Two-pronged kill mechanism at the end-Triassic mass extinction

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High-resolution biomarker and compound-specific isotope distributions, coupled with the degradation of calcareous fossil remnants reveal that intensive euxinia and decalcification (acidification) driven by Central Atlantic Magmatic Province (CAMP) activity formed a two-pronged kill mechanism at the end-Triassic mass extinction. In a newly proposed extinction interval for the basal Blue Lias Formation (Bristol Channel Basin, UK), biomarker distributions reveal an episode of persistent photic zone euxinia (PZE) that extended further upwards into the surface waters. In the same interval shelly taxa almost completely disappear. Beginning in the basal paper shales of the Blue Lias Formation, a Lilliput assemblage consisting of only rare calcitic oysters (Liostrea) and ghost fossils of decalcified aragonitic bivalves are preserved. The stressors of PZE and decalcification parsimoniously explain the extinction event and inform possible combined causes of other biotic crises linked to emplacements of large igneous provinces, notably the end-Permian mass extinction where PZE occurred on a broad and perhaps global scale.
Two-pronged kill mechanism at the end-Triassic mass extinction

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ABSTRACT

High-resolution biomarker and compound-specific isotope distributions, coupled with the degradation of calcareous fossil remnants reveal that intensive euxinia and decalcification (acidification) driven by Central Atlantic Magmatic Province (CAMP) activity formed a two-pronged kill mechanism at the end-Triassic mass extinction. In a newly proposed extinction interval for the basal Blue Lias Formation (Bristol Channel Basin, UK), biomarker distributions reveal an episode of persistent photic zone euxinia (PZE) that extended further upwards into the surface waters. In the same interval shelly taxa almost completely disappear. Beginning in the basal paper shales of the Blue Lias Formation, a Lilliput assemblage consisting of only rare calcitic oysters (*Liostrea*) and ghost fossils of decalcified aragonitic bivalves are preserved. The stressors of PZE and decalcification parsimoniously explain the extinction event and inform possible combined causes of other biotic crises linked to emplacements of large igneous provinces, notably the end-Permian mass extinction where PZE occurred on a broad and perhaps global scale.
INTRODUCTION

The end-Triassic extinction (ETE; ca. 202 Ma) is one of the largest mass extinction events of the Phanerozoic and temporally correlated with emplacement of the Central Atlantic Magmatic Province (CAMP) (Pálfy et al., 2001). Pulsed CAMP outgassing of CO$_2$ and SO$_2$ in large quantities is thought to have triggered the ETE through a cascading series of environmental perturbations, including global carbon cycle changes, rapid warming leading to ‘hyperthermal’ climatic events, and increased continental weathering. In many marine sedimentary basins such conditions led to stagnation, deoxygenation, and deposition of organic-rich laminated mudstones (e.g., Kasprak et al., 2015). However, the precise mechanism(s) responsible for the extinction event remain elusive.

The Bristol Channel Basin, SW UK, although not necessarily globally representative, has become a focal locality for ETE studies employing palynological, paleontological (Warrington et al., 2008 and refs therein), and geochemical analyses (Jaraula et al., 2013; Fox et al., 2020). The pronounced negative anomaly in the organic carbon isotope record ($\delta^{13}$C$_{\text{org}}$; initial CIE; Fig. 1) in the Lilstock Formation (Fm.) at St. Audrie’s Bay (Hesselbo et al., 2002) is routinely used to chemostratigraphically correlate the extinction event and CAMP volcanism among sections on a global scale (e.g., Hesselbo et al., 2002). However, this CIE is stratigraphically offset from the highest occurrences (HO) of key fossil taxa. For example, the HO of foraminiferal, ostracod, and bivalve fauna (Hallam, 1990) is in the overlying basal Blue Lias Fm. at the base of finely laminated organic carbon-rich mudstones termed the paper shales (Richardson, 1911). Furthermore, the HO of conodonts also sits in the lowermost Blue Lias Fm. (Swift, 1989). Based on these and other findings, including the HO of the reptile clade Phytosauria in the lowermost Blue Lias Fm. (Maisch and Kapitzke, 2010) and a Lilliput assemblage of bivalves at the very
base of the paper shales (Fox et al., 2020), recent studies have placed the ETE above the initial CIE in the paper shales, at a separate and slightly younger $\delta^{13}$C$_{org}$ anomaly (Fig. 1) (Wignall and Atkinson, 2020; Fox et al., 2020). Despite decades of study establishing the presence of extinction of fauna characteristic of the end-Triassic (Fig. 1) and a dearth of calcite- and aragonite-secreting organisms at the extinction horizon, little is known of the killing mechanism(s). To better investigate this critical interval and the cause(s) of the ETE, we undertook high-resolution (i.e. cm-scale) biomarker and compound-specific isotope analyses to disentangle ecological community shifts recorded in the fossil record at two sections in the Bristol Channel Basin: St. Audrie’s Bay [51.182833°, −3.286000°] and Lilstock [51.200757°, −3.176389°].

RESULTS AND DISCUSSION

Acidification and photic zone euxinia forcing the ETE

Decalcified bivalve taxa exhibiting low diversity (Fox et al., 2020) and a general lack of CaCO$_3$-secreting organisms (Hallam, 1990) above the Lilliput assemblage in the paper shales gives evidence of an acidification event that terminated with the return of calcareous nannoplankton and ammonites later in the sedimentary record (Fig. 1). Termed the biocalcification crisis, this event is placed between the HO of the ammonite *Choristoceras marshi* and lowest occurrence of *Psiloceras spelae* in European sections (McRoberts et al., 2012). Correlation between the HO of conodonts in the SW UK (Swift, 1989) to the HO of Triassic conodonts at the end of the *C. marshi* zone (Hillebrandt et al., 2013) provides correlative evidence of acidification at the ETE. In a global context, the biocalcification crisis is evidenced by major reduction in sedimentary carbonates and biogenic carbonates from secreting organisms,
particularly corals, calcareous nannoplankton, benthic foraminifera groups, and some bivalves (Cope and Hallam, 1991; Hautmann, 2004; van de Schootbrugge et al., 2007; Lindström et al., 2012; McRoberts et al., 2012; Fox et al., 2020). Likely driven by CAMP-induced rapid outgassing of CO$_2$, acidification is a plausible kill mechanism. However, our biomarker and compound-specific isotope investigation reveals that additional ecological stresses may play important roles in driving extinction.

The paper shales are characterized by low pristane to phytane ratios (Pr/Ph), high gammacerane index values, supporting anoxia in a well-stratified water column, and increases in C$_{40}$ carotenoids derived from purple sulfur bacteria (okenane) and green-pigmented (chlorobactane) and brown-pigmented (isorenieratane) green sulfur bacteria (Fig. 2). Whereas purple sulfur bacteria (Chromatiaceae) and green-pigmented green sulfur bacteria (Chlorobi) reported below this unit indicate the presence of microbial mats (Fox et al., 2020), coexistence with brown-pigmented Chlorobi and biomarkers for anoxia and stratification indicate photic zone euxinia (PZE), a condition in which toxic H$_2$S extends upward into the sun-lit region of an anoxic water column (e.g. Grice et al., 2005). Due to higher light intensity requirements of Chromatiaceae and green-pigmented Chlorobi compared to brown-pigmented Chlorobi (Grice et al., 1998; Brocks and Schaeffer, 2008; Overmann, 2008), the ratio of isorenieratane to okenane and chlorobactane (iso/oke + chlo) serves as a proxy for the relative depth of the chemocline, where higher values indicate predominance of low-light-adapted photosynthetic bacteria and therefore a deeper chemocline. Thus, the lower paper shales are characterized by a shallower chemocline compared to later in the record where iso/oke + chlo values increase. Below the Blue Lias Fm. iso/oke + chlo values are also low. However, this interval is characterized by
geochemical and sedimentological evidence for shallowing, freshening, and desiccation, but little
evidence for prolonged PZE (Fox et al., 2020 and refs therein).

Where okenane and chlorobactane abundances are highest, the $\delta^{13}$C$_{29}$ n-alkane mirrors
the minor negative $\delta^{13}$C$_{org}$ excursion, possibly related to the CAMP (Fig. 3). $\delta^{13}$C values of
regular isoprenoids (pristane and phytane) and n-alkanes (C$_{17-19}$) also show negative excursions,
albeit more variable (Fig. 3). Significant decreases in okenane and chlorobactane abundances
later in the paper shales (Fig. 2) are possibly related to lower-light availability due to a deepening
of the chemocline and/or due to increased algal productivity in the euphotic zone (Grice et al.,
1998; Brocks and Schaeffer, 2008; Overmann, 2008). Here, $\delta^{13}$C values of pristane, phytane and
C$_{17-19}$ n-alkanes show a positive isotope excursion, and based on their isotopic differences,
carbon fixation shifts to increased autotrophic production (Fig. 3) (Grice et al., 2005). Elevated
isorenieratane abundances in this interval show PZE continued but was limited to the lower
region of the photic zone, and low Pr/Ph and aryl isoprenoid ratios throughout the paper shales
demonstrate persistent PZE (Fig. 2; Data Repository) (Schwark and Frimmel, 2004).

These results suggest the paper shales formed in two sequential different depositional
environments which are related to chemocline depth and carbon isotope chemistry. First, at the
extinction horizon in the basal Blue Lias Fm., high abundances of Chromatiaceae and green-
pigmented Chlorobi biomarkers and low iso/oke + chlo values support a shallow chemocline
with PZE extending throughout much of the photic zone. Biomarker $\delta^{13}$C values of marine
organisms show a negative excursion, are variable compared to isotopic shifts in higher land
plants. In modern-day ecosystems, pH changes impact carbon leakage, mechanisms of carbon
concentration, and activity of carbonic anhydrase in dehydrating HCO$_3^-$, all of which affect
carbon isotope fractionation in phytoplankton (Wang et al., 2016). These effects of acidification
on phytoplankton, in conjunction with intense PZE and its associated precipitation of bio-
essential elements (Takahashi et al., 2014), possibly account for the marine $\delta^{13}$C variations at the extinction horizon. The second depositional environment is characterized by a decline in Chromatiaceae and green-pigmented Chlorobi and increases in brown-pigmented Chlorobi and iso/oke + chlo, consistent with contraction of sulfidic conditions. The coinciding shift to autotrophic production and positive $\delta^{13}$C excursions in biomarkers of marine organisms agree with a $^{13}$C-enriched euphotic zone due to increased carbon fixation and reduced light availability to Chromatiaceae and Chlorobi. Elevated abundances in brown-pigmented Chlorobi biomarkers support continued PZE but restricted to lower-light levels of the water column.

The invocation of H$_2$S toxicity as a driver for the ETE is supported by increases in isorenieratane, aryl isoprenoids (Richoz et al., 2012; Jaraula et al., 2013; Kasprak et al., 2015) or pyrite framboild diameter analysis (Atkinson and Wignall, 2019). However, for the first time we report PZE was not only persistent, but due to increased abundances of biomarkers derived from sulfur bacteria that require elevated light intensities and H$_2$S, PZE extended into shallower depths of the photic zone than previously thought. The presence of these organisms supports increased stress to epipelagic nektonic and planktonic communities. Furthermore, increased precipitation of bio-essential elements associated with periods of PZE have suppressive effects on marine life and its recovery during extinction events (Takahashi et al., 2014). Given that PZE biomarkers are observed in European and Canadian sections, which represent a range of depositional settings including open ocean (Richoz et al., 2012; Jaraula et al., 2013; Kasprak et al., 2015), PZE at the ETE may have global extent, although perhaps not everywhere simultaneously. Effects of euxinia on calcifying organisms are poorly understood, but short-term intervals have resulted in planktonic foraminifera extinction (Oba et al., 2011). In conjunction
with acidification, PZE may thus explain the near lack of fauna during the ETE biocalcification crisis. Additionally, we note that the importance of anoxia has been shown to be an important stressor on modern coral analogues experimentally (Altieri et al., 2017), and that ocean anoxic events frequently result in a species richness decline in calcareous and benthic communities (e.g. Watkins et al., 2005; Mattioli et al., 2008). Consequently, we argue that the development of persistent and intense PZE in conjunction with acidification leads to major ecological stress, and that these conditions together are important for driving the ETE. These features are the most compelling evidence of CAMP-induced environmental perturbations throughout the latest Rhaetian, and plausibly relate the negative $\delta^{13}$C anomaly in the lower Blue Lias Fm. to CAMP activity.

Organic-rich laminated lithologies are often host to Lagerstätten assemblages that preserve articulated fossils. Lack of bioturbation and preservation of microlaminations in lacustrine and marine settings indicates deposition below the wave base and persistent water column stratification and bottom water anoxia (Olsen, 1990). Although the facies of the paper shales conform to this model, the absence of fish or any articulated fossils (Hallam, 1991; confirmed by our field observations) is consistent with acidification and PZE driving extinction, although this may also be related to basin restriction. This lack of fossil content, in addition to the micro-laminations, is anomalous compared to superficially similar orbitally paced units above the paper shales that do have abundance fossils. From field observations, the paper shales immediately succeeding the Lilliput assemblage are nearly devoid of shelly taxa with the exception of decalcified bivalves, supporting acidification. However, Mander et al., (2008) report shelly taxa specimens (Modiolus sp., Liostrea sp., and L. hisingeri) in the upper-most layers, and Atkinson and Wignall (2019) report Liostrea sp. in the lower paper shales (Fig. 4) that could be
associated with the lilliput assemblage. Above the paper shales, shelly taxa species richness increases in close proximity to the lowest occurrence of organisms that preserve the aragonitic nacre; *Psiloceras planorbis* and other *Psiloceras* and *Neophyllites* ammonites (Warrington et al., 2008 and refs therein). Major increases in foraminifera species richness and preserved foraminiferal test linings occur above this interval (Bonis et al., 2010; Clémence and Hart, 2013), signaling diminishing effects of acidification (Fig. 4). Biomarker and pyrite frambooid analysis in shale/dark marl lithologies support cyclical euxinic conditions into the *P. planorbis* zone (Jaraula et al., 2013; Atkinson and Wignall, 2019), suggesting stable conditions with increased continental weathering during shale/dark marl deposition and storm events/mixing during limestone and light marl formation (Weedon et al., 2017). Above the lowest occurrence of *P. planorbis*, bivalve assemblages increase in diversity but not in abundance (Mander et al., 2008) suggesting localized effects of acidification and PZE inhibit the return of pre-extinction ecological conditions.

**CONCLUSIONS**

The fully marine expression of the ETE in the SW UK is in the basal Blue Lias Fm., during an acidification event with persistent and intense PZE and its associated redox conditions. This combination of ecological stressors explains many observations within the lower Blue Lias Fm., including the lack of well-preserved vertebrate fossils, near absence of shelly taxa in the paper shales, and subsequent increases in species richness upward toward the termination of the biocalcification crisis. Furthermore, acidic and euxinic conditions constitute the most compelling evidence of CAMP-induced environmental perturbations thought to drive the ETE throughout the latest Rhaetian. In future studies, high-resolution sampling for biomarkers and their $\delta^{13}C$
values, in conjunction with ecological community shifts, will be critical to properly evaluate the
global extent and significance of combined ecological stressors in the ETE and similar
extinctions.
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REFERENCES CITED


FIGURE CAPTIONS

Figure 1. δ\textsuperscript{13}C\textsubscript{org} records in the SW UK. ETE lithology and paleogeographic reconstruction (top) after Hesselbo et al., (2002), with CAMP lateral extent in red. HO of conodonts after Swift (1989). References for other ecological and geophysical data in figure.

Figure 2. Biomarker-inferred redox and PZE conditions at St. Audrie’s Bay (circles, solid lines) and Lilstock (squares, dashed lined) relative to δ\textsuperscript{13}C\textsubscript{org} and TOC. Two depositional environments indicated by green (shallow redoxcline) and pink (deeper chemocline) bars. Biomarkers below and ecological indicators above each profile. Pristane to phytane ratios and gammacerane, okenane, chlorobactane and isorenieratane indices up to the base of the Blue Lias Fm. reported in Fox et al., (2020). Details in the Data Repository.

Figure 3. Compound-specific carbon isotope analysis at St. Audrie’s Bay (circles, solid lines) and Lilstock (squares, dashed lines). Two depositional environments indicated by green (variable but negative excursions in regular isoprenoids and \textit{n}-alkanes) and pink (positive excursions and shift to more autotrophy) bars. Biomarkers below, and ecological indicators above each profile. δ\textsuperscript{13}C of biomarkers to the base of the Blue Lias Fm reported in Fox et al., (2020). Details in the Data Repository.

Figure 4. Ecological shifts relative to anoxia (paper shales), biocalcification crisis, and PZE in the Bristol Channel Basin. Note bivalve species richness increases after intense PZE and foraminifera species richness increase with return of \textit{P. planorbis}. Details in Data Repository.
Figure 1

[Diagram showing stratigraphic sections, with labels for Foraminifera Zones, Carbonate indicators, and lithological units.]

SW UK, sections
Kuhjoch, Austria
Kenneclott Point, Canada

Calcification crisis
Freshwater indicators
Microbial Mats
Lilliput Assemblage
Bivalve extinctions
Conodonts
Calcareous nannoplankton
Magnetostratigraphy

Foraminifera Zones
P. planorbis
C. thiergartii

Laminted shale
Limestone
Siltstone
Shale
Concretions
Wave ripples

δ13Corg [% VPBD]
-30 -28 -26 -24 -22

St. Audrie’s Bay

Lilstock
Langport Member
Cotham Member
Lilstock Formation

Initial CIE
Precursor CIE
Main CIE
Reducing Persistent Stratification

Deeper Chemocline

Typical Stratification Proxy

Water Column Redox

Prograde vs. Persistent PZE

Purple SB (Chromatiaceae)

Green-pigmented Green SB (Chlorobi)

Brown-pigmented Green SB (Chlorobi)

Low-light vs. High-light Requiring SB

Deeper Chemocline

Figure 2
<table>
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<th>Higher Land Plants</th>
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**Figure 3**

- **St. Audrie's Bay**: Lithology
  - Limestone
  - Laminated mudstone
  - Oscillatory ripples
  - Desiccation cracks
  - Sandstone

- **Lilstock**: Height (cm)
  - St. Audrie's Bay original height (cm)

- **Kerogen Type**: Limestone, Limonite
- **ETE**

- **Height (cm)**:
  - St. Audrie's Bay
  - Lilstock

- **UC - upper Cotham Member**
- **L - Langport Member**
- **BL - Blue Lias Formation**
- **SS - Sandstone**
- **Pr - Pristane**
- **Ph - Phytane**
- **Av - Average**
- **VPDB - Vienna Pee Dee Belemnite**

**Notes**:
- **Average** δ^{13}C
- **Autotrophy** (Algae & land plants)
- **Heterotrophy** (Bacteria)
Figure 4

Carbon Isotope Profile

Photic Zone Euxinia Biomarkers

Forams
Special richness
(Jaraula et al., 2013)

Bivalves
Special richness
Faculative mobility
Abundance
(Bonis et al., 2010)

Lower Trophic Organisms

Biocalification
Crisis

marine
non-marine

0 20 40 60 80 100
Percentage (%)

0 2 4 6 8 10 12 14
Isomer-richness
(Mander et al., 2008)

Species richness
(Atkinson et al., 2019)

Abundance
(Warrington et al., 2008)

Species richness

Dinoflagellate cysts
Acritarchs
Prasinophytes
Foraminiferal test linings
Botryococcus & Pediastrum

Test linings of foraminifera:
P. planorbis
C. thiergartii

St. Audrie’s Bay
(Hesselbo et al., 2002)

Liistock

Conodonts

Liliput assemblage (ETE)

St. Audrie’s Bay

Liistock

LIL - Liistock Formation
C - Coatham Member
G - Glomospira/Glomospirella Assemblage
PPSZ - pre Planorbis subzone

L - Langport Member
Fm - Formation
E - Eoguttulina iassica Assemblage
CJZ - C. Johnstoni zone

Okenane Index

Isorenieratane
(nmol TOC)
(Jaraula et al., 2013)

Isorenieratane

Index

0 0

δ¹³C
[‰ VPDB]

-30 -25 -20 -15 -10 -5 0 5 10 15 20 25 30

Concentrations
Shell concentrations
Wave ripples
Soft sediment deformation

Figure 4

Biocalification
Crisis

marine non-marine

0 20 40 60 80 100
Percentage (%)

0 2 4 6 8 10 12 14
Isomer-richness
(Mander et al., 2008)

Species richness
(Atkinson et al., 2019)

Abundance
(Warrington et al., 2008)

Species richness

Dinoflagellate cysts
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St. Audrie’s Bay
(Hesselbo et al., 2002)

Liistock

Conodonts

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St. Audrie’s Bay

Liistock

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L - Langport Member
Fm - Formation
E - Eoguttulina iassica Assemblage
CJZ - C. Johnstoni zone

Okenane Index

Isorenieratane
(nmol TOC)
(Jaraula et al., 2013)

Isorenieratane

Index

0 0

δ¹³C
[‰ VPDB]

-30 -25 -20 -15 -10 -5 0 5 10 15 20 25 30

Concentrations
Shell concentrations
Wave ripples
Soft sediment deformation
desiccation