Onset of environmental disturbances in the Panthalassic Ocean over one million years prior to the Triassic-Jurassic boundary mass extinction

Shane D. Schoepfer a,*, Jun Shen b, Hiroyoshi Sano c, Thomas J. Algeo b, d, e

a Department of Geoscience and Natural Resources, Western Carolina University, Cullowhee, NC 28723, USA
b State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, Hubei 430074, PR China
c Department of Earth and Planetary Sciences, Kyushu University, Fukuoka 812-8581, Japan
d Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA
e State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, Hubei 430074, PR China

ARTICLE INFO

Keywords:
CAMP
Central Atlantic Magmatic Province
Inuyama
Mercury
Volcanism
Paleoproductivity

ABSTRACT

While the end-Triassic mass extinction has been linked to emplacement of the Central Atlantic Magmatic Province (CAMP), evidence for environmental stresses appears hundreds of thousands of years prior to the extinction in some sections from the Panthalassic Ocean. In this study, we measured carbon, sulfur, and mercury concentrations in the Kurusu section, near Inuyama, Japan. These bedded radiolarian cherts are part of the Mino Terrane, an accretionary complex of late Paleozoic and Mesozoic sediments deposited at abyssal water depths in the open ocean, providing a unique window into the Triassic-Jurassic transition in pelagic settings. The rhythmically bedded nature of the sediments allowed construction of a floating astronomical age model tied to the radiolarian-defined Triassic-Jurassic boundary. Average linear sedimentation rates (LSR) of 0.07–0.48 cm kyr^{-1} and total organic carbon (TOC) concentrations of 0.07–0.22% yielded estimates of primary productivity rates (PPR) based on published transfer functions ranging from 2400 to 63,000 mg C cm^{-2} kyr^{-1}, which are generally comparable to PPRs in the modern equatorial and subtropical Pacific. While mercury (Hg) concentrations are strongly correlated with sedimentary sulfide content throughout the section, a distinct increase in the ratio of Hg to sulfide near the Triassic-Jurassic boundary may record Hg input from CAMP volcanism. Below this level, a series of discrete spikes in sulfide content appear during the ~ 1.2 Myr before the extinction, recording a precursor interval of environmental stress that also correlates with changes in the composition of the planktonic community. We infer that these changes reflect the development of stratification in the water column, with more reducing conditions characterizing the thermocline below the surface mixed layer. Based on the evidence from Kurusu and comparisons to other Panthalassic sections, we propose a model in which water-column stratification began to develop in the open Panthalassic Ocean over one million years before the Triassic-Jurassic boundary. Evidence from sections deposited at slope depths suggests that this rising chemocline may have begun to impinge on the slopes of island arcs and the South American continental margin by ~ 400 kyr before the boundary. The end-Triassic extinction coincided with both the main phase of CAMP eruptions and the irruption of acidic, reducing deep waters into photic zone and shelf environments.

1. Introduction

The end-Triassic mass extinction (ETME) is considered to have been one of the most significant biodiversity crises of the Phanerozoic (Raup and Sepkoski, 1982). While not the largest mass extinction in terms of overall magnitude (Alroy, 2010), it was the first major mass extinction experienced predominantly by the Modern Evolutionary Fauna (Sepkoski, 1981). It also coincided temporally with the Mesozoic Marine Revolution, a putative escalation of interspecies interaction as a driver of evolutionary novelty (Vermeij, 1977; McRoberts, 2001), and may have played a role in initiating this event. Despite its evolutionary significance, the degree to which the ETME represented a short-term extinction event rather than a prolonged interval of biodiversity depletion remains in debate (Bambach et al., 2004; Lucas and Tanner, 2008, 2018; Alroy, 2010). The beginning of the ETME has been linked to the emplacement of the Central Atlantic Magmatic Province (CAMP), with

* Corresponding author.
E-mail address: schoepfer@email.wcu.edu (S.D. Schoepfer).
the terrestrial extinction corresponding with the earliest eruptions beginning around 201.6 Ma (Blackburn et al., 2013; Marzoli et al., 2019) and the marine extinction potentially corresponding to intrusive activity beginning 50–100 kyr earlier (Davies et al., 2017). However, it is not yet clear if these events represent the initial onset of environmental stresses in an otherwise relatively stable world, or only one especially severe stage in a complex period of environmental deterioration.

Like many events in geologic history, our understanding of the ETME is biased by the distribution of the preserved rock record. Much of what we know about the event is derived from sections deposited on continental shelves in the peri-Tethyan ocean (Kürschner et al., 2007; Pauly et al., 2007; Bonif et al., 2011; Richoz et al., 2012; van de Schootbrugge et al., 2013), incipient North Atlantic basin (Hallam, 1996; Hesselbo et al., 2002), or terrestrial rift basins in eastern North America (Marzoli et al., 2004; Whiteside et al., 2007, 2010). Many of these sections exhibit major changes in sedimentary facies across the Triassic-Jurassic Boundary (TJB), which complicates interpretation of geochemical data (Hallam and Goodfellow, 1990; Hesselbo et al., 2004). The Panthalassic, or proto-Pacific, Ocean covered ~70% of Earth’s surface area at the end of the Triassic Period. Despite its great extent, records from the Panthalassic realm are sparse and difficult to correlate with sections from other parts of the world (Lindstrøm et al., 2017). Continental shelf sections are exposed in Nevada (Guex et al., 2004) and parts of Peru (Schaltegger et al., 2008; Yager et al., 2017), but the dynamics of the extinction in the open Panthalassic Ocean can be studied only in those locations where seafloor sediments have been accreted onto a continent, either as part of a larger arc terrane such as Wrangellia (i.e., Kasprak et al., 2015) or in an accretionary wedge complex (Hori, 1992). The Mino-Tamba-Ashio complex of central Honshu is the most extensive of the latter (Wakita, 1987), and it can be correlated with other Panthalassic sections (Carter and Hori, 2005). These preserved seafloor sediments provide us a novel perspective into the ETME as it occurred in the pelagic ocean.

Due to its strong association with the CAMP eruptions (Greene et al., 2012), the ETME has often been viewed as an example of the ‘greenhouse extinction’ model (Kump et al., 2005; Kidder and Worsley, 2010), in which rapid, CO2-driven warming of the oceans (Korte et al., 2017) results in the CAMP eruptions, which is composed of a complex late Paleozoic through Mesozoic succession of metamorphosed igneous rocks, limestones, siliciclastic rocks, and bedded radiolarian cherts (Sano et al., 1992; Wakita, 1987, 2019). This last lithofacies is interpreted to have been deposited below the carbonate compensation depth, in the low-latitude (peri-equatorial) Panthalassic Ocean (Ando et al., 2001; Carter and Hori, 2005), between the Early Permian and Late Jurassic (Sano, 1988; Wakita, 2013). The composition of the sediments reflects the variable fluxes of siliceous radiolarian tests and hemipelagic or windblown silt and clay components (Wignall et al., 2010), likely influenced by orbitally-driven changes in climate or productivity at Milankovitch periodicities (Ikeda et al., 2015).

The goal of this study is to assess the evidence for environmental degradation in the open Panthalassic Ocean in the interval prior to the end-Triassic biodiversity crisis. First, we examine evidence for reducing conditions in the water column, as reflected in sedimentary sulfides (cf. Algeo et al., 2007). Second, we examine evidence for volcanism, using sedimentary mercury, which has become a widely used proxy for volcanism even in distal sedimentary settings (cf. Sano et al., 2008; Shen et al., 2019a, 2019b). Accurate application of the Hg proxy requires determining the dominant Hg host phases and the mechanisms by which Hg was removed from the water column. Third, we examine evidence for changes in the primary productivity rate, as calculated from transfer functions using TOC content and sedimentation rate as inputs (Felix, 2014; Schoepfer et al., 2015). Since the major sedimentary component of the study section, radiolarian chert, is also biogenic in origin, the thicknesses of individual beds will be used as an alternative means to assess productivity variations. Lastly, we will compare evidence from Kurusu with sections from other Panthalassic sites, including accreted terranes such as Wrangellia (Kasprak et al., 2015; Schoepfer et al., 2016), and from continental shelf settings in North America (Guex et al., 2004; Ritterbush et al., 2014) and South America (Schaltegger et al., 2008; Yager et al., 2017) in order to better understand the degree to which the ETME can be viewed as a sudden mass extinction event consistent with the greenhouse model.

2. Geologic setting

2.1. The Mino Terrane of central Japan

Pelagic sediments, i.e., those deposited under several kilometers of marine water, overlying oceanic crust, and minimally influenced by detrital sediment input, are rarely preserved from earlier than the Jurassic Period. Those that are preserved are generally located in accretionary complexes in the circum-Pacific region, i.e., New Zealand, the Russian Far East, the Philippines, and Japan. In Japan, the Mino-Tamba-Ashio terrane complex runs from SW to NE across central Honshu (Fig. 1), while the approximately coeval Chichibu complex extends through southern Honshu into Shikoku and Kyushu (Wakita, 2013).

Our studied section is part of the Mino Terrane of central Honshu, which is composed of a complex late Paleozoic through Mesozoic succession of metamorphosed igneous rocks, limestones, siliciclastic rocks, and bedded radiolarian cherts (Sano et al., 1992; Wakita, 1987, 2019). This last lithofacies is interpreted to have been deposited below the carbonate compensation depth, in the low-latitude (peri-equatorial) Panthalassic Ocean (Ando et al., 2001; Carter and Hori, 2005), between the Early Permian and Late Jurassic (Sano, 1988; Wakita, 2013). The composition of the sediments reflects the variable fluxes of siliceous radiolarian tests and hemipelagic or windblown silt and clay components (Wignall et al., 2010), likely influenced by orbitally-driven changes in climate or productivity at Milankovitch periodicities (Ikeda et al., 2015).

The goal of this study is to assess the evidence for environmental degradation in the open Panthalassic Ocean in the interval prior to the end-Triassic biodiversity crisis. First, we examine evidence for reducing conditions in the water column, as reflected in sedimentary sulfides (cf. Algeo et al., 2007). Second, we examine evidence for volcanism, using sedimentary mercury, which has become a widely used proxy for volcanism even in distal sedimentary settings (cf. Sano et al., 2008; Shen et al., 2019a, 2019b). Accurate application of the Hg proxy requires determining the dominant Hg host phases and the mechanisms by which Hg was removed from the water column. Third, we examine evidence for changes in the primary productivity rate, as calculated from transfer functions using TOC content and sedimentation rate as inputs (Felix, 2014; Schoepfer et al., 2015). Since the major sedimentary component of the study section, radiolarian chert, is also biogenic in origin, the thicknesses of individual beds will be used as an alternative means to assess productivity variations. Lastly, we will compare evidence from Kurusu with sections from other Panthalassic sites, including accreted terranes such as Wrangellia (Kasprak et al., 2015; Schoepfer et al., 2016), and from continental shelf settings in North America (Guex et al., 2004; Ritterbush et al., 2014) and South America (Schaltegger et al., 2008; Yager et al., 2017) in order to better understand the degree to which the ETME can be viewed as a sudden mass extinction event consistent with the greenhouse model.

2. Geologic setting

2.1. The Mino Terrane of central Japan

Pelagic sediments, i.e., those deposited under several kilometers of marine water, overlying oceanic crust, and minimally influenced by detrital sediment input, are rarely preserved from earlier than the Jurassic Period. Those that are preserved are generally located in accretionary complexes in the circ-
et al., 2010; Ikeda and Hori, 2014; Ikeda et al., 2017). The sediments were subsequently accreted to continental East Asia in the late Mesozoic.

2.2. The Kurusu section

The Kurusu section (Fig. 1; Hori, 1988, 1992) is exposed on the southern bank of the Kiso River, approximately 6.5 km to the northeast of Inuyama, Aichi Prefecture, Japan (35.4209° N, 136.9652° E). It represents a conformable succession of only weakly deformed chert beds that dip ~60° to the south. The section is composed of continuous, tabular beds of radiolarian chert ranging in thickness from 1.5 to 10 cm (mean ~ 4 cm), separated by well-developed, millimeter-scale shale partings. Unlike other Mino-Tamba Terrane sections that show systematic variations in chert colour (Wignall et al., 2010; Ikeda and Tada, 2014), the chert beds at Kurusu are a relatively uniform grayish-green, although some show red to purple coloration in a continuous band running through the center of the bed.

Unlike many other Triassic-Jurassic boundary sections globally, there is no major facies change in the Kurusu section (Hori et al., 2007). In general, shale partings between beds are not as well developed in the upper part of the section; however, there are no major changes in lithofacies that are likely to be responsible for observed changes in geochemistry. One exception to the general lithologic uniformity is a prominent, ~20 cm-thick reddish-brown shale bed that marks the end of our section.

The Triassic-Jurassic boundary was identified in the Kurusu section by Hori et al. (2007), and slightly revised by Kuroda et al. (2010) on the basis of radiolarian and conodont biostratigraphy. The boundary occurs ~6.25 m above the lowest measurable beds of the section (overlying a prominent fold that deforms the underlying beds) and ~20 m below the prominent reddish-brown shale layer at the top of the section. On the basis of these stratigraphic tie-points, we can position the TJB at approximately Bed 155 of our measured section (Fig. 2A-D). This interpretation is supported by our geochemical results (see Section 4).

3. Methods

3.1. Field methods

We collected a total of 213 samples in outcrop at the Kurusu section, from a continuous interval spanning ~26 m of strata. The base of our section was located in the lowest (i.e., northernmost) accessible bed of this conformable succession. Strata below the base of the section are deformed by a tight NNW-SSE fold and cannot easily be tied into the TJB.
section. While the section is well exposed along the banks of the Kiso River when the water level is low, fluvial erosion has shaped the beds into a dissected and irregular surface that makes measuring a continuous transect difficult. For this reason, our section is a composite of four short sections correlated using field observations and photography.

On the basis of these correlations, we were able to identify 239 distinct chert beds in the lower 9.5 m of our section. The thickness of each of these beds (including the associated shale parting) was measured in the field with a measuring tape, and where accessible a sample of the chert was collected (Supplementary Table 1). Between 9.5 m and the reddish-brown shale bed at 26 m, the shale partings between chert beds became increasingly indistinct. Instead of measuring and sampling individual chert beds in this interval, samples were collected where they were easily accessible, and assigned a stratigraphic height in the composite section using a measuring tape.

3.2. Geochemical and Petrographic Methods

A total of 213 samples were trimmed to remove visible veins and weathered surfaces, and pulverized to ~200 mesh using an agate mortar and pestle. Aliquots of each sample were separated for different analytical procedures. Mercury concentrations (33 samples) were monitored via multiple analyses of the MESS-3 standard, yielding an average sedimentation rate for this interval is 0.20 cm kyr⁻¹, with a standard deviation of 0.09 cm kyr⁻¹.

The section continues above Bed 238, although the shale partings between chert beds become increasingly indistinct, and these beds were not sampled individually. To establish an age model for this part of the section (i.e., 9.5–26 m), we used a range of constant sedimentation rates. Applying the mean sedimentation rate from the lower well-bedded interval (0.20 cm kyr⁻¹) suggests that the red shale horizon at 26 m dates to 191.44 Ma, placing it in the late Sinemurian (Fig. 4B). To account for uncertainty in sedimentation rates of the upper part of the section, we apply rates that are one standard deviation lower (0.11 cm kyr⁻¹) and higher (0.29 cm kyr⁻¹) than the mean rate, yielding a range of potential ages for the top of the section from 184.33 Ma (Pliensbachian) to 194.06 Ma (Sinemurian). Because the “average” age model is most consistent with the better constrained bedded interval, it will be used for all paleoproductivity calculations, however these paleoproductivity values should be understood to have an additional 40% error due to uncertainties in sedimentation rate.

3.3. Age Model

To derive an age model for the Kurusu section, we employed an approach similar to that used by Ikeda and Tada (2014) at the nearby Katsuyama section. The bedded pelagic cherts of the Mino Terrane have been strongly linked to astronomical controls on either radiolarian productivity or detrital sediment flux, with each chert-shale couplet being associated with an orbital precession cycle (Ikeda and Tada, 2013, 2014). The effect of precession cycles on sedimentary systems reflects the varying contributions of several orbital components, which have changed in duration over geologic time (Laskar et al., 2004; Hinnov, 2013). We follow Ikeda and Tada (2014) in adopting a duration of 0.02 Myr (i.e., 20 thousand years) to represent the interaction of these various components.

To anchor this floating timescale for the Kurusu section to an absolute chronostratigraphy, we follow Ikeda and Tada (2014) in adopting an age of 201.4 Ma for the radiolarian turnover that marks the TJB in the Mino Terrane. This date is derived from biostratigraphic correlations with sections in Nevada (Schoene et al., 2010) and the Pucaré Basin of Peru (Gueux et al., 2012) that contain datable volcanic ashes. While these dates were recalculated by Wotzlaw et al. (2014), the revised date for the TJB (201.36 ± 0.17 Ma) agrees well with the Ikeda and Tada (2014) interpolated date. Due to a lack of macroscopic fauna in Japanese pelagic sections, the end-Triassic mass extinction and Triassic-Jurassic boundary are effectively equivalent, both defined by a turnover in the radiolarian fauna. However, it is worth noting that this event occurred later than both the onset of CAMP volcanism, as dated in North American rift basins (201.564 Ma, Blackburn et al., 2013), and the initial emplacement of recognized CAMP intrusives (201.635 Ma, Davies et al., 2017, Marzoli et al., 2019).

Based on the correlation of our section with that of Hori et al. (2007) and Kuroda et al. (2010), we assigned an age of 201.4 Ma to Bed 155 in our measured section (Fig. 3). Each identifiable bed above and below this point is assigned an age that differs by 0.02 Ma. Based on this model, the lowest bed in the study section, immediately above the bed surface (i.e., 0 m), can be dated to 204.50 Ma, within the Rhaetian stage (Ogg, 2012). Note that while Kuroda et al. (2010) interpret the top of the Bacteriolum deweveri radiolarian Zone as the Norian-Rhaetian boundary, this would imply a Rhaetian stage of substantially less than 4 Myr, which is inconsistent with even the ‘long Carnian’ model of Late Triassic chronostratigraphy (Wutzlaw et al., 2014; Maron et al., 2015). The highest individually identified bed, Bed 238 at 9.43 m, is assigned an age of 199.74 Ma, which places it in the late Hettangian (Fig. 4A, Ogg and Hinnov, 2012). Assuming that each chert-shale couplet represents ~20 kyr, we can calculate a “short-term” linear sedimentation rate for each individual bed. These range from 0.07 cm kyr⁻¹ to 0.48 cm kyr⁻¹. The average sedimentation rate for this interval is 0.20 cm kyr⁻¹, with a standard deviation of 0.09 cm kyr⁻¹.

Calculations of primary productivity rates (PPR) followed the approach developed in Schoepfer et al. (2015), which used a compilation of 94 marine sediment cores to develop transfer equations relating PPR in the modern ocean to sedimentation rate and organic carbon flux. Many of the cores used in Schoepfer et al. (2015) are from the equatorial or subtropical Pacific, and yield sedimentation rates comparable to those calculated from the Kurusu section. As a result, we consider the coefficients developed in that study to be applicable in pelagic environments, where the vast majority of sinking organic carbon is remineralized before reaching the seafloor.

These equations have been applied to Permian-Triassic sediments (Shen et al., 2015), as well as TJB sediments in Schoepfer et al. (2016).

Unlike those studies, which use biostratigraphically constrained estimates of sedimentation rate at the stage level, the astronomical timescale for the Kurusu section allows us to estimate the “short-term” sedimentation rate for any individual chert-shale couplet for which the thickness is known. The thickness of each measured bed was divided by 20 kyr (i.e., one precession cycle) to determine a linear sedimentation rate (LSR, cm kyr⁻¹). This was converted into a mass accumulation rate (MAR, g cm⁻² kyr⁻¹), by multiplying the sedimentation rate by a typical density for lithified marine sediments, 2.5 g cm⁻¹.

Primary productivity rates were calculated using transfer equations...
These equations are intended to yield first order estimates of changes in PPR over time, and the absolute values have associated errors as high as 100%. The full derivations of the equations, and methods of determining the associated error, are described in detail in that study.

Eq. (1) (Equation (18) of the source paper) is derived from the observed relationship between sedimentation rate and the rate of organic carbon preservation in sediments:

$$\text{PROD}_{\text{prim.}} = 1000 \times 10^{4.1} \times \frac{\text{TOC}}{\text{MAR}^{0.54}}$$

where PROD$_{\text{prim.}}$ is primary productivity in units of mg C cm$^{-2}$ kyr$^{-1}$, and TOC is the dimensionless weight proportion of organic carbon.

Eq. (2) (Equation (21) of the source paper) is based on empirical regressions between primary productivity and the accumulation rates of organic carbon in the Late Pleistocene-Holocene ocean.

$$\text{PROD}_{\text{prim.}} = 10^{8.55} \times (\text{OCAR})^{0.41}$$

where OCAR is the organic carbon accumulation rate (MAR $\times$ TOC) in units of mg cm$^{-2}$ kyr$^{-1}$.

To supplement the equations developed in Schoepfer et al. (2015), we also employed two older paleoproductivity equations, which were assessed by Felix (2014) and found to yield values consistent with measured modern productivity rates:

$$\text{PROD}_{\text{prim.}} = 100 \times (\text{TOC} \times \text{DBD}) \big/ (0.003 \times \text{LSR}^{0.3})$$

$$\text{PROD}_{\text{prim.}} = 531 \times (\text{TOC} \times \text{DBD})^{0.71} \times \text{LSR}^{0.07} \times \text{WD}^{0.45}$$

where WD is the water depth of the depositional environment and DBD is the assumed dry bulk density of the sediment (2.5 g cm$^{-3}$). Consistent with interpretations of the Mino Terrane depositional environment, we used a typical pelagic marine water depth of 4000 m. Eq. (3) is modified from Müller and Suess (1979) and Eq. (4) is modified from Stein (1986). A factor of 100 has been inserted in these equations in order to convert productivity estimates from units of g C m$^{-2}$ yr$^{-1}$ to units of mg C cm$^{-2}$ kyr$^{-1}$.

4. Results

4.1. Bed thickness

Measured bed thicknesses show systematic variability throughout the section. In the lowest part of the section, between 0 and 5.35 m, two complete cycles in bed thickness can be observed. The first of these cycles, which is estimated to represent the interval from ~204.3 to
~203.1 Ma, shows peak bed thicknesses of 10 cm. The second cycle, representing the interval from ~203.1 Ma to 202.0 Ma, shows lower peak bed thicknesses of 6.5 to 7.5 cm. These two cycles may represent the 1.2 Myr obliquity modulation cycle (Ikeda and Tada, 2013; Liu et al., 2019). A distinct sub-peak within the first cycle, centered around 203.3 Ma, may represent a 400-kyr long-eccentricity cycle.

Above 202.0 Ma, beds are generally thinner, with thicknesses rarely above 4 cm throughout the boundary interval. A small peak, reaching thicknesses as much as 4.5 cm, is centered around 201.84 Ma, and may represent a long-eccentricity cycle. Bed thicknesses start to increase again above 201.1 Ma, reaching values as high as 9.5 cm. A clear 1.2-Myr cyclicity cannot be observed in this part of the section, but the bed thicknesses may reflect a set of three 400-kyr long-eccentricity cycles. Above 9.5 m in the measured section, chert lithofacies becomes more massive in character, and the individual beds are insufficiently distinct from one another to be assigned thicknesses (Fig. 5).

### 4.2. Carbon and sulfur speciation

Total organic carbon (TOC) and total inorganic carbon (TIC) were measured in a total of 178 samples from the lower 15 m of the study section (Fig. 5). TOC is generally low throughout the section, ranging from 0.07 to 0.22%, with little systematic variation. Most values are clustered tightly around the mean value of 0.11% (st. dev. = 0.03%). The only substantial deviation from this baseline is a broad peak centered around 5.3 m, estimated to represent an age of 202.2 Ma, which reached values above 0.20%. TIC was not present at detectable levels in most of the measured samples (119 out of 178). Two peaks in TIC were observed in the lowermost part of the section, reaching values above 0.50%. Above 1.76 m, representing an estimated age of 203.9 Ma, detectable TIC is rarely observed, with only one value >0.30%.

Non-acid volatile sulfur (NAVS) content and acid-volatile sulfur content (AVS) were measured in 178 samples (Fig. 5). NAVS ranged from 0.02 to 0.45%, with a mean value of 0.11% (st. dev. 0.09%). NAVS content, although low overall, shows coherent secular variation, with several discrete spikes to values >0.20% throughout the section. The first two of these spikes occur in the first 3 m of the section, with estimated ages of 204.0 and 203.7 Ma. Another three spikes occur between 4.87 and 6.23 m, representing an interval from 202.5 to 201.7 Ma, i.e., in the 1.2 million years preceding the end-Triassic extinction. NAVS content is generally higher in the more massive cherts above 9.5 m (<199.56 Ma), with most samples in this interval yielding values >0.10%. A total of 62 out of 178 samples yielded detectable AVS. Spikes in AVS generally correspond to those in NAVS, with AVS reaching a maximum value of 0.19%.

### 4.3. Mercury content

Mercury content was measured in a total of 33 samples throughout the lower 15 m of the section, yielding values from <1 ppb to 29.5 ppb, with a mean value of 8 ppb (Fig. 5). No long-term secular trend is observed through the section, and the majority of samples yielded <10 ppb Hg. Single samples yielding Hg > 10 ppb are found at 2.64 m (14.4 ppb) and 5.56 m (12.2 ppb). A series of samples with elevated (>10 ppb) Hg values are found within the ~0.5-m interval underlying the inferred TJB; the highest values correspond with the TJB transition interval identified by Kuroda (Fig. 5). This interval of enhanced mercury concentrations is estimated to span from 202.1 to 201.4 Ma. A second interval of elevated mercury concentrations (>18 ppb) occurs from 9.33 to 12.54 m, coinciding with the transition from bedded cherts with well-
developed shale partings to more massive cherts. This interval has an estimated age of 199.8 Ma to 198.2 Ma, coinciding with the uppermost Hettangian to lower Sinemurian.

4.4. Paleoproductivity estimates

Quantitative paleoproductivity estimates were made for each sample for which TOC data were available, using the four equations presented in Section 3.4 (Fig. 5). In general, the resulting estimates were similar, usually varying by less than an order of magnitude, despite the partially independent bases for these equations. Secular trends in the calculated productivity rates were also generally consistent, with the most elevated values within the 1.2 million year interval preceding the TJB, between 4.87 and 6.63 m.

Eq. (1) (Schoepfer et al., 2015, their equation 18) yielded the highest productivity estimates, with a mean value of 21,721 mg C cm$^{-2}$ kyr$^{-1}$ (st. dev. = 8448 mg C cm$^{-2}$ kyr$^{-1}$). Maximum short-term productivity estimates in the pre-extinction interval are >60,000 mg C cm$^{-2}$ kyr$^{-1}$. Some cyclicity in calculated productivity rates is seen at the 400-kyr scale, especially in the lower part of the section. Eq. (2) (Schoepfer et al., 2015, their equation 21) yielded considerably lower estimates, with a mean value of 3530 mg C cm$^{-2}$ kyr$^{-1}$ (st. dev. = 685 mg C cm$^{-2}$ kyr$^{-1}$). Peak values were ~6000 mg C cm$^{-2}$ kyr$^{-1}$. Eq. (3) (Müller and Suess, 1979, their equation 6) yielded values very similar to Eq. (1), with a mean of 15,330 mg C cm$^{-2}$ kyr$^{-1}$ (st. dev. = 4852 mg C cm$^{-2}$ kyr$^{-1}$) and a peak value >36,000 mg C cm$^{-2}$ kyr$^{-1}$. Eq. (4) (Stein, 1986, their equation 8) was more similar to Eq. (2), yielding a mean productivity value of 8792 mg C cm$^{-2}$ kyr$^{-1}$ (st. dev. = 2819 mg C cm$^{-2}$ kyr$^{-1}$).

The paleoproductivity equations containing a sedimentation rate term in the denominator (Eqs. (1) and (3)) attempt to explicitly correct for the poor preservation of sinking organic carbon at low preservation rates. As a result, these equations give higher estimates for productivity in the surface ocean at the time of deposition, and they are sensitive to cyclical variability in sedimentation rate (see Section 4.1). Eqs. (2) and (4) do not attempt to correct for low sedimentation rates in the pelagic ocean, and thus they yield considerably lower values, although it is worth noting that Eq. (4), which yields intermediate values, accounts for preservation by including a water depth term (Felix, 2014).

5. Discussion

5.1. Episodes of sulfide deposition

Throughout the Kurusu cherts, an average of 93% of total sulfur is present in non-acid-volatile forms (NAVS), and acid-volatile sulfur (AVS) content generally mirrors the stratigraphic distribution of NAVS, likely reflecting post-depositional oxidation of the AVS component. In a pelagic depositional setting, NAVS is likely to be overwhelmingly in the form of sedimentary organic matter and stable sulfides such as pyrite (Shen et al., 2016). Pyrite can be readily identified in petrographic thin sections (Fig. 6 A-H), especially those coinciding with spikes in NAVS content (Fig. 6 D–H). Some pyrite grains show euhedral shapes or are associated with organic laminae, suggesting they formed diagenetically (Fig. 6 F–H), while others appear to be coarse framboids with diameters on the order of tens of microns (Fig. 6 A-D).

These larger framboids are more consistent with precipitation in dysoxic pore waters than a euxinic water column (Wilkin et al., 1996; Wignall and Newton, 1998). Despite their likely diagenetic origin, the stratigraphic distribution of sulfides (concentrated within a few discrete, rhythmically-spaced intervals) suggests they reflect early diagenetic processes controlled by the sediment porewater environment. Some of these larger framboids may represent diagenetic overgrowths of syntopic pyrite, a process that would be enhanced by low sedimentation rates in the pelagic ocean (Wilkin et al., 1996). Enhanced deposition of
labile organic matter (as discussed in Section 5.3) would also enhance diagenetic pyrite precipitation in dysoxic bottom water or sedimentary pore water. Lastly, because NAVS exceeds TOC as a weight percentage in most samples, it is likely that NAVS spikes at Kurusu at least partially reflect syngenetic sulfide deposition, enhanced by diagenetic precipitation (cf. Algeo et al., 2007, 2011).

Prior to the TJB, this sulfide deposition occurred in a series of discrete spikes, all of them defined by multiple sample points, reaching NAVS values >0.20%. These positive excursions share certain properties, including beginning abruptly, and having a characteristic duration of 4–6 individual beds, which suggests they had a duration of ~100 kyr and may have been paced by the short-eccentricity orbital cycle. The spikes are concentrated in two intervals of the Rhaetian succession. Two closely spaced spikes in NAVS are centered around 204.0 Ma and 203.7 Ma, meaning they are unlikely to be directly related to the TJB. The latest Rhaetian features three spikes in sulfide content, beginning at ~202.5 Ma and continuing until ~300 kyr prior to the TJB. This interval is highlighted in Fig. 5, and is plotted separately from other Triassic samples in Figs. 7 and 8 (n.b., we adopt the term ‘crisis interval’ for compatibility with Schoepfer et al., 2016, where an analogous interval was identified at Kennecott Point; it is not meant to imply a biological crisis at Kurusu). It is worth noting that, within this ‘crisis interval’, individual peaks in NAVS are separated by 15–20 individual beds, suggesting that the ~400-kyr long-eccentricity cycle modulated sulfide deposition when conditions were broadly favorable for sulfate reduction.

The presence of sulfide deposition events in the 1.2 million years preceding the TJB suggests a change in water-column redox conditions. Reducing conditions, in which available oxygen was locally consumed and oceanic sulfate was reduced to sulfide in the water column or sediments, may have developed as a result of increased productivity (see below) or intensified water-column stratification. An interval of environmental stress, lasting for hundreds of thousands of years prior to the radiolarian turnover that marks the TJB in Panthalassic sections, is also observed in the Kennecott Point section of British Columbia, where the ‘crisis interval’ is associated with the development of low-oxygen conditions in deep water (Kasprak et al., 2015; Schoepfer et al., 2016).

Upsection, in the Sinemurian interval, NAVS content is generally elevated relative to the Rhaetian and Hettangian intervals. Unlike the Rhaetian, Sinemurian sulfide deposition is not concentrated in a series of discrete spikes, but instead shows a broad increase to a new higher baseline value. Total sulfur measurements suggest that this secular increase in S deposition continued to the top of the measured section (likely upper Sinemurian; Supplementary Table 2). This increase in sulfide deposition is likely the key variable controlling increased Hg deposition in the same interval. The reasons for this increase in sulfide deposition...
deposition are not understood at present, but may be related to a widespread trend toward more reducing conditions in the Panthalassic realm during the Early Jurassic. Sulfur isotopes from the Kennecott Point section suggest near quantitative sulfate reduction in the Hettangian (Williford et al., 2009), and organic carbon isotopes from Levanto show a prolonged Hettangian positive excursion that may reflect burial of light organic carbon (Yager et al., 2017). However, both of these trends are primarily Hettangian, and thus predate the increase in sulfide at Kurusu.

5.2. Mechanisms of mercury deposition

Sedimentary mercury (Hg) concentrations are widely used as a proxy for volcanic activity (see reviews by Grasby et al., 2019; Shen et al., 2019a), and mercury excursions located around mass extinction boundaries and or oceanic anoxia events (e.g., OAE) have been ascribed to large igneous province (LIP) eruptions worldwide (Sanei et al., 2012; Grasby et al., 2013; Thibodeau et al., 2016; Percival et al., 2017; Shen et al., 2019b). The CAMP eruptions have been linked to a global episode of mercury deposition in the latest Triassic (Percival et al., 2017), in both marine and terrestrial settings (Lindström et al., 2019, Lindström et al., 2021), though records from the deep Panthalassic Ocean are lacking. The unusual depositional setting of the Mino Terrane provides an opportunity to assess the global impact of the CAMP eruptions, as the Kurusu site in the tropical Pacific was extremely distant from (almost antipodal to) the eruptive centers of the CAMP. Likewise, it was distal from any continent-margin setting or known oceanic volcanic arc that might have served as an alternative local source of mercury (Shen et al., 2021). As a pelagic section deposited at abyssal water depths, it may represent a more globally integrated signal of atmospheric mercury deposition than any other TJB site studied to date (c.f. Shen et al., 2019b). However, before interpreting mercury concentrations as a straightforward proxy for volcanic activity, the mechanisms by which Hg is transferred to the sedimentary environment as well the host of Hg in sediments must be considered (e.g., Shen et al., 2019c, 2020).

While volcanism may increase the flux of Hg to the surface ocean, dissolved Hg is particle reactive, and will generally be removed from the marine environment by sinking organic matter (Sanei et al., 2012; Bergquist, 2017). As a result, raw mercury concentrations may be driven more by variation in TOC fluxes than real changes in volcanic Hg input, and variation in Hg concentration may be attenuated after normalization to TOC. In our studied section, this does not appear to be the case;
due to the lack of variability in TOC content, the shape of the Hg/TOC curve largely reflects Hg concentrations, with several spikes immediately above the TJB and a broad increase to higher values in the Sinemurian (Fig. 5). Plotting Hg content against TOC shows no correlation (Spearman’s $\rho = -0.06$, $n = 32$, $p > 0.05$), though most samples fall within a field that likely indicates Hg scavenging by the sinking organic flux (Fig. 7A). This can be distinguished from a more linear “high-Hg” trend, defined mainly by ‘crisis interval’ and Sinemurian samples.

Mercury can also be sequestered from ocean water by association with sedimentary sulfides, due to the high stability constants of inorganic Hg-S complexes (Shen et al., 2016c). Hg generally shows a strong correlation with NAVS in our section (Spearman’s $\rho = +0.65$, $n = 32$, $p < 0.01$), suggesting that the sulfide flux, rather than TOC flux, may have been the primary control on Hg transfer to the sediment. The Sinemurian increase in Hg persists following normalization to NAVS (Fig. 5), with the most notable feature of the Hg/NAVS curve (Fig. 7B) being a series of distinct spikes, the most prominent of which coincides with the TJB interval as defined by Kuroda et al. (2010). These spikes can be discerned on the NAVS vs Hg crossplot as ‘crisis interval’ and Jurassic samples that deviate from the general linear correlation trend (which is even stronger when they are excluded; Spearman’s $\rho = +0.71$, $n = 29$, $p < 0.01$).

This suggests that the TJB-interval mercury spikes may represent the only time during deposition of the section when the flux of mercury to the surface ocean exceeded the capacity of the local TOC and sulfide fluxes to sequester Hg in sediments (cf. Sanei et al., 2012). The timing of these spikes strongly suggests a direct link to eruption of the CAMP basalts, the onset of which has been found to correspond well with the end-Triassic mass extinction (Blackburn et al., 2013; Percival et al., 2017). While these Hg excursions correlate with the radiolarians-defined TJB at Kurusu, they significantly postdate the onset of CAMP activity identified by Kuroda et al. (2010) based on increasingly unradiogenic osmium isotope ratios. Based on our age model, this osmium isotope trend began approximately 2 million years prior to the TJB, and is unlikely to be directly related to CAMP emplacement. The mercury evidence for CAMP activity also postdates the pre-extinction ‘crisis interval’ of sulfide deposition, suggesting that the reducing conditions prior to the TJB were not directly driven by the main phase of extrusive CAMP eruptions. These changes in the Panthalassic realm in the millions of years before the TJB will be considered in Section 5.5.

5.3. Primary productivity

All four paleoproductivity equations applied to the Kurusu section yield a realistic range of values comparable to some of the low-to-moderate productivity regions of the modern ocean. Eqs. (2) and (4), which yield average paleoproductivity estimates in the range of 3000 to 10,000 mg C cm$^{-2}$ kyr$^{-1}$, are consistent with oligotrophic subtropical gyre regions in the Indian and Pacific oceans (Longhurst et al., 1995; Schoepfer et al., 2015). Eqs. (1) and (3), which explicitly account for low sedimentation rates, yield average values in the 15,000 to 25,000 mg C cm$^{-2}$ kyr$^{-1}$ range that more closely resemble the Pacific equatorial divergence, as well as higher latitude regions of deeper mixing such as the subarctic Atlantic and southern subtropical convergence (Longhurst et al., 1995; Schoepfer et al., 2015). These estimates agree well with the inferred position of the Mino Terrane during the Triassic-Jurassic transition, which was located in the tropical Panthalassic Ocean where it may have been influenced by equatorial upwelling.

Eqs. (1) and (3) yield elevated productivity values for the ‘crisis interval’, generally in the 30,000 to 50,000 mg C cm$^{-2}$ kyr$^{-1}$ range. Productivity at this level is observed at longer time scales only in coastal and upwelling regions (Schoepfer et al., 2015), which are inconsistent with the inferred Kurusu environment. It is worth noting that an increase in calculated productivity in the Rhaetian ‘crisis interval’ is seen regardless of which equation is used, and results from elevated TOC in the numerator of these equations rather than from the sedimentation rate term in the denominator of Eqs. (1) and (3). While the thin bedding prior to the TJB accentuates the apparent spike in productivity in those equations that are sensitive to sedimentation rate (i.e., Eqs. (1) and (3)), maximum productivity values in the pre-extinction interval always exceed the average value for the section by a factor ranging from 1.7 to 2.9 depending on choice of equation.

The thin beds and low inferred sedimentation rates prior to the extinction are likely to be a reflection of low radiolarian productivity in the upper water column. One possibility is that this interval of environmental stress saw a decrease in the ecological importance of radiolarians and a proliferation of non-skeletonized algae such as dinoflagellates or cyanobacteria in response to water-column stratification and nutrient limitation (Schoepfer et al., 2016). Alternatively, the elevation in calculated productivity may be an artifact of organic carbon preservation. The periodic spikes in NAVS content in this interval suggest the development of more reducing conditions in the water column, and the small increase in TOC content may reflect more efficient preservation of the sinking organic carbon flux against a backdrop of consistent or even declining primary productivity. If this is the case, the thinning of the radiolarite beds may be a better indicator of productivity in the surface ocean than TOC content.

Plotting the organic carbon accumulation rate (OCAR) against the overall mass accumulation rate (MAR) in log-log space can be used to distinguish between these two possibilities (Schoepfer et al., 2015). In the Kurusu environment, where the predominant sedimentary component is biogenic silica with minimal dilution by detrital sediment, we would expect the slope of the MAR-OCAR relationship to be close to 1. This is indeed the case, with the full dataset having a slope of 0.90 in log-log space (Fig. 8). A slope lower than unity suggests that the small effect of dilution by detrital sediment is stronger than the effect of enhanced preservation at higher sedimentation rates in most of the section (Schoepfer et al., 2015; see their fig. 18).

Under these near-ideal conditions, the OCAR:MAR ratio will reflect the composition of the planktonic community, with higher ratios indicating a higher proportion of non-biomineralized phytoplankton relative to silica-producing radiolarians. In log-log space, the clusters of Jurassic samples and Rhaetian samples from before the ‘crisis interval’ overlap almost completely. They have slopes of 0.93 and 0.95 respectively, bracketing the overall trend line and suggesting similar mechanisms of preservation. The similar OCAR:MAR ratios (0.86 × 10$^{-3}$ and 0.98 × 10$^{-3}$, respectively) indicate a relatively uniform composition of the planktonic community.

The majority of samples from the latest Rhaetian ‘crisis interval’ fall above this OCAR:MAR trend. While the slope for this set of samples is slightly higher (1.02), it is barely above unity, suggesting that there is no strong preservational effect linked to sedimentation rate. This group shows an elevated OCAR:MAR ratio (1.31 × 10$^{-3}$), indicating a substantially greater ecological role for non-skeletonized phytoplankton. This may be a result of water-column stratification favoring those algae able to fix nitrogen directly from the atmosphere (i.e., non-biomineralized cyanobacteria, Schoepfer et al., 2016). Taken together, these observations suggest a real change in the phytoplankton community—thus, the thinning of the chert beds may not be indicative of declining overall primary productivity, but specifically a decline in the productivity of radiolarians. With only a small increase in the strength of the preservation effect, it is likely that the calculated increase in productivity in the pre-extinction interval reflects a real increase in the biomass of non-skeletonized algae in the upper water column.

5.4. Comparison to other sections

5.4.1. Katsuyama, Inuyama area, Japan

Kurusu is only one of several Japanese TJB sections exposed in the Mino-Tamba-Ashio terrane complex. The Katsuyama section, also located on the Kiso River north of Inuyama, has been extensively studied (Hori, 1992; Wignall et al., 2010; Ikeda et al., 2015; Fujisaki et al., 2016,
2018). While these two sections are less than 1 km apart in the modern day and composed of similar pelagic bedded chert-shale couplets, the evidence suggests that they were deposited in somewhat different environments (Fig. 9). Despite their proximity, the sites occupy different thrust sheets (Fujisaki et al., 2016), and astrochronological analysis yielded a mean sedimentation rate at Katsuyama of only ~0.14 cm kyr⁻¹ (Ikeda and Tada, 2014), which is lower than that estimated at Kurusu. Furthermore, unlike the relatively homogeneous gray-green cherts seen at Kurusu, the Katsuyama section shows substantial colour variation, with brick-red cherts through the Rhaetian and Hettangian grading into gray to white cherts in the upper Sinemurian.

At Katsuyama, Ikeda et al. (2015) identified an interval of purple chert linked to changes in iron minerology that approximately coincided with the ETME. They attributed this event to deep-ocean acidification. However, this event occurred over <100 kyr, and is roughly an order of magnitude shorter than the ‘crisis interval’ at Kurusu. A detailed study of the Katsuyama section by Fujisaki et al. (2016) identified three negative carbon isotope excursions (NCIEs), with durations ranging from 50 to 100 kyr, comparable to the individual NAVS spikes seen at Kurusu (this study). The first NCIE began in the late Rhaetian, approximately 1.8 m below the TJB and well below the base of the Globolaxtorum tozeri Zone. While not dated by Fujisaki et al. (2018), sedimentation rate calculations suggest deposition ~1.3 Myr prior to the TJB (Fig. 9). Much like the NAVS spikes at Kurusu, these NCIE events broadly coincide with increased TOC (although this is ambiguous evidence for changes in productivity). There is no notable enrichment in trace element redox proxies coinciding with these excursions.

5.4.2. Kennecott Point, British Columbia

The Kennecott Point section, located in the Haida Gwaii of British Columbia (Fig. 9), provides another window into environmental conditions in the Panthalassic Ocean during the Triassic-Jurassic transition (Ward et al., 2001, 2004; Longridge et al., 2007; Williford et al., 2007, 2009; Kasprak et al., 2015; Schoepfer et al., 2016). This section is interpreted to have been deposited at slope water depths on the flanks of Wrangellia (also called the Insular Terrane), which would have been a major low-latitude island arc far from the coast of North America at that time (Kasprak et al., 2015). While deposited in shallower water than Kurusu, the Kennecott section can be correlated with Kurusu using radiolarian biostratigraphy (Carter and Hori, 2005).

Like Kurusu, the Kennecott Point section shows a ‘crisis interval’ of increasing ecological stress, on the order of hundreds of thousands of years in duration (Schoepfer et al., 2016). Sedimentation rate calculations based on the long-Carnian model for the Late Triassic (Ogg, 2012),
which has been supported by recent studies (Wotzlaw et al., 2014; Maron et al., 2015), suggests a duration for this interval on the order of ~400 kyr. It is worth noting that the ‘crisis interval’ at Kennecott Point coincided almost completely with the G. tozeri radiolarian Zone, which our age model for Kurusu estimates to have lasted ~400 kyr. Much like Kurusu, the ‘crisis interval’ at Kennecott Point shows a decrease in radiolarian abundance, and biomarker data indicates an increasing importance of non-skeletonized algae such as prasinophytes and cyanobacteria (Kaspark et al., 2015).

Kennecott Point also resembles the Kurusu section in showing repeated disturbances to the sulfur cycle in the pre-extinction interval. Willford et al. (2009) identified two discrete positive sulfur isotope excursions, suggesting near-quantitative sulfate reduction, during the pre-extinction ‘crisis interval’. While these appear to have been episodes of more intense sulfate reduction than those seen at Kurusu, the timing is suggestive of a connection. If the ‘crisis interval’ at Kennecott Point was indeed ~400 kyr in duration, then the section may have only experienced the last two of the three disturbances to the sulfur cycle seen at Kurusu. Willford et al. (2009) also recognized a prolonged positive excursion in sulfide sulfur isotopes above the TJB. Bartolini et al. (2012) determined the age of this shift to be late Hettangian-early Sinemurian, which agrees reasonably well with the early Sinemurian increase in NAVS observed at Kurusu (Fig. 9).

Unlike Kurusu, the beginning of the ‘crisis interval’ at Kennecott Point coincided with the onset of bottom-water anoxia in the depositional environment (Schoepfer et al., 2016), and was linked to declining primary productivity as a result of enhanced water-column stratification and decreased nutrient availability (Ward et al., 2001, 2004; Schoepfer et al., 2016). These disparities may be the result of differences in depositional water depths and in the style of nutrient cycling between volcanic-arc and pelagic environments. If anoxia developed primarily at thermocline water depths, it may have coexisted with oxygenated abyssal waters at Kurusu, while intersecting the seafloor on the slopes of the Wrangellia volcanic arc. At Kennecott Point, the main effect of water-column stratification may have been to inhibit upward mixing of nutrients, while in the pelagic ocean shallower mixing may have been favorable for photosynthesis (see Section 5.5). These inhomogeneous conditions may have controlled the distribution of marine fauna in the latest Triassic, complicating biostatigraphic interpretation.

5.4.3. Levanto section, Peru

The Levanto site, in the Pucará Basin of Peru, is a stratigraphically expanded section extending from the Rhaetian into the Hettangian (Fig. 9). Due to a lack of sedimentary structures attributable to wave action and a general absence of bioturbation, the section is interpreted to have been deposited at slope water depths (Yager et al., 2017) and may represent an environment broadly comparable to that at Kennecott Point, albeit on the slope of continental South America rather than on an offshore volcanic arc.

The ETME was recognized in this section by the disappearance of the ammonoid genus Choristoceras, and the TJB defined by the first appearance of the genus Psiloceras (Schaltegger et al., 2008), both events that can also be recognized at Kennecott Point (Fig. 9). The onset of the pre-extinction environmental disturbance in this section can be recognized most readily as excursions in organic and inorganic carbon isotopes. The timing of the excursions can be constrained using the abundant dated volcanic ashes in the section (Schaltegger et al., 2008; Wotzlaw et al., 2014). These disturbances to the carbon cycle began significantly earlier than the ETME, or the earliest U–Pb ages of CAMP basalt emplacement (Blackburn et al., 2015; Davies et al., 2017; Marzoli et al., 2019).

While no major negative excursion in carbonate isotopes is seen until the TJB, a notable positive excursion in organic carbon isotopes began at 201.85 Ma, i.e., ~400 kyr prior to the TJB (Yager et al., 2017). This estimate for the onset of pre-extinction ecological disturbance is in good agreement with that from Kennecott Point, which may reflect similarities in depositional water depths. A short, discrete positive excursion in organic carbon isotopes occurred earlier, at 202.15 Ma (Yager et al., 2017), approximately coincident with the first spike in sulfide deposition at Kurusu, however this initial disturbance at Levanto is not sustained into the ‘crisis interval’.

5.4.4. Muller Canyon, Nevada, USA

Triassic-Jurassic boundary sections in the Gabbs Range of Nevada (Guex et al., 2004; Ward et al., 2007), on the paleomargin of the North American Craton, represent a significantly different environment than those of other sections considered in this study (Fig. 9). The Muller Canyon section, which is dominated by carbonate lithofacies, was deposited at significantly shallower water depths than Kurusu and the other sections considered above, in a shelf environment estimated to be at or near storm wave base (Corsetti et al., 2015). Environmental changes can be clearly recognized in these strata, in the form of a negative carbon isotope excursion (Ward et al., 2007), as well as a transition to siliciclastic-dominated lithofacies. The latter may result from changes in sea level (Hallam and Wignall, 1999) or enhanced continental runoff in the aftermath of a terrestrial extinction (van de Schootbrugge et al., 2009; Lindstrom et al., 2012; Steinthorsdottir et al., 2012), but may also reflect oceanographic processes that could have potentially stressed marine fauna, such as acidification (Hautmann et al., 2008; Greene et al., 2012; Ritterbush et al., 2014).

Unlike the other Panthalassic sections discussed above, the onset of pre-extinction disturbances at Muller Canyon coincided closely with the disappearance of Choristoceras crickmeyi, an indicator of the onset of the ETME in Panthalassic settings (Corsetti et al., 2015). This horizon also correlates with the beginning of an increase in the TOC-normalized Hg content of the sediment, which does not peak until the TJB (Thibodeau et al., 2016). The section can dated using a combination of ammonoid biostatigraphy and radiometric ash dating (Schoene et al., 2010), yielding an age of ~201.5 Ma for the transition to siliciclastic sedimentation. This age agrees well the earliest emplacement of CAMP basalts (Blackburn et al., 2013; Marzoli et al., 2019). If this transition does reflect marine ecological stresses in this comparatively shallow Panthalassic section (Ritterbush et al., 2014), it suggests a link between water depth and the development of environmental disturbances.

5.5. Mechanisms of environmental disturbance prior to the TJB

The episodic deposition of sulfide minerals at Kurusu in the 1.2 million years preceding the TJB suggests that biological oxygen demand exceeded the oxygen supply in parts of the water column, leading to the production of free hydrogen sulfide. While some studies have found no evidence for sulfidic conditions across the TJB in Mino Terrane strata, this outcome may have been a consequence of sampling strategies and the redox proxies applied. Wignall et al. (2010) did not detect pyrite framboids in the Kurusu section around the TJB, but given that evidence for sulfidic conditions across the TJB in Mino Terrane strata, this may be a consequence of their relatively low sampling resolution in an interval with no clear sedimentological evidence for anoxic conditions. Geochemical approaches to redox conditions based on redox-sensitive trace metal concentrations, which are local proxies reflecting the redox state of the bottom water (Algeo and Maynard, 2004, 2008), have yielded little to no evidence for the concentration of redox-sensitive elements in the TJB interval from Japanese pelagic sections (Hori et al., 2007; Fujisaki et al., 2016, 2018). These observations can be explained if we accept that the abyssal bottom waters of the pelagic ocean remained at least somewhat oxygenated throughout the TJB interval. This is consistent with sedimentological observations of the Inuyama area sections, where the boundary does not correspond with a clear change in sediment colour or the style of deposition, despite the Toarcian anoxic event being easily recognizable sedimentologically (Wignall et al., 2010; Ikeda et al., 2015). Direct evidence for bottom water anoxia is seen only in shallower
Panthalassic sections, such as Kennecott Point (Schoepfer et al., 2016).

Instead, sulfidic conditions are likely to have developed in the oxygen-minimum zone of the thermocline region, below the surface mixed layer, where decomposing organic matter consumes the available oxygen. The development of stratification, in which an unusually stable, shallow pycnocline separates the surface mixed layer from the deep ocean, would likely have provided conditions favorable to sulfide precipitation. A similar pattern, in which strong accumulation of pyrite frambooids is coupled with limited enrichment of redox-sensitive trace metals, has been observed in abyssal Permian-Triassic boundary (~251 Ma) sections in Japan, where it is interpreted as evidence for the expansion of ocean anoxia primarily in the thermocline region of the Panthalassic Ocean, rather than in its deep water mass (Algeo et al., 2010, 2011).

It is worth noting that, at Kurusu, evidence for stratification corresponds with an increase in calculated primary productivity rates, although the magnitude of this increase is likely exaggerated by some of the paleoproducitivity equations. This contrasts with Kennecott Point, where the onset of stratification coincided with declining productivity (Schoepfer et al., 2016). While volcanic influence from the distal CAMP eruptions could be invoked to explain “fertilization” of the pelagic ocean with iron and other micronutrients, we do not see evidence for direct volcanic inputs until the immediate TJB interval, where it appears in the form of high Hg/NAVS ratios. Instead, the divergence may reflect different modes of nutrient cycling in pelagic and arc-adjacent environments.

At Kennecott Point, intensification of water-column stratification appears to have inhibited nitrate recycling from deeper water, requiring direct N fixation by cyanobacteria and limiting productivity prior to the TJB (Kasprak et al., 2015; Schoepfer et al., 2016). In the subtropical gyre environment represented by the Kurusu section, nitrogen limitation was likely acute even prior to development of stratification. In this environment, the development of a relatively shallow mixed layer above a stable chemocline may have stimulated planktonic productivity by keeping phytoplankton within their critical depth, with more time spent in the photic zone (Sverdrup, 1953). While the critical-depth hypothesis has been called into question in high-latitude environments (Behrenfeld, 2010), it is supported as a model for the lower photic zone in oligotrophic subtropical settings (Letelier et al., 2004). Because of the energy requirements of N fixation, a shallow mixed layer may have been especially advantageous to diazotrophs (Dore et al., 2008). If shoaling of the mixed layer led to increased productivity of a non-skeletonized, largely microbial phytoplankton community with cyanobacteria as a major component, then the export of labile organic matter and its decomposition in the thermocline oxygen minimum and the sediments may have led to sulfate reduction and sulfide precipitation.

It is difficult to attribute the evidence for water-column stratification in the central Panthalassic Ocean to the CAMP eruptions, which it appears to have predated considerably. The earliest spike in sulfide content at Kurusu can be estimated at 202.5 Ma, almost a full million years before even the earliest CAMP-associated intrusive activity (201.635 Ma, Davies et al., 2017). Estimates of PCO2 from the Newark-Hartford Basin show carbon dioxide levels declining throughout the Rhaetian, before increasing rapidly following the onset of CAMP emplacement (Schaller et al., 2011, 2013), so there is little evidence of CO2 driving global warming during the ‘crisis interval’. The onset of CAMP intrusion does correspond fairly well to the Ir and Ce anomalies noted by Hori et al. (2007; Schoepfer et al., 2016). A sudden mass extinction occurring against a backdrop of complex and spatially heterogeneous environmental stress is consistent with the canonical ‘greenhouse extinction’ at the end of the Permian (Sun et al., 2012; Song et al., 2014), where diverse benthic communities persisted in shallow environments until the onset of the main phase of large igneous province eruption (Shen et al., 2018).

5.6 Water depth and the timing of environmental stresses

Based on the Panthalassic sections considered in this study, we can trace the onset of environmental stresses from deeper into progressively shallower environments (Fig. 10). These stresses, which likely reflect the development of ocean stratification and more reducing conditions in the oxygen-minimum zone, appear to have occurred in episodes with durations of ~50–100 kyr, separated by ~300–400 kyr intervals of reduced stress. Three of these episodes are identifiable at Kurusu in the form of spikes in sulfide deposition, and at the nearby Katsuyama section in the form of negative carbon isotope excursions (Fujisaki et al., 2018). In the pelagic environments represented by the Japanese sections, these disturbances are manifested as changes in the composition of the phytoplankton community, possible changes in primary productivity, and more reducing conditions in the thermocline region, thousands of meters above the seafloor; the seafloor itself seems to have remained oxygenated through the Triassic-Jurassic transition (Hori et al., 2007; Wignall et al., 2010; Fujisaki et al., 2016).

At slope depths of a few hundred meters, in environments such as those represented by Kennecott Point and Levanto, anoxic conditions in the thermocline region impinged directly on the seafloor. At Kennecott Point, the onset of water-column stratification coincided with the accumulation of redox-sensitive metals in the sediment (Kasprak et al., 2015; Schoepfer et al., 2016). In both slope sections, stressed conditions appear to have become persistent by ~400 kyr prior to the TJB, roughly coinciding with the Globolaxtorum tozeri radiolarian Zone. Only the latter two episodes of disturbance seen in the pelagic sections were felt in slope environments (the first may be present at Levanto as a brief positive carbon isotope excursion; Yager et al., 2017). These considerations imply that the pycnocline of the Late Triassic Panthalassic Ocean was relatively deep, and that it shallowed during the latest Rhaetian, between 1 Myr and 400 kyr prior to the TJB.

At Kennecott Point, this stratification surface impinged on the arc slope within the photic zone during the ETME, promoting ecological expansion of anaerobic bacteria such as sulfide oxidizers and methanotrophs, and introducing ammonium into the surface ocean (Kasprak Os isotopes began as early as 203 Ma, which is consistent the age proposed by Callegaro et al. (2012) for the Norian-Rhaetian boundary, but which cannot be easily reconciled with the most recent dates for the onset of CAMP emplacement (Marzoli et al., 2019) or the Norian-Rhaetian boundary (Wozlaw et al., 2014; Kent et al., 2017). One possibility is that magmatic intrusions into sediments (Heimdal et al., 2018, 2019) during early activity of the Central Atlantic Magmatic Province generated greenhouse gases, including thermogenic methane and halocarbons (Heimdal et al., 2020), well-before the emplacement of the well-dated CAMP volcanic rocks. While CAMP intrusive activity can currently only be dated to the ~100 kyr prior to CAMP eruptions (Davies et al., 2017), it is possible that additional sills related to earlier phases of Gondwanan rifting have yet to be identified (Svensen et al., 2018).

Extensive, extrusive CAMP volcanism (Blackburn et al., 2013; Percival et al., 2017; this study), recorded even in the distal setting of the central Panthalassic Ocean as a discrete interval of high mercury flux, does seem to have contributed to a major turnover in radiolarians across the Panthalassic basin (Carter and Hori, 2005; Hori et al., 2007; Kuroda et al., 2010), possibly due to some combination of acidification (Hautmann et al., 2008; Greene et al., 2012; Ikeda et al., 2015), and intense surface warming (McElwain et al., 1999; Ruhl et al., 2011) leading to water column stratification and shoaling of the chemocline (van de Schootbrugge et al., 2007; Richoz et al., 2012; Kasprak et al., 2015; Schoepfer et al., 2016). A sudden mass extinction occurring against a backdrop of complex and spatially heterogeneous environmental stress is consistent with the canonical ‘greenhouse extinction’ at the end of the Permian (Sun et al., 2012; Song et al., 2014), where diverse benthic communities persisted in shallow environments until the onset of the main phase of large igneous province eruption (Shen et al., 2018).
et al., 2015; Schoepfer et al., 2016). At Kurusu, it appears to have been linked to CAMP volcanism, with volcanic inputs of mercury exceeding the rate at which it could be sequestered in sulfides. These explanations need not be mutually exclusive, if the main phase of CAMP volcanism coincided with an interval of rapid warming (McElwain et al., 1999; Ruhl et al., 2011; Steinthorsdottir et al., 2011; Schaller et al., 2011, 2015). The strong link between the onset of CAMP volcanism and the development of acidic, inhospitable conditions in shelf environments in Nevada (Hautmann et al., 2008; Greene et al., 2012; Ritterbush et al., 2014) suggests that the main stage of the CAMP eruptions may have led to reducing, acidic deep waters impinging on shallow shelf environments along the western margin of the North American Craton.

6. Conclusions

The Kurusu section records a depositional interval extending from the Rhaetian to the late Hettangian or (probably) Sinemurian, thus spanning the Triassic-Jurassic boundary. While mercury is present throughout the section, it is strongly positively correlated with NAVS spanning the Triassic-Jurassic boundary. While mercury is present throughout the latest Rhaetian, modulated by climatic cyclicity at Milankovitch orbital periodicities. The drivers of this process remain mysterious, as they predate even the earliest dated CAMP activity, but may reflect as-yet unrecognized intrusions related to rifting of Gondwana. The Triassic-Jurassic boundary, which cannot be strongly distinguished from the ETME in Panthalassic environments, may represent the chemocline rising into the photic zone and impinging on continental shelf margins during the main phase of CAMP eruptions.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.earscirev.2021.103870.

Declaration of Competing Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to thank the University of Washington Earth and Space Sciences department and NSF GK-12 Ocean and Coastal Interdisciplinary Science Program for their financial support while completing fieldwork on the Kurusu section. We would also like to thank Sofie Lindström and an anonymous reviewer for providing valuable feedback that greatly improved this manuscript. JS acknowledges support from Natural Science Foundation of China (92055201, 42072037), 111 Project from National Bureau of Foreign Experts and the Ministry of Education of China (BP0820004). TJA acknowledges support from the National Science Foundation (EAR-1733977).

References


