Widespread upper-ocean deoxygenation in the Alpine-Mediterranean Tethys during the Toarcian Oceanic Anoxic Event

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Abstract

The early Toarcian (~183 Ma) was characterized by pronounced climate warming associated with massive release of ^{13}C-depleted carbon to the exogenic system, as evidenced by globally recognized negative carbon-isotope excursions (N-CIE) in biospheric carbon reservoirs. Global warming during this interval could have triggered a variety of environmental perturbations, of which the large-scale marine deoxygenation, as indicated by the presence of widespread organic carbon-rich deposits, is arguably diagnostic, thereby naming the interval in question the Toarcian Oceanic Anoxic Event (T-OAE). Nevertheless, the spatial variability of water-column redox is unclear because most sedimentological and geochemical methods applied for the evaluation of marine redox are more likely reflective of the bottom-water and/or pore-water state. This drawback prohibits us from uncovering the links between marine redox and biotic turnovers, especially given that 1) a second-order mass extinction occurred during the event; 2) shallow-water environments provided the necessary niche for most aerobic marine organisms. Here we report new I/(Ca+Mg) and Cerium (Ce)-anomaly data from two carbonate successions from northern Italy that encompass the T-OAE interval. Both successions were deposited in the Alpine-Mediterranean Tethys; one in a shallow-water platform setting and the other within a basinal pelagic environment. The successions record an abrupt drop in I/(Ca+Mg) values, coupled with positive excursions of Ce-anomaly records at the onset of the T-OAE N-CIE at both sites. The synchronized changes in marine iodate depletion and Ce enrichment at both sites suggest widespread and significant upper-ocean deoxygenation in the Alpine-Mediterranean

Tethys. This redox pattern is attributed to an expanded oxygen minimum zone (OMZ) formed as a result of sluggish oceanic circulation under climate warming, augmented by enhanced dissolved oxygen consumption due to increased nutrient availability and the consequent eutrophication in both proximal and distal settings. Because reduced seawater dissolved oxygen [O_2] would increase the ecological stress and constrict any potentially hospitable habitats, the broad synchroneity between biotic turnovers and upper-ocean deoxygenation in the Alpine-Mediterranean Tethys is compatible with a potential causal link.

1. Introduction

The Early Jurassic witnessed an interval of pronounced climatic and environmental upheaval, known as the Toarcian Oceanic Anoxic Event (T-OAE, ~183 Ma; Jenkyns, 1988) or Jenkyns Event (Müller et al., 2017). This event is stratigraphically constrained by a globally identified negative carbon-isotope ($\delta^{13}C$) excursion (N-CIE) in biospheric reservoirs of carbon, and is interpreted to have been caused by massive ^{13}C-depleted carbon release into the exogenic system (Hesselbo et al., 2000). This major carbon-cycle perturbation and climate warming (6–7 °C increase in seawater temperatures; e.g., Bailey et al., 2003) caused marked environmental disturbance (see Remírez and Algeo, 2020 for a review), of which the most significant was the widespread deposition of organic carbon-rich facies (Jenkyns, 1988; Kemp et al., 2022a), suggesting expanded ocean deoxygenation through the event, in particular in the European Epicontinental Shelf (EES; Fig. 1A). Analyses of redox-sensitive metal elements (e.g., Mo, Re, and U; Kunert and Kendall, 2023) and multiple isotopic systems (e.g., S-, Mo-, and Tl-isotopes; Gill et al., 2011; Dickson, 2017; Dickson et al., 2017; Them et al., 2018) confirm significant deoxygenation at many sites, and an expansion in the areal extent of anoxic/euxinic conditions to 2–10% of the seafloor during the T-OAE. The intense reducing conditions even extended into the near-surface ocean at some sites in the European Epicontinental Shelf, where biomarker proxies have revealed at least intermittent photic-zone euxinia (e.g., Schouten et al., 2000; Pancost et al., 2004; French et al., 2014). Nevertheless, the spatial variability of water-column redox, and in particular the upper-ocean redox conditions (which could have significantly affected biotic turnovers since the shallow-water ecosystem would have provided the necessary niche for most aerobic marine organisms) is poorly understood, given that the majority of sedimentological and geochemical methods are indicative of bottom-water and/or pore-water redox conditions (e.g., Chen et al., 2021, 2023; Kemp et al., 2022b; Gambacorta, et al., 2024).

Carbonate-associated iodine (as denoted by I/(Ca+Mg)) has in the last two decades been increasingly used to trace the redox conditions of the upper oceans in Earth history (e.g., Lu et al., 2010, 2018; He et al., 2022), allowing a nuanced distinction between oxic and hypoxic conditions. The long residence time of iodine (~ 300 kyr) in the modern oceans means a relatively uniform marine iodine concentration of ~0.45 µmol/L (Elderfield and Truesdale, 1980). Iodine speciation (i.e., iodate and iodide) is, however, redox-dependent. Specifically, iodate (IO_3^-) is the thermodynamically stable form of iodine under oxic conditions. IO_3^- is, however, readily reduced to iodide (I^-) under low-oxygen conditions and converts to the oxidized counterpart when seawater dissolved oxygen increases significantly (Luther and Campbell, 1991). Nevertheless, the kinetics of I^- oxidation is slow relative to those of IO_3^- reduction, potentially leading to surface seawater with low IO_3^- concentrations albeit with relatively high dissolved oxygen contents (Chance et al., 2014). IO_3^- is the only geochemical species that can be incorporated into the carbonate crystal lattice by substituting for the CO_3^{2-}

ion, thereby allowing the ratio of I/(Ca+Mg) in carbonates to be used as a direct tracer for water-column (normally upper ocean where carbonates are precipitated or secreted) redox conditions (Lu et al., 2010). In detail, relatively high I/(Ca+Mg) values in bulk carbonate rocks imply oxic seawater, whereas lower values suggest oxygen-depleted conditions (Lu et al., 2010).

In addition to the I/(Ca+Mg) ratios, the Ce-anomaly proxy is also widely used to assess the local to regional upper-ocean redox conditions due to its unique redox characteristic (Lawrence et al., 2006). In detail, Ce (III) is readily oxidized to insoluble Ce (IV) and then adsorbed on the surface of manganese (oxyhydr)oxide minerals or accumulates as discrete Ce oxide particles. These processes result in a marked depletion of marine Ce compared to its REE neighbors, thus leaving seawater with a negative Ce-anomaly signal under oxygenated conditions. Under manganous/anoxic conditions, instead, these oxide minerals and particles experience reductive dissolution with excess Ce releasing back to the water column and a consequent positive Ce anomaly (De Baar et al., 1985, 1988; German et al., 1991).

Here we present I/(Ca+Mg) data encompassing the T-OAE from two carbonate successions (Dogna core and Colma di Malcesine section, northern Italy), deposited in the Alpine-Mediterranean Tethys at widely differing paleo-depths. In combination with Ce-anomaly data, our study reveals abrupt upper-ocean deoxygenation at both sites at the onset of the T-OAE N-CIE. Integrated with previous studies, we find widespread oxygen-depleted conditions in the upper oceans outside of the European Epicontinental Shelf. This redox state is attributed to an expanded OMZ, which could have caused the regional biotic turnovers due to increased ecological stress.

2. Geological setting

The study sites (Dogna core and Colma di Malcesine section) are both located in the southern Alps (northern Italy, NW Tethys), which occupied a segment of the passive Tethyan continental margin that experienced extensional movements during the Early Jurassic synchronously with the break-up of Pangea (Winterer and Bosellini, 1981).

2.1 Dogna, Belluno Basin

The Belluno Basin was a relatively deep (1500–2000 m), narrow, and elongated basin, located on the continental margin of the Apulian Plate in the Alpine-Mediterranean Tethys (Bosellini et al., 1981). The formerly extensive carbonate-platform belt disintegrated during the Early Jurassic due to active rifting and the opening of the Central North Atlantic Ocean, with a 'horst and graben' zone formed in a pelagic setting (Bosellini et al., 1981). During the Early Jurassic, the Belluno Basin was bounded by the Trento Platform/Plateau to the west and the Friuli Platform to the east (Fig. 1B), with the Igne Formation (Fig. 2I) spanning the Toarcian–Aalenian interval comprising calcareous and clay-rich facies (Bosellini et al., 1981). The Dogna core was deposited at a paleo-latitude of ~23°N in the Belluno Basin, with an estimated paleo-depth of ~1000 m. The material in the Dogna core is characterized by pelagic limestones and interbedded manganoan carbonates, marls, and calcareous shales. In stratigraphically equivalent sections nearby, the occurrence of *Dactylioceras* cf. *anguiforme* 60 cm above the top of the diagnostic manganoan carbonate-shale sequence indicates the upper *falciferum* Zone. Multiple *Hildoceras* species at a stratigraphically higher level indicates the *bifrons* Zone. Thus, the manganoan carbonate-shale sediments in the Dogna core were assigned to the lower *falciferum* Zone (Jenkyns et al., 1985). On this biostratigraphic basis, the N-CIEs (spanning a thickness of ~18 m) in both organic and inorganic carbon archives in the Dogna core unambiguously constrain the T-OAE chemostratigraphically

(Jenkyns et al., 2001; Fig. 2I-A).

2.2 Colma di Malcesine, Trento Platform

The Trento Platform is an offshore Bahamian-type platform bordered by the Lombardian Basin to the west and the Belluno Basin to the east in the Early Jurassic (Fig. 1B). Biostratigraphic analyses of ammonites, nannofossils and bivalves have assigned the base of the Tenno Formation to the *tenuicostatum* Zone (Geyer et al., 1986; Picotti and Cobianchi, 1996). Thus, the Tenno Formation and the underlying Misone Formation (Fig. 2II), consisting mainly of micritic limestones, span the Pliensbachian–Toarcian boundary (Bosellini, 1972; Masetti, 1998). The platform experienced regional deepening in the early Toarcian. This quasi-drowning event caused a marked change in the depositional environment, as reflected by a lithological transition from peritidal shallow-water carbonate to clay-rich facies (Castellarin, 1972). The Colma di Malcesine section is located at the western margin of the Trento Platform, where the impact of flooding was relatively minor in the early Toarcian, with paleo-depths likely in the range of tens of meters (Woodfine et al., 2008). In the Colma di Malcesine section, the clay-rich limestones (indicative of possible local deepening) are sandwiched by massive oolitic limestones below and chert-bearing limestones above, with the identification of the N-CIE (spanning a thickness of ~35 m) in the inorganic carbon archive constraining the T-OAE chemostratigraphically (Woodfine et al., 2008; Fig. 2II-A).

3. Materials and methods

3.1 $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ in the Dogna core

Twenty-eight bulk carbonate samples from the Dogna core spanning the T-OAE N-CIE interval (defined by Jenkyns et al., 2001, as denoted by brown hollow circles in Fig. 2I-A) were selected and analyzed for carbonate carbon and oxygen isotopes ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$). Powdered bulk carbonate samples from the Dogna core, in the mass range 200 to 700 µg (depending on the $CaCO_3$ content, see methods in the Supplementary materials) were analyzed for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ at the Department of Earth Sciences, University of Oxford, using a Thermo Delta V Advantage gas-source mass spectrometer fitted with a Gas Bench II peripheral. Within the Gas Bench II sample block, the powdered samples were reacted with purified phosphoric acid (H_3PO_4) at 50 °C. The relative $^{13}C/^{12}C$ and $^{18}O/^{16}O$ values are reported in the conventional $\delta^{13}C$ (‰) notation and $\delta^{18}O$ (‰) notation relative to the

Vienna Pee Dee Belemnite (V-PDB), following a within-run laboratory standard calibration with NBS-18 and NBS-19. Analytical reproducibility of an in-house marble standard (NOCZ) was better than 0.1‰ for both δ^{13}C and δ^{18}O (1SD).

3.2 I/(Ca+Mg)

Forty-nine carbonate samples encompassing the T-OAE N-CIE interval were taken from the Dogna core (n = 28) and the Colma di Malcesine section (n = 21) for the measurements of carbonate-associated iodine concentrations at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan) using a simplified but effective method modified after Lu et al. (2010). In detail, sample powders from the bulk carbonate rocks were collected by microdrill to avoid veins and weathered material. Around 10 mg of sample powder were weighed and rinsed with deionized water to remove surface-bound iodine. The sample powder was then dried and treated with ~10 g of 2% pre-distilled nitric acid to react with the carbonate portion. The carbonate-leaching step was strictly limited to <15 minutes to minimize the iodine loss at low pH conditions. 5 mL of the supernatant was then taken out to determine the concentrations of carbonate-associated iodine using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700X). Recent laboratory data show that the addition of 0.5% tertiary amine (as an iodine stabilizer, suggested by Lu et al., 2010) has little impact on iodine recovery as long as the measurement is performed within 15 minutes (see Huang et al., 2022 for more details). Thus, tertiary amine was not used in this study for iodine stabilization, but the time for the carbonate leaching reaction was tightly controlled. Multiple replicate analyses of carbonate standards GSR-23, GSR-25, and GSR-28 yielded relative standard deviations (RSDs) of <3%. An aliquot of 1 mL of acid-digested supernatant was diluted to 30 mL using 2% pre-distilled nitric acid and measured for concentrations of Ca and Mg using an inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Avio 500). Multiple replicate analyses of the carbonate standards GSR-23 and GSR-25 yielded RSDs of <5%.

3.3 Trace elements

The same sample batch (n = 49) was also selected for trace-element analysis (Rare Earth Elements (REE), Mn, Sr, etc.). In detail, ~50 mg sample powder was treated with 5 mL 10% acetic acid for 12 hours. 0.5 mL supernatant was then transferred into a new Teflon beaker. Subsequently, the aliquot was dried using 1 mL concentrated HNO_3 three times to transform the dissolved samples into nitrate. This procedure was followed by the dilution using 10 mL 2% HNO_3 before the final elemental determination via an Agilent 7700X ICP-MS at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan). The analytical precision was better than 3% (RSD) for all selected elements. The Ce-anomaly proxy used herein is expressed as $(Ce/Ce^*)_N = Ce_N/(Pr_N{*}Pr_N/Nd_N)$ following Lawrence et al. (2006). Pr and Nd refer to Praseodymium and Neodymium, respectively. The subscript N refers to REE normalized to post-Archean Australian Shale (PAAS) (Taylor and Mclennan, 1985).

4. Results

4.1 Dogna core

The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data from the Dogna core bulk carbonate samples are plotted against the stratigraphy in Fig. 2I-A and 2I-B. $\delta^{13}C_{carb}$ values range between –1.5‰ and +3.7‰ through the succession and show a clear N-CIE between 28.01 m and 10.45 m. In detail, $\delta^{13}C_{carb}$ values are relatively stable (~+2.1‰) between 28.86 m and 28.01 m core depths, followed by a progressive decrease to –1.5‰ at 20.4 m core depth. Subsequently, $\delta^{13}C_{carb}$ values increase to +3.7‰ at 10.45 m core depth before dropping to the pre-event baseline values (~+1.7‰) stratigraphically upwards. Based on the T-OAE N-CIE morphology, our $\delta^{13}C_{carb}$ data are readily correlatable with previous higher resolution results from the same core by Jenkyns et al. (2001). $\delta^{18}O_{carb}$ values range from –5.3‰ to –1.1‰, with a mean of –3.0‰ in the Dogna core (Fig. 2I-B). Albeit with some fluctuations, $\delta^{18}O_{carb}$ values generally decline over the N-CIE onset interval (i.e., decreasing $\delta^{13}C$ values) and reach a minimum of –5.3‰ at 20.4 m core depth. This value is followed stratigraphically upwards by a marked increase up to ~–1.1‰ at the top of the core.

The I/(Ca+Mg) values in the Dogna core increase abruptly from ~1 μmol/mol to the maximum of 3.97 μmol/mol at 28.01 m core depth at a level below the T-OAE N-CIE interval (Fig. 2I-C), concurrent with generally negative Ce-anomaly records (~0.8; Fig. 2I-D). Higher in the stratigraphy there follows a marked drop in I/(Ca+Mg) values to 0.84 μmol/mol at 26.4 m core depth, coinciding with an abrupt increase in the Ce-anomaly to 1.4 during the N-CIE onset interval. Upwards, in parallel with the decreasing $\delta^{13}C$ that pass to the interval recording the late recovery phase of the T-OAE N-CIE (i.e., rising δ^{13}C values), despite some minor fluctuations, the I/(Ca+Mg) values remain relatively stable with a mean of 0.72 μmol/mol from 26.4 m to 12.52 m core depth. Coevally, Ce-anomalies remain predominantly positive (with a maximum of 1.6) up to the level of the late N-CIE recovery phase (15.36 m core depth), followed by a gradual decrease upwards with a minimum of ~0.4 at the top of the core. Following the interval of generally low I/(Ca+Mg) values, an increase to 3.34 μmol/mol is observed at the end of the T-OAE N-CIE before declining to the background value (0.42 μmol/mol at the top of the core) post-dating the event.

4.2 Colma di Malcesine section

The δ^{13}C$_{carb}$ and δ^{18}O$_{carb}$ data in the Colma di Malcesine section (Fig. 2II-A and 2II-B) are from Woodfine et al. (2008). The I/(Ca+Mg) values at this site increase from ~1 μmol/mol to ~1.7 μmol/mol at the very beginning of the T-OAE N-CIE, coupled with negative Ce-anomalies ranging from <0.2 to 0.9. Similarly to the Dogna core, the I/(Ca+Mg) values then drop markedly to 0.96 μmol/mol at 1.5 m section height, concurrent with decreasing δ^{13}C values during the N-CIE onset interval. Following a subsequent increase to 1.61

μmol/mol at 5.5 m section height, a general decline is observed upwards in the N-CIE recovery phase, with the I/(Ca+Mg) values revolving around 0.8 μmol/mol to the end of the event at 33.5 m section height (Fig. 2II-C). The Ce-anomaly values fluctuate through the succession with the majority (18 out of 21) <1. The maximum (1.3) is reached at 19.5 m section height, followed by a gradual drop moving stratigraphically upwards (Fig. 2II-D).

5. Discussion

5.1 Preservation of geochemical signals and Ce-anomaly as an indicator of local redox conditions

Geochemical parameters such as Mn and Sr concentrations, Mn/Sr ratios, and $\delta^{18}O_{carb}$ have been extensively applied to assess carbonate diagenetic alteration (Brand and Veizer, 1980; Kaufman and Knoll, 1995; Jacobsen and Kaufman, 1999). We thus compared our I/(Ca+Mg) values to these geochemical parameters to assess the potential diagenetic effects on our analyzed samples.

There is no or only a weak correlation between our I/(Ca+Mg) values and these indicators of diagenesis (i.e., Mn/Sr and $\delta^{18}O_{carb}$) at both sites (Fig. 3A–3D), suggesting negligible diagenetic imprints on our carbonate samples.

Generally high $\delta^{18}O_{carb}$ values (>–5‰) at both sites (all samples have $\delta^{18}O_{carb}$ values >–5‰ at Colma di Malcesine, 24 out of 28 samples have $\delta^{18}O_{carb}$ values >–5‰ at Dogna) further support the contention that our samples are little altered (Table S1; Kaufman and Knoll, 1995). The lack of correlation between Mg/Ca and I/(Ca+Mg) implies that the effects of dolomitization are limited as well at both sites (Fig. 3E and 3F). Thus, the carbonate rocks we analyzed likely preserve primary seawater signals, and our I/(Ca+Mg) and Ce-anomaly data likely capture local/regional upper-ocean redox conditions.

5.2 Ce-anomaly as an indicator of local *vs* global redox conditions

Ce has a very short residence time (50–130 yr as opposed to 1500 yr for the global ocean mixing time) in modern oceans (Alibo and Nozaki, 1999), which makes it sensitive to local redox changes. Nevertheless, on a global basis, significant changes in marine redox would impact widespread oxic sinks (e.g., the manganese (oxyhydr)oxide pool), thereby leaving a similar ocean-wide Ce-anomaly potentially recorded in many depositional environments: geochemical processes that would mask the signal of local redox changes (Jenkyns et al., 2017). For example, in the modern oceans where oxic sinks are widespread, the negative Ce-anomaly is likely a ubiquitous characteristic given its large adsorption onto the manganese (oxyhydr)oxide minerals (Tostevin, 2021). By contrast, during OAEs, globally expanded marine deoxygenation would have greatly reduced the size of the manganese (oxyhydr)oxide sink, thereby releasing massive quantities of Ce back into the water columns leading to a globally distributed positive Ce-anomaly (e.g., Dickens and Owen, 1995; Bodin et al., 2013). Consequently, it is necessary to evaluate the roles of local and global redox in marine Ce signals before using the Ce-anomaly as an indicator of local upper-ocean redox.

As mentioned in Section 4, the Ce-anomaly data at our studied sites show clearly different patterns; at the pelagic Dogna site, the significant positive Ce-anomaly during the N-CIE onset interval was followed by a continued decline to background values in the N-CIE recovery phase (Fig. 2I-D). By contrast, in the shallow-water Colma di Malcesine section, Ce-anomaly records fluctuated more abruptly throughout the N-CIE interval (Fig. 2II-D). The clear inconsistency between these two sites under widely differing depositional environments suggests a crucial role of local redox in the Ce-anomaly records.

5.3 Widespread upper-ocean deoxygenation in the Alpine-Mediterranean Tethys

The I/(Ca+Mg) ratios at both of the study sites are higher than those from the Proterozoic and Paleozoic, though a marked increase in the Devonian suggests a rise in atmospheric and marine dissolved oxygen, which is likely associated with increased abundance of vascular land plants (Lu et al., 2018). The higher I/(Ca+Mg) ratios in the Mesozoic suggest more oxygenated oceans, possibly due to a marked radiation of eukaryotic phytoplankton (Lu et al., 2018).

On a shorter time scale, however, to the first approximation, I/(Ca+Mg) and Ce-anomaly data indicate abrupt upper-ocean deoxygenation at both sites throughout the T-OAE (Fig. 2). Specifically, just before the T-OAE N-CIE, markedly increased I/(Ca+Mg) and negative Ce-anomalies suggest oxygenated upper oceans at the pelagic site. On the shallow-water platform, oxygenated conditions could have persisted to the very beginning of the T-OAE N-CIE. Subsequently, local upper ocean waters in both platform and basinal environments shifted abruptly to oxygen-depleted conditions during the decreasing δ^{13}C interval, as reflected by a clear drop in I/(Ca+Mg) and a positive shift in Ce-anomaly records. The deoxygenation was sustained through the event, as illustrated by generally low I/(Ca+Mg) values at both sites. Nevertheless, in more detail, on the platform the oxygen-depleted state appears to have been not as strong as that at the pelagic site. Specifically, in the platform setting (Colma di Malcesine section), the Ce-anomaly records barely cross the anoxic threshold (1.2) with most data indicating suboxic conditions (Fig. 2II-D), and I/(Ca+Mg) values fluctuate markedly in the N-CIE recovery phase, reflecting episodic oxygenation (Fig. 2II-C). By contrast, the environment deteriorated at Dogna, where the local upper ocean waters became anoxic during the N-CIE onset interval as illustrated by clearly positive Ce-anomalies (Fig. 2I-D). The intense reducing conditions started to improve following the late N-CIE recovery phase, as indicated by gradational negative excursions of Ce-anomalies into the oxic/suboxic sector. The Ce-based inference of gradually more oxygenated conditions appears to have occurred earlier than that indicated by the I/(Ca+Mg) ratios, which suggests a recovery of local upper-ocean conditions at the end of the T-OAE N-CIE. This upper-ocean redox mismatch likely results from the relatively slow I^- oxidation process (Chance et al., 2014), which can maintain low IO_3^- concentrations in the upper oceans despite a potential recovery of dissolved oxygen contents during the T-OAE N-CIE recovery phase. The fact that the cerium anomaly was likely related to both local and global processes could also have been a complicating factor.

Commonly observed organic-rich deposits in the European Epicontinental Shelf across the T-OAE (even post-dating the T-OAE) are commonly attributed to the development of sustained local/regional marine anoxia/euxinia and low rates of clastic sedimentation (Kemp et al., 2022a), which was associated with geographic barriers and runoff-induced watermass stratification (McArthur et al., 2008; Ruvalcaba Baroni et al., 2018). Outside of the European Epicontinental Shelf, however, for example in the Alpine-Mediterranean Tethys, reducing conditions throughout the water column do not appear to have been particularly intense even during the T-OAE, as inferred from compiled geochemical, sedimentological, and paleontological data (Gambacorta et al., 2024). This geochemical state was likely due to open-ocean connectivity and the proximity to oxygen-rich currents from equatorial regions (Ruvalcaba Baroni et al., 2018). Nevertheless, in the Belluno Basin the occurrence of high-molecular-weight porphyrins (diagnostic of green sulfur bacteria) in the Longarone section (close to the Dogna core) suggests photic-zone euxinia, albeit intermittent in character, at this pelagic site (Farrimond et al., 1989). This interpretation is broadly consistent with our I/(Ca+Mg) and Ce-anomaly data from Dogna. On the Adriatic Carbonate Platform (i.e., a continuation of the Friuli Platform, east of the Belluno Basin; Fig. 1B), the enrichment of sedimentary Mn prior to and extending to the onset of the T-OAE in the Velebit-A section, Croatia (site 3 in Fig. 1A) suggests local shallow-water deoxygenation (Sabatino et al., 2013). This interpretation is supported by the enrichment of redox-sensitive metal elements (e.g., V, Ni, and Mo) in the Kovk section (site 4 in Fig. 1A) on the same platform, which indicates intensified reducing conditions in the photic zone (Ettinger et al., 2021). A similar marine chemistry has also been inferred in the Marche-Umbria Apennines (central Italy), where the enrichment of maleimides (degraded products of tetrapyrrole pigments that are diagnostic of green sulfur bacteria) in the pelagic Valdorbia section (site 5 in Fig. 1A) indicates that upper-ocean euxinia could have, at least transiently, extended to the upper oceans (Pancost et al., 2004).

On the Campania–Lucania Platform of the southern Apennines that constituted an epi-oceanic carbonate platform of the Alpine-mediterranean Tethys during the Jurassic (Channell et al., 1979), I/Ca work has been carried out in the Monte Sorgenza section (site 6 in Fig. 1A; Lu et al., 2010). The section was deposited in a shallow-water setting with a likely paleo-depth of a few meters and consists mainly of skeletal packstones, ooid grainstones, and wackstones in the Lower Jurassic (Woodfine et al., 2008 and references therein). Biostratigraphic analyses, combined with the identified N-CIEs, chemostratigraphically define the T-OAE at this site (Woodfine et al., 2008; Trecalli et al., 2012). A similar pattern (i.e., depleted marine iodate at the onset of the T-OAE N-CIE; Fig. 4A) was observed, suggesting similar oxygen-depleted conditions (Lu et al., 2010) to those present on carbonate platforms and adjacent pelagic environments in the Southern Alps (Fig. 4B and 4C). The deoxygenation in the Monte Sorgenza section was sustained throughout the interval of the N-CIE, even extending into post-event times. Further I/Ca work on belemnites in the Yorkshire section in the north of the European Epicontinental Shelf (Cleveland Basin, UK) shows comparable results, suggesting upper-ocean deoxygenation was at least a trans-regional characteristic during the T-OAE (Lu et al., 2010). In North Africa, the sporadic occurrence of aryl isoprenoids (products of aromatic carotenoids that are linked to the biosynthesis by photo-autotrophic sulfur bacteria) in the Chaabet El Attaris section, Tunisia (site 7 in Fig. 1A) implies at least episodic photic-zone euxinia at the margin of northern Gondwana during the T-OAE

(Ruebsam et al., 2022). In the Austro-Alpine sector (Fig. 1A), where regional seawater was hydrographically less restricted and better ventilated than the European Epicontinental Shelf, deoxygenation conditions also deteriorated in the T-OAE N-CIE interval. In detail, the occurrence and accumulation of isorenieratane in the Reka Valley section, Hungary (site 8 in Fig. 1A) on the northeastern West Tethys shelf suggests that photic-zone euxinia could have extended to the open oceans during the T-OAE (Ruebsam et al., 2018). Based on multiple geochemical proxies (e.g., the size of pyrite framboids, sedimentary sulfur contents, and pyrite sulfur-isotopes), a detailed analysis of T-OAE marine sulfur cycling at Zázrivá, a transitional spot between the European shelf and the Tethyan continental margin in Slovakia (site 9 in Fig. 1A) also reveals an expansion of shallow-water euxinia proximal to the open oceans (Suan et al., 2018).

5.4 An OMZ model for upper-ocean deoxygenation across the T-OAE, and implications for biotic turnover

Upper-ocean deoxygenation during the T-OAE outside of the anoxic/euxinic European Epicontinental Shelf, for example, in the Alpine-Mediterranean Tethys was likely associated with an expanded OMZ, which caused marked depletion of iodate in surface oceans as observed at both of our study sites. Earlier work has linked the widespread organic-rich deposits in Tethys to an expanded OMZ model (Jenkyns, 1988; Farrimond et al., 1989), which would have been associated with sluggish circulation and weakened capacity of marine dissolved oxygen due to T-OAE climate warming. Moreover, warming-driven enhancement of hydrological cycling and increased silicate chemical weathering would have significantly increased terrigenous fluxes, as evidenced by globally recognized positive shifts to more radiogenic values in Os- and Sr-isotopes (e.g., McArthur et al., 2000; Cohen et al., 2004; Kemp et al. 2020; Yang et al., 2024) and widely distributed coarser sediments and increased terrestrial material (e.g., increased terrestrial phytoclast abundance) across the T-OAE (e.g., Kemp and Izumi, 2014; Kemp et al., 2019). Increased terrigenous inputs would have elevated nutrient availability, which was likely augmented by active local upwelling (e.g., Jenkyns et al., 2001). Movement of nutrient-rich waters up into the photic zone would have stimulated marine productivity, potentially leading to eutrophication and the consequent deterioration of local/regional marine environments (i.e., an expanded OMZ) due to intensified remineralization of planktonic organic matter (Jenkyns, 2010).

The widespread oxygen-depleted conditions could have been exacerbated by a protracted rise in global sea level during the T-OAE (e.g., Hesselbo and Jenkyns, 1998; Hallam, 2001; Hesselbo, 2008), as evidenced by the commonly observed lithological transitions (from oolitic limestones to marlstones, or even shales) and the local drowning of carbonate platforms in the Alpine-Mediterranean Tethys (e.g., Woodfine et al. 2008; Ettinger et al., 2021). This OMZ model is further supported by the widely distributed manganese carbonate rocks in the Alpine-Mediterranean Tethys (e.g., in Austria, Germany, Italy and Hungary), which are interpreted to have formed as the result of enhanced land-derived Mn transport (mainly in the form of dissolved reduced Mn^{2+}) to basins with an expanded OMZ and precipitated as $MnCO_3$ in sediment under less reducing conditions (Jenkyns et al., 1991; Gambacorta et al., 2024), though a local hydrothermal/volcanic Mn source cannot be excluded. Outside the Alpine-Mediterranean Tethys, the OMZ even extended into the abyssal environment of the central Panthalassic (= paleo-Pacific) Ocean during the T-OAE, as indicated by the bottom-water anoxia/euxinia in reconstructed for the exotic terrain of the Sakahogi section, central Japan (Kemp et al., 2022b; Chen et al., 2023).

A second-order (i.e., a species-level event) mass extinction could have begun around the time of the Pliensbachian/Toarcian boundary and likely peaked during the T-OAE (Hallam, 1986; Little and Benton, 1995; Dera et al.,2010). Earlier work has taken marine anoxia/euxinia as the controlling factor of the coeval biotic turnovers (e.g., Wignall et al., 2005; Caswell and Coe, 2013; Danise et al., 2015) because reduced seawater [O_2] would have threatened marine organisms by reducing oxygen availability and compromising aerobic metabolism (Diaz and Rosenberg, 2008). For example, in the Yorkshire section (Cleveland Basin) in the European Epicontinental Shelf, the horizons where most benthic species disappeared are unambiguously organic-rich, which suggests the predominance of intense reducing conditions, and thus a potential cause-and-effect link between an anoxia-induced increase in ecological pressure and marine invertebrate extinction (Wignall et al., 2005). A multivariate approach that combines multiple geochemical proxies (e.g., TOC, C-, O-, S-, and Mo-isotopes) with quantitative invertebrate fossil data in the Cleveland Basin further underlines the crucial role of anoxia/euxinia in biotic turnovers given a clear correlation between increasing Mo-isotopes and declining benthic diversity (Danise et al., 2015).

Our work, by reconstructing upper-ocean redox across the T-OAE in the

Alpine-Mediterranean Tethys, allows for the evaluation of the relationships between regional marine redox and biotic turnovers. In detail, in the shallow-water Colma di Malcesine section, the lack of bioturbation and fauna in the clay-rich carbonates, coupled with depleted marine iodate and increased marine Ce abundance during the N-CIE onset interval (Fig. 2II) implies reduced seawater [O_2] as a potential threat to the local marine fauna. The sparse occurrence of sponge spicules in these clay-rich horizons suggests episodic oxygenation events, an interpretation supported by our fluctuating I/(Ca+Mg) values and generally low marine Ce abundance (Fig. 2II). The subsequent occurrence of bivalves and echinoderms in the interval of the N-CIE recovery phase at this site (Woodfine et al., 2008) suggests improved marine environments, which is broadly consistent with our proxy-based inferences. Similar findings are also observed in the nearby sections on the Trento Platform where, for example, bioturbation is absent in the Sega d'Ala section at the onset level of the T-OAE N-CIE, whereas abundant benthic fossils are present in the interval recording the recovery phase and after the event (Woodfine et al., 2008). Although direct paleontological information from the pelagic Dogna core itself is lacking, detailed biostratigraphic work on multiple sections nearby in the Belluno Basin has revealed an absence of benthos and paucity of planktonic biota in the T-OAE clay-rich interval, underlain by massive belemnite-bearing limestone with sporadic ammonites, foraminifera, radiolarians and sponge spicules, and overlain by pelagic limestone containing diagnostic ammonites (Jenkyns et al., 1985). Moreover, biotic turnovers have been widely reported in the Alpine-Mediterranean sector during the T-OAE. For example, reduced abundance and dwarfism of pelagic calcareous nannofossils has been observed in Italy and Portugal (e.g., Erba, 2004; Suan et al., 2008; Ettinger et al., 2021), accompanied by marked turnovers of dinoflagellates (Palliani and Riding, 1999; Correia et al., 2021). A turnover in the benthos (e.g., bivalves, brachiopods, foraminifera) and nekton (e.g., ammonites, ostracods) also occurred in Morocco, Algeria, Portugal, and Italy (e.g., Boomer et al., 1998; Cecca and Macchioni, 2004; Soulimane et al., 2017; Reolid et al., 2019), with a loss of benthos in the Peniche section, Portugal (Rita et al., 2016) and in the Ratnek El Kahla section, Algeria (Ruebsam et al., 2020).

Given the unequivocal evidence for upper-ocean deoxygenation (even anoxia/euxinia) in the Alpine-Mediterranean region at the onset of the T-OAE N-CIE based on the I/(Ca+Mg), redox-sensitive metal elements, and biomarkers (Section 5.3), a causal link between marine redox and biotic turnovers may have also existed in the Tethyan realm lying to the south of the European Epicontinental Shelf. Even in this region, oxygen-depleted conditions may have been in excess of the tolerance of marine aerobic organisms, leading to at least regional extinction. This temporary or permanent loss of biota could have been exacerbated by the local occurrence of free H_2S in the upper ocean, which was toxic to organisms living in shallow-water settings. Nevertheless, multiple stressors (e.g., temperature, pH, sea level, and seawater [O_2]) could have had synergistic impacts on the regional biotic turnovers during the T-OAE. For example, the northward migration of the Mediterranean ammonite fauna was likely a consequence of the eustatic sea-level rise and increased seawater temperatures (Suan et al., 2008; Dera et al., 2011). The regional carbonate-production crisis may have also resulted from the increase in eustatic sea level, and was exacerbated by possible ocean acidification (Müller et al., 2020b) associated with massive carbon emissions during the T-OAE (Trecalli et al., 2012).

6. Conclusion

Newly determined new I/(Ca+Mg) data from two carbonate successions with widely differing paleo-depths in northern Italy, combined with Ce-anomaly records, reveal upper-ocean deoxygenation in the Alpine-Mediterranean Tethys at the onset of the T-OAE. The oxygen-depleted conditions are attributed to an expanded OMZ and are broadly consistent with regional faunal turnovers. This association is compatible with a causal link between deoxygenation and extinction. Most likely a cause-and-effect relationship existed between upper-ocean [O_2] scarcity and increased ecological stress even outside of the European Epicontinental Shelf, where regional reducing conditions in hydrographically restricted basins were extremely intense and persistent.

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Appendix A. Supplementary materials

Supplementary materials related to this article can be found on-line at https://

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FIGURE CAPTIONS

Fig. 1 (A) Paleogeographic map of the Western Tethys in the Early Jurassic (modified after Müller et al., 2020a), illustrating the locations of the studied Dogna core (site 1, blue circle) and Colma di Malcesine section (site 2, purple circle). Sites 3–9 indicate possible photic-zone anoxia/euxinia during the T-OAE. See main text for details. EES: European Epicontinental Shelf; A-A: Austro-Alpine Sector; A-M: Alpine-Mediterranean Sector; NGPM: Northern Gondwana Paleomargin. (B) Present configuration of Early Jurassic carbonate platforms and basins of the northern peri-Adriatic domain in the Southern Alps, showing the platform and basinal environments for the Colma di Malcesine section and the Dogna core, respectively. Modified after Ettinger et al. (2021).

Fig. 2 (I) Litho- and bio-stratigraphy, and geochemical data ($\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, I/(Ca+Mg) and Ce-anomaly) from the Dogna core of the Lower Toarcian. The lithological log was drawn schematically based on the calcium carbonate content ($CaCO_3$ wt%) data (see Supplementary materials). Biostratigraphy is after Jenkyns et al. (1985). The $\delta^{13}C_{carb}$ data denoted by black solid triangles and brown hollow circles are from this study and Jenkyns et al. (2001), respectively, which constrain the T-OAE stratigraphically. (II) Lithostratigraphy and geochemical data ($\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$, I/(Ca+Mg), and Ce-anomaly) from the Lower Toarcian of the Colma di Malcesine section. The lithological log, $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data are from Woodfine et al. (2008). Note the black dashed line in the I/(Ca+Mg) profile at both sites representing a three-point moving average. *D. tenu.* = *Dactylioceras tenuicostatum*. Plien. = Pliensbachian. Fm. = Formation.

Fig. 3 Cross-plots of I/(Ca+Mg) versus Mn/Sr, $\delta^{18}O_{carb}$ and Mg/Ca from the Dogna core (panels A, C, and E) and the Colma di Malcesine section (panels B, D, and F).

Fig. 4 Paired $\delta^{13}C_{carb}$ and I/(Ca+Mg) from Monte Sorgenza (A), Colma di Malcesine (B), and Dogna (C) in Italy, with a potential water-depth gradient from shallower (platform) to deeper (basin) environments. Note the I/Ca ratios at Monte Sorgenza (Lu et al., 2010), as opposed to I/(Ca+Mg) ratios at Colma di Malcesine and Dogna. The shaded area denotes the T-OAE interval defined by biostratigraphy and the identified N-CIEs (Woodfine et al., 2008; Trecalli et al., 2012; Jenkyns et al., 1985, 2001). Note an abrupt drop in marine iodate at all three sites concurrent with the T-OAE N-CIEs, suggesting widespread upper-ocean deoxygenation in the Alpine-Mediterranean Tethys.

Table. S1 All geochemical data presented and discussed in the main manuscript from the Colma di Malcesine section and Dogna core.