

**Patterns of local and global redox variability during the Cenomanian–Turonian Boundary
Event (Oceanic Anoxic Event 2) recorded in carbonates and shales from central Italy**

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Abstract

Careful evaluation of the local geochemical conditions in past marine settings can provide a window to the average redox state of the global ocean during episodes of extensive organic-carbon deposition. These comparisons aid in identifying the interplay between climate and biotic feedbacks contributing to and resulting from these events. Well-documented examples are known from the Mesozoic Era, which is characterized by episodes of widespread organic-carbon deposition known as Oceanic Anoxic Events (OAEs). This organic-carbon burial typically leads to coeval positive carbon-isotope excursions. **Geochemical data are presented** here for several palaeoredox proxies (Cr/Ti, V, Mo, Zn, Mn, Fe speciation, I/Ca and sulfur isotopes) from a section exposed at Furlo in the **Marche–Umbrian** Apennines of Italy that spans the Cenomanian–Turonian boundary. Here, OAE 2 is represented by a ~1-m thick radiolarian-rich millimetre-laminated organic-rich shale known locally as the Bonarelli Level. Iron speciation data for thin organic-rich intervals observed below the Bonarelli Level imply a local redox shift going into the OAE, with ferruginous conditions (i.e., anoxic with dissolved ferrous iron) transiently developed prior to the event and euxinia (i.e., anoxic and sulfidic bottom waters) throughout the event itself. Pre-OAE enrichments of elements sensitive to anoxic water columns were due to initial development of locally ferruginous bottom waters as a precursor to the event. However, the greater global expanse of dysoxic to euxinic conditions during the OAE greatly reduced redox-sensitive **trace-metal** concentrations in seawater. Carbonate I/Ca ratios were generally low, suggesting locally reduced bottom water oxygen conditions preceding the event and relatively increased O₂ concentrations post-event. Combined, the Furlo geochemical data suggest a redox-stratified water column with oxic surface waters and a shallow chemocline overlying locally ferruginous bottom waters preceding the event, globally widespread euxinic bottom waters during the OAE, followed by chemocline shallowing but sustained local redox stratification following the event.

Keywords

Oceanic anoxic event, OAE 2, redox conditions, geochemistry, trace metals, sulfur

Introduction

Sediments linked to the Cenomanian-Turonian boundary are well exposed at Furlo Gorge in Marche–Umbria, central Italy (Fig. 1), with a nearly 30 m-thick succession containing foraminiferal-nannofossil limestone, chert and organic-rich facies, including a ~1 m-thick black shale/radiolarian sand unit (Bonarelli Level) representing the local expression of Oceanic Anoxic Event: OAE 2 (Beaudoin et al., 1996; Turgeon and Brumsack, 2006; Lanci et al., 2010; Gambacorta et al., 2015). OAE 2 represents the most severe global climatic perturbation in the Cretaceous Period (Schlanger et al., 1987; Kuroda and Ohkouchi, 2006; Takashima et al., 2006; Jenkyns, 2010), marked by globally distributed organic-carbon deposition (Schlanger and Jenkyns, 1976) that is expressed in a large coeval positive carbon-isotope excursion in marine carbonates and marine and terrestrial organic matter (Scholle and Arthur, 1980; Arthur et al., 1990; Hasegawa, 1997). The event is generally marked by indicators of relatively elevated temperatures and atmospheric CO₂ (Berner, 2006; Takashima et al., 2006; Friedrich et al., 2012), high sea level (Haq et al., 1987; Jarvis et al., 2001), enhanced phosphorus regeneration/recycling (Van Cappellen and Ingall, 1994; Nederbragt and Fiorentino, 1999; Mort et al., 2008; Kraal et al., 2010), increased hydrothermal activity or other forms of basalt-seawater interaction (Jones and Jenkyns, 2001; Snow et al., 2005; Kuroda et al., 2007; MacLeod et al., 2008; Du Vivier et al., 2014; Du Vivier et al., 2015; Jenkyns et al., 2017), increased continental weathering (Blättler et al., 2011; Blumenberg and Wiese, 2012; Pogge von Strandmann et al., 2013) and major changes in the movement of marine water masses (Martin et al., 2012; Zheng et al., 2013). The physical and chemical oceanographic changes during the OAE resulted in evolutionary turnover of marine organisms, including molluscs (Elder and Kirkland, 1985; Elder, 1991), calcareous nannofossils (e.g., Bralower, 1988; Erba, 2004), radiolarians (Erbacher et al., 1996; Erbacher and Thurow, 1997; Musavu-Moussavou et al., 2007) and benthic and planktic foraminifera (e.g., Leckie, 1985; Kaiho and Hasegawa, 1994; Premoli Silva and Sliter, 1999; Leckie et al., 2002; Parente et al., 2008).

Understanding the dynamics of de-oxygenation during this short-lived event, estimated as lasting between 450 and 900 thousand years (Arthur and Premoli Silva, 1982; Kuhnt et al., 2005; Sageman et al., 2006; Voigt et al., 2008; Eldrett et al., 2015; Batenburg et al., 2016), and similar organic-carbon burial events throughout Earth history, has been a major priority in a search to unravel the climate forcing, biological feedbacks and related redox dynamics of the ocean during

biotic extinction events (Bambach, 2006). There is mounting evidence for widespread anoxic and specifically euxinic conditions during OAE 2 based on diverse geochemical proxies for local bottom-water redox at multiple locations (Brumsack, 2006; Turgeon and Brumsack, 2006; Jenkyns et al., 2007; Pearce et al., 2009; van Bentum et al., 2009; Lu et al., 2010; Hetzel et al., 2011; Owens et al., 2012; Westermann et al., 2014; Dickson et al., 2016a; Goldberg et al., 2016; Owens et al., 2016), including evidence for photic-zone euxinia (Sinninghe Damsté and Köster, 1998; Kuypers et al., 2002; Pancost et al., 2004; van Bentum et al., 2009). Numerical ocean modelling suggests that 50% (by volume) of the global ocean was anoxic during the OAE (Monteiro et al., 2012). However, sulfur- and molybdenum-isotope mass balance models suggest more limited extents of euxinia specifically, with a maximum of 7% of the seafloor (Owens et al., 2013; Dickson et al., 2016a; Dickson et al., 2016b). By contrast, the global redox conditions prior to and following the OAE remain less known, although several studies have suggested reduced oceanic oxygenation prior to the event (Lu et al., 2010; Westermann et al., 2014; Zhou et al., 2015; Owens et al., 2016). This possibility is particularly relevant as the observed extinctions of radiolaria begin prior to the event, followed by the main biotic turnover recorded in the middle of the Bonarelli Level (Erbacher and Thurow, 1997; Musavu-Moussavou et al., 2007). The decline of other fossil groups during the OAE has been attributed to an expansion of anoxic and euxinic conditions that were unfavourable and even toxic to life (Leckie et al., 2002; Snow et al., 2005). Furthermore, the wide extent of euxinia during the OAE appears to have drawn down bio-essential trace metals (Algeo and Maynard, 2004; Reinhard et al., 2013; Owens et al., 2016), which are important for nitrogen fixation (Fe, Mo and V; Zerkle et al., 2006; Bellenger et al., 2011) and play an integral role in controlling primary production.

The dataset presented here combines several geochemical tracers of marine redox from both shales and carbonates with the goal of constraining local surface- and bottom-water redox conditions prior to, during and subsequent to the OAE, as well as the global redox landscape during this event. It has historically been difficult to assess the stratigraphic record of oxygen dynamics leading into and out of the OAEs due to lithological changes—specifically, transitions from carbonates to organic-rich shales and back to carbonates. Many of the most widely used palaeoredox proxies were developed for use with shales. Recently, however, there have been significant geochemical advances toward more robust assessments of local and global oxygen

conditions recorded in carbonate lithologies (Lu et al., 2010; Gill et al., 2011a; Gill et al., 2011b; Owens et al., 2013; Hardisty et al., 2014; Zhou et al., 2015).

The $\delta^{13}\text{C}_{\text{organic}}$ proxy is here specifically used as a tracer for global burial of isotopically light organic carbon as a reliable tool for stratigraphic correlation. Furthermore, use of the shale iron geochemistry to inform local redox conditions allows for a more sophisticated interpretation of trace-metal geochemistry. In particular, armed with independent constraints on local redox conditions, interpretations of trace-metal enrichments allow tracking of global redox shifts between oxic, anoxic (V, Cr/Ti, Zn) and euxinic (Mo) conditions. Lastly, integration of carbonate-associated-sulfur (CAS) isotopes, a proxy for the global biogeochemical sulfur cycle, and carbonate I/Ca proxy as a fingerprint of local oxic versus anoxic conditions and the relative chemocline position, provides additional constraints. Finally, pyrite $\delta^{34}\text{S}$ has the potential to constrain local environmental conditions, and $\Delta^{34}\text{S}$, the isotopic difference between marine sulfate (from CAS) and pyrite, can provide additional environmental information, such as marine sulfate concentration as related to the extent of marine anoxia and associated pyrite burial.

Materials and methods

Geological Setting

This study focused on sedimentary rocks from the Marche–Umbria region of Italy near the village of Furlo (Fig. 1)—specifically, outcrops exposed in a disused quarry located approximately 25 km SE of Urbino. The exposed rocks are pelagic deposits laid down on the continental margins of the Tethyan Ocean (Bernoulli and Jenkyns, 2009). Of particular interest is the Bonarelli Level, represented by a 110-cm-thick laminated organic-rich interval with clay and thin radiolarian sands (Turgeon and Brumsack, 2006; Jenkyns et al., 2007; Mort et al., 2007; Lanci et al., 2010). Carbonates and organic-rich facies were sampled extending ~12.5 m below the base of the Bonarelli Level, where the section consists of (1) rhythmic layers or couplets of alternating light grey micritic limestone rich in nannofossils and planktic foraminifera (the so-called Scaglia Bianca), (2) black and gray chert and (3) intercalated thin (millimetre-to-centimetre) black organic-rich shales (Beaudoin et al., 1996; Jenkyns et al., 2007; Mitchell et al., 2008; Gambacorta et al., 2015). These thin black shales constitute only a few percent of the section by thickness and are missing in many other OAE 2 localities in Marche–Umbria. Their presence elevates the value and novelty of this study. The overall sequence shows a cyclic

stratigraphic pattern of cherts, shales and limestones, which is attributed to astronomical forcing in the Alpine Tethys–Central Atlantic Ocean. Specifically, the thin black shale levels have been assigned to formation during eccentricity minima with reduced deep-water circulation favouring transient anoxia (Lanci et al., 2010).

The samples were collected in the middle of individual facies to avoid any gradational redox effect associated with adjacent lithologies, but generally the boundaries between lithological units are sharp and distinct. For this study we avoided all the chert-dominated layers, which are not well suited to proxy approaches. Five carbonate samples were collected from above the top of the Bonarelli Level. Weathered surfaces were avoided for all samples collected, especially the carbonate-lean shale intervals, in order to minimize any post-depositional oxidation effects that would most adversely affect Fe speciation. Additionally, for the Bonarelli Level itself, we excavated as deeply as possible (generally 5–7 cm) to reveal the freshest non-fissile material, which is less likely to have been exposed to post-depositional oxidation. This approach was deemed especially important because of the likelihood of pyrite oxidation given that the rocks below the black shale are stained rust-orange (Fig. 1).

Methods

Samples of both carbonates and organic-rich shales were collected for whole-rock geochemical analysis. All samples were trimmed prior to powdering to ensure that geochemical analyses were performed on the most pristine materials possible. All samples were powdered using a trace-metal-clean ball mill. For organic-carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$), all samples were de-carbonated using 4 M hydrochloric acid until effervescence ceased. The samples were then rinsed several times using deionized water and ultimately combusted by elemental analyzer (EA) coupled, under continuous flow, to a Delta V Thermo IRMS (Isotope Ratio Mass Spectrometer) at the University of California, Riverside. The isotope ratio ($^{13}\text{C}/^{12}\text{C}$) was calculated as:

$$\delta^{13}\text{C}(\text{‰}) = \left[\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}} - 1 \right] \cdot 1000. \quad (\text{Equation 1})$$

All values are presented in the standard delta notation as per mil (‰) deviation from Vienna Pee Dee Belemnite (V-PDB), with replicate analyses yielding a standard deviation of 0.05‰. Total carbon (TC) and total sulfur (TS) were measured by combustion of 100 mg of sample in an Eltra CS-500 carbon/sulfur analyzer with high-temperature furnace (1400°C). Total inorganic carbon

(TIC) was measured using an acidification module in combination with the Eltra instrument, and total organic carbon (TOC) was calculated as the difference between TC and TIC.

A standard chromium reduction method was used to quantify pyrite sulfur concentrations (Canfield et al., 1986). Chromium reduction was performed on all bulk samples of organic-rich shale, as well as the residue remaining following the carbonate-associated sulfate (CAS) extraction (see below). Specifically, pyritic sulfur (S_{pyrite}) was extracted using a boiling solution of chromous chloride with hydrochloric acid for 2 hours, a technique that evolves hydrogen sulfide gas. This sulfide was trapped by precipitation as zinc sulfide (ZnS). The precipitate was quantified by titration, yielding wt% S_{pyrite} . For isotopic analysis of $\delta^{34}S_{\text{pyrite}}$, the hydrogen sulfide was instead precipitated as silver sulfide using the same chromium reduction method but with a solution trap containing silver nitrate with ammonium hydroxide.

All samples analyzed for $\delta^{34}S_{\text{CAS}}$ contained carbonate contents of greater than 65 wt% and up to 95 wt%. A standard procedure was followed for extracting CAS (Gellatly and Lyons, 2005; Gill et al., 2011a; Gill et al., 2011b). Briefly, approximately 10 to 20 g of powdered sample were treated with a solution of 10% sodium chloride and then 125 ml of concentrated sodium hypochlorite, with each step being followed by multiple rinses of deionized water to prevent the incorporation of any non-CAS sulfur-bearing phases. The samples were then dissolved using 4 M hydrochloric acid for less than 1 hour and immediately vacuum-filtered, minimizing any oxidation of pyrite. Pyrite oxidation was further limited by the low ferric iron contents of the samples and generally low amounts of pyrite. A barium chloride solution was added to precipitate the extracted sulfate as barium sulfate.

The precipitated silver sulfide and barium sulfate was filtered, homogenized and weighed into pressed tin capsules with excess vanadium pentoxide. The samples were combusted by EA coupled, under continuous flow, to a Delta V Thermo IRMS. The isotope ratio ($^{34}S/^{32}S$) was calculated as:

$$\delta^{34}S(\text{‰}) = \left[\frac{{}^{34}S/{}^{32}S_{\text{sample}}}{{}^{34}S/{}^{32}S_{\text{standard}}} - 1 \right] \cdot 1000. \quad (\text{Equation 2})$$

All sulfur-isotope compositions are reported in standard delta notation as per mil (‰) deviation from Vienna Canyon Diablo Troilite (V-CDT). The data were analyzed in the Lyons' stable isotope laboratory at the University of California, Riverside, using a series of in-house standards

(IAEA S-1, S-2, and S-3) and international standards (IAEA SO-5, IAEA SO-6, and NBS 127), with a replicate analyses agreement of 0.2‰ or better.

Trace-element analysis was performed using ~100 mg of powder weighed into ceramic vials and heated for ~12 hours at 450°C to volatilize all organic material. The samples were subsequently weighed after cooling to determine the loss on ignition and then transferred into trace-metal-clean Savillex vials and completely dissolved using a standard sequential acid protocol (nitric acid/hydrochloric acid/hydrofluoric acid) at ~150°C. Subsequent to complete dissolution, the samples were dried down and then re-constituted in ~0.35 M HNO₃ for major- and trace-element analysis. All acids used in this method were Aristar/trace-metal grade. Elemental concentrations (Al, Fe, Ti, Mo, V, Cr and Zn) were measured using an Agilent 7500ce quadrupole inductively coupled plasma mass spectrometry (ICP-MS) housed in the Lyons' laboratory at the University of California, Riverside. Standard reference materials (SDO-1 shale) were digested along with the samples and analyzed with each batch of digestions and were within the accepted analytical error for all elements. Procedural blanks were below detection limits, and analytical reproducibility on separate dissolved samples was better than 5% for all elements.

Iron speciation analysis was performed on all of the shales samples. Per convention, we operationally define highly reactive iron (Fe_{HR}) as pyrite Fe (Fe_{py}), Fe carbonate (Fe_{carb}), Fe oxides (Fe_{ox}) and magnetite Fe (Fe_{mag}). All these phases are assumed to be reactive toward hydrogen sulfide on early diagenetic time scales (Canfield et al., 1992; Raiswell and Canfield, 1998; Poulton and Canfield, 2005). Highly reactive iron is thus calculated as Fe_{py} + Fe_{carb} + Fe_{ox} + Fe_{mag}. Pyrite-Fe concentrations are calculated using the chromium method described above, with Fe_{py} calculated from the pyrite-S concentrations assuming a stoichiometry of FeS₂. Unpyritized reactive Fe (Fe_{carb}, Fe_{ox} and Fe_{mag}) was analyzed using a three-step sequential extraction (Poulton and Canfield, 2005; Poulton and Raiswell, 2005). Briefly, ~100 mg of sample were weighed into a 15 ml centrifuge tube and processed as follows: (1) a 1 M sodium acetate extraction adjusted to a pH of 4.5 with constant shaking for 24 hours to extract Fe_{carb}, (2) extraction of the sample residue for Fe_{ox} using 50 g/L sodium dithionite buffered to a pH of 4.8 for 2 hours with constant shaking and (3) extraction of Fe_{mag} from the remaining residue using an ammonium oxalate/oxalic acid-buffered solution at a pH of 3.2 for 6 hours. All extracts were analyzed using an ICP-MS in the Lyons laboratory.

Iodine/calcium ratios (I/Ca) in carbonate lithologies were determined by quadrupole ICP-MS (Bruker M90) at Syracuse University. Measurements of iodine and calcium were determined by dissolving ~1-5 mg of sample in **trace-metal-clean** vials using 0.54 M nitric acid (Lu et al., 2010). Tertiary amine (0.5%) was added to all samples and standards to stabilize iodine, since it is volatilized in acidic solutions. The resulting solutions were analyzed the same day. Standard reference materials (JCP-1 coral) were digested along with the samples and analyzed in parallel, which resulted in an average iodine value of 5.59 ± 0.11 ppm ($n = 5$), which is similar to previous results of 5.47 ± 0.07 ppm (Lu et al., 2010) and 5.5 ± 0.2 ppm (Chai and Muramatsu, 2007). The sample reproducibility was better than 5% for both I and Ca.

Results

Carbon

The $\delta^{13}\text{C}_{\text{org}}$ analyses at Furlo reveal a ~4‰ excursion across the organic-rich Bonarelli Level that marks the OAE at this locality. Below this organic-rich unit, within the thin black shales interbedded between the pelagic limestones, the values range between -28.1‰ and -26.4‰, with an average of -27.4‰. Within the OAE, values range between -26.5‰ and -23.4‰, with an average of -24.8‰ (Fig. 2). These values agree well with data in Jenkyns et al. (2007) from the same location. The TOC values below and above the Bonarelli Level (black shales and carbonates below; carbonate above) are all below 2.2 wt%, and a majority of the samples are near 0.5 wt%. In contrast, the TOC values increase to an average of 7.0 wt% in the Bonarelli Level itself, with a maximum recorded value of 13.4 wt%. The carbonate content of the sub-Bonarelli Level black shales were all below 33 wt%, and the carbonates below and above the Bonarelli Level had averages of 90.7 and 78.7 wt%, respectively. Carbonate contents for the Bonarelli Level itself were below the detection limit and are reported as zero. However, Jenkyns et al. (2007) reported TOC values between 0 and 20 wt% in the stratigraphically lower thin black shales, implying considerable non-homogeneity in these organic-rich levels. Elsewhere in Marche–Umbria, TOC contents of parts of the Bonarelli Level locally exceed 20 wt% (Farrimond et al., 1990; Tsikos et al., 2004; Gambacorta et al., 2015).

Iron and trace-metal geochemistry

Iron and trace-metal analyses were performed on all samples with carbonate contents below 35 wt%, which included all organic-rich shales. These samples all had total Fe (Fe_T) contents in excess of 0.5 wt%, which is consistent with established protocols (Clarkson et al., 2014). Normalizing Fe_T to Al can reveal enrichments beyond the detrital average, which for Phanerozoic mudstones and shales is 0.51 (± 0.1 ; Raiswell et al., 2008), and thereby suggest anoxic deposition (Lyons and Severmann, 2006). Shales deposited before the OAE have an average ratio of 0.49, with a range from 0.44 to 0.51; within the Bonarelli Level itself, however, the shales have an average of 0.85 and range from 0.52 to 1.18.

The ratio of highly reactive Fe (Fe_{HR}) to Fe_T can also indicate anoxic depositional conditions because of the comparatively large proportion of reactive Fe that is typical of such settings (Raiswell and Canfield, 1998; Poulton and Canfield, 2011). Modern marine muds deposited under oxic conditions have an upper limit of 0.38 for $\text{Fe}_{HR}/\text{Fe}_T$ (Raiswell and Canfield, 1998). The black shales below the Bonarelli Level average 0.57, with all samples above 0.50, and during the event average 0.68, with a range of 0.55 and 0.82. For all but one sample, 90% of the Fe_{HR} is from the pools of Fe_{py} , Fe_{carb} , Fe_{ox} so that Fe_{mag} makes up a small portion of the reactive Fe pool. Furthermore, the removal of Fe_{mag} from the calculations has minimal effects on the ratios and interpretations. It is unlikely that these values are driven by diagenetic artifacts as there is a large amount of pyrite and minimal amounts of secondary oxides as the magnetite contents are low. The ratio of pyrite Fe (Fe_{py}) to Fe_{HR} is a measure of the fraction of the reactive Fe pool that has been pyritized through exposure to hydrogen sulfide. Values above 0.7, when combined with elevated ratios of $\text{Fe}_{HR}/\text{Fe}_T$, convincingly point to deposition beneath euxinic waters (März et al., 2008; Poulton and Canfield, 2011). Black shales deposited prior to deposition of the Bonarelli Level have $\text{Fe}_{py}/\text{Fe}_{HR}$ ratios averaging 0.48, with a range between 0.40 and 0.53, whereas those recording the OAE average 0.78, with all values above 0.73 (Fig. 3). The average pyrite S concentrations in the black shales below the Bonarelli Level are 0.17 wt%, whereas in the OAE interval the average is 0.79 wt%, with a maximum value of 1.01 wt%. These high pyrite contents also attest to the freshness of the samples, consistent with the lack of obvious signs of post-depositional oxidation for the Bonarelli Level black shales.

Trace-metal analysis of the organic-rich shales at Furlo also speaks to investigation of the depositional redox conditions (Fig. 3). Manganese concentrations in sediments deposited prior to the OAE (average of 190 ppm) are well below the average shale value of 850 ppm (Turekian and

Wedepohl, 1961) and drop to 32 ppm within the Bonarelli Level itself. Vanadium is enriched in pre-OAE black shales (578 ppm) compared to average shale values of 130 ppm (Turekian and Wedepohl, 1961). Similarly, average Cr/Ti is also enriched prior to the OAE black shales (77×10^{-2} ppm/ppm) compared to the normalized average shale of Cr/Ti of 2.0×10^{-2} (ppm/ppm) (Turekian and Wedepohl, 1961). Chromium is normalized to Ti content due to substantial detrital inputs (Reinhard et al., 2013). Averages for V and Cr/Ti in the Bonarelli Level are 152 ppm and 7×10^{-2} (ppm/ppm), respectively. Prior to the OAE, Zn concentrations range from 314 to 964 ppm (compared to 95 ppm for average shale; Turekian and Wedepohl, 1961), with an average of 613 ppm. Zinc averages 91 ppm in the Bonarelli Level, with a range of 48 to 191 ppm. Black shales deposited prior to the OAE have an average Mo content of 6 ppm with the highest value reaching 9 ppm (compared to 2.6 ppm for average shales; Turekian and Wedepohl, 1961) and Mo content averages 22 ppm with a range from 14 to 40 ppm within the Bonarelli Level. Aluminum concentrations average 1.15 wt% in the black shales prior to the OAE and show a slight increase within the Bonarelli Level (average of 1.61 wt%). These Al concentrations are low compared to the average upper continental crustal composition (8.00 wt%; Turekian and Wedepohl, 1961), a phenomenon that was documented previously at this and nearby locations (Turgeon and Brumsack, 2006; Westermann et al., 2014). This observation is likely due to dilution from organic matter and siliceous radiolarians. The ratios of a given metal to Al ratio do not significantly alter the trends (Fig. 3) or our interpretations relative to the absolute concentrations, although normalization does smooth some of the overall trends.

The averages and ranges for trace-metal contents in the pre-OAE organic-rich layers and the Bonarelli Level are similar to those reported previously from this location (Turgeon and Brumsack, 2006) and a nearby section (Westermann et al., 2014), with Zn being the lone exception. The average Zn data for the Bonarelli Level are lower compared to earlier reports even though they are from the same site and similar lithologies (Turgeon and Brumsack, 2006), but the average values of the thin black shales prior to the OAE are similar. Directly comparing and using trace-metal enrichments to resolve local redox environments is challenging because the local conditions, i.e. Fe speciation, may not be completely resolved at all sites due to possible global trace-metal drawdown during the event (see discussion).

Pyrite sulfur isotopes

Pyrite isotope data were generated from for all the black shales (Fig. 4). Also, a few of the carbonate samples yielded enough pyrite to determine an isotopic value, but the concentrations were too low to measure the amount of pyrite using the gravimetric method. Generally, the average $\delta^{34}\text{S}_{\text{pyrite}}$ values for carbonate and shale are in good agreement, but carbonates show greater variability. Average $\delta^{34}\text{S}_{\text{pyrite}}$ for all samples stratigraphically below the Bonarelli Level is -47.1‰, with a range from -45.2‰ to -51‰. However, the average $\delta^{34}\text{S}_{\text{pyrite}}$ across the Bonarelli Level increases to -38.8‰, with a range from -36.8‰ to -42.6‰. Two analyzed samples post-dating the Bonarelli Level yielded values of -34.2‰ and -36.4‰. From these data it is unclear whether the $\delta^{34}\text{S}_{\text{pyrite}}$ returns to pre-OAE baseline in strata post-dating the event.

Carbonate sulfur isotopes and I/Ca ratios

$\delta^{34}\text{S}_{\text{CAS}}$ data were only generated for the carbonate-rich intervals. From the base of the section to the base of the Bonarelli Level, $\delta^{34}\text{S}_{\text{CAS}}$ is relatively stable with a range from 15.8‰ to 18.3‰ with a trend toward more positive values as it approaches the Bonarelli Level black shales. This trend of increasing $\delta^{34}\text{S}_{\text{CAS}}$ continues in the carbonate facies that follows the OAE black shale interval, rising to values near 22‰ at 3.5 m above the top of the Bonarelli Level. The $\Delta^{34}\text{S}$, defined as the difference between $\delta^{34}\text{S}_{\text{CAS}}$, representing seawater sulfate (Kampschulte and Strauss, 2004), and $\delta^{34}\text{S}_{\text{pyrite}}$, was calculated for the six samples with both $\delta^{34}\text{S}_{\text{CAS}}$ and $\delta^{34}\text{S}_{\text{pyrite}}$ values. From these data, a trend in $\Delta^{34}\text{S}$ is suggested, with values rising up section going into the OAE and falling again higher in the section (Fig. 4).

Overall the I/Ca results reveal a systematic trend most easily described in three stages: (1) the I/Ca ratios are stable at ~0.6 $\mu\text{mol/mol}$ for the stratigraphically lowest 5 m and (2) decrease to an average of 0.25 $\mu\text{mol/mol}$ from 5 m to the base of the Bonarelli Level and then (3) steadily increase from near 0.25 $\mu\text{mol/mol}$ to > 1 $\mu\text{mol/mol}$ at higher stratigraphic levels (Fig. 4). No iodine or CAS data are available for the Bonarelli Level because of the absence of carbonate.

Discussion

Local geochemical conditions

The trace-metal record for Furlo has been discussed previously (Turgeon and Brumsack, 2006) and at a nearby section (Scopelliti et al., 2006; Westermann et al., 2014). However, this

study provides the first independent geochemical measure of the local redox conditions in multi-lithology section deposited prior to, during and subsequent to the OAE—as an essential interpretive framework for the trace-metal data. For example, the Fe speciation results provide an independent constraint on the local redox environment prior to and during the OAE but not following due to the presence of carbonate-dominated lithologies. The $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ values of black shales throughout the section are elevated relative to typical oxic modern marine sediments (Raiswell and Canfield, 1998; Poulton and Canfield, 2011), suggesting deposition within anoxic bottom waters. The $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ratio in the organic-rich layers deposited prior to the OAE must be viewed with caution, as there are only a few results from thin shale interbeds. However, they are all below the euxinic threshold of 0.7 (März et al., 2008), suggesting ferruginous conditions locally (Poulton and Canfield, 2011). Relatively short-term ferruginous conditions have also been documented from Tarfaya in the proto-North Atlantic before and during OAE 2 (Poulton et al., 2015), which is attributed to orbitally forced enhanced continental weathering flux, and similar results are documented for Cretaceous OAE 3 (März et al., 2008). Samples from the Bonarelli Level deposited during the OAE exhibit elevated $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ and $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ consistent with at least local euxinic deposition for these sediments. Therefore, the $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ and $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ data point to the possibility of a shift from pre-OAE anoxic-ferruginous to euxinic bottom-water conditions during the OAE for the organic rich-sediments of the Bonarelli Level.

Ferruginous and euxinic conditions, as suggested by Fe speciation, typically enrich Fe relative to Al, but the samples deposited prior to the OAE that otherwise suggest ferruginous conditions fall within the crustal average, while the euxinic OAE samples in the Bonarelli Level are relatively enriched in total Fe. A possible explanation for the lower than expected total Fe content in the black shales deposited prior to the OAE is a lower than typical detrital Fe/Al ratio. On the other hand, the enrichments in the Bonarelli Level suggest either a more active Fe transport efficient trapping (as in the Fe 'shuttle'; Owens et al., 2012) or a larger hydrothermal contribution during the OAE proper (Jenkyns et al., 2007), with enrichment facilitated by locally euxinic conditions and associated Fe scavenging as pyrite. Significantly, pyrite framboid diameters in the Bonarelli Level at Furlo average $\sim 7 \mu\text{m}$, whereas those in the underlying black shales are larger and less common, with an average diameter of $9.8 \mu\text{m}$, further suggesting euxinic conditions once the OAE began (Jenkyns et al., 2007).

Manganese concentrations in the black shales deposited prior to the OAE are below the shale average and decrease further within the Bonarelli Level, which we attribute to local syn-sedimentary reduction of Mn-oxides under low-oxygen conditions and recycling into the water column (Turgeon and Brumsack, 2006). Trace-metal proxies requiring low oxygen but not necessarily sulfidic conditions—Cr/Ti, V and Zn (Algeo, 2004; Sahoo et al., 2012; Reinhard et al., 2013; Scott et al., 2013)—show enriched values in sediments deposited prior to the Bonarelli Level. However, all three elements decline to near crustal values within the Bonarelli Level, despite indications from the Fe speciation for more reducing (sulfidic) local conditions that should have continued to enrich these trace metals (Algeo and Maynard, 2004) (see discussion below). Moreover, Mo, a reliable indicator of redox variability, especially euxinic conditions, shows minimal enrichment in sediments deposited prior to the Bonarelli Level and elevated values ($\leq \sim 40$ ppm) in the Bonarelli Level. These OAE black shale enrichments are on the low end of those typical of modern open-ocean euxinic basins (Scott and Lyons, 2012). The Mo values recorded prior to the OAE suggests sulfide was accumulating in, but was largely restricted to, the sedimentary pore fluids underlying the sea floor (Scott and Lyons, 2012). The somewhat muted Mo values characteristic of the Bonarelli Level point to euxinia but with somewhat limited Mo uptake related to global inventory control (see discussion below). It is important to point out that prior to the deposition of the Bonarelli Level, that trace-metals suggest only local to regional reduction of oxic conditions, as confirmed by Fe speciation results. However, at the onset of the Bonarelli Level, trace-metals began to record the onset of reducing conditions in the entire ocean (see discussion below).

The $\delta^{34}\text{S}_{\text{CAS}}$ record at Furlo is very similar to other high-resolution Italian datasets (Ohkouchi et al., 1999; Owens et al., 2013; Gomes et al., 2016). All of the published $\delta^{34}\text{S}_{\text{CAS}}$ data from Italy show a ~ 6 to 7‰ excursion coincident with the carbon-isotope excursion. However, the absolute values for the baseline and associated maximum from the new dataset are most similar to those of Ohkouchi et al. (1999), who sampled a nearby outcrop of the pelagic Scaglia Bianca. Somewhat different is the record from shallow-water platform carbonates situated much further south at Raia del Pedale, which might have formed from a watermass with a different and perhaps stronger local overprint (Owens et al., 2013). At Furlo, the $\delta^{34}\text{S}_{\text{pyrite}}$ record is relatively stable prior to the event with a large $\Delta^{34}\text{S}$, which suggests pyrite formation in an open system (Sageman et al., 2014) likely near the sediment-water interface but not in the water column,

based on the relatively large framboid size (Jenkyns et al., 2007) and minimal Mo enrichment. Through the Bonarelli Level, $\delta^{34}\text{S}_{\text{pyrite}}$ shifts to more positive values and continues to increase above the black shale. This rise in $\delta^{34}\text{S}_{\text{pyrite}}$ was more rapid than that of $\delta^{34}\text{S}_{\text{CAS}}$, which causes the $\Delta^{34}\text{S}$ fractionation to decrease slightly from $\sim -62.5\text{‰}$ to $\sim -55\text{‰}$ —similar to the shift seen in the Western Interior Seaway over approximately the same interval (Adams et al., 2010). It is unlikely that this shift was due to local redox changes since the Fe speciation data suggest that local redox conditions became more reducing (i.e., switched from ferruginous to euxinic). If anything, it would be expected that $\Delta^{34}\text{S}$ values would be more steady and/or larger during the OAE because the pyrite would be forming in a relatively open-system euxinic water column.

I/Ca ratios reflect concentrations of iodate (IO_3^-) in the water column, because IO_3^- is the only iodine species that is incorporated into precipitating carbonate minerals (Lu et al., 2010). Importantly, local IO_3^- accumulation requires the presence of dissolved oxygen. Quantitative reduction to iodide occurs in oxygen-poor waters with reducing potentials similar to those supporting manganese reduction and denitrification (Wong and Brewer, 1977; Emerson et al., 1979; Rue et al., 1997). On the most basic level, the simple presence of carbonate-bound iodine at Furlo implies that oxygen was present in the shallow waters, which is also confirmed by the presence of pelagic carbonate formed from nannofossils and planktonic foraminifera (Lu et al., 2010, 2016; Zhou et al., 2015).

The I/Ca dataset from below the Bonarelli Level shows rather low values throughout the section ($<1\text{ }\mu\text{mol/mol}$), similar to other recent results for pre-OAE I/Ca ratios at multiple globally dispersed localities (Zhou et al., 2015). Beyond presence–absence, these I/Ca ratios are extremely low relative to those found in modern well-oxygenated settings, which are typically greater than $2.6\text{ }\mu\text{mol/mol}$ (Glock et al., 2014; Lu et al., 2016). I/Ca ratios $< 2.6\text{ }\mu\text{mol/mol}$ can be linked to water-column IO_3^- concentrations $< 250\text{ nM}$ (Lu et al., 2010; Glock et al., 2014; Lu et al., 2016), which are typically observed in marine settings within the oxycline directly overlying anoxic waters (Rue et al., 1997; Lu et al., 2016). By comparison to modern marine IO_3^- concentration profiles and associated sedimentary I/Ca ratios, values of $< 2.6\text{ }\mu\text{mol/mol}$ from the Furlo profile are most parsimoniously linked to carbonate secretion by micro- and nannoplankton within the oxycline in a redox-stratified water column (Lu et al., 2016). Similar ranges in I/Ca ratios have been observed at other OAE localities (Lu et al., 2010; Zhou et al., 2015), as well as those crossing the Permian–Triassic boundary (Loope et al., 2013) and from the

Palaeoproterozoic (Hardisty et al., 2014), a time of transitional oxygenation with the likelihood of still common anoxic deep waters. Given that the carbonate secretion would be linked to shallower waters relative to deposition of the studied black shales, the combined Cr/Ti, V, Mo and $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ data from deeper waters and the carbonate I/Ca results from shallow waters strongly suggest a redox-stratified water column—with the possibility of ferruginous bottom waters underlying an oxic surface layer prior to the deposition of the Bonarelli Level. Importantly, the increasing but still low I/Ca ratios relative to modern oxic settings following the OAE suggest a deepening oxycline but with sustained local water-column redox stratification following the event.

Global implications

The Fe geochemistry suggests that this site experienced local euxinic deposition during the OAE, even though trace-metal enrichments are relatively muted for a site experiencing euxinic conditions. An analogous relationship is observed at another OAE 2 locality—namely ODP site 1258, Demerara Rise, eastern equatorial Atlantic (Hetzl et al., 2009; Algeo and Rowe, 2011; Owens et al., 2016)—which suggests global expansion of reducing condition during the OAE. Such a hypothesized expansion of reducing conditions would have depleted the marine inventories of redox-sensitive metals. At this ODP site, molybdenum concentrations do increase at the onset of the OAE, reflecting the beginning of local euxinia, but the values are muted relative to those in modern euxinic settings (Scott and Lyons, 2012). In general, marginal marine sediments lack large trace-metal enrichments during the OAE because there is a global overabundance of sinks (anoxic waters and sediments) in many areas of the ocean compared to the relatively small supply (ocean inventory) of redox-sensitive trace metals. This trend, observed at Furlo as well as other contemporaneous localities, strongly suggests global drawdown of the marine Mo reservoir (reviewed in Owens et al., 2016; Dickson et al., 2017). Previous studies have attributed similar trends to non-euxinic local conditions during the OAE, which would limit the intensity of local Mo scavenging (i.e. Turgeon and Brumsack, 2006; Westermann et al., 2014). However, the addition of Fe speciation data indicates persistent local euxinia throughout the OAE interval at Furlo, suggesting that the ultimate control on enrichment was ocean-scale expansion of euxinic conditions leading to drawdown of trace elements in seawater on a global scale. The same argument can now be made for other OAE 2 locations.

501 Additionally, the Mo/TOC ratio drops through the Bonarelli Level to levels that are low
502 even when compared to the non-euxinic **deposits developed** prior to the OAE, which further
503 highlights the likelihood of Mo burial under a highly depleted marine reservoir (Algeo and
504 Lyons, 2006; Lyons et al., 2009). The Mo-TOC relationship is well documented in the modern
505 and ancient ocean for euxinic deposition and manifests itself as strong positive co-variation, but
506 the specifics of that relationship varies among different marine basins and intervals of time
507 (Algeo and Lyons, 2006; Scott et al., 2008). It is likely that different mean ratios (slopes of the
508 lines of co-variation) track the size of the Mo inventory as related to either local or global factors
509 (Algeo and Lyons, 2006). As such, varying Mo/TOC ratios allow for interpretations that ‘see
510 through’ local organic-matter controls to isolate possible reservoir relationships. Within the
511 Bonarelli Level, the Mo/TOC data average ~3.2 (slightly higher than the 2.8 observed at site
512 1258 on Demerara Rise). The Mo/TOC values recorded during the OAE at both Furlo and
513 Demerara Rise are lower than those of the Mo-depleted modern Black Sea (average of ~4.5),
514 while the Mo-replete Cariaco Basin records Mo/TOC values above ~20 (Algeo and Lyons,
515 2006). In the case of these two modern settings, levels of enrichment are controlled by the
516 strength of the basin’s connection to the open ocean and thus the renewal time of deep waters
517 relative to the rates of Mo uptake, as well as the timescales and magnitudes of water-column
518 sulfide accumulation. The data from Furlo and many other localities (Owens et al., 2016;
519 Dickson et al., 2017) mirror this inventory relationship where the sediment enrichment in
520 reducing basins outpaces the renewal rate. Thus, the Mo, and likely other redox-sensitive trace-
521 metals, drawdown is best explained as an expansion of euxinia during the OAE—compared to
522 conditions before and after the event and in today’s ocean.

523 **Trace-metal** availability may have played a role in controlling the spatial and temporal
524 patterns of evolution during the Proterozoic when widespread ferruginous and euxinic conditions
525 depleted the seawater concentrations of key elements (Anbar and Knoll, 2002; Scott et al., 2008;
526 Dupont et al., 2010; Planavsky et al., 2010; Reinhard et al., 2013), and similar conditions may
527 have existed for short periods in the Phanerozoic (Gill et al., 2011b). For example, widespread
528 reducing conditions can limit the availability of Mo and V, which are linked to the nitrogen cycle
529 as enzymatic co-factors in nitrogen fixation (Glass et al., 2009; Bellenger et al., 2011; Reinhard
530 et al., 2013). Additionally, Zn is known to be essential for eukaryotic development through
531 protein-DNA interactions (Dupont et al., 2006). Somewhat surprisingly, existing trends suggest

that Zn was not limiting in the widely ferruginous and euxinic Proterozoic ocean (Scott et al., 2013). However, concentrations of Zn during the OAE at Furlo and Demerara Rise (Hetzl et al., 2009; Owens et al., 2016) average 91 and 162 ppm, respectively, which is approaching the shale average of ~95 ppm (Turekian and Wedepohl, 1961). In particular, these muted enrichments stand out relative to the average pre-OAE values of 612 ppm observed in the shales. Furthermore, even these higher concentrations are on the low end of what is observed generally during the Precambrian and Phanerozoic in euxinic settings—that is, values commonly above 500 and extending to values greater than 1000 ppm (Scott et al., 2013). A drawdown of Zn concentrations may have played an important role ecologically during the OAE (Dupont et al., 2006). It is difficult to separate the relative importance of each bio-essential trace element, but collectively limitations are likely to have had important ecological and evolutionary impacts during this time interval.

The sulfur-isotope data for CAS show a positive excursion just below the Bonarelli Level and the pyrite excursion that starts at the base of the Bonarelli Level, with both continuing toward more positive values into the post-event interval. This excursion, despite the likelihood of regional differences and related local controls, is observed at numerous locations and basins and thus suggests a global perturbation in the sulfur-isotope composition of the ocean. This perturbation is reasonably attributed to a global increase in pyrite burial as the ocean became more reducing, leaving the marine sulfate reservoir isotopically heavy (Ohkouchi et al., 1999; Adams et al., 2010; Owens et al., 2013; Gomes et al., 2016). Specifically, the $\delta^{34}\text{S}_{\text{CAS}}$ expression of this excursion has now been observed at seven sections worldwide but with varying magnitudes (2 to 7‰), highlighting the combined global and local controls. It is noteworthy that the data of the present study show the global S isotope trend in both CAS and pyrite isotope data, including pyrite extracted from both shales and carbonate lithologies. Furthermore, the timing and lag following the carbon-isotope excursion are nearly identical at all localities (Ohkouchi et al., 1999; Adams et al., 2010; Owens et al., 2013). However, our positive $\delta^{34}\text{S}_{\text{pyrite}}$ excursion of ~12‰ has not been reproduced at other sites (Gautier, 1987; Böttcher et al., 2006; Hetzel et al., 2009; Adams et al., 2010), and the $\Delta^{34}\text{S}$ recorded at Furlo prior to the OAE (64.5 ‰) is the largest known for this event, although it is similar to the values recorded in the Western Interior Seaway (Adams et al., 2010). It is also important to point out that organic S likely plays an important role during this large carbon burial event but there are very limited data. Finally, it is

apparent that $\Delta^{34}\text{S}$ decreases post-OAE, but the timing is unclear as there are no CAS data at this site from the carbonate-free Bonarelli Level (Fig. 4).

The I/Ca trend and magnitudes observed at Furlo are consistent with data obtained from previously studied OAE 2 localities, with a switch to low I/Ca ratios beginning below the onset of the positive carbon-isotope excursion (Lu et al., 2010; Zhou et al., 2015). However, unlike the trace-metal records, this response is not easily linked to global iodine inventory shifts, as I/Ca tracks IO_3^- not total dissolved iodine. A lack of a prominent inventory control on I/Ca is supported by OAE 2 trends that vary in timing and magnitude among sites recording intervals preceding and during the OAE (Zhou et al., 2015). Indeed, organic carbon cycling plays a role in modulating I/Ca ratios, as iodine is a biophilic element whose reservoir size is most strongly linked to organic-carbon burial and remineralization (Lu et al., 2010). Consequently, a reservoir shift to lower iodine concentrations might be expected in association with the increase in organic-carbon burial that drove the positive carbon-isotope excursion of OAE 2 (Lu et al., 2010). However, the onset of this shift would be anticipated to propagate similarly among localities and to track the change in carbon isotopes if I/Ca ratios were mostly mirroring the total dissolved iodine inventory. As such, the combined I/Ca evidence from Furlo and other localities (Lu et al., 2010; Zhou et al., 2015) instead provide strong evidence for the onset of mildly reducing conditions and a shift toward redox-stratified water columns that decreased local IO_3^- concentrations prior to the OAE. The observed inter-site differences in the timing of I/Ca decreases are consistent with shifts toward low-oxygen, redox-stratified water columns that differed among settings on local and regional scales and may provide new perspectives on the mechanisms behind OAEs (Zhou et al., 2015). Toward that goal, this study is the first to integrate I/Ca ratios from carbonates with other proxy measurements from shales, such as V and Cr/Ti, which are similarly sensitive to subtle variations in dissolved oxygen (Rue et al., 1997). Overall, agreement among our diverse proxies further validates the suggestion of an early onset of low-oxygen conditions prior to the OAE.

Conclusions

Paired lithofacies and geochemical data from Furlo, Marche–Umbria, Italy illuminate the local and global redox landscape before and the onset of OAE 2. New Fe speciation data delineate local redox conditions during the deposition of the thin black shales below the

Bonarelli Level and suggest deposition under ferruginous conditions, with $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} > 0.38$ but $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ well below 0.7. In this pre-OAE interval, redox-sensitive elements that first respond to pronounced oxygen deficiency—Mn, V, Cr/Ti and Zn—are enriched, relative to average shale, prior to the OAE, with the exception of Mn, which shows a depletion. Furthermore, Mo, a euxinic proxy, shows very limited enrichment in sediments deposited before the Bonarelli Level, consistent with dissolved sulfide being restricted to pore waters in the underlying sediment column. The entire suite of geochemical data from just below the Bonarelli Level point toward local reducing bottom waters that lacked oxygen and sulfide.

Coincident with the initial onset of deposition at the Bonarelli Level, the Fe proxies suggest bottom-water euxinia, as indicated by parallel enrichments in $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ and $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ and supported by the size distribution of pyrite framboids. Molybdenum values are enriched by up to ~40 ppm, which is similar to euxinic enrichments seen at Demerara Rise in the OAE 2 black shales (Hetzl et al., 2009). These values, however, are relatively subdued compared to modern open-ocean euxinic conditions despite analogously open conditions, suggesting deposition within a depleted dissolved marine Mo reservoir due to global expansion of euxinia (reviewed in Owens et al., 2016; Dickson et al., 2017). Similar relationships have been observed for other intervals in Earth history (Reinhard et al., 2013). Importantly, V, Cr and Zn associated with the euxinic OAE interval are present at close to crustal averages, suggesting analogous drawdown of the marine inventories. Importantly, the expansion of anoxia and euxinia specifically during the OAE likely reduced the global marine metal supplies to levels that might have become biologically limiting. Again, local redox controls are ruled out because of the independent indications of anoxia and euxinia that derive from the Fe proxies.

The carbonate proxies show trends similar to those of previous studies (Ohkouchi et al., 1999; Adams et al., 2010; Lu et al., 2010; Owens et al., 2013; Zhou et al., 2015). Specifically, the $\delta^{34}\text{S}_{\text{CAS}}$ data show a ~6‰ positive excursion with a slight rise before the OAE that continues post-OAE, suggesting continued euxinic burial of pyrite on a large scale that waned with time (Owens et al., 2013). The relatively low I/Ca ratios recorded prior to the OAE point to an oxic surface ocean in direct exchange with laterally and vertically proximal anoxic watermasses, suggesting a shallow pre-OAE chemocline. Following the OAE, the data suggest a deepening of the chemocline related to an expansion of oxygenated waters.

This new multi-proxy lithofacies approach applied to carbonates and shales reveals strong consistency prior to the OAE **interval, and** the environmental drivers that spawned alternating shale and carbonate deposition are not straightforwardly linked to major changes in bottom-water redox conditions. However, no such comparison can be made for the Bonarelli Level due to its lack of carbonate. The stratigraphically higher levels above the Bonarelli Level lack organic-rich shales. Nonetheless, for the first time the combined shale-carbonate strategy suggests relatively low-oxygen conditions during the deposition of the pre-Bonarelli Level limestones and ferruginous conditions for the interbedded black shales—and thus consistently low O₂ conditions prior to the OAE at this location. Rather than changing redox, the rhythmic deposition was likely tied to other astronomically forced climatic and environmental changes (Galeotti et al., 2009; Lanci et al., 2010). The dataset presented here increases our understanding of the spatial extent of reducing conditions and euxinia specifically during OAE 2, with euxinia previously modelled to have affected between 2 and 10% of the seafloor (Owens et al., 2013; Dickson et al., 2016a; Dickson et al., 2016b). Consistent with these models, this dataset can be added to the growing list of localities that experienced low-oxygen and even ferruginous conditions prior to OAE 2 but it is unlikely these conditions prevailed globally as trace-metal enrichments remain high (Hetzl et al., 2009; Owens et al., 2016)—perhaps as a first step towards the more extreme conditions of the oceanic anoxic event proper.

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References

- Adams, D.D., Hurtgen, M.T. and Sageman, B.B.** (2010) Volcanic triggering of a biogeochemical cascade during Oceanic Anoxic Event 2. *Nature Geoscience*, **3**, 201–204, doi: 10.1038/ngeo811.
- Algeo, T.J.** (2004) Can marine anoxic events draw down the trace element inventory of seawater? *Geology*, **32**, 1057–1060, doi: 10.1130/G20896.1.
- Algeo, T.J. and Lyons, T.W.** (2006) Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography*, **21**, PA1016, doi: 10.1029/2004pa001112.
- Algeo, T.J. and Maynard, J.B.** (2004) Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chemical Geology; Geochemistry of Organic-Rich Shales: New Perspectives*, **206**, 289–318, doi: 10.1016/j.chemgeo.2003.12.009.

661 **Algeo, T.J. and Rowe, H.** (2011) Paleooceanographic applications of trace-metal concentration data.
662 *Chemical Geology*, **324–325**, 6–18, doi: 10.1016/j.chemgeo.2011.09.002.

663 **Anbar, A.D. and Knoll, A.H.** (2002) Proterozoic ocean chemistry and evolution: A bioinorganic bridge?
664 *Nature*, **297**, 1137–1142, doi: 10.1126/science.1069651.

665 **Arthur, M.A., Jenkyns, H.C., Brumsack, H.J. and Schlanger, S.O.** (1990) *Stratigraphy, geochemistry, and*
666 *paleoceanography of organic carbon-rich Cretaceous sequences*, in: Ginsburg, R.N. and Beaudoin, B.
667 (Editors) *Cretaceous Resources Events and Rhythms*, NATO ASI Series C, 304, Kluwer Academic
668 Publishers, 75–119.

669 **Arthur, M.A. and Premoli Silva, I.** (1982) Development of widespread organic carbon-rich strata in the
670 Mediterranean Tethys, in: Schlanger, S.O. and Cita, M.B. (Editors), *Nature and origin of Cretaceous*
671 *carbon-rich Facies*, Academic Press: 7–54.

672 **Bambach, R.K.** (2006) Phanerozoic Biodiversity Mass Extinctions. *Annual Review of Earth and Planetary*
673 *Sciences*, **34**, 127–155, doi: doi:10.1146/annurev.earth.33.092203.122654.

674 **Batenburg, S.J., De Vleeschouwer, D., Sprovieri, M., Hilgen, F.J., Gale, A.S., Singer, B.S., Koeberl, C.,**
675 **Coccioni, R., Claeys, P. and Montanari, A.** (2016) Orbital control on the timing of oceanic anoxia in the
676 Late Cretaceous. *Clim. Past*, **12**, 1995–2009, doi: 10.5194/cp-2015-182.

677 **Beaudoin, B., M'Ban, E.P., Montanari, A. and Pinault, M.** (1996) *Lithostratigraphie haute resolution*
678 *(<20 ka) dans le Cénomanién du bassin d'Ombrie-Marches*, *Comptes Rendus de l'Académie des*
679 *Sciences, Paris, Série IIa*, **323**, 689–696.

680 **Bellenger, J.P., Wichard, T., Xu, Y. and Kraepiel, A.M.L.** (2011) Essential metals for nitrogen fixation in a
681 free-living N₂-fixing bacterium: chelation, homeostasis and high use efficiency. *Environmental*
682 *Microbiology*, **13**, 1395–1411, doi: 10.1111/j.1462-2920.2011.02440.x.

683 **Berner, R.A.** (2006) GEOCARBSULF: A combined model for Phanerozoic atmospheric O₂ and CO₂.
684 *Geochimica et Cosmochimica Acta: A Special Issue Dedicated to Robert A. Berner*, **70**, 5653–5664, doi:
685 10.1016/j.gca.2005.11.032.

686 **Bernoulli, D. and Jenkyns, H.C.** (2009) Ancient oceans and continental margins of the Alpine-
687 Mediterranean Tethys: deciphering clues from Mesozoic pelagic sediments and ophiolites.
688 *Sedimentology*, **56**, 149–190, doi: 10.1111/j.1365-3091.2008.01017.x.

689 **Blättler, C.L., Jenkyns, H.C., Reynard, L.M. and Henderson, G.M.** (2011) Significant increases in global
690 weathering during Oceanic Anoxic Events 1a and 2 indicated by calcium isotopes. *Earth and Planetary*
691 *Science Letters*, **309**, 77–88, doi: 10.1016/j.epsl.2011.06.029.

692 **Blumenberg, M. and Wiese, F.** (2012) Imbalanced nutrients as triggers for black shale formation in a
693 shallow shelf setting during the OAE 2 (Wunstorf, Germany). *Biogeosciences*, **9**, 4139–4153, doi:
694 10.5194/bg-9-4139-2012.

695 **Böttcher, M.E., Hetzel, A., Brumsack, H.J. and Schipper, A.** (2006) Sulfur–iron–carbon geochemistry in
696 sediments of the Demerara Rise. In: Mosher, D.C., Erbacher, J., Malone, M.J. (Eds.), *Proceedings of the*
697 *Ocean Drilling Program. Scientific Results*, vol. 207. *Ocean Drilling Program*, College Station, TX, pp. 1–
698 23, doi.

699 **Bralower, T.J.** (1988) Calcareous nannofossil biostratigraphy and assemblages of the Cenomanian-
700 Turonian boundary interval: Implications for the origin and timing of oceanic anoxia. *Paleoceanography*,
701 **3**, 275–316, doi: 10.1029/PA003i003p00275.

702 **Brumsack, H.-J.** (2006) The trace metal content of recent organic carbon-rich sediments: Implications for
703 Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **232**, 344–361,
704 doi: 10.1016/j.palaeo.2005.05.011.

705 **Canfield, D.E., Raiswell, R. and Bottrell, S.H.** (1992) The reactivity of sedimentary iron minerals toward
706 sulfide. *American Journal of Science*, **292**, 659–683, doi: 10.2475/ajs.292.9.659.

Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M. and Berner, R.A. (1986) The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology*, **54**, 149–155, doi: 10.1016/0009-2541(86)90078-1.

Chai, J.Y. and Muramatsu, Y. (2007) Determination of Bromine and Iodine in Twenty-three Geochemical Reference Materials by ICP-MS. *Geostandards and Geoanalytical Research*, **31**, 143–150, doi: 10.1111/j.1751-908X.2007.00856.x.

Clarkson, M.O., Poulton, S.W., Guilbaud, R. and Wood, R.A. (2014) Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments. *Chemical Geology*, **382**, 111–122, doi: 10.1016/j.chemgeo.2014.05.031.

Dickson, A.J., Jenkyns, H.C., Porcelli, D., van den Boorn, S. and Idiz, E. (2016a) Basin-scale controls on the molybdenum-isotope composition of seawater during Oceanic Anoxic Event 2 (Late Cretaceous). *Geochimica et Cosmochimica Acta*, **178**, 291–306, doi: 10.1016/j.gca.2015.12.036.

Dickson, A.J., Jenkyns, H.C., Porcelli, D., van den Boorn, S., Idiz, E. and Owens, J.D. (2016b) Corrigendum to “Basin-scale controls on the molybdenum-isotope composition of seawater during Oceanic Anoxic Event 2 (Late Cretaceous)”. *Geochimica et Cosmochimica Acta*, **189**, 404–405, doi: 10.1016/j.gca.2016.06.025.

Dickson, A.J., Saker-Clark, M., Jenkyns, H.C., Bottini, C., Erba, E., Russo, F., Gorbanenko, O., Naafs, B.D.A., Pancost, R.D., Robinson, S.A., van den Boorn, S. and Idiz, E. (2017) A Southern Hemisphere record of global trace-metal drawdown and orbital modulation of organic-matter burial across the Cenomanian–Turonian boundary (Ocean Drilling Program Site 1138, Kerguelen Plateau). *Sedimentology*, **64**, doi: 10.1111/sed.12303, in press.

Du Vivier, A.D.C., Selby, D., Condon, D.J., Takashima, R. and Nishi, H. (2015) Pacific $^{187}\text{Os}/^{188}\text{Os}$ isotope chemistry and U–Pb geochronology: Synchronicity of global Os isotope change across OAE 2. *Earth and Planetary Science Letters*, **428**, 204–216, doi: 10.1016/j.epsl.2015.07.020.

Du Vivier, A.D.C., Selby, D., Sageman, B.B., Jarvis, I., Gröcke, D.R. and Voigt, S. (2014) Marine $^{187}\text{Os}/^{188}\text{Os}$ isotope stratigraphy reveals the interaction of volcanism and ocean circulation during Oceanic Anoxic Event 2. *Earth and Planetary Science Letters*, **389**, 23–33, doi: 10.1016/j.epsl.2013.12.024.

Dupont, C.L., Butcher, A., Valas, R.E., Bourne, P.E. and Caetano-Anollés, G. (2010) History of biological metal utilization inferred through phylogenomic analysis of protein structures. *Proceedings of the National Academy of Sciences*, **107**, 10567–10572, doi: 10.1073/pnas.0912491107.

Dupont, C.L., Yang, S., Palenik, B. and Bourne, P.E. (2006) Modern proteomes contain putative imprints of ancient shifts in trace metal geochemistry. *Proceedings of the National Academy of Sciences*, **103**, 17822–17827, doi: 10.1073/pnas.0605798103.

Elder, W. and Kirkland, J. (1985) Stratigraphy and depositional environments of the Bridge Creek Limestone Member of the Greenhorn Limestone at Rock Canyon Anticline near Pueblo, Colorado. In: Pratt, L., Kauffman, E.G., Zelt, F.B. (Eds.), *Fine-grained deposits and biofacies of the Cretaceous Western Interior Seaway: evidence of cyclic depositional processes*. SEPM Annual Mid-year Meeting, Field Trip No. 9, pp. 122–134., doi.

Elder, W.P. (1991) Molluscan paleoecology and sedimentation patterns of the Cenomanian-Turonian extinction interval in the southern Colorado Plateau region. *Geological Society of America Special Papers*, **260**, 113–138, doi.

Eldrett, J.S., Ma, C., Bergman, S.C., Lutz, B., Gregory, F.J., Dodsworth, P., Phipps, M., Hardas, P., Minisini, D., Ozkan, A., Ramezani, J., Bowring, S.A., Kamo, S.L., Ferguson, K., Macaulay, C. and Kelly, A.E. (2015) An astronomically calibrated stratigraphy of the Cenomanian, Turonian and earliest Coniacian from the Cretaceous Western Interior Seaway, USA: Implications for global chronostratigraphy. *Cretaceous Research*, **56**, 316–344, doi: 10.1016/j.cretres.2015.04.010.

Emerson, S., Cranston, R.E. and Liss, P.S. (1979) Redox species in a reducing fjord: equilibrium and kinetic considerations. *Deep Sea Research Part A. Oceanographic Research Papers*, **26**, 859–878, doi: 10.1016/0198-0149(79)90101-8.

Erba, E. (2004) Calcareous nannofossils and Mesozoic oceanic anoxic events. *Marine Micropaleontology*, **52**, 85–106, doi: 10.1016/j.marmicro.2004.04.007.

Erbacher, J. and Thurow, J. (1997) Influence of oceanic anoxic events on the evolution of mid-Cretaceous radiolaria in the North Atlantic and western Tethys. *Marine Micropaleontology*, **30**, 139–158, doi: 10.1016/S0377-8398(96)00023-0.

Erbacher, J., Thurow, J. and Littke, R. (1996) Evolution patterns of radiolaria and organic matter variations: A new approach to identify sea-level changes in mid-Cretaceous pelagic environments. *Geology*, **24**, 499–502, doi: 10.1130/0091-7613(1996)024<0499:eporao>2.3.co;2.

Farrimond, P., Eglinton, G., Brassell, S.C. and Jenkyns, H.C. (1990) The Cenomanian/Turonian anoxic event in Europe: an organic geochemical study. *Marine and Petroleum Geology*, **7**, 75–89, doi: 10.1016/0264-8172(90)90058-O.

Friedrich, O., Norris, R.D. and Erbacher, J. (2012) Evolution of middle to Late Cretaceous oceans—A 55 m.y. record of Earth's temperature and carbon cycle. *Geology*, **40**, 107–110, doi: 10.1130/g32701.1.

Galeotti, S., Rusciadelli, G., Sprovieri, M., Lanci, L., Gaudio, A. and Pekar, S. (2009) Sea-level control on facies architecture in the Cenomanian-Coniacian Apulian margin (Western Tethys): A record of glacio-eustatic fluctuations during the Cretaceous greenhouse? *Palaeogeography, Palaeoclimatology, Palaeoecology*, **276**, 196–205, doi: 10.1016/j.palaeo.2009.03.011.

Gambacorta, G., Jenkyns, H.C., Russo, F., Tsikos, H., Wilson, P.A., Faucher, G. and Erba, E. (2015) Carbon- and oxygen-isotope records of mid-Cretaceous Tethyan pelagic sequences from the Umbria–Marche and Belluno Basins (Italy). *Newsletters on Stratigraphy*, **48**, 299–323, doi: 10.1127/nos/2015/0066.

Gautier, D.L. (1987) Isotopic composition of pyrite: Relationship to organic matter type and iron availability in some North American Cretaceous shales. *Chemical Geology: Isotope Geoscience section*, **65**, 293–303, doi: 10.1016/0168-9622(87)90009-1.

Gellatly, A.M. and Lyons, T.W. (2005) Trace sulfate in mid-Proterozoic carbonates and the sulfur isotope record of biospheric evolution. *Geochimica et Cosmochimica Acta*, **69**, 3813–3829, doi: 10.1016/j.gca.2005.01.019.

Gill, B.C., Lyons, T.W. and Jenkyns, H.C. (2011a) A global perturbation to the sulfur cycle during the Toarcian Oceanic Anoxic Event. *Earth and Planetary Science Letters*, **312**, 484–496, doi: 10.1016/j.epsl.2011.10.030.

Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H. and Saltzman, M.R. (2011b) Geochemical evidence for widespread euxinia in the Later Cambrian ocean. *Nature*, **469**, 80–83, doi: 10.1038/nature09700.

Glass, J.B., Wolfe-Simon, F. and Anbar, A.D. (2009) Coevolution of metal availability and nitrogen assimilation in cyanobacteria and algae. *Geobiology*, **7**, 100–123, doi: 10.1111/j.1472-4669.2009.00190.x.

Glock, N., Liebetrau, V. and Eisenhauer, A. (2014) I/Ca ratios in benthic foraminifera from the Peruvian oxygen minimum zone: analytical methodology and evaluation as a proxy for redox conditions. *Biogeosciences*, **11**, 7077–7095, doi: 10.5194/bg-11-7077-2014.

Goldberg, T., Poulton, S.W., Wagner, T., Kolonic, S.F. and Rehkämper, M. (2016) Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. *Earth and Planetary Science Letters*, **440**, 81–91, doi: 10.1016/j.epsl.2016.02.006.

Gomes, M.L., Hurtgen, M.T. and Sageman, B.B. (2016) Biogeochemical sulfur cycling during Cretaceous oceanic anoxic events: A comparison of OAE1a and OAE2. *Paleoceanography*, **31**, 233–251, doi: 10.1002/2015PA002869.

Haq, B.U., Hardenbol, J.A.N. and Vail, P.R. (1987) Chronology of Fluctuating Sea Levels Since the Triassic. *Science*, **235**, 1156–1167, doi: 10.1126/science.235.4793.1156.

Hardisty, D.S., Lu, Z., Planavsky, N.J., Bekker, A., Philippot, P., Zhou, X. and Lyons, T.W. (2014) An iodine record of Paleoproterozoic surface ocean oxygenation. *Geology*, **42**, 619622, doi: 10.1130/g35439.1.

Hasegawa, T. (1997) Cenomanian-Turonian carbon isotope events recorded in terrestrial organic matter from northern Japan. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **130**, 251–273, doi: 10.1016/S0031-0182(96)00129-0.

Hetzel, A., Böttcher, M.E., Wortmann, U.G. and Brumsack, H.-J. (2009) Paleo-redox conditions during OAE 2 reflected in Demerara Rise sediment geochemistry (ODP Leg 207). *Palaeogeography, Palaeoclimatology, Palaeoecology*, **273**, 302–328, doi: 10.1016/j.palaeo.2008.11.005.

Hetzel, A., März, C., Vogt, C. and Brumsack, H.-J. (2011) Geochemical environment of Cenomanian - Turonian black shale deposition at Wunstorf (northern Germany). *Cretaceous Research*, **32**, 480–494, doi: 10.1016/j.cretres.2011.03.004.

Jarvis, I.A.N., Murphy, A.M. and Gale, A.S. (2001) Geochemistry of pelagic and hemipelagic carbonates: criteria for identifying systems tracts and sea-level change. *Journal of the Geological Society*, **158**, 685–696, doi: 10.1144/jgs.158.4.685.

Jenkyns, H.C. (2010) Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems*, **11**, Q03004, doi: 10.1029/2009gc002788.

Jenkyns, H.C., Dickson, A.J., Ruhl, M. and Van Den Boorn, S.H.J.M. (2017) Basalt–seawater interaction, the Plenius Cold Event, enhanced weathering and geochemical change: Deconstructing **Oceanic Anoxic Event 2** (Cenomanian–Turonian, Late Cretaceous). *Sedimentology*, **64**, doi: 10.1111/sed.12305, in press.

Jenkyns, H.C., Matthews, A., Tsikos, H. and Erel, Y. (2007) Nitrate reduction, sulfate reduction, and sedimentary iron isotope evolution during the Cenomanian-Turonian oceanic anoxic event. *Paleoceanography*, **22**, PA3208, doi: 10.1029/2006pa001355.

Jones, C.E. and Jenkyns, H.C. (2001) Seawater Strontium Isotopes, Oceanic Anoxic Events, and Seafloor Hydrothermal Activity in the Jurassic and Cretaceous. *American Journal of Science*, **301**, 112–149, doi: 10.2475/ajs.301.2.112.

Kaiho, K. and Hasegawa, T. (1994) End-Cenomanian benthic foraminiferal extinctions and oceanic dysoxic events in the northwestern Pacific Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **111**, 29–43, doi: 10.1016/0031-0182(94)90346-8.

Kampschulte, A. and Strauss, H. (2004) The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. *Chemical Geology; Applications of Stable Isotope Techniques to Geological and Environmental Problems*, **204**, 255–286, doi: 10.1016/j.chemgeo.2003.11.013.

Kraal, P., Slomp, C.P., Forster, A. and Kuypers, M.M.M. (2010) Phosphorus cycling from the margin to abyssal depths in the proto-Atlantic during oceanic anoxic event 2. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **295**, 42–54, doi: 10.1016/j.palaeo.2010.05.014.

Kuhnt, W., Luderer, F., Nederbragt, S., Thürow, J. and Wagner, T. (2005) Orbital-scale record of the late Cenomanian-Turonian oceanic anoxic event (OAE-2) in the Tarfaya Basin (Morocco). *International Journal of Earth Sciences*, **94**, 147–159, doi: 10.1007/s00531-004-0440-5.

Kuroda, J., Ogawa, N.O., Tanimizu, M., Coffin, M.F., Tokuyama, H., Kitazato, H. and Ohkouchi, N. (2007) Contemporaneous massive subaerial volcanism and late cretaceous Oceanic Anoxic Event 2. *Earth and Planetary Science Letters*, **256**, 211–223, doi: 10.1016/j.epsl.2007.01.027.

Kuroda, J. and Ohkouchi, N. (2006) Implication of spatiotemporal distribution of black shales deposited during the Cretaceous Oceanic Anoxic Event-2. *Paleontological Research*, **10**, 345–358, doi: 10.2517/prpsj.10.345.

Kuypers, M.M.M., Pancost, R.D., Nijenhuis, I.A. and Sinninghe Damsté, J.S. (2002) Enhanced productivity led to increased organic carbon burial in the euxinic North Atlantic basin during the late Cenomanian oceanic anoxic event. *Paleoceanography*, **17**, 1051, doi: 10.1029/2000PA000569.

Lanci, L., Muttoni, G. and Erba, E. (2010) Astronomical tuning of the Cenomanian Scaglia Bianca Formation at Furlo, Italy. *Earth and Planetary Science Letters*, **292**, 231–237, doi: 10.1016/j.epsl.2010.01.041.

Leckie, R.M. (1985) Foraminifera of the Cenomanian-Turonian Boundary Interval, Greenhorn Formation, Rock Canyon Anticline, Pueblo, Colorado, in: Pratt, L., Kauffman, E.G., Zelt, F.B. (Eds), Fine-grained deposits and biofacies of the Cretaceous Western Interior Seaway: evidence of cyclic depositional processes. *SEPM Annual Mid-year Meeting, Field Trip No. 4*, 5–19, doi.

Leckie, R.M., Bralower, T.J. and Cashman, R. (2002) Oceanic anoxic events and plankton evolution: Biotic response to tectonic forcing during the mid-Cretaceous. *Paleoceanography*, **17**, PA000623, doi: 10.1029/2001pa000623.

Loope, G.R., Kump, L.R. and Arthur, M.A. (2013) Shallow water redox conditions from the Permian-Triassic boundary microbialite: The rare earth element and iodine geochemistry of carbonates from Turkey and South China. *Chemical Geology*, **351**, 195–208, doi: 10.1016/j.chemgeo.2013.05.014.

Lu, Z., Hoogakker, B.A.A., Hillenbrand, C.-D., Zhou, X., Thomas, E., Gutchess, K.M., Lu, W., Jones, L. and Rickaby, R.E.M. (2016) Oxygen depletion recorded in upper waters of the glacial Southern Ocean. *Nat Commun*, **7**, doi: 10.1038/ncomms11146.

Lu, Z., Jenkyns, H.C. and Rickaby, R.E.M. (2010) Iodine to calcium ratios in marine carbonate as a paleo-redox proxy during oceanic anoxic events. *Geology*, **38**, 1107–1110, doi: 10.1130/g31145.1.

Lyons, T.W., Anbar, A.D., Severmann, S., Scott, C. and Gill, B.C. (2009) Tracking Euxinia in the Ancient Ocean: A Multiproxy Perspective and Proterozoic Case Study. *Annual Review of Earth and Planetary Sciences*, **37**, 507–534, doi: 10.1146/annurev.earth.36.031207.124233.

Lyons, T.W. and Severmann, S. (2006) A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins. *Geochimica et Cosmochimica Acta*, **70**, 5698–5722, doi: 10.1016/j.gca.2006.08.021.

MacLeod, K.G., Martin, E.E. and Blair, S.W. (2008) Nd isotopic excursion across Cretaceous ocean anoxic event 2 (Cenomanian-Turonian) in the tropical North Atlantic. *Geology*, **36**, 811–814, doi: 10.1130/G24999A.1.

Martin, E.E., MacLeod, K.G., Jiménez Berrocoso, A. and Bourbon, E. (2012) Water mass circulation on Demerara Rise during the Late Cretaceous based on Nd isotopes. *Earth and Planetary Science Letters*, **327–328**, 111–120, doi: 10.1016/j.epsl.2012.01.037.

März, C., Poulton, S.W., Beckmann, B., Küster, K., Wagner, T. and Kasten, S. (2008) Redox sensitivity of P cycling during marine black shale formation: Dynamics of sulfidic and anoxic, non-sulfidic bottom waters. *Geochimica et Cosmochimica Acta*, **72**, 3703–3717, doi: 10.1016/j.gca.2008.04.025.

Mitchell, R.N., Bice, D.M., Montanari, A., Cleaveland, L.C., Christianson, K.T., Coccioni, R. and Hinnov, L.A. (2008) Oceanic anoxic cycles? Orbital prelude to the Bonarelli Level (OAE 2). *Earth and Planetary Science Letters*, **267**, 1–16, doi: 10.1016/j.epsl.2007.11.026.

Monteiro, F.M., Pancost, R.D., Ridgwell, A. and Donnadieu, Y. (2012) Nutrients as the dominant control on the spread of anoxia and euxinia across the Cenomanian-Turonian oceanic anoxic event (OAE2): Model-data comparison. *Paleoceanography*, **27**, PA4209, doi: 10.1029/2012pa002351.

Mort, H., Jacquat, O., Adatte, T., Steinmann, P., Föllmi, K., Matera, V., Berner, Z. and Stüben, D. (2007) The Cenomanian/Turonian anoxic event at the Bonarelli Level in Italy and Spain: enhanced productivity and/or better preservation? *Cretaceous Research*, **28**, 597–612, doi: 10.1016/j.cretres.2006.09.003.

Mort, H.P., Adatte, T., Keller, G., Bartels, D., Föllmi, K.B., Steinmann, P., Berner, Z. and Chellai, E.H. (2008) Organic carbon deposition and phosphorus accumulation during Oceanic Anoxic Event 2 in Tarfaya, Morocco. *Cretaceous Research*, **29**, 1008–1023, doi: 10.1016/j.cretres.2008.05.026.

897 **Musavu-Moussavou, B., Danelian, T., Baudin, F., Coccioni, R. and Fröhlich, F.** (2007) The Radiolarian
898 biotic response during OAE2. A high-resolution study across the Bonarelli level at Bottaccione (Gubbio,
899 Italy). *Revue de Micropaléontologie*, **50**, 253–287, doi: 10.1016/j.revmic.2007.07.002.

900 **Nederbragt, A.J. and Fiorentino, A.** (1999) Stratigraphy and palaeoceanography of the Cenomanian-
901 Turonian Boundary Event in Oued Mellegue, north-western Tunisia. *Cretaceous Research*, **20**, 47–62,
902 doi: 10.1006/cres.1998.0136.

903 **Ohkouchi, N., Kawamura, K., Kajiwara, Y., Wada, E., Okada, M., Kanamatsu, T. and Taira, A.** (1999)
904 Sulfur isotope records around Livello Bonarelli (northern Apennines, Italy) black shale at the
905 Cenomanian-Turonian boundary. *Geology*, **27**, 535–538, doi: 10.1130/0091-
906 7613(1999)027<0535:SIRALB>2.3.CO;2.

907 **Owens, J.D., Gill, B.C., Jenkyns, H.C., Bates, S.M., Severmann, S., Kuypers, M.M.M., Woodfine, R.G.
908 and Lyons, T.W.** (2013) Sulfur isotopes track the global extent and dynamics of euxinia during
909 Cretaceous Oceanic Anoxic Event 2 *Proceedings of the National Academy of Sciences*, **110**, 18407–
910 18412, doi: 10.1073/pnas.1305304110.

911 **Owens, J.D., Lyons, T.W., Li, X., Macleod, K.G., Gordon, G., Kuypers, M.M.M., Anbar, A., Kuhnt, W. and
912 Severmann, S.** (2012) Iron isotope and trace metal records of iron cycling in the proto-North Atlantic
913 during the Cenomanian-Turonian oceanic anoxic event (OAE-2). *Paleoceanography*, **27**, PA3223, doi:
914 10.1029/2012pa002328.

915 **Owens, J.D., Reinhard, C.T., Rohrsen, M., Love, G.D. and Lyons, T.W.** (2016) Empirical links between
916 trace metal cycling and marine microbial ecology during a large perturbation to Earth's carbon cycle.
917 *Earth and Planetary Science Letters*, **449**, 407–417, doi: 10.1016/j.epsl.2016.05.046.

918 **Pancost, R.D., Crawford, N., Magness, S., Turner, A., Jenkyns, H.C. and Maxwell, J.R.** (2004) Further
919 evidence for the development of photic-zone euxinic conditions during Mesozoic oceanic anoxic events.
920 *Journal of the Geological Society*, **161**, 353–364, doi: 10.1144/0016764903-059.

921 **Parente, M., Frijia, G., Di Lucia, M., Jenkyns, H.C., Woodfine, R.G. and Baroncini, F.** (2008) Stepwise
922 extinction of larger foraminifers at the Cenomanian-Turonian boundary: A shallow-water perspective on
923 nutrient fluctuations during Oceanic Anoxic Event 2 (Bonarelli Event). *Geology*, **36**, 715–718, doi:
924 10.1130/G24893A.1.

925 **Pearce, M.A., Jarvis, I. and Tocher, B.A.** (2009) The Cenomanian-Turonian boundary event, OAE2 and
926 palaeoenvironmental change in epicontinental seas: New insights from the dinocyst and geochemical
927 records. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **280**, 207–234, doi:
928 10.1016/j.palaeo.2009.06.012.

929 **Planavsky, N.J., Rouxel, O.J., Bekker, A., Lalonde, S.V., Konhauser, K.O., Reinhard, C.T. and Lyons, T.W.**
930 (2010) The evolution of the marine phosphate reservoir. *Nature*, **467**, 1088–1090, doi: doi:
931 10.1038/nature09485.

932 **Pogge von Strandmann, P.A.E., Jenkyns, H.C. and Woodfine, R.G.** (2013) Lithium isotope evidence for
933 enhanced weathering during Oceanic Anoxic Event 2. *Nature Geoscience*, **6**, 668–672, doi:
934 10.1038/ngeo1875.

935 **Poulton, S.W. and Canfield, D.E.** (2005) Development of a sequential extraction procedure for iron:
936 implications for iron partitioning in continentally derived particulates. *Chemical Geology*, **214**, 209–221,
937 doi: 10.1016/j.chemgeo.2004.09.003.

938 **Poulton, S.W. and Canfield, D.E.** (2011) Ferruginous Conditions: A Dominant Feature of the Ocean
939 through Earth's History. *Elements*, **7**, 107–112, doi: 10.2113/gselements.7.2.107.

940 **Poulton, S.W., Henkel, S., März, C., Urquhart, H., Flögel, S., Kasten, S., Sinninghe Damsté, J.S. and
941 Wagner, T.** (2015) A continental-weathering control on orbitally driven redox-nutrient cycling during
942 Cretaceous Oceanic Anoxic Event 2. *Geology*, **43**, 963–966, doi: 10.1130/g36837.1.

- Poulton, S.W. and Raiswell, R.** (2005) Chemical and physical characteristics of iron oxides in riverine and glacial meltwater sediments. *Chemical Geology*, **218**, 203–221, doi: 10.1016/j.chemgeo.2005.01.007.
- Premoli Silva, I. and Sliter, W.V.** (1999) Cretaceous paleoceanography: Evidence from planktonic foraminiferal evolution. *Geological Society of America Special Papers*, **332**, 301–328, doi: 10.1130/0-8137-2332-9.301.
- Raiswell, R. and Canfield, D.E.** (1998) Sources of iron for pyrite formation in marine sediments. *American Journal of Science*, **298**, 219–245, doi: 10.2475/ajs.298.3.219.
- Raiswell, R., Newton, R., Bottrell, S.H., Coburn, P.M., Briggs, D.E.G., Bond, D.P.G. and Poulton, S.W.** (2008) Turbidite depositional influences on the diagenesis of Beecher's Trilobite Bed and the Hunsrück Slate; sites of soft tissue pyritization. *American Journal of Science*, **308**, 105–129, doi: 10.2475/02.2008.01.
- Reinhard, C.T., Planavsky, N.J., Robbins, L.J., Partin, C.A., Gill, B.C., Lalonde, S.V., Bekker, A., Konhauser, K.O. and Lyons, T.W.** (2013) Proterozoic ocean redox and biogeochemical stasis. *Proceedings of the National Academy of Sciences*, **110**, 5357–5362, doi: 10.1073/pnas.1208622110.
- Rue, E.L., Smith, G.J., Cutter, G.A. and Bruland, K.W.** (1997) The response of trace element redox couples to suboxic conditions in the water column. *Deep Sea Research Part I: Oceanographic Research Papers*, **44**, 113–134, doi: 10.1016/S0967-0637(96)00088-X.
- Sageman, B.B., Lyons, T.W. and Joo, Y.J.** (2014) 9.6 - Geochemistry of Fine-Grained, Organic Carbon-Rich Facies A2 - Holland, Heinrich D. In: *Treatise on Geochemistry (Second Edition)* (Ed K.K. Turekian), pp. 141–179. Elsevier, Oxford.
- Sageman, B.B., Meyers, S.R. and Arthur, M.A.** (2006) Orbital time scale and new C-isotope record for Cenomanian-Turonian boundary stratotype. *Geology*, **34**, 125–128, doi: 10.1130/g22074.1.
- Sahoo, S.K., Planavsky, N.J., Kendall, B., Wang, X., Shi, X., Scott, C., Anbar, A.D., Lyons, T.W. and Jiang, G.** (2012) Ocean oxygenation in the wake of the Marinoan glaciation. *Nature*, **489**, 546–549, doi: 10.1038/nature11445.
- Schlanger, S.O., Arthur, M.A., Jenkyns, H.C. and Scholle, P.A.** (1987) The Cenomanian-Turonian Oceanic Anoxic Event, I. Stratigraphy and distribution of organic carbon-rich beds and the marine $\delta^{13}\text{C}$ excursion, in *Marine Petroleum Source Rocks*, edited by J. Brooks and A. J. Fleet. *Geological Society, London, Special Publications*, **26**, 371–399, doi: 10.1144/GSL.SP.1987.026.01.24.
- Schlanger, S.O. and Jenkyns, H.C.** (1976) Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw*, **55**, 179–184, doi: 10.1016/j.chemgeo.2005.10.010.
- Scholle, P.A. and Arthur, M.A.** (1980) Carbon isotope fluctuations in Cretaceous pelagic limestones; potential stratigraphic and petroleum exploration tool. *AAPG Bulletin*, **64**, 67–87, doi: 10.1016/j.chemgeo.2005.10.010.
- Scopelliti, G., Bellanca, A., Neri, R., Baudin, F. and Coccioni, R.** (2006) Comparative high-resolution chemostratigraphy of the Bonarelli Level from the reference Bottaccione section (Umbria–Marche Apennines) and from an equivalent section in NW Sicily: Consistent and contrasting responses to the OAE2. *Chemical Geology*, **228**, 266–285, doi: 10.1016/j.chemgeo.2005.10.010.
- Scotese, C.R.** (2008) The PALEOMAP Project PaleoAtlas for ArcGIS, Volume 2. *Cretaceous Paleogeographic and Plate Tectonic Reconstructions, PALEOMAP Project*, doi: 10.1016/j.chemgeo.2012.05.012.
- Scott, C. and Lyons, T.W.** (2012) Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chemical Geology*, **324–325**, 19–27, doi: 10.1016/j.chemgeo.2012.05.012.
- Scott, C., Lyons, T.W., Bekker, A., Shen, Y., Poulton, S.W., Chu, X. and Anbar, A.D.** (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature*, **452**, 456–459, doi: 10.1038/nature06811.
- Scott, C., Planavsky, N.J., Dupont, C.L., Kendall, B., Gill, B.C., Robbins, L.J., Husband, K.F., Arnold, G.L., Wing, B.A., Poulton, S.W., Bekker, A., Anbar, A.D., Konhauser, K.O. and Lyons, T.W.** (2013)

Bioavailability of zinc in marine systems through time. *Nature Geoscience*, **6**, 125–128, doi: 10.1038/ngeo1679.

Sinninghe Damsté, J.S. and Köster, J. (1998) A euxinic southern North Atlantic Ocean during the Cenomanian/Turonian oceanic anoxic event. *Earth and Planetary Science Letters*, **158**, 165–173, doi: 10.1016/S0012-821X(98)00052-1.

Snow, L.J., Duncan, R.A. and Bralower, T.J. (2005) Trace element abundances in the Rock Canyon Anticline, Pueblo, Colorado, marine sedimentary section and their relationship to Caribbean plateau construction and oxygen anoxic event 2. *Paleoceanography*, **20**, PA3005, doi: 10.1029/2004PA001093.

Takashima, R., Nishi, H., Huber, B.T. and Leckie, M. (2006) Greenhouse World and the Mesozoic Ocean. *Oceanography*, **19**, 82–92, doi.

Tsikos, H., Jenkyns, H.C., Walsworth-Bell, B., Petrizzo, M.R., Forster, A., Kolonic, S., Erba, E., Premoli Silva, I., Baas, M., Wagner, T. and Sinninghe Damsté, J.S. (2004) Carbon-isotope stratigraphy recorded by the Cenomanian–Turonian Oceanic Anoxic Event: correlation and implications based on three key localities. *Journal of the Geological Society*, **161**, 711–719, doi: 10.1144/0016-764903-077.

Turekian, K.K. and Wedepohl, K.H. (1961) Distribution of the Elements in Some Major Units of the Earth's Crust. *Geological Society of America Bulletin*, **72**, 175–192, doi: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

Turgeon, S. and Brumsack, H.-J. (2006) Anoxic vs dysoxic events reflected in sediment geochemistry during the Cenomanian-Turonian Boundary Event (Cretaceous) in the Umbria-Marche Basin of central Italy. *Chemical Geology*, **234**, 321–339, doi: 10.1016/j.chemgeo.2006.05.008.

van Bentum, E.C., Hetzel, A., Brumsack, H.-J., Forster, A., Reichart, G.-J. and Sinninghe Damsté, J.S. (2009) Reconstruction of water column anoxia in the equatorial Atlantic during the Cenomanian-Turonian oceanic anoxic event using biomarker and trace metal proxies. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **280**, 489–498, doi: 10.1016/j.palaeo.2009.07.003.

Van Cappellen, P. and Ingall, E.D. (1994) Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography*, **9**, 677–692, doi: 10.1029/94pa01455.

Voigt, S., Erbacher, J., Mutterlose, J., Weiss, W., Westerhold, T., Wiese, F., Wilmsen, M. and Wonik, T. (2008) The Cenomanian – Turonian of the Wunstorf section – (North Germany): global stratigraphic reference section and new orbital time scale for Oceanic Anoxic Event 2. *Newsletters on Stratigraphy*, **43**, 65–89, doi: 10.1127/0078-0421/2008/0043-0065.

Westermann, S., Vance, D., Cameron, V., Archer, C. and Robinson, S.A. (2014) Heterogeneous oxygenation states in the Atlantic and Tethys oceans during Oceanic Anoxic Event 2. *Earth and Planetary Science Letters*, **404**, 178–189, doi: 10.1016/j.epsl.2014.07.018.

Wong, G.T.F. and Brewer, P.G. (1977) The marine chemistry of iodine in anoxic basins. *Geochimica et Cosmochimica Acta*, **41**, 151–159, doi: 10.1016/0016-7037(77)90195-8.

Zerkle, A.L., House, C.H., Cox, R.P. and Canfield, D.E. (2006) Metal limitation of cyanobacterial N₂ fixation and implications for the Precambrian nitrogen cycle. *Geobiology*, **4**, 285–297, doi: 10.1111/j.1472-4669.2006.00082.x.

Zheng, X.-Y., Jenkyns, H.C., Gale, A.S., Ward, D.J. and Henderson, G.M. (2013) Changing ocean circulation and hydrothermal inputs during Ocean Anoxic Event 2 (Cenomanian-Turonian): Evidence from Nd-isotopes in the European shelf sea. *Earth and Planetary Science Letters*, **375**, 338–348, doi: 10.1016/j.epsl.2013.05.053.

Zhou, X., Jenkyns, H.C., Owens, J.D., Junium, C.K., Zheng, X.-Y., Sageman, B.B., Hardisty, D.S., Lyons, T.W., Ridgwell, A. and Lu, Z. (2015) Upper ocean oxygenation dynamics from I/Ca ratios during the Cenomanian-Turonian OAE 2. *Paleoceanography*, **30**, 510–526, doi: 10.1002/2014PA002741.

Figure 1. Palaeogeographic locations of Furlo (red circle) and Demerara Rise (white circle) adapted from the PALEOMAP Project (Scotese, 2008) with an inset photo of the Furlo outcrop, illustrating the Bonarelli Level (c. 1 metre thick) and the under- and overlying grey pelagic limestones (so-called Scaglia) at the time of sampling.

Figure 2. Organic-carbon isotopes ($\delta^{13}\text{C}_{\text{org}}$) from both shales (squares) and carbonates (circles). Total organic carbon and carbonate data for both the organic-rich shales and carbonates. Total organic carbon is low before the OAE (denoted with the dark grey bar) in both lithologies and increases during the OAE (shales). Stratigraphic column was based on the field campaign but is similar to previous studies (Jenkyns et al., 2007; Mort et al., 2007).

Figure 3. Palaeoredox geochemical data from the organic-rich black shales. The Bonarelli Level recording the OAE is denoted by the grey bar and nearly all of the parameters show a major perturbation, with the Fe proxies increasing and Mo illustrating a small increase in concentration. The low-oxygen trace-metal proxies, Mn, V, Cr/Ti and Zn, all show a significant decline in concentration during the event, attributed to global drawdown of these elements due to worldwide increase of euxinic sinks. The dashed vertical lines represent the average shale value for elemental concentration except for Cr, which is based on Cr/Ti values.

Figure 4. Sulfur-isotope and carbonate geochemical paleoredox data. The sulfur-isotope data shift to more positive values leading into the Bonarelli Level and increase post OAE-level, albeit with a decline in $\Delta^{34}\text{S}$. The ratio of I/Ca shows significant scatter but generally the interval below the Bonarelli Level shows relatively low values, indicating deposition in an oxygen-depleted environment for the pelagic limestones, before rebounding to higher values at the top of the section.