Marine Deoxygenation Predates the End-Triassic Mass Extinction Within the Equatorial Panthalassa and its Influence on Marine Ecosystems Before the Biotic Crisis

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ABSTRACT

The end-Triassic Mass Extinction (ETME) was one of the "Big 5" mass extinctions of the Phanerozoic and is thought to have been caused by a series of environmental changes triggered by the emplacement of the Central Atlantic Magmatic Province (CAMP). While the overall driver of the ETME is well-accepted, the specific roles of subsequent environmental changes in driving the extinction remain unresolved due to both spatial and temporal biases within existing geochemical records. Additionally, recent studies suggest that environmental deterioration may have preceded the emplacement of both CAMP and the ETME. Here, we present nitrogen isotope ($\delta^{15}N$) and iron speciation data from a sedimentary succession located in Grotto Creek, Alaska in order track changes in the marine nitrogen cycle and redox across the upper Norian Stage of the Triassic through lower Hettangain Stage of the Jurassic (~215 to 198 million years ago). The geologic succession at Grotto Creek represents deeper water marine deposition in eastern equatorial Panthalassa, likely capturing regional oceanic redox trends. $\delta^{15}N$ records from Grotto Creek show a pronounced positive excursion of +3% that initiates in the upper Norian, peaks near the Norian-Rhaetian boundary (NRB; ~208.5), and declines through the ETME and into the Hettangian. Throughout this interval, iron speciation data show persistent anoxic conditions and occasional euxinia occurred in the local bottom waters. We propose that the positive δ^{15} N and iron speciation data from Grotto Creek reflect a progressive deoxygenation of the upper water column with the expansion of the equatorial oxygen minimum zone (OMZ). Specifically, the δ^{15} N excursion reflects a shift in the dominant processing of bioavailable nitrogen from uptake and nitrification under oxic conditions to incomplete denitrification followed by complete denitrification as deoxygenation progressed. Records from existing study sites in other regions of the Panthalassa reflect similar redox fluctuations and support that this deoxygenation was a regional phenomenon. Other recent studies of the Late Norian and Rhaetian also document declines in biodiversity that predate the ETME, as well as, carbon isotope excursions, likely reflecting perturbations to the carbon cycle. Together, this evidence suggests that increasingly lowoxygen conditions initiated at least ~ 8 Ma before the emplacement of CAMP and likely paved the way for the ETME.

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GENERAL AUDIENCE ABSTRACT

The end-Triassic mass extinction (ETME) occurred ~ 201 million years ago and was associated with a large drop in global diversity. The extinction is thought to be due to a warming climate resulting from greenhouse gasses released during the eruption of the Central Atlantic Magmatic Province (CAMP). Although the ETME is one of the largest extinction events of the last ~500 million years, the environmental changes leading to the extinction, and before the CAMP eruption, are not well understood. We studied the Grotto Creek section in Alaska which is a sequence of sedimentary rocks that record the deep ocean environment from the ancient Panthalassa or Paleo-Pacific Ocean. This section also provides a relatively complete record of the time before, during, and after the ETME. Here, we present the stable isotopes of nitrogen ($\delta^{15}N$) from these rocks that show disturbances to the nitrogen cycling that occurred in the ocean more than ~ 8 million years before the ETME. We show that δ^{15} N and iron data from Grotto Creek document falling ocean oxygen levels before the ETME. We also find that our $\delta^{15}N$ agrees with other environmental proxies that also reflect declining oxygen levels in the oceans along with decreases in marine animal diversity well before the ETME. These geochemical records help to show a more complete picture of how environments changed in the Panthalassa before the ETME

Dedication

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Introduction

The Latest Triassic ($\sim 237 - 201.3$ Ma) represents a time of disturbance to marine and terrestrial ecosystems that culminated with the End-Triassic Mass Extinction (ETME). The ETME was characterized by $\sim 63\%$ loss of marine invertebrate diversity at the genus-level as well as major changes in environments and perturbations to biogeochemical cycles that occurred immediately before the Triassic-Jurassic transition (Alroy et al., 2008, Rigo et al., 2020). Although punctuated intervals of environmental instability have been identified throughout the Triassic, the ETME remains the most notable of these events in terms of total diversity lost, particularly within the marine realm (Korte et al., 2019; Rigo et al., 2020). While there is a consensus on the ultimate cause of the ETME, the emplacement of the Central Atlantic Magmatic Province or CAMP, the proximate causes of extinction have long been a subject of study. These proximate causes include global warming driven by input of greenhouse gasses into the atmosphere (Huynh and Poulsen 2005); sea-level fluctuations (Hallam and Wignall 1999); wildfires (Fox et al., 2022a; Fox et al. 2022b); soil erosion (van de Schootbrugge et al., 2020); ocean acidification (Greene et al., 2012), and marine deoxygenation (He et al., 2020). One proximate extinction mechanism, marine deoxygenation, or oxygen decline, also has the potential to induce environmental instability through the alteration of biogeochemical cycles and control on oceanic productivity and biodiversity (Naafs et al., 2019). However, the spatial extent of deoxygenation during and around the interval that contains the ETME is under-constrained.

Along with the proximate causes of the ETME, how marine environments changed leading up to the ETME remains a subject of interest. Recent studies suggest that several minor and localized extinctions potentially preceded the ETME by ~7 Ma near the boundary between the Norian-Rhaetian stages of the Triassic (NRB; Rigo et al., 2020, Zaffani et al., 2017). In addition, evidence of a carbon cycle perturbation, recorded as a negative carbon isotope excursion (δ^{13} C), has been identified at the NRB (Rigo et al., 2020). This δ^{13} C excursion has been found in multiple sedimentary successions representing deposition in the Panthalassa and Tethys oceans and suggests a potentially global scale disruption to the carbon cycle (Rigo et al., 2020). However, age dating of CAMP emplacements suggest that the earliest phases of eruption (201.635 ± 0.029 Ma) post-date the NRB carbon excursion and extinctions by up to ~ 6 Ma (Davies et al., 2017; Blackburn et al., 2013) and thus cannot be invoked as the drivers of these events. Therefore, the trigger of this earlier carbon cycle disruption remains unresolved.

To better evaluate the potential role of deoxygenation before and during the ETME, we present redox proxy data from the sedimentary succession at Grotto Creek located in the Wrangellia terrane of Alaska (Fig. 1; Caruthers et al., 2022; Witmer, 2007). The McCarthy Formation, exposed at Grotto Creek, is of particular interest as it represents a relatively complete record of deep water deposition in the ancient Panthalassa leading up to, during, and in the wake of the ETME (Caruthers et al., 2022). Because of this, Grotto Creek has the potential to capture the record of environmental change within the equatorial Panthalassa before the ETME. Here, we utilize the stable isotopes of sedimentary nitrogen (δ^{15} N) and iron speciation in order to evaluate the initiation, duration, and extent of redox and environmental changes that led up to the ETME.



Fig. 1. **A.** Modern location of Grotto Creek field site in Alaska with an annotated photo of the area visited during the two field campaigns, 2017 and 2019, where samples used for this study were collected. **B.** General stratigraphic framework of the Grotto Creek site,

along with the broader Wrangell Mountains, based on Veenma et al., (2022), Witmer (2007), and Caruthers et al., (2022). This study focuses on the lower member of the McCarthy Formation.

Nitrogen as a proxy

Nitrogen is an essential component of the building blocks of life (Mettam and Zerkle, 2021) and because of this, bioavailable nitrogen (in the form of NH₃, NH₄⁺, NO₂⁻, and NO₃⁻) is a vital nutrient in the oceans. Nitrogen is also cycled in marine environments by several biologically mediated processes (Fig. 2) and many of these processes are sensitive to the redox conditions of the environment. Importantly these processes fractionate, or partition, the isotopes of nitrogen differently and different biological pathways impart different fractionations depending on the mechanism of the reaction taking place (Table 1.; as reviewed by Mettam and Zerkle, 2021). The sum of those fractionations is captured by the nitrogen isotopes (δ^{15} N) of sedimentary organic matter and when the dominant biological pathways of nitrogen cycling and/or the source of bioavailable nitrogen change, the local δ^{15} N of marine organic matter will change. As noted above biologically available sources of nitrogen include ammonia (NH₃) and ammonium (NH₄⁺) and the oxidized species nitrite (NO₂⁻) and nitrate (NO₃⁻); their availability is dictated by redox dependent microbially mediated pathways. These pathways and their net isotopic effects are summarized next.

Pathway	Overall	Fractionation	Net isotopic
	Reaction		effect
N fixation	$N_2 \rightarrow NH4^+$	-2‰	~ 0‰
Nitrification	$\rm NH4^+ \rightarrow \rm NO3^-$	$\rm NH4^+ \rightarrow \rm NO2^- ~(\sim 12 - 16\%)$	~ 0‰
		$NO_2^- \rightarrow NO_3^- (\sim -13\%)$	
Denitrification	$NO_3 \rightarrow N_2$	Up to -25‰	~ 2‰ - 25‰

Sedimentary	$NO_3 \rightarrow N_2$	Up to -25‰	~ -3‰ - 0‰
denitrification			
Anammox	$\mathrm{NH_4^+}$ + $\mathrm{NO_2^-}$	Up to -25‰	~ 2‰ - 25‰
	\rightarrow N ₂		
N assimilation	NH4 ⁺ or NO3 ⁻	~ 0‰	~ 0‰
	$\rightarrow N_{Org}$		
Respiration/ uptake/			
remineralization	$N_{Org} \rightarrow NH4^+$	~ 4‰	≥ 3‰

Table 1. Dominant pathways controlling the different species of bioavailable nitrogen within the oceans. These reactions are microbially mediated and have fractionations associated with the reaction(s) but may have a different net isotopic effect on the resulting organic nitrogen pool captured sedimentary organic matter.



Fig. 2. Graphic representation of the dominant reactions involved in the marine nitrogen cycle (Summarized in Table 1). The dark blue shaded area represents an oxygen minimum

zone (OMZ) and the brown shaded area represents sediments on the ocean floor. Black arrows indicate reactions while dashed gray arrows indicate the release of N_2 gas into the atmosphere. Modified from Robinson et al. (2012).

Nitrogen cycle pathways and oxygen concentrations

If a water column is well oxygenated, nitrogen uptake through respiration, and to a lesser extent nitrification, is dominant and nitrate (NO₃⁻) is the most abundant pool of bioavailable nitrogen (Fig 2.; Mettam and Zerkle, 2021). Nitrogen uptake through respiration results in a negative fractionation of ~ - 3‰ which can enrich the local residual dissolved δ^{15} N pool by a few permille (Fig. 3; Somes et al., 2010). The fractionations resulting from nitrification, the oxidation of ammonium, is the result of net isotope effect of two processes, firstly from the conversion of NH₄⁺ → NO₂⁻ (~ 12 - 16‰) and the subsequent conversion of NO₂⁻ → NO₃⁻ (~ -13‰) preferentially utilizing ¹⁵N bearing NO₂⁻ (Sigman, 2009). In the modern oceans, the net isotope effect of nitrification is generally negligible due to the quantitative conversion of NH₄⁺ to NO₃⁻ (Stüeken et al., 2016; Mettam and Zerkle., 2021).

During episodes of oxygen depletion to suboxic levels, denitrification (the reduction of nitrate by organic carbon) is the dominant microbially mediated pathway and NH4⁺ becomes more abundant in the local bioavailable nitrogen pool (Fig. 2; Algeo et al., 2014; Higgins et al., 2012; Robinson et al., 2012; Mettam and Zerkle, 2021). Denitrification preferentially utilizes ¹⁴N bearing nitrate and subsequently leaves behind residual nitrate enriched in ¹⁵N resulting in more ¹⁵N incorporated into the organic matter (Table 1.; Mettam and Zerkle, 2021). However, in oxygenated oceans like the modern, denitrification is constrained to oxygen minimum zones (OMZ) that can be found at depths in excess of 200 meters and often occur underneath areas of high primary productivity (Algeo et al., 2014; Higgins et al., 2012; Robinson et al., 2012). The expansion of OMZs, through the increased export of organic matter from the photic zone, can result in increased denitrification, subsequently leaving behind a pool of residual NO3⁻ that is enriched in δ^{15} N (Fig. 3; Algeo et al., 2014; Higgins et al., 2012; Robinson et al., 2012; Robinson et al., 2012; Sephton et al., 2002).

As the residual NO₃⁻ is assimilated into organic matter its δ^{15} N values will be enriched in ¹⁵N (Higgins et al., 2012; Robinson et al., 2012). If oxygen concentrations continue to decline and denitrification consumes all the available nitrate, nitrogen fixation becomes the dominant source of bioavailable nitrogen (Fig. 3). Nitrogen fixation, the process where diazotrophs convert atmospheric N₂ into the bioavailable forms of nitrogen NH₃ and NH₄⁺, results in a residual δ^{15} N value of ~ 0 ‰ (Table 1; Fig. 2; Brandes and Devol., 2002). The progressive deoxygenated conditions result in a pathway shift from denitrification to nitrogen fixation forming a less ¹⁵N enriched δ^{15} N signature through the incorporation of the newly fixed nitrogen into the biomass (Fig 3; Mettam and Zerkle, 2021; Higgins et al., 2012; Robinson et al., 2012).



Fig. 3. Qualitative graph displaying the relationship between bulk $\delta^{15}N$ and oxygen concentrations within marine systems. Modified from Quan et al. (2013).

Iron speciation as an additional redox proxy

In addition to δ^{15} N, we also present iron speciation records spanning the same interval from the Norian though the Hettangian at Grotto Creek. Iron speciation is used to distinguish water column redox conditions using the ratio of highly reactive iron (Fe_{HR}) to the total iron (Fe_T) within a sample (Poulton and Canfield, 2005; He et al., 2022). Fe_{HR} refers to iron found in mineral phases that will react with hydrogen sulfide to form pyrite or that found in the pyrite itself. It is delivered to sedimentary basins predominantly as iron oxide minerals, however under anoxic conditions, these oxides are reductively dissolved, releasing aqueous ferrous iron. This ferrous iron can be transported and further cycled along chemoclines (a vertical chemical gradient within bodies of water) underlain by anoxic water where it eventually can form minerals that are deposited in the sediments. This process is known as the iron shuttle and results in enrichments of Fe_{HR} in sediments that can be tracked with Fe_{HR}/Fe_T (Poulton and Canfield, 2005; Poulton and Raiswell, 2002; reviewed by Raiswell et al., 2018).

Studies of modern and ancient sedimentary systems provide a framework for the interpretation of Fe_{HR}/Fe_T. Fe_{HR}/Fe_T < 0.22 are indicative of sediments deposited under oxic water columns; Fe_{HR}/Fe_T > 0.38 indicates deposition under anoxic water columns; and Fe_{HR}/Fe_T in between 0.22 and 0.38 can reflect deposition under oxic or anoxic water columns (as reviewed by Poulton, 2021; Poulton & Canfield, 2011; Raiswell & Canfield, 2012). Sediments determined as deposited under anoxic water column conditions (Fe_{HR}/Fe_T > 0.38) can be further classified based on the proportion of the Fe_{HR} pool found in pyrite (Fe_{py}): Fe_{py}/Fe_{HR} < 0.6 indicates an anoxic and iron-rich (ferruginous) water column; > 0.8 is representative of anoxic and sulfidic (euxinic) water column. Fe_{py}/Fe_{HR} between 0.6 to 0.8 are considered equivocal and could represent deposition under either ferruginous or euxinic water column (Anderson & Raiswell, 2004; Benkovitz et al., 2020; Poulton, 2021; Raiswell et al., 2018).

When interpreting paleoredox conditions, there can be apparent discrepancies between interpretations drawn from sedimentological, paleontological, and geochemical data based solely on one type of data (e.g., Poulton, 2021). For example, it is not uncommon to have geochemical data that suggest water-column anoxia in sedimentary intervals that contain benthic fauna (e.g., Dahl et al., 2019; Kenig et al., 2004). These disparate phenomena can be resolved by understanding that sedimentary deposits record temporally - and spatially - integrated signals. Benthic colonization that requires bottom water oxygenation can occur on short time scales (annual, decadal, etc.) while some geochemical proxies (including iron speciation) record water-column redox conditions over the longer time frames (e.g., Kenig et al., 2004; Sageman & Lyons, 2003). Conversely, geochemical evidence of short intervals of anoxia can be destroyed when the water column becomes oxygenated, and especially if the sediment is later mixed by bioturbation or currents. The combination of the $\delta^{15}N$ and iron speciation can be leveraged together to reconstruct redox in different depths in the water column (e.g., Stüeken et al., 2016; Poulton and Canfield, 2005; Robinson et al., 2012). Stücken et al. (2016) notes the iron speciation proxy as an indicator of bottom water redox conditions, while nitrogen isotopes in organic matter reflect the redox control reactions sources of bioavailable nitrogen to the photic zone. Thus, $\delta^{15}N$ can be used to reconstruct the redox state of the upper water column while iron speciation represents the lower water column. The insight gained from understanding the time-and spatial integration of these signals help us to interpret the conditions of Grotto Creek data below.



Fig. 4. Late Triassic global paleogeographic reconstruction displaying the approximate location of the Central Atlantic Magmatic Province (CAMP) during the ETME,, and the Grotto Creek field site (marked as a star). Orange and green circles indicate sites in Panthalassa and the Tethys, respectively, where nitrogen isotope data from the interval around the ETME are available. Map modified from Blakey (2014) and; Caruthers et al., (2022.

Geologic setting

The Grotto Creek site sits within the remnants of the Wrangellia Terrane now located in the Wrangell Mountains of southcentral Alaska (Fig 1A). The Triassic to lower Jurassic successions are exposed in sections of the northern block of the terrane, in the Wrangell Mountains, as well as the southern block, in southwestern Canada. Previous studies, including paleomagnetic, geochronologic, paleontologic data, have determined that Wrangellia sat in the tropical latitudes of the eastern Panthalassa during the late Triassic and Early Jurassic (Fig. 4; Caruthers and Stanley, 2008). The Upper Triassic succession order consists of, in ascending order, the Chitistone and Nižná limestones and McCarthy Formation (Fig. 1B). The Chitistone and Nižná limestones are composed of carbonate ramp and reef facies that hosted a diverse shallow marine ecosystem (Caruthers et al., 2022; Veenma et al, 2022). These units are overlain by the McCarthy Formation that is mainly composed of calcareous and siliceous mudstones deposited outboard of a mixed carbonate-siliceous ramp (Fig. 1B; Witmer, 2007; Caruthers et al., 2022; Veenma et al., 2022). The transition between these units is hypothesized to represent the drowning of the carbonate platform that took place in the later Norian resulting from thermal subsidence of northern Wrangellia (Armstrong et al., 1969).

Caruthers et al. (2022) established geochronology of the succession at Grotto Creek through a combination of biostratigraphic, carbon isotope, and U-Pb zircon data. The late Norian Cordilleranus ammonoid biozone spans from the section base (-30 m) to ~4m as indicated by the presence of *Monotis*, ammonoids and age-specific conodonts. The NRB occurs at ~4m as evidenced by overlapping examples of Norian fauna (e.g. Rhacophyllites debilis) and the lowest occurrence of Rhaetian ammonoids (Vandaites cf. suttonensis). U-Pb dates, taken from bentonite beds, bracket the NRB and place the Grotto Creek NRB at ~ 209 Ma. Additionally, organic carbon isotopes start low in this interval, presumably capturing the nadir of the NRB negative carbon isotope excursion. Rhaetian ammonoids are present in the section above the NRB until ~29m where lowest in situ Jurassic ammonoid co-occurs with the highest in situ example of Triassic conodonts. However, poor preservation combined with the next robust biostratigraphic indication of the Hettangian ~6m above the Triassic-Jurassic co-occurrence interval requires the T-J transition to be defined as an interval between ~29-35 m. The T-J transition interval is followed by lower-mid Hettangian ammonoids, composed of both in situ and float samples (Cauthers et al., 2022). The carbon isotope record across the T-J transition corroborates these age assignments with three negative excursions associated with the end-Triassic observed in stratigraphic sections globally.

Methods and Materials

Whole rock samples were collected at approximately 0.5 m - 1 m intervals, when conditions allowed, over the course of two field campaigns that took place in the summer

of 2017 and 2019. Samples were subsequently cleaned, cut to reveal an unweathered face, and powdered at the Virginia Tech Biogeochemistry lab. For nitrogen isotope analyses, sample powders were then treated with 2 M HCl to remove all carbonate before. Residues were rinsed and flushed with deionized water until attaining a pH of 5 or higher, dried in a 55° C oven and then ground, using a mortar and pestle, into a homogeneous powder. Samples were weighed into tin capsules standards USGS 25 (-30.41 \pm 0.16 ‰) and USGS 26 (+53.75 \pm 0.15 ‰) and the commercial standard low organic soil were run between every 8-14 samples to calibrate reference gas, monitor instrument drift, and normalize data to the AIR scale. Isotopic analyses were performed using an Isoprime isotope ratio mass spectrometer (IRMS) with an Elementar vario Isotope Cube, elemental analyzer (EA). Nitrogen isotopic data were corrected for drift over the course of the run and then normalized to the AIR scale to determine δ^{15} N values. Reproducibility of nitrogen isotope analyses yielded standard deviations for the USGS25 and USGS26 standards of 0.21 and 0.26 respectively. The organic total nitrogen content of each sample was determined using the area of the N₂ peak measured by the elemental analyzer calibrated to a size series of low organic soil elemental standards. In addition, low organic soil standards, utilized for nitrogen contents, were spaced throughout the run in order to accommodate instrument drift over the course of the run. Nitrogen contents calculated using this method averaged less than 5% error from the known composition of the standards. We use the total organic carbon (TOC) contents of these samples as reported by Carauthers et al. (2022) to calculate carbon and nitrogen ratios below.

The sequential iron extractions used for this study followed the method of Poulton and Canfield (2005). Briefly, 0.1 to 0.2 g of sample powder was reacted sequentially with three different reagents used to target specific iron bearing mineral phases in the rock: (1) 1 M sodium acetate solution buffered to pH 4.5 for 48 h at 50°C to target iron in carbonate minerals (Fe_{carb}) such as siderite and ankerite; (2) sodium dithionite (50 g/L) solution buffered to pH 4.8 for 2 h to target iron in oxides and hydroxides (Fe_{ox}) such as goethite and hematite; and (3) 0.2 M ammonium oxalate and 0.17 M oxalic acid buffered to pH of 3.2 for 6 h to target iron in magnetite (Fe_{mag}). After each extraction, iron concentrations in

the solutions were quantified by spectrophotometry using the modified version of the ferrozine method of Stookey (1970) and Viollier et al., (2000). Replicate sample extractions from each extraction yielded reproducibility better than 7%.

Pyrite iron determined was extracted using the chromium reducible sulfur (CRS) extraction of Canfield et al., (1986). In this method, ~0.1 to 0.3 g of sample powder was reacted with a 1 M chromous chloride solution while being heated for 2 h on a distillation line. The sulfur in pyrite liberated as H₂S gas was subsequential flushed into a vessel filled with a zinc acetate solution using nitrogen gas precipitating solid ZnS. This ZnS was then converted to Ag₂S by adding AgNO₃ solution to the zinc acetate solution with the captured ZnS. The precipitate was dried and weighed to determine the pyrite iron contents (Fe_{py}) by assuming a 2:1 stoichiometric relationship between sulfur and iron from the original pyrite (FeS₂). Recovery of sulfur from pure pyrite run at the same time as the samples was within 95% of the expected value. Replicate analyses of the samples via this method were within 5%.

Total iron (FeT) contents were determined following a modified version of the method of Aller et al., (1986). Here 0.3 g of sample powder was placed in crucibles and heated in a muffle furnace to 900°C for 6 h. The ashed powders were weighed, homogenized, and placed in sealed Savillex vials with concentrated 12 M HCl, sealed, and heated to 145° C for 48 h. After this, an aliquot of solution was analyzed to determine its iron contents using the ferrozine spectrophotometry method described above and replicate analyses of the samples were within 5%.

Results

$\delta^{15}N$ results

We observe two nitrogen isotope excursions in the Triassic-Jurassic succession at Grotto Creek: The δ^{15} N record displays an overall +3‰ excursion initiating the middle Norian

and peaks near the Norian-Rhaetian boundary (Fig. 4). Pre-excursion $\delta^{15}N$ values of ~ 0.5 - 2‰, occur within the middle Norian (-30 m - 20 m). $\delta^{15}N$ values gradually become more positive at -20 m within the section. The $\delta^{15}N$ values reach their most positive values (3 - 3.7‰) just past the Norian-Rhaetian boundary (~ 209 Ma at ~ 15 m). While the most positive $\delta^{15}N$ values occur in a cluster around ~15 m elevated $\delta^{15}N$ values occur from 0 - 30 m within the section. $\delta^{15}N$ values decline back to near pre-excursion values (1 - 2‰) at ~ 37 m across the ETME and into the Hettangian. Higher in the section, further into the Hettangian, another $\delta^{15}N$ positive excursion initiates near 60 m. This excursion occurs over a relatively short stratigraphic interval (60 m - 65 m), but is of a similar magnitude, $\delta^{15}N$ values of ~3.5‰, to the one found lower in the section.



Fig. 5. Stratigraphic plots of nitrogen isotope and iron speciation proxy data from Grotto Creek displayed with the biostratigraphic, geochronologic, and lithologic framework established by Caruthers et al., (2022). Nitrogen isotopes are depicted in blue, Fe_{HR}/Fe_{T} in red, Fe_{PY}/Fe_{HR} in yellow, and organic carbon isotopes from Caruthers et al., (2022) in green. Thresholds for Fe speciation, defined by Poulton and Canfield (2005), are displayed as dashed lines in both the Fe_{HR}/Fe_{T} (0.38) and Fe_{PY}/Fe_{HR} (0.6 and 0.8) plots. Ash bed dates

established in Caruthers et al., (2022) are shown next to the corresponding stratigraphic height of the sampled bentonite. Please note that the ETME is displayed as the gray shaded interval.

Iron speciation results

The dominant highly reactive iron pools in the succession from Grotto Creek are pyrite and iron carbonate that both contain reduced (ferrous) iron and indicate reducing conditions within the sedimentary porewaters. Total iron contents average 1.00 ± -0.6 wt%. The majority of Fe_{HR}/Fe_T data have Fe_{HR}/Fe_T > 0.38 and indicate deposition under an anoxic water column (Fig. 5.; Poulton and Canfield, 2011). Fe_{HR}/Fe_T values remain well above the 0.38 threshold, reflecting anoxic conditions throughout the section (-30 m - 60 m), with an average Fe_{HR}/Fe_T ratio of ~0.83. The Fe_{PY}/Fe_{HR} ratios, however, are more variable through the section, but do indicate the majority of the samples were deposited under anoxic, ferruginous conditions as the majority plot below 0.6. It should be noted that samples that plot above the 0.6 threshold and near, and occasionally above, the 0.8 threshold occur most commonly from ~25 m - 40 m in the section (Fig. 5).

Discussion

Reliability of the ancient $\delta^{15}N$ archive

The δ^{15} N of marine sediments preserved in the geologic record can reflect the composition of fixed marine nitrogen but can also be influenced by additional sources of organic matter and/or later alteration during burial. Here, we investigate the potential effects of thermal maturity, selective volatilization, and the addition of terrestrial organic matter to evaluate whether the δ^{15} N signal observed at Grotto Creek is reflective of original marine organic matter.

Thermal maturation

The nitrogen isotopic composition of sedimentary organic matter can be altered by thermal maturation experienced by the organic matter during burial and metamorphism. Thermal denitrogenation, the thermal loss of nitrogen, increases sedimentary C/N ratios but studies suggest the alteration of the $\delta^{15}N$ of the residual organic matter may be as low as 1‰ through lower greenschist facies (Ader et al., 1998; 2006; 2016; Algeo et al., 2014). The thermal maturity of the McCarthy Formation was previously evaluated by Witmer (2007, Appendix C) using Rock-Eval pyrolysis that yielded T_{max} values of ~ 461 - 482°C. These T_{max} values indicate the maturation stage of organic matter within the bulk rock sample determined through heating the sample in a specialized pyrolysis oven (Peters and Cassa, 1994). However, it should be noted these temperatures are higher than the rock has physically experienced. Conodonts from Grotto Creek have a Conodont Alteration Index (CAI), a proxy for the maximum temperature experienced by sedimentary rocks, of 3 that corresponds to a temperature range of 110 - 200°C (McMillin and Golding, 2019). It should be noted that the max temperature experienced by the succession likely did not exceed the threshold necessary for thermal alteration of the nitrogen isotope signal (Algeo et al., 2014; Robinson et al., 2012). Burial related diagenesis, where thermal maturation is low but was the dominant alteration mechanism, may result in the transformation of organic matter bound nitrogen into clay bound ammonium but remains within 1-2‰ of bulk δ^{15} N values (Mingram et al., 2005; Ader et al., 2016). While each of these processes may impart small alterations of the bulk δ^{15} N values, we would expect to observe increasing δ^{15} N values with depth, assuming temperature increases with depth, if they were the main mechanism controlling $\delta^{15}N$ variation in the succession at Grotto Creek. Instead the positive $\delta^{15}N$ excursions we observe at the Grotto Creek section are likely to reflect other processes with potentially only a small overall shift (1-2‰) in the data population attributable to thermal alteration.

Microbial alteration during early diagenesis

During early diagenesis microbial activity may result in the alteration of primary sedimentary $\delta^{15}N$ values through several processes dictated by pore water oxygen

concentrations. Remineralization of organic matter in oxic pore waters can enrich the residual organic matter in 15 N by up to ~ 4‰ through nitrification of liberated nitrogen in the form of ammonium (NH4⁺) (Ader et al., 2016; Prokopenko et al., 2006; Stüeken et al., 2016). Although nitrification has the potential to impart a large negative fractionation, the presence of oxygen hampers the isotopic effect through rapid oxidation of ammonia (Mettam and Zerkle, 2021). Deamination, or the release of ¹⁵N depleted NH₄⁺ into sediment pore waters during organic matter decomposition (remineralization), occurs first followed by the partial oxidation of the NH_4^+ (Prokopenko et al., 2006; Algeo et al., 2014). However, if the NH₄⁺ produced by remineralization is bound by clay minerals, the bulk δ^{15} N values may experience little to no alteration (Prokopenko et al., 2006). Under anoxic pore water conditions the release of NH4⁺ into the water column above, however, can also produce fractionations resulting in the depletion of 15 N by <1 ‰ (Altabet et al., 1999). Sedimentary denitrification also has the potential to alter $\delta^{15}N$ values up to -3 % however the fractionation tends to be notably weaker (~0‰) due to pore water diffusion related limitations (Sigman et al., 2009). While each of these processes have the potential to alter the primary isotopic signature of sedimentary organic matter δ^{15} N they are unlikely to be the main source of stratigraphic trends. Instead, we suggest that the sample-to-sample variation of ~ 1 - 2 ‰ δ^{15} N observed at Grotto Creek may be associated with the smaller (1 - 2‰) fractionations from microbial alteration during early diagenesis.

Mixing organic matter sources

Mixing of organic matter sources, such as the input of terrestrial organic matter, has the potential to significantly modify bulk δ^{15} N values and must be considered when evaluating nitrogen isotope records. Marine organic matter tends to exhibit lower C:N ratios (< 10) terrestrial nitrogen exhibits substantially higher C:N ratios (~20 - 200; Meyers et al., 1997). This allows for the evaluation of the contribution of terrestrial organic matter to bulk δ^{15} N through the utilization of C:N ratios of Grotto Creek. We find that the Grotto Creek C:N ratios average in the 7-10 range and reflect the dominant contribution of marine organic matter to the observed δ^{15} N record with little if any contribution from terrestrial sources (Fig. 5). Additionally, terrestrially derived nitrogen can also be incorporated into clay

mineral phases that are later deposited in the marine environment (Robinson et al., 2012). However the low aluminum contents (~ 4 wt%) found in the succession at Grotto suggests low detrital clay contents indicate minimal terrestrially derived organic matter (Veenma et al., 2022). Further, the benthic fauna observed at Grotto Creek are associated with distal marine settings and, when combined with the low aluminum contents, suggest the $\delta^{15}N$ record was not significantly influenced by terrestrial nitrogen sources (Caruthers et al., 2022).

Through the techniques outlined above, we determine that Grotto Creek $\delta^{15}N$ trends are unlikely to be the result of additional organic matter sources, diagenetic alteration, or thermal maturation and instead primarily reflect the composition of fixed marine nitrogen. Thus, we view Grotto Creek $\delta^{15}N$ as primary signals and interpret them accordingly.



Fig. 6. Plot of the carbon to nitrogen ratios versus δ^{15} N values from Grotto Creek. The linear correlation through the data is represented by the dashed line. The green box is the approximate values of terrestrial organic matter (Meyers, 1997 and Algeo et al., 2014).

Record of changes to marine nitrogen cycling and oxygen concentrations within eastern Panthalassa

The δ^{15} N record at Grotto Creek shows two pronounced positive excursions of +3‰ that likely were the result of major changes in the marine nitrogen cycle within the equatorial Panthalassa. Iron speciation data from the same interval shows local bottom waters were persistently anoxic were predominantly ferruginous with occasional episodes of euxinia. This data, along with the paleogeographic location of Grotto Creek, indicate that it was deposited within the equatorial OMZ. With this in mind, we propose that the (~+3‰) δ^{15} N excursion that starts in the middle Norian and peaks near the Noran-Rhaetian boundary indicates a progressive deoxygenation of the lower part of the upper water column near the photic zone or, in other words, an expansion of the local oxygen minimum zone (Fig. 7).



Fig. 7. Illustrative diagrams outlining the scenario of progressive deoxygenation of the upper water column near the photic zone to anoxic conditions from the Norian through

Hettangian at Grotto Creek. A) Norian; B) Latest Norian and first half of Rhaetian; C) later Rhaetian and early Hettangian; D) Qualitative graph displaying the interpreted evolution of δ^{15} N with oxygen concentrations from Norian through Rhaetian. Modified from Quan et al. (2013).

In this scenario, pre-excursion δ^{15} N values of ~ 1 - 2‰ during the middle Norian reflect dominant nitrogen uptake and nitrification ($0\% \pm 2-3\%$) established under broadly oxic conditions (Fig 7A; Robinson et al, 2012) in the upper water column. At the same time Fe speciation data indicate that local bottom water conditions were predominantly anoxic and ferruginous (Fig. 7A). Following these initial conditions, δ^{15} N values gradually increased, with the most positive values found around the Norian-Rhaetian boundary (Fig. 5). We interpret the increased $\delta^{15}N$ values to be the result of denitrification becoming more favored, as dissolved oxygen declined in the upper water column upon the vertical expansion of the OMZ (Fig. 7B). Denitrification preferentially utilizes ¹⁴N bearing nitrate and subsequently leaves behind ¹⁵N enriched nitrogen resulting in organic matter with more positive δ^{15} N values. Fe_{HR}/Fe_T values show that bottom waters remained anoxic during this time. As oxygen concentrations continued to fall in the upper water column, below the photic zone, and anoxia became persistent, $\delta^{15}N$ declined back to near pre-excursion values (1 - 2‰) across the ETME. This occurred as denitrification led to the eventual loss of nitrate within the locally and ammonium became the primary source of bioavailable nitrogen through nitrogen fixation.

Several lines of evidence suggest progressively more reducing marine conditions after the peak of the δ^{15} N excursion and during and after the ETME at both Grotto Creek and more broadly in eastern Panthalassa. Iron speciation data, specifically the Fe_{HR}/Fe_T, from Grotto Creek indicates that the bottom waters continued to be anoxic. However, Fe_{PY}/Fe_{HR} values begin to plot more consistently toward the euxinic threshold (Fig. 5), suggesting a possible shift towards more reducing and potentially sulfidic bottom waters. Bivalves, while not common at Grotto Creek, become notably less abundant after the NRB with monotis becoming extinct in the Norian (Caruther et al. 2022). Although these organisms only

record a fraction of time compared to the surrounding sediments, and geochemical proxies contained within, their occurrence is indicative of brief windows of habitable and potentially oxygenated bottom waters. Further, the drop in their abundance following the NRB suggests more anoxic and therefore less habitable conditions become more consistent (Caruthers et al., 2022). Additionally, biomarker and redox sensitive trace metal data, from a succession deposited on the southern end of the Wrangellia Terrane (now located in Kennecott Point, Canada), indicate reducing benthic conditions with episodes of photic zone euxinia during the ETME interval (Kasprak et al. 2015; Schoepfer et al., 2016; discussed in more detail below). In summary, Grotto Creek δ^{15} N and Fe speciation data, along with data from elsewhere on Wrangellia, likely reflect the vertical expansion of the OMZ followed by episodes of photic zone euxinia across the ETME in eastern Panthalassa.

In context of the above scenario, we suggest that the second, more brief $\delta^{15}N$ excursion, at ~ 60 m, in the Hettangian (Fig. 5) reflected a transient shift to more oxygenated conditions where partial denitrification resumed. This interpretation is supported by the Fe speciation data, which show a decline in the FePY enrichments and Fe_{HR}/Fe_T that are confined to the same interval (Fig. 5). The increase in Fe_{HR}/Fe_T coincident with the brief $\delta^{15}N$ excursion indicates this oxygenation was likely transient and followed by a return to anoxic conditions in the local bottom waters.

Alternative scenarios

The above interpretations of δ^{15} N records from Grotto Creek could reflect a different sequence of changes to local redox as the δ^{15} N values are non-unique (Mettam and Zerkle, 2021). Specifically, the longer-term positive nitrogen excursion observed in the Upper Triassic at Grotto Creek (Fig. 5) could reflect 1) local redox conditions could have started more reducing with the positive excursion reflecting oxygenation followed by a return to a more anoxic conditions (Fig. 8A); 2) the local depletion of oxygen below the photic zone, as outlined above, but the subsequent return to a more oxygenated redox state (Fig. 8B); or 3) local conditions that started reducing and the excursion was generated by progressive

oxygenation (Fig. 8C). Here, we will evaluate the plausibility of these alternative scenarios in light of the available evidence.



Fig. 8. Schematic depictions of potential scenarios relating the nitrogen isotope composition to marine oxygen concentrations. Arrows depict temporal trajectory of δ^{15} N due to changing O₂ contents A) depletion of oxygen below the photic zone and subsequent return to a more oxygenated redox state; B) initially more reducing conditions with the excursion reflecting oxygenation followed by a return to a more anoxic conditions; or C) local conditions that started reducing and the excursion was generated by progressive oxygenation. Base schematic modified from Quan et al., 2013 (see figure 1A).

In terms of isotopic effects of the dominant reactions that influence bioavailable nitrogen, those that occur under both oxic and anoxic conditions have the potential to produce the low (~ 0.5-2‰) δ^{15} N values. Therefore, the low δ^{15} N we observe in the middle Norian could point to more complete denitrification with anoxia near the base of the photic zone column instead of oxygenated conditions — similar to the scenario we suggest for during and after the ETME. While iron speciation broadly reveals anoxic conditions in the local bottom waters during this time, the occurrence of benthic fauna is the highest in the middle Norian (Caruthers et al., 2022) and suggests more frequent transient oxygenation events in the deeper water column and likely more oxygenated conditions in the upper water column. Moreover, the later shift to more positive δ^{15} N with the decline in occurrence of benthic fauna suggests increased deoxygenation not oxygenation.

The shift to less positive δ^{15} N values in the later Rhaetian, across the ETME, and into the Hettangian (Fig. 5) could reflect a shift back towards more oxic conditions as oxygenation suppresses denitrification (Fig. 8B; Robinson et al., 2012; Sigman, 2009). However, as mentioned earlier, the low occurrence of benthic fauna, iron speciation data and other geochemical data from elsewhere on Wrangellia suggest a shift to more reducing conditions regionally. Therefore, we advocate that the lower δ^{15} N in the upper Rhaetian and lower Hettangian at Grotto Creek reflect further deoxygenation rather than oxygenation.

Relationship between environmental changes and late Triassic faunal turnover

Our interpretations of δ^{15} N combined with iron speciation records from Grotto Creek illuminate the progressively more reducing redox state of the equatorial Panthalassa in the lead up to the ETME. Additional evidence of redox fluctuations has been documented by previous studies of other successions deposited in other locations along the Wrangellia terrane (Sephton et al., 2002; Kasprak et al., 2015; Schoepfer et al., 2016) as well as elsewhere in Panthalassa (Fujisaki et al., 2020). Next we will compare our observations to these records from Panthalassa, as well as, to those from the better studied Tethys in order to cast our data in a more global context and better understand what was happening in the nitrogen cycle and marine redox during this time.

Panthalassa records

Nitrogen isotopes are a local proxy dictated by the state of the resident nitrogen cycle, but a better understanding of nitrogen cycling, and redox dynamics within a region can be gleaned from comparison of local records. Kasprak et al. (2015) and Schoepfer et al. (2016) both utilized a site on the southern side of the Wrangellia terrane, known as Kennecott Point (Haida Gwaii, British Columbia, Canada), that contains a positive $\delta^{15}N$ excursion of similar magnitude (3-4‰) that occurs in the Rhaetian (Fig. 9). The peak of the positive excursion at Kennecott Point occurs in the middle Rhaetian and post-dates the one at Grotto Creek; however, similar to the record at Grotto Creek, the $\delta^{15}N$ fall to pre-excursion values by the interval of the ETME. These δ^{15} N fluctuations could reflect the same progressive expansion of the equatorial OMZ we interpret from the data at Grotto Creek. In line with this interpretation, Kasprak et al. (2015) and Schoepfer et al. (2016) presented additional redox proxies, such as biomarkers and trace metal abundances, that show evidence of progressively more reducing conditions into the ETME. The delay of the δ^{15} N peak may reflect the later expansion of the OMZ in that portion of Wrangellia. In addition, another Panthalassa site located at Black Bear Ridge (BBR) in British Columbia, located on the northwestern margin of Pangaea, potentially displays a similar positive δ^{15} N excursion (Fig. 9.; Sephton et al., 2002). There is elevated δ^{15} N (2 to 4 ‰) in the Norian that drops to 0‰ in the lowest Hettangian. However, this dataset has a low stratigraphic sampling density and the Nortian, Rhaetian and Hettangian stages were subsequently revised by the biostratigraphic study of Hall and Pitaru (2004). In any case, elevated δ^{15} N values in the Norian at BBR are broadly reflective of the same excursion interval at both Grotto Creek and Kennecott Point, implying the observation is regional as opposed to a strictly local signal.



Fig. 9. Compilation of nitrogen isotope records from the Panthalassa and Tethys oceans spanning the ETME. Panthalassa records include Kennecott Point, Canada (Schoepfer et al., 2016; Kasprak et al., 2015), Black Bear Ridge, Canada (Sephton et al., 2002), and Katsuyama, Japan (Fujisaki et al., 2020). Tethys records include Mariental, Germany (Richoz et al., 2012), Mingolsheim, Germany (Quan et al., 2008), and Doniford Bay, England (Paris et al., 2010) and were correlated using the framework established by

Lindström et al., (2017). Gray area on the vertical timeline indicate missing time in each record/succession.

Elsewhere in Panthalassa, the δ^{15} N records from the deep sea chert succession at Katsuyama, Japan show a decline from 1‰ to 0‰ from the latest Rhaetian and into the earliest Hettangian (Fujisaki et al. 2020). Note, that these data do not span the interval of the Norian and Rhaetian that contains the δ^{15} N excursion seen at Grotto Creek and only represent a narrow window of time around the ETME. The facies and redox proxy data from the Katsuyama succession suggest the sequence was deposited under oxic conditions in the oligotrophic portion of Panthalassa (Fujisaki et al. 2016). Given this context, it seems unlikely that the fall in δ^{15} N at this location represents deoxygenation and complete denitrification. Fujisaki et al. (2020) suggested that the 1‰ negative shift represented a partial nitrate assimilation by the phytoplankton in this portion of Panthalassa.

In summary, we suggest that the rise in δ^{15} N found in the early Rhaetian at Grotto Creek (and maybe Black Bear Ridge) and the mid Rhaetian at Kennecott Point represent an increase in denitrification in the water column as the OMZ expanded in the eastern equatorial Panthalassa. The difference in timing between the sites reflects the spatial expansion of the OMZ. The δ^{15} N in the late Rhaetian and rebound in the early Hettangian represented increased deoxygenation, an interpretation that is supported by redox sensitive trace metal enrichments and organic biomarker data. The biomarker proxies indicate that euxinic conditions developed in the photic zone latest Rhaetian with the ETME and into the earliest Hettangian (Kasprak et al., 2015).

Tethys records

A large number of studies have investigated environmental changes over the ETME from sites representing the Tethys (e.g., Hesselbo et al., 2002; Zaffani et al., 2017; Quan et al., 2008; Richoz et al. 2012; Jaraula et al., 2013; Fox et al., 2022) and a few of these studies have utilized nitrogen isotopes (Paris et al., 2010; Quan et al., 2008; Richoz et al. 2012). All of the published δ^{15} N datasets come from successions representing deposition in an epicontinental seaway that was on the westernmost margin of the Tethys ocean basin.

Paris et al. (2010) presented a δ^{15} N record spanning the ETME taken from Doniford within the Bristol Channel Basin in the United Kingdom along with micropaleontological and Rock-Eval analyses. This section records a gradual $\delta^{15}N$ decline starting with values between around 5‰ to 3.5‰ and falling to +1.7‰ from the latest Rhaetian to earliest Hettangian, but with notable short-term fluctuations superimposed on this trend. Paris et al. (2010) attributed the higher $\delta^{15}N$ values found in the uppermost Rhaetian due to microbial degradation of the organic matter just after deposition based on Rock-Eval data in line with tidal flat facies they occur in. For the earliest Hettangian portion of the record, Paris et al. (2010) was uncertain as to the cause of short-term fluctuations found within the continued decline in $\delta^{15}N$, but suggested that $\delta^{15}N$ could have reflected a number of processes active as organic matter accumulation varied locally. However, biomarker data from the same sequence but at the nearby sites of St. Audrie's Bay and Lilstock indicate that photic zone euxinia developed in earliest Hettangian within the basin (Jaraula et al., 2013; Fox et al., 2022; Atkinson and Wignall, 2019) and suggests that the decline in $\delta^{15}N$ may have been driven by deoxygenation, the local loss of nitrate, and the shift to nitrogen fixation as primary source of bioavailable nitrogen.

Two studies present δ^{15} N records from sites within the Germanic Basin in southern Germany: the Mingolsheim and Mariental-1 cores (Fig. 9; Quan et al., 2008; Richoz et al. 2012). Both records record relatively high, but variable, δ^{15} N in the uppermost Rhaetian in comparison the in ETME interval and overlying Hettangian: between -0.3‰ and +2.2‰ for the Mingolsheim core (Quan et al., 2008) and +3‰ and +5‰ for the Mariental-1 core (Richoz et al. 2012). Both studies attributed the variability in these records to fluctuating

oxygen levels in the water column and subsequently variable amounts of denitrification. Quan et al., (2008) attributed the lower $\delta^{15}N$ during the ETME interval to a declining influence of denitrification on the nitrate pool, and higher levels of water column oxygenation during that time. Richoz et al. (2012) attributed the shift to lower $\delta^{15}N$ (<+3‰) during the ETME at Mariental-1 to reflect declining primary productivity, oxygen demand, and denitrification.

The Mariental-1 record ends in the lowest Hettangian and shows slightly higher (~+3‰), but variable, δ^{15} N which was attributed to slightly higher levels of denitrification in a less oxygenated water column (Richoz et al. 2012). Biomarker data from the Mariental-1 core and nearby Rosswinkel FR 204–201 core indicate episodes of photic zone euxinia also occurred in the earliest Hettangian and drops in δ^{15} N coincident with these biomarker occurrences point to transient intervals of nitrate loss with deoxygenation and the expansion of euxinia (Richoz et al. 2012).

The record from Mingolsheim contains an unconformity and is missing a record of the earliest Hettangian. Above the unconformity there is a record of the rest of the Hettangian into the Sinemurian where $\delta^{15}N$ then increases up the section from +1.5‰ to +2‰. This shift in $\delta^{15}N$ values was interpreted as the result of enhanced denitrification under increasing deoxygenation driven by enhanced terrestrial input from enhanced weathering induced by CAMP volcanism (Quan et al., 2008). Supporting this scenario, trace metal enrichments (Mo and U) from the later Hettangian in the Mingolsheim also suggest euxinic development in the basin during this time.

Overall the geochemical data from the Tethyan locations, like those in from eastern Panthalassa, indicate progressive deoxygenation across the ETME and into the Early Jurassic. However, the specific δ^{15} N records across the ETME show a variety of local signals that vary in their response to local oxygenation and deoxygenation. It should be noted that these sites were likely affected by the development of local anoxia that occurred in the epicontinental seaways as opposed to OMZs that are associated with deeper marine

settings (Diaz, 2016). This kind of anoxia could have persisted well through the ETME and therefore caused a more consistent δ^{15} N signal that does reflect significant changes in the dominant source nitrogen pathways affecting bioavailable nitrogen. The utility of these records in understanding the broader history of marine nitrogen cycling and oxygenation in the Tethys over this time interval is hampered since the records: 1) only represent the time interval of the ETME and its immediate aftermath and 2) contain major hiatuses and/or the facies changes associated with sea level fluctuations in these shallow epeiric basins. This second factor resulted in more localized signals in the δ^{15} N and redox proxy records. All this highlights the need for additional work to determine whether the change in the nitrogen cycle and deoxygenation that predate the ETME seen in eastern Panthalassa also occurred in the Tethys. Future work should focus on Tethys sites less proximal to Pangea that contain the interval leading up the ETME, Norian and Rhaetian, where the geologic record permits.

Broader implications for the ETME: Diversity, drivers, and timing

Based on our proxy records from Grotto Creek and others from the region, the interval leading up to the ETME exhibits a record of progressive marine deoxygenation within eastern Panthalassa. Our dataset adds to the growing body of evidence of environmental and biological change in the Norian and Rhaetian that preceded the ETME. Whiteside and Ward (2011) presented a mid-Norian carbon isotope record from Kennecott Point and defined what they term a "chaotic" carbon interval that contains two positive carbon isotope excursions that precede the NRB (Fig. 10). It is unclear whether these excursions represent regional or global changes to the carbon cycle and their underlying cause, but they immediately precede a major drop in ammonoid diversity in eastern Panthalassa (Fig. 10; discussed more below). This decline in ammonoid diversity and the "chaotic" carbon interval correlate to the beginning of the δ^{15} N excursion and the inferred start of OMZ expansion that we interpret at Grotto Creek. Further, Rigo et al. (2020) recently presented a compilation of δ^{13} C records from across the NRB that record a negative isotope excursion. Given the global distribution of this δ^{13} C excursion, it suggests that it represents a global perturbation to the carbon cycle at this time. The δ^{13} C record from Grotto Creek

also displays this negative excursion across the NRB (Fig. 5; Caruthers et al., 2022) and the nadir of this excursion occurs near the peak of the δ^{15} N excursion.



Fig. 10. Timeline of the events around the ETME with a generalized carbon and nitrogen isotope curves in addition to North American (Eastern Panthalassa) generic ammonoid diversity (modified from Whiteside and Ward, 2011). Major positive carbon isotope excursions (PCIE) and negative carbon isotope excursions (NCIE) are named in accordance with the established conventions (i.e. pre-cursor, initial, and main; Rigo et al., 2020).

There is no current consensus regarding the proximate causes that explain the records of environmental change captured by geochemical proxies during the Norian-Rhaetian transition. Potential drivers of NRB negative δ^{13} C excursions (along with additional proxy signals) include 1) emissions of greenhouse gasses due to large-scale volcanic activity and 2) extraterrestrial impact (Rigo et al. 2020). Both processes would have injected ¹³C depleted carbon into the exogenic carbon cycle. The oldest CAMP activity dates to 201.63

Ma (Davies et al., 2017) much younger than events around the NRB. Another potential LIP active in the late Triassic, known as the Angayucham volcanic terrane and exposed in southern Alaska. Its volcanics yield age dates of 214 ± 7 Ma (Pallister et al., 1989; Ernst and Buchan, 2001), which overlap with this interval. However, the areal extent of this terrane is poorly constrained and more precise age dates are both needed to better understand its potential impact on the environment during this time. The Manicouagan impact structure (~90 km diameter; Spray et al., 2010) is dated to the Middle Norian (~215.5 Ma), but this places the impact up to ~6 Ma prior to the NRB (Clutson et al., 2018). Further there have been no strata found in the Norian that bear impact related features (melt glass spherules, Ir anomalies, etc.). In summary, underlying drivers of the changes in Norian-Rhaetian are yet to be thoroughly investigated and further work should seek to do so.

The environmental disruptions recorded in carbon and nitrogen cycling alongside changes to marine redox, regardless of the drivers, clearly had profound impacts on marine ecosystems. As mentioned above, eastern Panthalassa ammonoid diversity declined starting in the mid-Norian, reached a low at the Norian-Rhaetian Boundary, and remained low into the ETME (Whiteside and Ward 2011; Lucas, 2018a). At the same time, bivalves experienced elevated extinction rates and their global diversity declined into the Rhaetian after reaching a high in the Norian (Ros et al., 2012; Wignall et al., 2007). Gastropods saw their highest extinction rates in the Norian and brachiopods had elevated extinction rates in both the Norian and Rhaetian (Kiessling et al. 2007). Notably these drops in diversity and elevated extinction rates occurred when the initial phases of deoxygenation occurred in eastern Panthalassa. Additionally conodont diversity also saw stepped declines across the Norian and Rhaentian (Rigo et al. 2016). Overall analyses of all benthic genera indicate that 41% of all those that crosses the Norian–Rhaetian boundary became extinct within the Rhaetian, while at the same time their origination rates fell (Kiessling et al. 2007). These extinctions may be associated with the progression of deoxygenation observed in eastern Panthalassa. In addition to marine diversity, groups of terrestrial taxa experienced extinctions across the Norian and Rhaetian (Lucas, 2018b) like the cynodonts, a group of Gondwanan herbivores, (Abdala and Gaetano, 2018) along with additional terrestrial species. This suggests that the environmental driver(s) behind these declines in diversity impacted both marine and terrestrial ecosystems.

Conclusions

Overall our data from the Grotto Creek succession, in addition to data from other studies, suggest progressive deoxygenation in eastern Panthalassa during the late Triassic. This is evidenced by the positive excursion captured in the δ^{15} N record, and iron speciation data, which suggest an expansion of the local oxygen minimum zone into the shallow water column. Importantly, a drop in regional ammonoid diversity within eastern Panthalassa, along with major drops in global bivalve diversity, coincide with the onset of deoxygenation at Grotto Creek and may be linked with this environmental change (Wignall et al., 2007). Further, other sites in this region of Panthalassa also indicate a shift to more reducing marine conditions and the occurrence of photic euxinia later during ETME (Kasprak, et al., 2015; Schoepher et al., 2016), supporting the scenario of a progressive expansion of the OMZ in equatorial Panthalassa.

The onset of deoxygenation seen in eastern Panthalassa suggests that environmental deterioration, at least in Panthalassa, started in the later Norian, predating the ETME by at least ~8 million years. This finding supports other studies that have recently documented additional evidence of both environmental and ecological stress (e.g. perturbations to the carbon cycle) during the later Norian and Rhaetian. The underlying drivers of these earlier changes to the Earth system are at present unclear as they predate the emplacement of CAMP. Future work should focus on identifying potential drivers of these changes, since recognizing these mechanisms is critical to understanding how long-term environmental stressors shaped ecosystems and ultimately led to one of the largest mass extinctions of the Phanerozoic.

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