic trend, indicating that the water column was likely not euxinic (Fig. 7). Wignall et al. (2010) reported pyrite framboids with a small and narrow size range from the "Griesbachian black shale" in the Mj section, corresponding to Bed 36 in the MjL-2 section. However, this should be revised to the lowest Spathian. We confirm the small average diameters for pyrite framboids from the same strata, suggesting that the results are consistent.

For the Spathian MjU section, pyrite morphologies have previously been reported by Takahashi et al. (2015). Multiple types of pyrite appear (framboids, crystals), suggesting that this section records a reducing depositional and diagenetic environment (Takahashi et al., 2015). Pyrite framboids with a small and narrow size range occur in the middle part of the section (Beds 12–19), suggesting a euxinic water column.

5.2.2. Iron speciation systematics

Fe-speciation is a proxy for reconstructing regional water column redox conditions (Poulton and Canfield, 2011; Poulton, 2021). Enrichments in Fe_{HR} ($Fe_{HR}/Fe_T > 0.38$) commonly characterize deposition under anoxic water column conditions, whereas ratios <0.22 commonly occur under oxic bottom water conditions, and ratios between 0.22-0.38 are considered equivocal (Poulton and Canfield, 2011). For anoxic samples, the extent of pyritization of the Fe_{HR} pool (Fe_{py}/Fe_{HR}) provides an indication of whether the water column was ferruginous ($Fe_{py}/Fe_{HR} < 0.6$) or euxinic ($Fe_{py}/Fe_{HR} > 0.8$), with Fe_{py}/Fe_{HR} ratios between 0.6-0.8 being equivocal (Poulton, 2021).

These threshold values are not absolute, however, and can be influenced by high sedimentation rates (particularly during turbidite deposition; e.g., Canfield et al., 1996). However, sedimentation rates for Spathian siliceous claystone successions that are similar to lithofacies of this study have been estimated as < 10 mm per kiloyear (Muto et al., 2020; Muto, 2021). Thus, the impact of rapid sedimentation on Fe speciation systematics is not a consideration for this study. Transfer of Fe_{HR} to clay minerals (such as glauconite) during diagenesis can also affect Fe-speciation records and can be important in organic-rich, non-sulfidic sediments (e.g., Poulton and Raiswell, 2002; Poulton et al., 2010). However, we found no evidence for glauconite formation in the samples from MjL and MjU. Hutchings and Turchyn (2020) note that reductive diagenesis promotes iron-sulphide formation, which may result in an overestimation of Fe_{py}/Fe_{HR} ratios. However, Fe-speciation has been extensively calibrated on ancient marine rocks (Raiswell et al., 2001; Poulton and Raiswell, 2002; Clarkson et al., 2014), which by definition have undergone diagenesis (c.f. Pasquier et al., 2021), and hence diagenetic pyrite formation is accounted for in these redox thresholds. Nevertheless, a more robust interpretation of redox conditions can be achieved by utilizing multiple independent proxies (Poulton, 2021), and hence we take the common approach of considering our Fe-speciation data alongside pyrite framboid size distributions and redox-sensitive trace metal systematics (see below).

In the lower part of MjL-2 (Beds 3–7a), Fe_{HR}/Fe_T ratios fall in the equivocal range, except for Bed 3, which shows a slightly elevated value (Fig. 7). Bed 8a has a low Fe_{HR}/Fe_T value (<0.22), indicative of an oxic depositional environment. Then, starting from Bed 9a to the top of MjL-2 (Bed 36), Fe_{HR}/Fe_T ratios are consistently elevated (>0.38), suggesting a shift towards a persistently anoxic depositional environment. Within these anoxic layers, Beds 9a–14b have fluctuating Fe_{py}^*/Fe_{HR} ratios, with several samples plotting in the equivocal range or above (Fig. 7), consistent with fluctuations between ferruginous and euxinic water column conditions. In the overlying Beds 15–36, Fe_{py}^*/Fe_{HR} ratios also show a degree of fluctuation, but values are persistently higher, suggesting more persistent euxinia.

In the MjU section, Fe_{HR}/Fe_T ratios are generally lower, with many samples falling at the low end of the equivocal range or below (Fig. 8), suggesting an oxic depositional environment. However, Beds 12–19 have higher Fe_{HR}/Fe_T ratios, indicative of anoxic depositional conditions. This interval coincides with higher Fe_{py}^*/Fe_{HR} ratios, particularly in Beds 12, 13, 14, 15 and 17, suggesting possible (at least intermittent) euxinia. Above this interval, Fe_{HR}/Fe_T ratios are mostly low (<0.38), except for Beds 27 and 40, suggesting dominantly oxic conditions. Higher Fe_{HR}/Fe_T ratios and low Fe_{py}^*/Fe_{HR} ratios in Beds 27 and 40 suggest possible short-lived transitions to ferruginous anoxia.

5.2.3. Redox-sensitive trace element systematics

Uranium and Mo exist as soluble oxyanions in oxic seawater (see Tribovillard et al. 2006), with a globally homogenous distribution in the modern oxygenated ocean because of their long residence times relative to the mixing time of the ocean. Under reducing conditions, U transforms to tetravalent U(IV) and is sequestered within anoxic sediments regardless of whether sulphide is present (McManus et al., 2006). Molybdenum may be removed from the water column into sediments in the presence of significant concentrations of hydrogen sulphide (>11μM H_2S; Helz et al., 2011). Mo enrichments in sediments occur due to the formation of thiomolybdates and subsequent scavenging by pyrite, or via the formation of Mo-Fe-S compounds or Mo-organic matter complexes (Vorlicek et al., 2004; Chappaz et al., 2014; Ardakani et al., 2016; Dahl et al., 2017; Wagner et al., 2017). However, moderate Mo enrichments can also occur in the absence of dissolved sulphide, via uptake by Fe (oxyhydr)oxide minerals formed in ferruginous settings (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012; Li et al., 2023).

Bennett and Canfield (2020) recommend using U/Al and Mo/Al ratios as the most objective normalization approach for minimizing potential influence from detrital inputs. They suggest that euxinic conditions are indicated when U/Al and Mo/Al ratios exceed ~5 (μg/g), and oxygen-poor sea floor sediments ($O_2 \geq 10$ μM) are indicated when U/Al ratios are

>1 (µg/g), based on a compilation of modern settings. Furthermore, local baseline values and thresholds for redox interpretations are region-specific (Algeo and Li, 2020; Poulton, 2021; Li S. et al., 2023), and hence calibration of local redox thresholds should be performed wherever possible. Following these recommendations, we calibrated the trace metal thresholds for identification of different redox conditions in the MjL and MjU sections.

An Fe_{HR}/Fe_T ratio of <0.22, which is highly indicative of an oxic depositional environment (Poulton and Canfield, 2011; Poulton, 2021), is observed in Bed 8a of MjL-2 (Fig. 7; Table S1). U/Al and Mo/Al values for this sample are 0.4 and 0.1, respectively. The samples from Beds 5 and 7a have intermediate Fe_{HR}/Fe_T values (0.22–0.38). Among them, Bed 7a has minimum trace element ratios (U/Al = 0.1 and Mo/Al = 0.04). We therefore set the local baseline values for oxic deposition as 0.1–0.4 for U/Al and 0.04–0.1 for Mo/Al. In the MjU section, Fe_{HR}/Fe_T ratios of < 0.22 were detected in nine horizons (Beds 5, 9, 10, 11, 24, 30, 31, 36 and 48; Fig. 8; Table S2). The range of elemental ratios for these horizons is 0.2–0.4 for U/Al, and 0.04–0.12 for Mo/Al. This gives MjU oxic baseline values for U/Al and Mo/Al of 0.2–0.4 and 0.04–0.12, respectively, which are very similar to the ranges defined for section MjL-2, thus supporting the validity of our approach. Indeed, the estimated oxic baseline values for both study sections are consistent or slightly lower than the oxic values of Bennet and Canfield (2020), which were based on a compilation of modern settings.

U/Al and Fe_{HR}/Fe_T ratios are expected to vary synchronously (e.g., He et al., 2022; Li S. et al., 2023) because they have a similar redox potential (Zheng et al., 2002). However, some samples with high Fe_{HR}/Fe_T ratios indicative of anoxia (notably in the upper half of the MjL-2 section, with the exception of the top; Fig.7) have U/Al values similar to the baseline range. This difference is likely due to different depths being recorded by the Fe_{HR}/Fe_T and U/Al proxies. While U drawdown occurs in the sediments, increases in Fe_{HR}/Fe_T can occur due to Fe mineral precipitation in the upper part of the water column, for example, at the depth of the oxygen minimum zone (OMZ), which may be several hundred to ~1000 m deep. Therefore, in a deep ocean environment such as this, where the water depth was likely in the range of 3000-4000 m, an increase in Fe_{HR}/Fe_T without any increase in U/Al may represent the development of an OMZ in the upper part of the water column.

However, the generally consistent trends between Fe_{HR}/Fe_T and U/Al in both the MjL and MjU sections (Figs. 7 and 8), support a redox control on both proxies. Increased U/Al ratios (>0.5 and reaching up to 1.3 in Bed 11a of MjL-2) occur coincident with high Fe_{HR}/Fe_T (>0.38) ratios (Fig. 7). This U/Al range is significantly lower than the oxic-anoxic threshold proposed by Bennet and Canfield (2020), potentially suggesting that the somewhat elevated

U/Al ratios (relative to our defined oxic baseline) may reflect dysoxic to suboxic levels at the bottom of the water column, rather than fully anoxic conditions. Alternatively, U depletion from Early Triassic seawater as a consequence of expanded anoxia (mentioned in Elrick et al., 2017) may have masked the enrichment of this element under fully anoxic conditions. We also evaluate Mo/Al using the different redox proxies to investigate the relative intensity of sulfide availability. Some Mo/Al ratios are low, falling close to the baseline value, although Fe speciation implies euxinic conditions (i.e., Fe_{HR}/Fe_T >0.38 and Fe_{py}^*/Fe_{HR} >0.8). This is observed in the upper half of the MjL-2 section (Fig. 7), and suggests that euxinia occurred at this level, but was likely weak and/or short-lived, and thus did not exceed the relatively high hydrogen sulfide concentrations required to activate Mo drawdown into the sediments. Somewhat elevated Mo/Al ratios, in the range of 0.2–1.0, coincide with high Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} ratios, in the absence of pyrite framboids with a small and narrow size range indicative of water column, in Beds 9b-12b of the MjL-2 section and Beds 13-15 and 17 of the middle of the MjU section (Figs. 7 and 8). This also suggests weak or short-lived euxinia. The highest Mo/Al ratios (1-6) coincide with euxinic Fe-speciation signals and abundant small-sized pyrite framboids in Bed 36 of the top of the MjL-2 section and Beds 12, 16, 18 and 19 of the MjU section (Figs. 7 and 8). The upper value for these samples exceeds the threshold of 5 proposed by Bennet and Canfield (2020) for the detection of euxinia, strongly supporting the development of euxinic conditions.

5.2.4. Enrichment factor of molybdenum and uranium

To determine covariation between Mo and U in the study section, we recast elemental concentrations as enrichment factors (Mo_{EF} and U_{EF}) and plot these data in Fig. 12. In the study section, most of the Mo_{EF} and U_{EF} results align with the lower to middle part of the open marine redox elevation trend, with a low Mo_{EF}/U_{EF} ratio (<10; Fig. 12). This suggests that redox state variability around the sediment-water interface controlled the Mo and U concentrations of the sediments (Algeo and Tribovillard, 2009; Tribovillard et al., 2012). Meanwhile, high Mo_{EF}/U_{EF} ratios (greater than 10) are observed in the uppermost part of MjL-2 (Bed 36) and in the middle of MjU (Beds 12, 16, 17 and 18). The corresponding Mo_{EF} and U_{EF} values plot in the Mo particle shuttle area (Fig. 12). This indicates that Mo deposition in association with Fe-Mn (oxyhydr)oxide minerals formed in the water column at this level (Algeo and Tribovillard, 2009; Scholz et al., 2013).

5.2.5. Redox records for the MjL-2 section (middle Smithian to latest Smithian)

Based on the redox parameters for the MjL-2 section described above, we define four redox stages (Stages 1 to 4; Figs. 7 and 13). Stage 1 documents a period of oxic conditions in the lower part of MjL-2 (Beds 1 through 8a), as characterized by low Fe_{HR}/Fe_T ratios (<0.38), low trace metal ratios (U/Al and Mo/Al) and low enrichment factors (U_{EF} and Mo_{EF}) (Figs. 7 and 12). Thus, oxic conditions occurred in the water column and bottom waters during the middle Smithian (Fig. 13). The presence of euhedral pyrite rather than small framboids (Figs. 7 and 13) is consistent with this interpretation.

Stage 2 in the middle to late Smithian corresponds to the cherty claystone and thin black claystone beds between Beds 10a and 15 of MjL-2 (Fig. 7). This interval has increases in Fe_{HR}/Fe_T ratios (>0.38) and U/Al ratios (above the baseline range) peaking at Bed 11a. These increased values of redox proxies suggest anoxic water development at the water column and deoxygenation at the bottom water, respectively (Fig. 13). There is a distinct decrease in both Fe_{HR}/Fe_T and U/Al ratios in Beds 13-15. It may indicate more intermittent anoxia. Fe_{py}^*/Fe_{HR} and Mo/Al ratios vary in this part of the section, suggesting that the water column fluctuated between ferruginous and euxinic, with most values falling either in the ferruginous or equivocal zones (Fig. 7). The frequent occurrence of small-sized pyrite framboids (Figs. 7 and 11) also supports periodic water column euxinia (see Fig. 13).

Stage 3, represents a prolonged period of persistent anoxia through the late Smithian (Bed 15 through 35 of MjL-2), as indicated by elevated Fe_{HR}/Fe_T ratios. U/Al ratios in this interval are slightly high or within the base line range (Fig. 7). High Fe_{HR}/Fe_T combined with relatively low U/Al ratio suggests that anoxic water developed in the upper part of the water column above the sediment-water interface. Fe_{py}^*/Fe_{HR} ratios are commonly >0.6 and sometimes >0.8 (Fig. 7), Mo/Al ratios are relatively low, while pyrite is mainly euhedral with rare irregularly-shaped framboids. Thus, the precise chemistry of the water column may have varied across this interval, from ferruginous through to the possible limited development of intervals of weak and/or short-lived euxinia (Fig. 13).

Stage 4 is recorded in the black claystone bed at the top of the MjL-2 section, which was deposited in the latest Smithian to possibly earliest Spathian. This interval has elevated Fe_{HR}/Fe_T and Fe_{py}^*/Fe_{HR} ratios, while U/Al and Mo/Al ratios progressively increase (with the increase in Mo/Al beginning towards the top of Stage 3; Fig. 7). Increased U/Al ratios (Fig. 13) suggest anoxic bottom water conditions (since U drawdown occurs in porewaters;

Anderson et al., 1989; Klinkhammer and Palmer, 1991), while high Fe_{HR}/Fe_T, Fe_{py}^*/Fe_{HR} and Mo/Al ratios occurring coincident with small-sized pyrite framboids indicate the progressive development of euxinic conditions in the water column. Algeo et al. (2011) studied another Panthalassic deep-sea Permian-Triassic section and interpreted such small-sized pyrite framboids as being derived from an oxygen minimum zone (OMZ) in the upper part of the water column (several hundreds to ~1000 m in depth). Mo_{EF} values also increase relative to U_{EF} at this stage (Fig. 12), resulting in high Mo_{EF}/U_{EF} ratios potentially indicative of increased Mo drawdown from the water column to the sediment due to uptake and sequestration by Fe-Mn (oxyhydr)oxide minerals (Algeo and Tribovillard, 2009; Tribovillard et al., 2012). This suggests that an enhanced particulate shuttle was occurring between anoxic bottom waters and the overlying OMZ, with better oxygenated conditions between these depths (Fig. 13).

5.2.6. Redox records in the MjU section (middle Spathian)

There is a hiatus between deposition of the MjU and MjL-2 sections (see Fig. 1). However, we here consider the interval recorded by the MjU section to be Stage 5, which we further subdivide into Stages 5a to 5c (Fig. 8). Stage 5a documents the lower half of the MjU section (Beds 1 through 11), and has low Fe_{HR}/Fe_T ratios (<0.38), limited pyritization, low U/Al and Mo/Al ratios, and also low U_{EF} and Mo_{EF} values (Figs. 8 and 12). These combined observations strongly support oxic water column conditions (Fig. 13). Stage 5b is recorded in a chert and siliceous claystone sequence with black laminae (Beds 12 through 17), and black claystone and black chert (Beds 18 and 19). These beds have high Fe_{HR}/Fe_T suggesting anoxic water column conditions (Fig. 8). The U/Al ratio also increases in this interval suggesting oxygen-poor bottom water condition. Takahashi et al. (2015) considered that these strata record suboxic bottom water because of relatively low U_{EF} values. Fe_{py}^*/Fe_{HR} and Mo/Al ratios fluctuate through this interval in a generally consistent manner, while pyrite framboids in Beds 16 and 19 are small, with a narrow size range, suggesting that the water column varied between ferruginous and euxinic (Figs. 11 and 13). Increased Mo_{EF}/U_{EF} ratios with high Mo_{EF} (Fig. 12) suggest additional Mo drawdown by the Fe-Mn particle shuttle, with a non-sulfidic water column separated from sulfidic water depths, similar to Stage 4 in the MjL section (Fig. 13). Dominantly oxic water column conditions then returned during Stage 5c (Beds 22 through 53), as evidenced by low Fe_{HR}/Fe_T, U/Al and Mo/Al values (Fig. 8). However, enrichments in Fe_{HR}/Fe_T and U/Al in Beds 26, 29 and 40 suggest short-lived transitions to anoxic ferruginous water column conditions.

5.2.7. Oceanic productivity proxies across redox stage variations

Biogenic barium (Ba_{bio}) in the sedimentary rocks is a potential proxy for paleo-oceanic productivity, because of authigenic barite formation in sinking organic particles or aggregates (Dehairs et al., 1980, 1987, 1992; Jaccard et al., 2013). Authigenic barite is preserved in the sediment especially under oxic to suboxic conditions (Dymond et al., 1992). However, under reducing conditions, authigenic barite may be reductively dissolved and lost to the water column through diffusion out of the sediment (Dymond et al., 1992).

In this study, the calculated Ba_{excess} values reflect the sum of Ba_{bio} and Ba absorbed on other minerals (Eagle et al., 2003). In the MjL-2 section through the overlying MjU section, Ba_{excess} shows relatively low values of 100-200 ppm (Fig. 14), compared with up to 800-1000 ppm reported for other Permian-Triassic oceanic strata ranging from shallow to deep environments (Shen et al., 2015). Decreases in Ba_{excess} are observed in the euxinic black claystone layers of Stage 2 and Stage 4, and Stage 5b (Fig. 14). This suggests that authigenic barite would have been lost under sulfidic sedimentary conditions. Thus, these specific data provide little insight into paleo-productivity during deposition.

$SiO_{2(bio)}$ indicates preservation of siliceous biocrusts in sedimentary rocks, and reflects the biotic silica flux from the water column into the sediment (e.g., Onoue 2018 and references therein). In MjL-2, $SiO_{2(bio)}$ varies around a value of 40-60 wt%, and decreases to a value of less than 30 wt%, especially in the black claystone layers in Stage 2 and Stage 4 (Fig. 14). This suggests that the biotic silica flux varied rhythmically, potentially controlled by astronomical cycles (e.g., Ikeda et al., 2014), and decreased during the development of anoxic water during the Smithian Stage 2 (temporal) and Stage 4. In the Spathian MjU section, the variability in $SiO_{2(bio)}$ is relatively large (between about 30 and 70 wt%), reflecting muddy and siliceous radiolarian-rich cherty layers (Fig. 14). Among these variations, the minimum value of $SiO_{2(bio)}$ occurs in the black claystone bed in Stage 5b (17 wt% in Bed 18), which we interpret above to reflect the development of an anoxic-euxinic water column.

It has been proposed that the formation of the organic matter-enriched black claystone at the Permian-Triassic boundary (PTB) of the Pelagic Panthalassa was the result of a decrease in biogenic SiO_2 from the radiolarian chert, where biogenic SiO_2 accounts for about 90%, resulting in a smaller dilution effect from SiO_2 and a relative increase in the organic matter and clay fractions (Algeo et al., 2009, 2010). In fact, the data of Algeo et al. (2009, 2010) show that biogenic SiO_2 decreased 0.6-0.7 times and TOC increased about 4 times from the Late Permian chert to the earliest Triassic black claystone. In the case of the Smithian black claystone, biogenic SiO_2 ($SiO_{2(bio)}$ in this study) decreases from about 53-59 wt% in the cherty claystone beds to about 33-35 wt% in the black claystone beds (i.e., about 0.6-0.8 times; Figure 14, Table S5). A black claystone interbed in Stage 2 (Bed 12b in the MjL-2) and the bed below (Bed 12a in the MjL-2) contain similar amounts of $SiO_{2(bio)}$ (53 wt% and 56 wt%, respectively). The TOC content of these black claystone layers increases from about 0.1 wt% to about 1.5-2 wt% (Fig. 7, Table S5). The magnitude of these increases compared to the beds below is 10- to 20-fold (Fig. 7, Table S5). This is overwhelmingly greater than the decrease in SiO_2 dilution during the same interval. This comparison suggests that the organic-rich black claystone beds in the Mj section document an increase in organic matter sinking flux from the water column, possibly due to high surface primary productivity supplying organic matter to the pelagic Panthalassa. While beyond the scope of the current work, in the future, normalizing the TOC flux to an absolute timescale, such as the cyclo-stratigraphy for this interval, may provide further insight.

5.2.8. Weathering conditions in hinterland based on CIA values

The CIA is a proxy for the intensity of chemical weathering in sediment source regions due to variations in humidity or temperature (Nesbitt and Young, 1982; Goldberg and Humayun, 2010). The MjL-2 section shows a constant value of 69-70 throughout. These values are consistent with normal average shale values (e.g., PAAS) which have a CIA value of 70-75 (Taylor and McLenann, 1985). This range of values continues in the lower half of the MjU interval (Fig. 14). Meanwhile, the upper part of the MjU section shows a slightly higher value of 77-80. A higher CIA value indicates an increase in the contribution of native material subjected to chemical weathering. For example, clay minerals have high CIA values such as 75-85 for illite and 85-100 for kaolinite (Nesbitt and Young, 1982; Taylor and McLennan, 1985; Bahlburg and Dobrzinski, 2011). The CIA record in the MjU section may have increased in the Middle Spathian, although not significantly, and the hinterland may have changed slightly in terms of provenance. However, the local oceanic redox changes described above (sections 5.2.5 and 5.2.6) do not synchronize with this CIA trend, suggesting that changes in chemical weathering intensity did not drive the changes in oceanic redox conditions.

5.3. Oceanic anoxia at the Smithian–Spathian transition and possible triggering mechanism

Oceanic redox records at the Smithian–Spathian transition have also been reported from other regions, such as shallow marine Paleo-Tethys (South China; Huang et al., 2017, Sun et al., 2015, Song et al., 2019), Neo-Tethys (Arabian margin; Clarkson et al., 2016) and Boreal shelf seas (Smith Creek Canada; Grasby et al. 2013; Spitsbergen, Norway; Wignall et al. 2016). Although there are records from the southern middle latitude Panthalassa (New Zealand; Hori et al., 2007; Grasby et al., 2021), the late Smithian and the early to middle Spathian have not been reported from this area. During the N3 δ^{13}C negative trough of the middle to late Smithian, dysoxic conditions have been reported from the shallow Paleo-Tethys and mid-slope of Neo-Tethys (Fig. 15), although organic-rich sediments are rarely reported. Oxygen-poor but non-sulfidic redox conditions are common in the shallow marine Tethys and Boreal latitudes. Redox conditions at our low-latitude Panthalassa site changed from oxic to ferruginous anoxic, with the occasional development of water column euxinia (Stages 1 to 3; Fig. 15). Based on these data, we suggest that widespread dysoxic to anoxic (but non-euxinic) shallow marine conditions developed in the middle to late Smithian, with the deep ocean showing evidence of generally more reducing conditions (the bottom right panel of Figure 15). Primary productivity during this stage was likely low overall, because of the rare occurrence of organic-rich sediments in Tethys and Panthalassa(Fig. 15 and reference therein), and this may explain the general absence of anoxia in shallower waters.

Climate warming is a possible trigger for this ocean deoxygenation. The $\delta^{18}O_{apatite}$ record suggests high sea surface temperatures during the middle to late Smithian, around the N3 δ^{13}C excursion (Sun et al., 2012; Fig. 1). Seawater warming would have reduced dissolved O_2 solubility and contributed to marine deoxygenation. In addition, thermohaline circulation driven by subduction of warm saline surface water formed in mid- and low- latitudes would have potentially contributed to the development of a stratified ocean structure with anoxic deeper waters (Kidder and Worsley, 2004). Indeed, some epi-continental oceanic regions in the Paleo-Tethys and Neo-Tethys provide evidence of a highly stratified ocean structure based on a δ^{13}C gradient (2–5‰) from shallow to deep settings (Song et al., 2013; Li H.X. et al., 2023). If such stagnant conditions occurred during the late Smithian, deoxygenation in the deep-sea Panthalassa would have been promoted. Low productivity and anoxic conditions during the late Smithian has also been reported from the Boreal Sea based on low nitrogen isotope compositions (Grasby et al., 2016).

Suggested low oceanic productivity in the middle to late Smithian would relate to the frequent appearance of oxygen-poor and non-sulfidic ferruginous anoxia, including in the pelagic deep-sea Panthalassa. Low surface productivity limits the organic matter sinking flux, making it difficult to establish and sustain water column euxinia (Ozaki et al., 2011; Winguth and Winguth, 2012). Low oceanic productivity during this time-interval could be due to multiple possible factors. Sun et al. (2012) argued that surface photosynthesis could be inhibited under high surface water temperatures (above 40°C) in tropical regions during the late Smithian thermal maximum. In addition, nutrient limitation also controls primary productivity. However, Sr isotopes ($^{87}Sr/^{86}Sr$), as a proxy for input of terrestrial material (including nutrients) to the ocean on a global scale, shows an increasing trend during this interval, suggesting an increase, rather than decrease, in nutrient supply from land to sea (Fig. 1; Sedlacek et al., 2014 and Song et al., 2015). Furthermore, the CIA^* values in the study section do not show significant changes across these intervals, suggesting only a small change in weathering conditions in the provenance area (Fig. 13). Therefore, it is difficult to ascribe terrestrial weathering conditions as a possible cause of the late Smithian oligotrophic ocean in each region. Instead, we suggest that ocean stratification under the warming climate described above likely limited regional nutrient upwelling to shallow waters.

From the N3 $\delta^{13}C$ trough toward the P3 $\delta^{13}C$ increase across the SSB, argillaceous lithofacies appear in shallow marine carbonate sections from Paleo-Tethys (Fig. 15). Galfetti et al. (2007) recognized organic-rich black shale in the off-shore Jinya section, South China (Fig. 15). The South Majiashan and west Pindinshan sections in Chaohu, South China, comprise ramp deposits that show evidence of a euxinic water column around the SSB (high Fe_{py}^*/Fe_{HR} ratios and small-sized pyrite framboids; Huang et al., 2017; Shen et al., 2019; Fig. 15). Oceanic redox conditions in Boreal shelf seas and mid-slope regions in Neo-Tethys also became euxinic and ferruginous, respectively (Fig. 15; Clarkson et al., 2016, Grasby et al., 2013; Li H.X. et al. 2023). The pelagic Panthalassa also records the development of a euxinic water column at this time (Stage 4; Figs. 7 and 15).

The evidence above suggests that intense oceanic anoxia occurred widely during the latter part of the N3 $\delta^{13}C$ trough and the P3 $\delta^{13}C$ interval across the SSB (the middle right panel of Fig. 15). Organic matter-enriched sediments (black shale and black claystone) appear at off-shore Paleo-Tethys and pelagic Panthalassa sites. This implies that high primary productivity developed in the surface waters of continental margins and the pelagic Panthalassa (the middle right panel of Fig. 15). The silicic biomass flux, which represents radiolarians, decreased in the pelagic Panthalassa during this interval (Fig. 14).

According to the $\delta^{18}O_{apatite}$ records, sea surface temperatures decreased during this period (Fig. 1: Song et al. 2012). However, as the estimated water temperature was still high (> 35°C) it could have contributed to marine deoxygenation due to low oxygen solubility at such temperatures. The structural water mass changes in Tethys have been debated based on a $\delta^{13}C$ depth gradient across the SSB. The $\delta^{13}C$ depth gradient regionally declined in the Paleo-Tethys and Neo-Tethys during the end of the N3 to P3 $\delta^{13}C$ positive excursion (except in the Paleo-Tethyan Lower Yangtze Basin; Li H.X. et al., 2023). This suggests a loss of the ocean stratification during the mid-late Smithian. However, since the $\delta^{13}C$ gradient decline postdates the development of anoxic-euxinic conditions in each SSB section, this challenges the explanation that structural water mass changes preceded and caused high primary production and euxinia (as proposed by Song et al., 2019). Instead, nutrient-rich surface water formation in the pelagic Panthalassa occurred during the latter stages of N3 and continued toward the P3 $\delta^{13}C$ excursions. Considering this timing, if this nutrient-rich Panthalassic water was transported laterally, it would also have contributed to eutrophication and anoxia in peripheral oceanic areas such as the western marginal Panthalassa. To make this pelagic open-ocean highly productive and euxinic, it is reasonable to assume that surface water eutrophication was driven by equatorial upwelling (Fig. 15). The enhancement of upwelling in open-ocean settings such as Panthalassa is generally driven by increased surface wind and water-current intensity (Fig. 15; e.g., Winguth and Winguth, 2013), which would be an expectation during cooling across the SSB (as inferred by the $\delta^{18}O_{apatite}$ temperature decrease). On the other hand, ocean eutrophication due to increased input of terrigenous and/or volcanic material, as suggested in a case study of the end-Permian (Grasby et al., 2023), is not an appropriate scenario at this time. No significant provenance change inferred from the CIA was detected over this interval of the MjL section.

During the middle Spathian, short-lived anoxic and euxinic waters have been reported from the Paleo-Tethys platform and ramp (Guizhou: Tian et al., 2014; Chaohu: Huang et al., 2017), and the northern margin of Pangea (Smith Creek: Grasby et al., 2013) (Fig. 15). This study also presents evidence for anoxic water column conditions in the pelagic-Panthalassa during the N4 $\delta^{13}C$ negative excursion (Stage 5b of MjU section). The deposition of organic-rich sediments, represented by black claystone layers in the low-latitude pelagic-Panthalassa, points towards increased surface productivity and a greater depositional flux of organic matter, with a decrease in the silicic biomass flux. To increase or maintain surface primary productivity, there must also have been a supply of nutrients within the pelagic ocean. Notably, terrigenous weathering sources are unlikely to have been the primary cause, as the

$^{87}Sr/^{86}Sr$ ratio shows no significant variation during this interval (Fig. 1). Also, no significant change in CIA value is detected in the central Panthalassa (Fig. 13). Instead, other factors, such as equatorial upwelling in the central Panthalassa, likely played a major role in promoting high surface productivity. However, empirical evidence concerning the vertical structure of the Spathian low-latitude Panthalassa ocean remains limited.

6. Conclusions

In this study, we have reconstructed the Panthalassic deep-sea lithologic sequence of the middle Smithian to latest Smithian exposed in Inuyama, central Japan, using conodont fossils and $\delta^{13}C_{org}$ correlations. Based on our new data, we have revised the lithostratigraphy of the studied section for decoding the Panthalassic record in response to significant environmental changes. Geochemical analyses and pyrite morphology observations were conducted to reconstruct paleo-seawater redox conditions. Water column redox conditions in the pelagic Panthalassa changed in the middle to late Smithian, from oxic to anoxic ferruginous. Prevailing euxinic water column conditions developed in the latest Smithian to earliest Spathian. Ferruginous conditions in the late Smithian and the development of euxinia across the SSB also occurred in other oceanic regions, such as the shallow Tethys and north Pangea. By the middle Spathian, redox conditions in the pelagic Panthalassa were dominantly oxic, interrupted by short-lived intervals of water column euxinia. These redox records for the pelagic Panthalassa are noteworthy for filling gaps in our understanding of the spatial extent of ocean redox variability across the Smithian–Spathian.

The occurrence of organic-rich black claystone deposits at Inuyama suggests that an increased organic matter flux played a key role in the transition from late Smithian ferruginous anoxia to latest Smithian euxinia in the equatorial Panthalassa Ocean. If driven by increasing productivity, then the increased nutrient supply is likely to be a result of enhanced ocean circulation and upwelling. An increase in terrigenous weathering and nutrient input to the oceans is unlikely to have been directly responsible for increased productivity because the setting that was many thousands of kilometres from the nearest landmass. Changes in oceanic structure and associated frequent development of anoxic and euxinic seawater were therefore important environmental factors during the decline of nekton animal diversity at the SSB.

Declaration of Competing Interest

None.

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Figure Captions

Figure 1. Geochemical profiles of strontium isotopes ($^{87}Sr/^{86}Sr$; Song et al., 2015), oxygen isotopes in conodont apatite ($\delta^{18}O_{apatite}$; Sun et al., 2015), and carbonate carbon isotopes ($\delta^{13}C_{carb}$; Payne et al., 2004) during the Early Triassic and Middle Triassic from compiled shallow-water carbonate sections. The deep-water siliceous sedimentary sections of the Momotaro–Jinja lower section (this study) and Momotaro-Jinja upper section (Takahashi et al., 2015, central Japan), as well as a paleogeographic map (by Ziegler et al., 1998) showing depositional areas of Lower–Middle Triassic sediment from South China and Japan, are also shown. For $\delta^{13}C_{org}$ (organic carbon isotope) of the Momotaro-Jinja sections, a three-point running mean (blue line) and $\pm 2\sigma$ standard deviation (sky blue area) are shown. Absolute age values are obtained from the timescale in Sun et al. (2012) and Burgess et al. (2014).

Figure 2. Location and geological context of the Momotaro–Jinja section, central Japan. The geologic map around the section is based on Sugiyama (1997).

Figure 3. Geologic map of the Momotaro-Jinja lower section (MjL) and the Momotaro-Jinja upper section (MjU). The locations of the five subsections of MjL and a studied interval of MjU are marked by white rectangles.

Figure 4. Photographs of thin sections from the Momotaro-Jinja lower section (MjL) and Momotaro-Jinja upper section (MjU). a to h are observed with transmitted light, and i to l are observed under reflected light. a: Siliceous claystone of Bed 3 of MjL. b: Cherty claystone of Bed 17 of MjL. Small pyrite forms are observable. c: Dolostone layer of Bed 24 of MjL. Rhombic dolomite crystals are observable. d: Black claystone of Beds 9b of MjL. Round siliceous microfossils are scattered. e: Black claystone bed of Bed 36 of MjL. f: Black chert of Bed 19 in MjU. Abundant siliceous microfossils are observed. g: muddy chert of Bed 29 in MjU. Siliceous microfossils and clayey matrix are observed. h: muddy chert of Bed 46 in MjU. Clayey materials and slight siliciclastic materials and siliceous bioclasts are observed. i: Black claystone bed of Bed 36 of MjL. Arrows with PF indicates pyrite framboids. j: Black claystone of Bed 9b of MjL. Arrows with Apm indicate aggregated pyrite microcrystals. k: Black claystone bed of Bed 36 of MjL. Arrows with IP indicate irregular-shaped pyrite. l: Cherty claystone of Bed 16 of MjL. Arrows with EP indicate the appearance of euhedral pyrite.

Figure 5. Outcrop photographs of the Momotaro-Jinja lower section-2. (a) lower part. (b) upper part. The white dashed line indicates bedding planes.

Figure 6. Lithostratigraphy and conodont occurrences for the Momotaro-Jinja lower section.

Figure 7. Lithologic column of the Momotaro-Jinja lower section-2 (MjL-2), with the abundance of pyrite morphologies in thin sections, and Fe speciation and trace metal profiles. Local background values of U/Al and Mo/Al (Bed 7a) are shown as vertical dashed lines with “baseline” notation. Open circles in the vertical plots indicate a dolostone sample. These data are eliminated from our paleo-redox interpretation.

Figure 8. Lithologic column of the Momotaro-Jinja upper section (MjU section), with the abundance of pyrite morphologies in thin sections (Takahashi et al., 2015), and Fe speciation and trace metal profiles. Local background values of U/Al and Mo/Al (Bed 24) are shown as vertical dashed lines with “baseline” notation. Open circles in the vertical plots correspond to results from the samples affected by carbonate veins. These data were eliminated from the paleoenvironmental interpretation.

Figure 9. Ba-Al crossplots for the studied sections. Left: Momotaro jinja lower section-2 (MjL-2 section), Right: Momotaro jinja upper section (MjU section). Minimum values of Ba/Al assumed as detrital Ba/Al ratio are 69 for MjL-2 and 50 for MjU, respectively.

Figure 10. Stereo-photographs of selected conodont specimens recovered from the Momotaro-Jinja lower section. The sketch of the specimen and photographs of the holotype of each species are also shown in the left and right panels, respectively.

1-2. *Conservatella conservativa*, from Bed 1 of MjL-2

3-4. *Guanxidella bransoni*, 3 is from Bed 3 of MjL-2, 4 is from Bed 6 of MjL-3. Holotype-image is obtained from Müller (1956).

5. *Neospathodus waageni*, from Bed 8a of MjL-2. Holotype-image is obtained from Sweet (1970b).

6. *Chirodella*? *igoi*, Beds 27-28 from MjL-2. Holotype-image is obtained from Koike (1996).

7. *Spathicuspus spathi*, Bed 30 of MjL-2. Holotype-image is obtained from Sweet (1970b).

8. *Neostrachanognathus tahoensis*, Bed 33 of MjL-2. Holotype-image is obtained from Koike (1998).

9. *Scythogondolella milleri*, Bed 2 of MjL-5. Holotype-image is obtained from Müller (1956).

10. *Neospathodus dieneri*, Bed 2 of MjL-5. Holotype-image is obtained from Sweet (1970a).

Figure 11. Cross plot of mean values and standard deviation of diameters of pyrite framboids from the Momotaro-Jinja lower section (MjL section; this study) and Momotaro-Jinja upper section (MjU section; Takahashi et al., 2015). The boundary between fields for anoxic and dysoxic environments is based on data from modern sediments (Wilkin et al., 1996).

Figure 12. Vertical plot (left) and cross plot (right) of molybdenum (Mo) and uranium (U) enrichment factors (Mo_{EF} and U_{EF}, respectively) for the Momotaro Jinja section. Vertical plot of the ratio of Mo_{EF}/U_{EF} is also shown. Superimposed grey-coloured areas in the cross-plot representing modern oceanic sediments are from Algeo and Tribovillard (2009) and Tribovillard et al. (2012). The U/Mo_{SW} is the weight ratio in modern seawater (SW), which ranges from 3.0 to 3.1 (modern Pacific and Atlantic, respectively; Anderson, 1987; Bruland, 1983; Chen et al., 1986; Emerson and Huested, 1991).

Figure 13. Schematic diagram showing interpretations of the redox conditions in the low latitude pelagic Panthalassa during the middle Smithian to earliest Spathian, and middle Spathian (see main text for details).

Figure 14. Lithologic column of the Momotaro-Jinja section (MjL-2 section and MjU section), with the excess fraction of barium (Ba_{excess}), biotic silica oxide ($SiO_{2(bio)}$), and modified chemical index of alternation following McLennan (1993) (CIA^*; see explanation in the main text). Legends for lithologic columns are the same as in Figs. 7 and 8.

Figure 15. Compilation of oceanic redox conditions across the Smithian–Spathian boundary. Data are modified from Galfetti et al. (2007), Huang et al. (2017), Song et al. (2019), Grasby et al. (2013), and Clarkson et al. (2016). Schematic diagrams of the possible evolution of oceanic anoxia are also shown.

Figure S1. Iron-speciation profiles for the MjL-2 section.

Figure S2. Iron-speciation profile for the MjU section.

Figure S3. Conodont fossils recovered from the Momotaro-Jinja lower section.

1. *Ellisonia triassica* S4 element, 2-4. "*Neohindeodella*" *triassica*, 5. *Conservatella* sp.? 6.

Conservatella P2 element, 7. *Parachirognathus* sp.?, 9-11.*Chirodella breviramulis*. All figures are normally arranged pairs.

Figure S4. Conodont recovered from the Momotaro-Jinja lower section. 1-3. *Ellisonia triassica* S4 element, 4. *Ellisonia triassica* S3 element (cf.), 5-10. .? 3-5. *Hadrodontina* sp. 6. *Hadrodontina*?, 7. *Parachirognathus* sp., 8-10. "*Neohindeodella" triassica*, 11-12. *Chirodella breviramulis,* 13. *Chirodella breviramulis* S2 element*,* 15. *Chirodella* cf. *breviramulis*. All figures are normally arranged pairs.

Figure S5. Conodont recovered from the Momotaro-Jinja lower section. 1, 5. *Ellisonia triassica* S4 element, 2. "*Neohindeodella*" *triassica*, 3. "*Neohindeodella*" sp., 4. *Ellisonia triassica* S3 element, 6. *Ellisonia* sp., 7-8. "*Neohindeodella"* sp.. All figures are normally arranged pairs.

Figure S6. Conodont recovered from the Momotaro-Jinja lower section. 1. *Ellisonia triassica* S3 element, 2. *Ellisonia triassica* S4 element, 3. "*Neohindeodella" triassica*, 4. "*Neohindeodella" kobayashii*, 5-7. "*Neohindeodella"* sp.. All figures are normally arranged pairs.

Figure S7. Conodont recovered from the Momotaro-Jinja lower section. 1-2. *Ellisonia triassica* S3 element, 3. *Ellisonia triassica* S3 element (cf.), 4. *Ellisonia triassica* S4 element, 5. "*Neohindeodella"* sp., 6. *Chirodella breviramulis* P1 element, 7. Ellisonia cf. triassica. *Nevadensis*. All figures are normally arranged pairs.

Figure S8. Conodont recovered from the Momotaro-Jinja lower section. 1. *"Neohindeodella" triassica,* 2. *Ellisonia triassica* S3/4 element, 4. *Ellisonia triassica* S4 element, 5-8. "*Neohindeodella"* sp.. All figures are normally arranged pairs.

Figure S9. Conodont recovered from the Momotaro-Jinja lower section. 1-3. *Ellisonia triassica* S3 element, 4. *Ellisonia triassica* S4 element, 5. "*Neohindeodella*" *triassica*, 6. *Ellisonia triassica* S3 element (cf.), 7. "*Neohindeodella"* sp.. All figures are normally arranged pairs.

Figure S10. Conodont recovered from the Momotaro-Jinja lower section. 1. *Parachirognathus* aff. *ethingtoni* of Koike (1982), 2. *Ellisonia triassica,* 3. *Ellisonia triassica* S4 element, 4. *Ellisonia triassica* S3 element. All figures are normally arranged pairs.

Figure S11. Conodont recovered from the Momotaro-Jinja lower section.
1-2. *Ellisonia triassica* S4 element, 3. *Ellisonia triassica* S3 element. All figures are normally arranged pairs.

Figure S12. An aerial photo of the Momotaro-Jinja section.
The image (taken by a drone aircraft (DJI mavic 2)) is comparable to the geologic map of Figure 3 in the main text.

Paleontological notes

Conservatella conservativa (Müller, 1956) Figures. 8-1, 8-2
  Ctenognathus conservativa Müller, 1956, p. 821, pl. 95, fig. 25.
  Conservatella conservativa (Müller, 1956). Maekawa et al., 2018, figs. 14.1-14.3
  Conservatella conservativa (Müller, 1956). Maekawa and Jenks 2021, figs 13.1-13.13

Remarks: Illustrated specimen is identified by the following features.
(1) Pointed spike-like denticles. (2) The denticles are straight and slightly reclined posteriorly, discrete in the upper, fused in the lower. (3) Basal margin is straight in the anterior half and upturned in the middle to posterior. It is distinguished from *Discretella,* which has fewer denticles (up to 7) and are more discrete. The specimen of Fig.8-1 is broken in the posterior part, but those features described above are observable.

Age: Lower to middle Smithian

Guangxidella bransoni (Müller, 1956) Figures 8-3, 8-4
  Neoprioniodus bransoni Müller, 1956, p. 829, pl. 95, figs. 19–21.
  Guangxidella bransoni (Müller). Maekawa and Igo, 2014, p. 211, figs. 152.16–152.18, 153–159, 160.1–160.4.
  Guangxidella bransoni (Müller). Maekawa and Jenks, 2021 Figures 14.14–14.20, 15.1–

15.20

Remarks: Illustrated specimen is identified by the following features. (1) Discrete denticles (around 8 to 9). (2) Basal margin arched upwards. (3) Posteriorly expanded basal cavity. (4) Large cusp at the posterior end. The specimen from the MjL-2 section (Fig. 8-3) is broken in the anterior part, but the features described above are observable.
Age: Middle Smithian

Neospathodus waageni (Sweet, 1970a) Figures 8-5

Neospathodus waageni Sweet, 1970a, p. 260, pl. 1, figs. 11, 12.

Remarks: The illustrated specimen is identified by the following features. (1) Arch-shaped upper edge with at least nine denticles. (2) The denticles are fused in the lower half. (3) Basal margin is straight.
Age: Smithian

Chirodella? *Igoi* (Koike), Figure 8-6

Cornudina igoi Koike, 1996. p. 119–120, Figs. 4.1–4.20.

Remarks: The illustrated specimen is identified by the following features. (1) Long cusp in posterior end. (2) Short anterior process that bears two denticles. This species is tentatively included in the genus *Chirodella* following the original assignment to *Cornudina* (a junior synonym of *Chirodella*), but typical *Chirodella* has a posterior process, *C. igoi* may not belong to this genus.
Age: the upper Smithian to Anisian

Spathicupsus spathi Sweet, Figure 8-7

Spathicupsus spathi Orchard, 2010 Figure 7 19-20
Neospathodus spathi n. sp., Sweet 1970a, p. 257-260, pl. 1, figs. 5, 6
Neospathodus spathi Sweet Tian et al., 1983, p. 379, pl. 97, fig. 1

Remarks: The illustrated specimen is identified by the following features. (1) Short segminate element. (2) A large prominent cusp in the posterior. (3) Low number of anterior denticles (around 4-5). (4) Weak lateral expansion of the basal cavity.

Age: Orchard (2007) summarizes this species yields during the late Smithian and early to middle Spathian.

Neostrachanognathus tahoensis Koike, 1998 Figure 8-8

Neostrachanognathus tahoensis Koike 1998, Fig. 9K–M

Remarks: The illustrated specimen is identified by the following features. (1) A coniform element. (2) Posteriorly elongated basal area (3) A small denticle in the anterior end.
Age: Spathian to Anisian

Scythogondolella milleri Müller, 1956. Figure 8-9

Gondolella milleri Müller, 1956, p. 823, pl. 95, figs. 1–9
Neogondolella milleri (Müller). Sweet et al., 1971, pl. 1, fig. 37

Remarks: This species is a segminiplanate P1 element which bears denticulation on the lateral platform margins. The illustrated specimen in this study is broken around the posterior half, but denticulation on the lateral platform rib, a short free blade, and low carina in the middle are observable.
Age: Middle to upper Smithian

Neospathodus dieneri Sweet, Figure 8-10

Neospathodus dieneri Sweet, 1970a, p. 9, pl.1, fig. 17
Remarks: This species is identified by the following features. (1) A thin segminiplanate element. (2) Denticles discrete in the upper half. (3) Denticles are pointed and reclined to erect. (4) Height of the denticles gradually decreases from posterior to anterior. (5) Basal margin is upturned on the posterior side. (6) Basal cavity is expanded, subrounded and oval.

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1703