



# Latest Pliensbachian to Early Toarcian depositional environment and organo-facies evolution in the North-German Basin (Hondelage Section)

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## Abstract

The Pliensbachian/Toarcian boundary interval represents a transition from a coldhouse into a hothouse climate state, involving the demise of a land-based cryosphere, initiating a third-order global sea-level rise. Within the intensely studied Northwest Tethyan shelf region, the South-German Basin has been investigated in more detail than the North-German Basin (NGB). We here provide a palaeoenvironmental reconstruction of the Pliensbachian/Toarcian transition from the Hondelage fossil excavation site located in the NGB employing organic, isotope, and major/trace element proxies. Here, the late Pliensbachian was characterized by cold climate, low sea level, and a slow hydrological cycle, causing minor terrigenous sediment and nutrient fluxes to the basin, instigating low marine productivity. Shallow, well-mixed shelf waters of normal salinity favored aerobic degradation of planktonic biomass, preventing sedimentary accumulation of organic matter. These conditions changed in the earliest Toarcian, where increased temperatures led to sea-level rise via meltdown of land-based ice and accelerated the hydrological cycle, causing salinity stratification. Enhanced riverine sediment and nutrient supply from nearby landmasses promoted marine primary productivity, which caused anoxic conditions in bottom and pore waters favoring enhanced preservation and accumulation of organic matter. A short-lived sea-level fall at the Lower Elegans Bed coincided with lowered productivity and enhanced carbonate precipitation, due to reduced runoff and recovery of the carbonate factory. Increased redox-sensitive trace element concentrations above the Lower Elegans Bed suggest a renewed inflow of low-salinity arctic water masses via the Viking Corridor and potentially increased freshwater input, promoting water column stratification, enhanced planktonic productivity, and re-establishment of bottom water anoxia/euxinia.

**Keywords** Redox assessment · Organic matter preservation · Toarcian Oceanic Anoxic Event · Global warming · Toarcian sea level

## Introduction

The latest Pliensbachian to early Toarcian was characterized by major climate swings that were paralleled by rapid high-amplitude sea-level cycles (Fig. 1) (e.g., Morard et al. 2003; Suan et al. 2010; Pittet et al. 2014; Korte et al. 2015; Krencker et al. 2019; Ruebsam et al. 2020a). Climate and sea-level dynamics have been related to orbitally forced glacial–interglacial cycles, which is supported by the occurrence of glacial deposits in strata of latest Pliensbachian age (e.g., Kaplan 1978; Suan et al. 2011; Teichert and Luppold 2013; Ruebsam and Schwark 2021; Merkel and Munnecke 2023). Latest Pliensbachian to early Toarcian environmental instabilities affected marine and continental ecosystems (e.g., Little and Benton 1995; Harries and Little 1999; Mattioli et al. 2008; Danise et al. 2015; Slater et al. 2019), as

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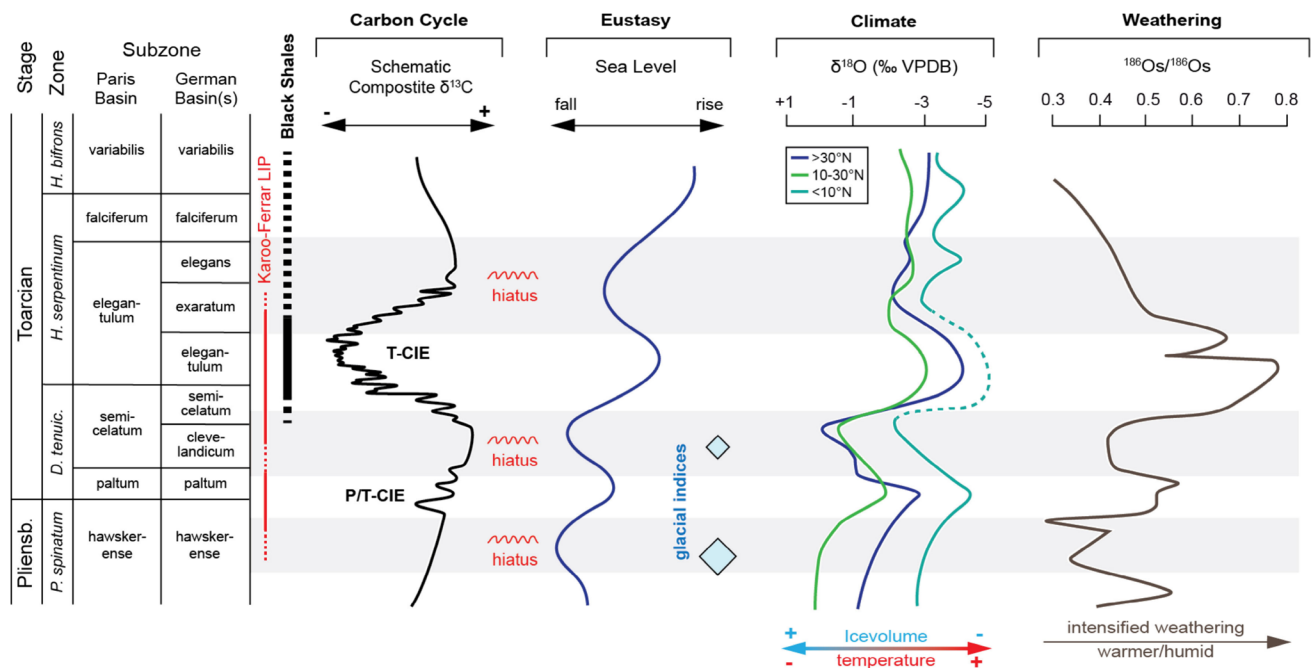
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**Fig. 1** Generalized evolution of carbon cycle (P/T-CIE: Pliensbachian/Toarcian carbon isotope excursion; T-CIE: Toarcian carbon isotope excursion), eustatic sea level, climate and weathering during the latest Pliensbachian and early Toarcian in the EEBS (European Epicontinental Basin System) (modified from Ruebsam et al. 2020b). The T-CIE coincides with the onset of widespread black shale deposition at shelf seas. Early Toarcian environmental change was poten-

tially triggered by the emplacement of the Karoo-Ferrar Large Igneous Province (LIP) shown by a thin red line. Ammonite zonation schemes for the German and Paris basins are after Page (2003). The thick black line marks intervals of global black shale deposition, the stippled line indicates regional black shale deposition (Ruebsam and Schwark 2024)

well as depositional conditions at shallow shelf areas. In particular, high-amplitude sea-level changes resulted in recurrent erosive events and stratigraphic condensation (e.g., Morard et al. 2003; Krencker et al. 2019; Ruebsam et al. 2019; Ruebsam and Al-Husseini 2020; Bodin et al. 2023).

Climate fluctuations culminated in an early Toarcian greenhouse that reconciles the genesis of the Toarcian Oceanic Anoxic Event (T-OAE Fig. 1), also termed “Jenkyns Event” (Müller et al. 2017; Gambacorta et al., 2023), a major organic carbon burial event of trans-regional, potentially global extent (Jenkyns 1988, 2010; Kemp et al. 2022). Deposition of organic carbon (OC)-rich strata (black shales, sensu lato) was most extensive across the northern part of the northwest Tethys shelf, an intensively structured shallow shelf area (Ziegler 1990), where black shale deposition was promoted by the interplay of local, regional, and global factors. These include sea-level changes, hydrological cycling, hydrological restriction, surface water freshening, freshwater stratification, and substantial nutrient supply via increased riverine discharge (e.g., Jenkyns 1988, 2010; Saelen et al. 1996; Cohen et al. 2004; Hermoso et al. 2013).

Warming phases at the Pliensbachian/Toarcian boundary interval and in the early Toarcian (Tenuicostatum–Serpentinum zonal boundary interval) were accompanied by

perturbations of the global carbon cycle (Fig. 1) that manifested in negative carbon isotope excursions, i.e., Pliensbachian/Toarcian Carbon Isotope Excursion: P/T-CIE and Toarcian Carbon Isotope Excursion: T-CIE (Hesselbo et al. 2000, 2007; Kemp et al. 2005; Suan et al. 2011; for a review see Ruebsam and Al-Husseini 2020). Although frequently used as synonyms, the T-CIE and the T-OAE show a disparity depending on regional conditions of sedimentation (Ruebsam and Schwark 2024). Carbon cycle perturbations were related to recurrent events of  $^{12}\text{C}$ -enriched carbon release (Beerling and Brentnall 2007). The potential carbon sources discussed include emissions from gas hydrates, wetlands, cryosphere (Hesselbo et al. 2000; Kemp et al. 2005; Them et al. 2017; Ruebsam et al. 2019) as well as volcanic processes, including intrusions into organic rich strata associated with thermogenic methane release, linked to the emplacement of the Karoo-Ferrar Large Igneous Province (K-F-LIP) in southern Gondwana (e.g., Svensen et al. 2007; Percival et al. 2015).

The response of depositional environments and marine ecosystems to late Pliensbachian to early Toarcian environmental change has been extensively studied from sediment successions in North Africa (e.g., Reolid et al. 2012, 2013; Baghli et al. 2022; Krencker et al. 2022; Ruebsam et al.

2022a), the Mediterranean realm (e.g., Jenkyns 1988; Mattioli and Pittet 2002, 2004; Reolid et al. 2018; Ruebsam et al. 2020a; Visentin and Erba 2021), the Paris Basin (e.g., van Breugel et al. 2006; Hermoso et al. 2009, 2013; Ruebsam et al. 2022b), the South-German Basin (Prauss et al. 1991; Röhl et al. 2001; Frimmel et al. 2004; Schwark and Frimmel 2004; Montero-Serrano et al. 2015; Ajuaba et al. 2022), and the British Islands (e.g., Jenkyns and Clayton 1986, 1997; McArthur et al. 2008; Xu et al. 2018). Detailed and stratigraphically well-constrained data from the central area of the NGB are, however, relatively rare. Pioneer work (Wunnenberg 1927; Hoffmann 1966, 1968; Riegel et al. 1986; Loh et al. 1986; Brumsack 1991; Prauss 1996) provided detailed palynological, geochemical, and sedimentological information, but lacked a detailed stratigraphic context. Furthermore, several studies focusing on maturity and source rock potential have been conducted on Posidonia Shale from the Hils syncline (Rullkötter et al. 1988; Littke et al. 1991a, b; Song et al. 2017; Stock et al. 2017). Recently, studies from the NGB (van de Schootbrugge et al. 2019; Mutterlose et al. 2022; Visentin et al. 2022; Burnaz et al. 2024; Ruebsam et al. 2024) presented sedimentological, palaeontological, and geochemical data embedded in a robust bio- and chemostratigraphic framework.

In this study, we investigate the latest Pliensbachian to early Toarcian strata of the stratigraphically well-defined Hondelage succession of the NGB (Fig. 2). Whereas previous work (Mutterlose et al. 2022) documented the ecological response of nannofossils and marine invertebrates, we here present inorganic, bulk organic and isotope geochemical data to assess changes in depositional conditions and organo-facies in response to latest Pliensbachian to early Toarcian environmental changes. In particular, this study aims to improve the understanding of Toarcian environmental variations in the NGB, where they have been insufficiently studied.

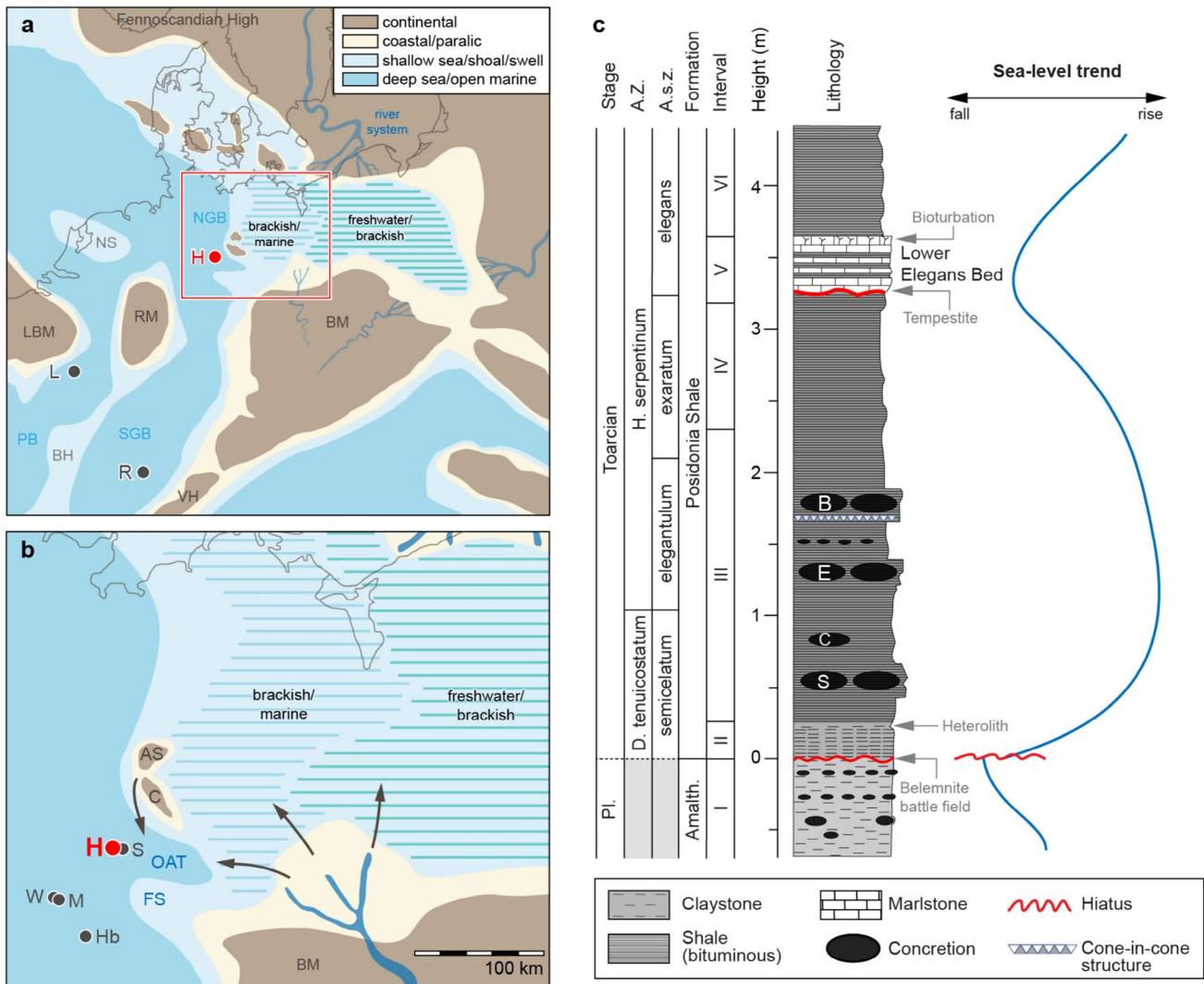
## Geological setting and stratigraphy

The NGB was part of the European Epicontinental Basin System (EEBS), a large epicontinental sea in the northern part of the Northwest Tethyan Shelf. The EEBS was intensively structured into several basins, such as the Paris Basin, the Lorraine Basin, the South-German Basin, the North-German Basin, the Dutch basins, or the British basins. These basins were separated by shoals, swells, and islands of variable size (Ziegler 1990). The EEBS was connected to the Arctic Ocean through the Viking Corridor (Fig. 2). South of the EEBS the North-West Tethys Shelf opened to the Tethys toward the southeast. Water-mass exchange between the Tethys Ocean and open North-West Tethyan Shelf with the EEBS was limited by numerous islands and swells, which

varied in size depending on eustatic sea-level fluctuations (Ziegler 1990).

The current study site, the Hondelage pit, a Fossilagerstätte famous for its rich fossil inventory is located 1 km north of the village Hondelage, near Braunschweig (Germany). The pit is currently mined for fossils by the Natural History Museum Braunschweig. Throughout the last 20 years, the section has provided rich fossil material of a marine ecosystem. The entire suite from single celled primary producers, via rich mollusc assemblages (bivalves, belemnites, gastropods, ammonites) up to fishes and ichthyosaurs has been recovered (Klopschar 2006; Mutterlose et al. 2022). As such, Hondelage offers an ideal opportunity to understand not only the palaeoenvironmental evolution of the Pliensbachian–Toarcian but also the response of the marine fauna. In the Early Jurassic, the study site was located in the south-eastern part of the NGB at a palaeolatitude ~45°N (van Hinsbergen et al. 2015) within a local depression, the Oberaller Through (Fig. 2b). This depression was bordered by the Calvörde Island and Altmark Swell to the north, and by the Fallstein Swell to the south (Ruebsam et al. 2024). Regional factors, such as halotectonically induced uplift, most probably caused a formation of small-scaled basins and swells. To the east, in proximity to the Bohemian Massif, a shallow marine depositional setting is indicated by a more sandy facies (Ott 1967).

The Hondelage succession is mainly composed of claystones and calcareous claystones of latest Pliensbachian (Amaltheenton Formation) to lower Toarcian age (Posidonia Shale Formation) (Fig. 2c). For the Hondelage outcrop, a detailed biostratigraphic framework is based on ammonites and calcareous nannofossils (Mutterlose et al. 2022). As the Amaltheenton Formation lacks diagnostic ammonites, a late Pliensbachian age was inferred from the calcareous nannofossil *Crepidolithus impontus* that is characteristic for the late Pliensbachian Nannofossil Zone NJ5b (Mutterlose et al. 2022). The Posidonia Shale Formation contains a rich marine flora and fauna including calcareous nannofossils, ammonites, fishes, and marine reptiles. Ammonite findings allow to differentiate the *semicelatum* Subzone of the *D. tenuicostatum* Zone, as well as the *elegantulum*, *exaratum*, and *elegans* subzones of the overlying *H. serpentinum* Zone. Calcareous nannofossil assemblages further allow to assign the Posidonia Shale Formation to the Nannofossil Zone NJ6 (Mutterlose et al. 2022). The calcareous nannofossil calcification crises, recorded from the nearby Schandelah core (Visentin et al. 2022), is not well expressed in Hondelage due to the hiatus at the base of the Toarcian. Nevertheless, the onset of a nannofossil bloom slightly postdates the onset of the negative T-CIE (Mutterlose et al. 2022). The  $\delta^{13}\text{C}_{\text{org}}$  data show a negative carbon isotope excursion in strata corresponding to the upper *D. tenuicostatum* and the lower *H. serpentinum* zones (Mutterlose et al. 2022). This



**Fig. 2** **a**: Palaeogeographic map of the Early Toarcian in northern Europe, showing the study site (*H* Hondelage) and localities mentioned in the text (*R* Rietheim and *L* Luxemburg) (*BM* Bohemian Massif, *RM* Rhenish Massif, *LBM* London Brabant Massif, *VH* Vindelician High, *PB* Paris Basin, *SGB* South-German Basin, *NGB* North-German Basin). The palaeogeographic map is modified from Ziegler (1990), Barth et al. (2018), and Ruebsam et al. (2020c, 2024). **b**: Detailed palaeogeographic reconstruction of the study area, the south-eastern North-German Basin. Localities mentioned in the text are: *S*: Schandelah, *W*: Wickensen, *M*: Mainzholzen, and *Hb*: Hainberg. Regional palaeogeographic elements, such as the Oberaller Trough (OAT), the Calvörde Island (*C*), the Altmark Swell (*AS*), and

the Fallstein Swell (*FS*) are indicated. Sediment supply (arrows) was sourced from small islands in the north and from the Bohemian Massif (*BM*) in the southeast (Zimmermann et al. 2018; Barth et al. 2018; Ruebsam et al. 2024; Ott 1967). **c**: Lithostratigraphic column with ammonite biostratigraphy (Mutterlose et al. 2022) and simplified sea-level trend (Hallam 1997; Morard et al. 2003; Wignall 2005; Ruebsam and Al-Husseini 2021). A. Z.: Ammonite Zone; A. s.z.: Ammonite subzone; Interval I: Pliensbachian; Interval II: basal Posidonia Shale Formation; Interval III: T-CIE; Interval IV: post-CIE; Interval V: Lower Elegans Bed; Interval VI: upper Posidonia Shale Formation. *S*: siemensi concretion layer; *C*: capillatum concretion layer; *E*: elegantulum concretion layer *B*: borealis concretion layer

characteristic chemostratigraphic feature has been interpreted to reflect the T-CIE, which has been reported from coeval strata worldwide and acts as important chemostratigraphic marker (e.g., Hesselbo et al. 2000, 2007; Röhl et al. 2001; Kemp et al. 2005; Suan et al. 2011; Them et al. 2017; for a review see Ruebsam and Al-Husseini 2020).

Biostratigraphy and carbon isotope-based chemostratigraphy indicate a hiatus at the Pliensbachian/Toarcian

boundary. In particular, most of the lower part of the *D. tenuicostatum* zone, including the *semicelatum*, *tenuicostatum*, *clevelandicum*, *crossbeyi*, and *paltum* biohorizons, as well as the Pliensbachian/Toarcian boundary interval appear to be absent. The upper part of the *D. tenuicostatum* Zone rests unconformably on the underlying Amaltheenton Formation of the Pliensbachian. At comparable stratigraphic intervals, pronounced hiatuses of variable duration have

been reported from numerous sites and most likely resulted from erosive events during a major sea-level lowstand (e.g., Jenkyns 1985; Riegel et al. 1986; Hallam 1997; Morard et al. 2003; Wignall 2005; van Breugel et al. 2006; Suan et al. 2011; Ruebsam and Al-Husseini 2020). At Hondelage, this hiatus/erosive horizon is marked by the “Belemnite Battlefield”, a distinctive bed enriched in belemnites that have been corroded (Mutterlose et al. 2022). In addition, the erosive/reworked base at the Lower Elegans Bed (Fig. 2c) suggests deposition by a tempestite pointing toward a lowered sea level. Stratigraphic gaps, resulting from erosive events occurring in the same stratigraphic interval, have been described from several sections (e.g., Thibault et al. 2018; Ruebsam and Al-Husseini 2020).

## Methods

### Sample preparation

In total, 109 samples were collected at the Hondelage outcrop, covering uppermost Pliensbachian to lower Toarcian strata, covering ~ 3 Ma. The Pliensbachian Amaltheenton Formation is represented by 16 samples and the Toarcian Posidonia Shale Formation by 93 samples. To minimize the impact of contamination, rock surfaces were removed using sandpaper. Cleaned samples were crushed and powdered using a mortar. Afterward, samples were dried at ~ 40 °C for 48 h to remove residual moisture.

### CNS analysis

The original sample material was analyzed for its total nitrogen (TN), total sulfur (TS), and total carbon (TC) contents using an Elementar Vario CNS Elemental Analyzer EL III. Reproducibility and accuracy were assured by running replicate analysis of laboratory reference materials and duplicate analysis of samples. The relative standard deviation was < 2%.

### XRF

X-ray fluorescence measurements were carried out employing a Spectro XEPOS ED-XRF device. Here, 5 g of sample material was analyzed. To assure reproducibility and accuracy, a reference material was measured every 20 samples and the instrument was recalibrated, if the reference material (NCS DC 73326) was out of the certified limits. The relative standard deviation for the major elements (Si, Al, Ca, Fe, K, Na, P, Ti) was better < 1.5%. For trace elements (Mo, Zr, V, Cu, Mo, Cr) relative standard deviation was < 4% without U and including U < 6.5%.

## Programmed pyrolysis

Programmed pyrolysis afforded a HAWK (Wildcat Technologies, US) instrument operated in pyrolysis and oxidation mode. An aliquot of 70 mg of sediment was weighted into a crucible and inserted by an autoloader into the HAWK device. Determination of thermo-vaporized bitumen (S1 in mg HC/g rock) occurred isothermally at 300 °C. The amount of kerogen was determined via the hydrocarbon yield upon pyrolysis (S2 in mg HC/g rock) through heating in an inert environment using a ramp rate of 25 °C from 300 to 650 °C. The pyrolysis measurements of both CO and CO<sub>2</sub> (S3CO in mg CO<sub>2</sub>/g rock and S3CO<sub>2</sub> in mg CO<sub>2</sub>/g rock) gave the oxygen concentration of the kerogen. The temperature of maximum pyrolysis yields recorded by the S2 peak is given as T<sub>max</sub> (°C). The TOC was determined as the sum of reactive carbon (sum of bitumen and kerogen), analyzed in programmed pyrolysis mode in an inert environment, and the amount of non-generative carbon that was detected in oxygenated combustion mode. The carbonate content was determined via the release of CO<sub>2</sub> upon heating from 500 to 850 °C in oxidation mode and converted to calcite carbonate equivalents using a stoichiometry factor of 8.33.

## Organic carbon isotope geochemistry

Organic carbon isotope analysis was performed on sample material decalcified by treatment with 10% and 25% HCl. Afterward, the decalcified sample residue was washed with deionized water until a pH of about 6. Measurements were carried out using a Thermo Finnigan Delta V isotope ratio mass spectrometer coupled to a Flash EA via a ConFlow III interface. The isotope ratio is expressed in the delta notation:  $\delta_{sample}(\text{‰}) = \left( \frac{R_{Sample} - R_{Standard}}{R_{Standard}} - 1 \right) * 1000$  with R being the ratio of <sup>13</sup>C/<sup>12</sup>C with V-PDB as reference material. Reproducibility and accuracy were assured by running replicate analysis of laboratory reference materials and duplicate analysis of samples.

## Results

Results are described in stratigraphic order for the Intervals I–VI, which were defined by lithological criteria and geochemical data (I: Pliensbachian Amaltheenton Formation; II: basal Posidonia Shale Formation—pre T-CIE; III: Posidonia Shale Formation—T-CIE; IV: Posidonia Shale Formation—post T-CIE; V: Posidonia Shale Formation—Lower Elegans Bed; VI: upper Posidonia Shale Formation).

## Bulk sediment composition

Relative abundances of the elements Si, Ti, Zr, and Al vary in dependency of the mineral content of sedimentary rocks,

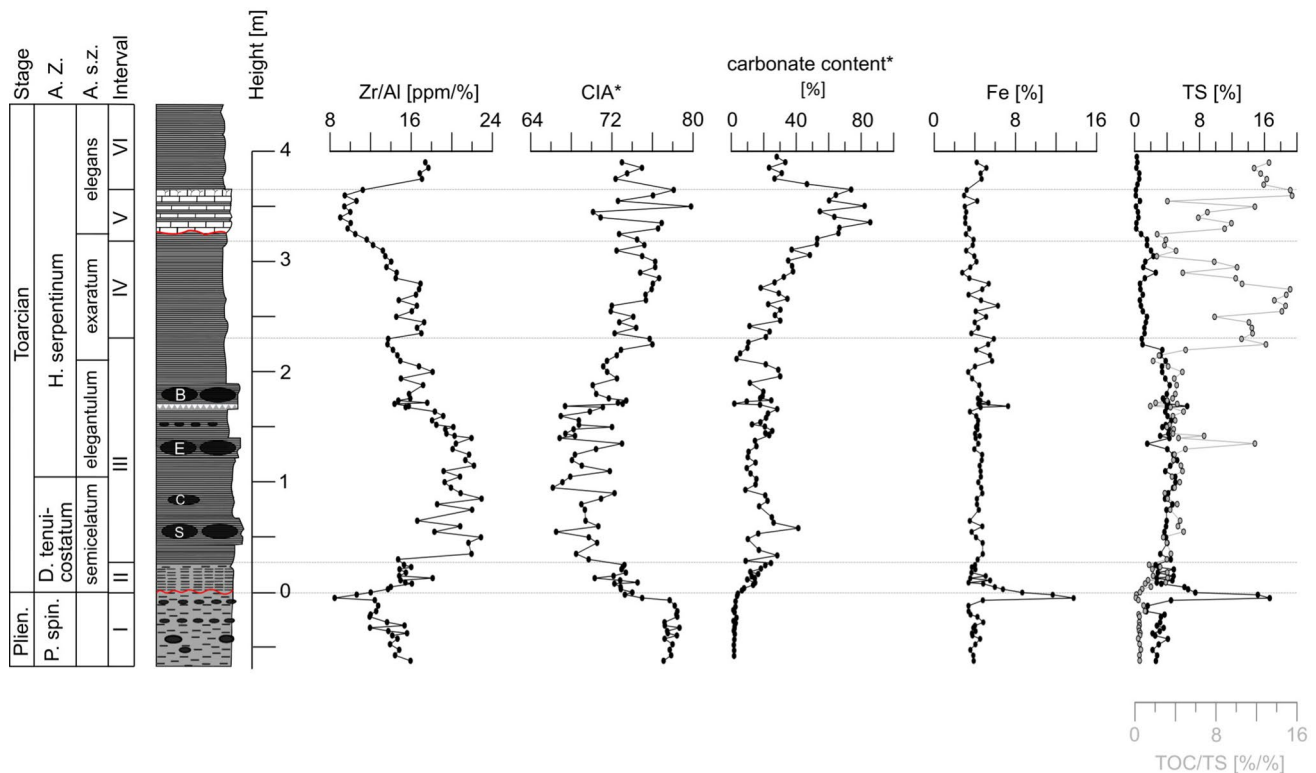
such as the abundance of Al-rich clay minerals, Si-rich quartz and Zr-, Ti-rich heavy minerals (Taylor and McLennan 1985; Nesbitt and Young 1982; Brumsack 1991). Accordingly, Si/Al, Ti/Al, and Zr/Al ratios (supplement Table S1) can provide information on the composition of the clastic sediment fraction, in terms of mineral composition and grain size (sand, silt, clay). All ratios show a parallel evolution and correlation (supplement Fig. S1, Fig. S2). Accordingly, only the Zr/Al ratios is described here. The Zr/Al (ppm/%) ratios range from 22.9 to 8.5 (Fig. 3). In interval I, the ratio declines, reaching a minimum of 8.5 followed by a rapid increase in the uppermost part. This trend continues in the lowermost part of interval II and reaches values of about 16. An abrupt increase in Zr/Al ratios to values of about 22 occurs in the lowermost part of interval III. High but variable values of 16–23 are seen in lower and middle part of interval III, before a decrease to values of about 14 occurs in the upper part of interval III (Fig. 3). Interval IV shows an abrupt increase in the Zr/Al ratio to values around 17, followed by a plateau with steady values and a return to lower ratios of about 12 (Fig. 3). Mainly low Zr/Al ratios in the range 9–11 appear in interval V, while remaining higher of 16–18 in samples from interval VI (Fig. 3).

The chemical index of alteration (CIA) allows quantifying the chemical weathering intensity, whereby weathering

and mineral hydrolysis will form Al-rich clay minerals, such as smectite and kaolinite (Nesbitt and Young 1982). The CIA adapted for carbonate-rich lithologies is calculated as  $CIA^* = 100 * Al / (K + Na + Al)$ . In the samples analyzed, the  $CIA^*$  falls in the range of 66–80 (Fig. 3). The  $CIA^*$  shows mainly high and steady values of 76–80 in samples from interval I, then decreases throughout the upmost part of intervals I and II. Mainly low but variable values of 66–76 occur in interval III (Fig. 3). An increase in the  $CIA^*$  to about 75 occurs in the uppermost part of interval III. Increased by variable values in the range 70–80 were determined for intervals IV–VI, with more variable values in interval V (Fig. 3).

The carbonate contents range between 1 and 86% (Fig. 3, supplement Table S1). Carbonate contents are low in samples from interval I (1–3%) and successively increase in interval II to 24%. A sharp drop occurs in a heterolithic sample at the top of interval II (9%). Interval III is characterized by carbonate contents ranging from 9 to 41%. Toward the top of interval III, the values decrease and subsequently increase during interval IV before reaching a maximum of 86% in interval V. Samples from interval VI show carbonate contents in the range of 20–30% (Fig. 3).

Pyrite minerals can be considered the major host of the elements Fe and S (Bernier and Raiswell 1983). The content



**Fig. 3** Stratigraphic trends in Zr/Al ratios, the  $CIA^*$  (modified Chemical Index of Alteration), carbonate content, as well as in the Fe and TS contents. For the lithological key, abbreviations and definition of the intervals, see Fig. 2

of Fe ranges from 3 to 13.7% (Fig. 3). Samples from interval I exhibit values mainly between 3 and 4%. The top of this interval is characterized by a horizon in which Fe abundances increase to values of 13.7%. In interval II, Fe abundances decrease to values in the range of 4–5%. Interval III is marked by mainly steady values in the range of 3–5%, with the exception of one sample with 7% and an increase to 4–5% in the uppermost part of the interval. In interval IV, the values remain in a similar range and drop toward the top to values of about 3%. Comparable values can be seen in interval V and increase to about 4–5% in interval VI (Fig. 3).

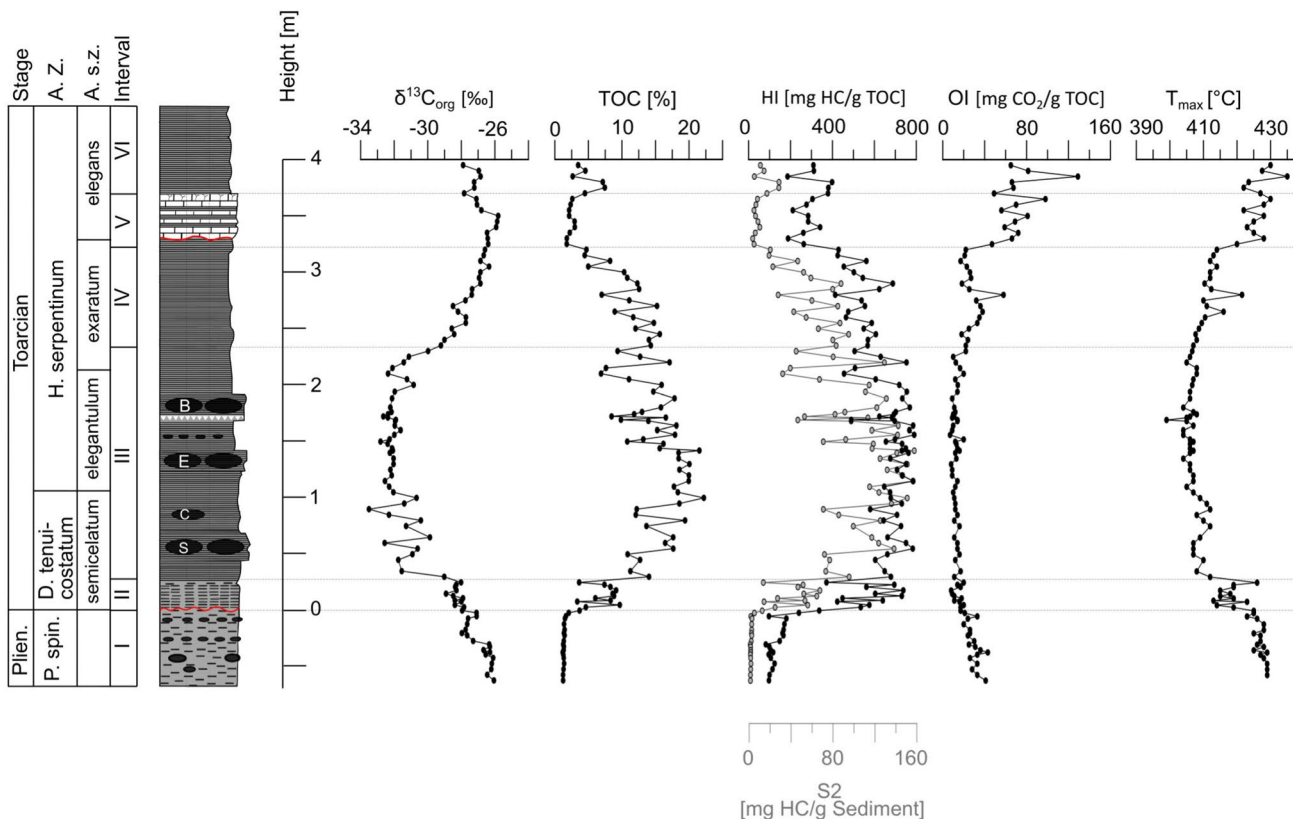
The TS contents fall in the range of 0.2–16.7% (Fig. 3, supplement Table S1). Throughout the intervals I–III, TS values mirror the trend seen in the Fe content. A drop in the TS content to values of about 1% is seen in the upper part of interval III. Lowered TS contents (mainly < 1%) are seen in samples from the intervals IV–VI (Fig. 3).

### Bulk organic geochemical proxies

The  $\delta^{13}\text{C}_{\text{org}}$  values range from  $-26$  to  $-33.5\text{‰}$  (Fig. 4, supplement Table S1). In intervals I and II,  $\delta^{13}\text{C}_{\text{org}}$  steadily declines from  $-26$  to  $-29\text{‰}$ . An abrupt change in the  $\delta^{13}\text{C}_{\text{org}}$  from  $-30$  to  $-33.5\text{‰}$  is seen at the base of interval

III that shows the overall lowest  $\delta^{13}\text{C}_{\text{org}}$  values. An increase in  $\delta^{13}\text{C}_{\text{org}}$  to values of about  $-27\text{‰}$  occurs in interval IV (Fig. 4). In intervals V and VI,  $\delta^{13}\text{C}_{\text{org}}$  values range from  $-28$  to  $-26\text{‰}$ .

The TOC content varies from 1.2 to 22.2% (Fig. 4, supplement Table S1). Mainly low TOC abundances in the range of 1–7% are seen in intervals I, V, and VI. Increased TOC abundances of 3.3–9.7%, 6.9–22.2%, and 7–15.7% occur in intervals II, III, and IV, respectively (Fig. 4). The S2 values vary between 1 and 157 [mg HC/g sediment] (Fig. 4). The S2 trend mirrors the observed TOC trend with mainly low values in the range of 1–5 [mg HC/g sediment] in the intervals I, V, and VI and increased S2 values of 12–95 [mg HC/g sediment], 32–157 [mg HC/g sediment], and 23–88 [mg HC/g sediment] in intervals II, III, and IV, respectively (Fig. 4). The HI ranges from 97 to 790 [mg HC/g TOC] (Fig. 4), with low HI values of 100–240 [mg HC/g TOC], 188–430 [mg HC/g TOC], and 186–400 [mg HC/g TOC] in intervals I, V, and VI, respectively. By contrast, high HI values of 337–790 [mg HC/g TOC] occur in intervals II–IV (Fig. 4). The OI values range from 7 to 129 [mg  $\text{CO}_2$ /g TOC] (Fig. 4). In interval I, OI values are 20–41 [mg  $\text{CO}_2$ /g TOC] and decline throughout this interval. Lowest OI values of 7–20 [mg  $\text{CO}_2$ /g TOC] occur in samples



**Fig. 4** Stratigraphic trends in  $\delta^{13}\text{C}_{\text{org}}$ , TOC, HI, S2, OI, and  $T_{\text{max}}$  values. For the lithological key, abbreviations, and definition of the intervals, see Fig. 2

from intervals II and III. Slightly increased OI values in the range of 17–58 [mg CO<sub>2</sub>/g TOC] were observed in interval IV. The highest OI values of 21–129 [mg CO<sub>2</sub>/g TOC] are seen in samples from intervals V and VI (Fig. 4). The  $T_{\max}$  values vary between 399 and 435 °C (Fig. 4, supplement Table S1). Intervals I, V, and VI are characterized by high values of 413–435 °C. The intervals II, III, and IV show lowered values of 413–426 °C, 399–412 °C, and 407–416 °C, respectively.

## Redox proxies

The content of selected redox-sensitive elements is expressed as abundance (ppm) and as enrichment factor (EF), relative to average shale values (Wedepohl, 1971, 1991). Enrichment factors were calculated as  $X_{EF} = (X_{\text{sample}} / Al_{\text{sample}}) / (X_{\text{average shale}} / Al_{\text{average shale}})$ , with X representing the abundance of a redox-sensitive element (ppm) in the sample and average shale, respectively.

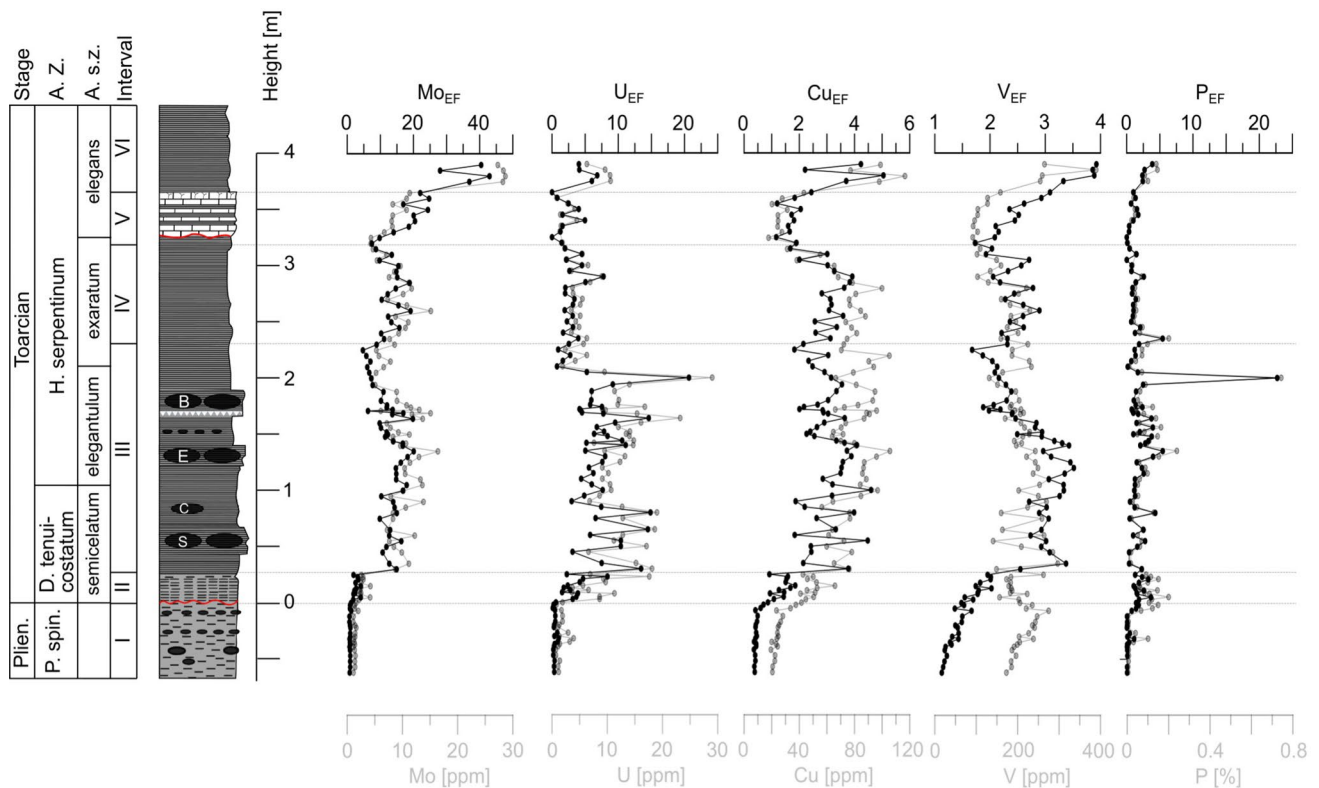
The abundances of Mo are 1.1–28.7 ppm, the  $Mo_{EF}$  values are 0.7–43 (Fig. 5). Interval I is characterized by low values of 0.7–1.2 increasing to 1–4 in interval II. At the base of interval III, enrichment factors strongly increase to 9.8–16.3. Lowered  $Mo_{EF}$  are observed in the upper part of interval III and lower part of interval IV (Fig. 5). Increased

$Mo_{EF}$  of about 30 are seen in the middle part of interval IV, before declining in the upper part. Within the lower part of interval V, low values range around 7.4–9.8. Subsequently the values increase reaching a maximum of 43 in interval VI.

Uranium abundance varies from 0 to 29 ppm.  $U_{EF}$  values range from 0 to 20.7 (Fig. 5, supplement Table S1). In interval I, low abundances of 0.1–1.1 were observed, thereafter increasing to 0.6–8.4 and 0.67–20.7 for intervals II and III, respectively. Shortly below the top of interval III, the values drop and remain low for intervals IV and V ranging from 0 to 7.8. In interval VI the values increase to 4.1–6.8.

The Cu abundances range from 17.7 to 116 ppm. The  $Cu_{EF}$  values are within the range of 0.4–5.1 (Fig. 5). Interval I shows low values between 0.4 and 0.7, thereafter increasing to values from 0.9 to 1.9 in interval II. In intervals III and IV, high values in the range of 1.8–4.1 were observed. The values decrease in interval V and range between 1.1 and 2.4. Interval VI is characterized by elevated values from 3.7 to 5.1.

The abundances of V vary from 91.6 to 389.4 ppm.  $V_{EF}$  values range between 1.1 and 3.9 for the succession. The trend closely resembles that of  $Cu_{EF}$  with elevated values in the range of 1.5–2, 1.7–3.4, 1.9–2.9, 1.7–3.1, and 3.3–3.9 for intervals II, III, IV, V, and VI, respectively, and low values ranging from 1.1 to 1.7 in interval I.



**Fig. 5** Stratigraphic trends in abundances and enrichment factors (EF) of redox-sensitive elements. For the lithological key, abbreviations, and definition of the intervals see Fig. 2



P abundance varies from 0.0018 to 0.74%.  $P_{EF}$  values range between 0 and 22.7. Interval I is characterized by low values on the order of 0.1–1.8. Subsequently, the values remain elevated for intervals II, III, and IV although with large fluctuations ranging from 0.1 to 22.7. At the beginning of interval V, the values are decreased at 0–1.5 but subsequently increase and exhibit high values ranging from 2.4 to 3.9 for interval VI. The highest value of 22.7 is attributed to fish debris (Delaney 1998).

## Discussion

### Sample quality

Surface samples, collected in an outcrop, such as those studied here, can be affected by weathering, resulting in alteration of mineral assemblages (Littke et al. 1991a, b), element contents (Marynowski et al. 2017) and organic matter composition (Bordenave et al. 1993). Pyrite/sulfides and organic matter are most sensitive toward weathering (Littke et al. 1991a, b; Marynowski et al. 2017; Ruebsam et al. 2018). Accordingly, weathering-related alteration of the sample material can be inferred from characteristic TOC/TS ratios (Ruebsam et al. 2018).

Suspiciously high TOC/TS ratios of 4–18 occur in samples from intervals VI, V, and IV, suggesting oxidation of pyrite/sulfides via meteoric waters. Comparable TOC/TS ratios of 4–24 were determined for the Toarcian Hainberg outcrop section located app. 70kms SSW of Hondelage by Arp et al. (2023). In contrast, the TOC/TS ratios determined for the nearby Schandelah core by Ruvalcaba Baroni et al. (2018) yielded TOC/TS ratios for the T-OAE of around 2.2, indicative of pristine pyrite. A compilation (Brumsack 1991) of TOC/S ratios for the NGB gave an average value of 2.3. Core data lacking effects of weathering, thus, yield TOC/S ratios in the region proposed for the average anoxic marine shale value of 2.5 (Bernier and Raiswell 1983). The close proximity between the Hondelage and Schandelah sites precludes drastic changes in environmental conditions, e.g., sulfate depletion by brackish waters, affecting the TOC/TS ratios and, thus, support the interpretation that both the Hondelage and Hainberg outcrop section are affected by pyrite weathering. This is compatible to the T-OAE section in Reka Valley (Ruebsam et al. 2018), where TOC/S ratios in the weathered part of the section increased to on average values of 26, whereby the hydrophobic organic matter showed almost no effect of oxidation (see supplement Fig. S3).

Uranium dissolves easily when exposed to oxidative fluids (Perkins and Mason 2015), which may explain the abrupt decline in U concentrations and  $U_{EF}$  in the upper part of interval III (Fig. 5). This indicates that U has potentially been altered over parts of intervals IV–VI and data must

be interpreted with caution. The redox-sensitive elements Mo, Cu, V, and P show no evidence for strong weathering-related alterations. Abundances and enrichment factors are lowered in the Lower Elegans Bed (interval V) but increase in interval IV to values comparable to those seen in interval III, which appears to be unaffected by surface weathering. Mo even reaches its strongest enrichment in interval VI (Fig. 5). Sedimentary organic matter can also be affected by outcrop weathering leading to a decline of HI and TOC, as well as to an increase in OI (Bordenave et al. 1993; Ruebsam et al. 2018). Lowered TOC and HI values accompanied by increased OI values occur in intervals V and VI. Samples from both intervals show increased  $T_{max}$  values (Fig. 4). This pattern may point to syndepositional changes in organic matter preservation, superimposed by weathering-related changes in organo-facies. In particular, high OI values accompanied by high/moderate TOC and moderate HI values point to oxidation of sedimentary organic matter via surface weathering. Consequently, data from the intervals V and VI are most likely altered by outcrop weathering, and U, TS, and organic proxies should be interpreted with caution.

### Stratigraphic evaluation and correlation

Precise stratigraphic correlation can be based on the combination of bio- and chemostratigraphic approaches (see review by Gröcke (2020) and references therein). For the late Pliensbachian and the early Toarcian, characteristic trends in organic carbon isotopes, such as the P/T-CIE and the T-CIE, have proven their chemostratigraphic correlation potential (e.g., Hesselbo et al. 2000, 2007; Ruebsam and Al-Husseini 2020). Combined application of bio- and chemostratigraphic approaches further allows to assess the stratigraphic completeness of a sediment archive and to detect potential hiatuses as well as condensed intervals (Pittet et al. 2014; Gröcke 2020; Ruebsam and Al-Husseini 2020).

For the Hondelage succession, the presence of stratigraphic gaps is indicated by biostratigraphic and lithological data (Mutterlose et al. 2022), which suggests a substantial gap at the Pliensbachian/Toarcian boundary (boundary interval I/II), covering the lower part of the *D. tenuicostatum* Zone. A belemnite battle field, consisting of corroded rostra, marks the boundary. Comparable lack of the basal Toarcian strata has been reported for the Wickensen and Mainzholzen sites of the Hils Syncline (Burnaz et al. 2024). The Lower Elegans Bed (*H. serpentinum* Zone; interval V) exhibits an erosive base, the potential hiatus is in this case minor.

The stratigraphic completeness of the Hondelage succession can further be assessed by chemostratigraphic correlation with coeval sediment archives for which detailed bio- and chemostratigraphic data are available. We here discuss the chemostratigraphy of the Hondelage section and its correlation with the nearby Schandelah Core (N-German

Basin; Ruvalcaba Baroni et al. 2018, van de Schootbrugge et al. 2019; Visentin et al. 2022; Ruebsam et al. 2024), the Rietheim core (SW-German Basin; Montero-Serrano et al. 2015) and core FR-210-078 (Lorraine Sub-Basin, Paris Basin, Luxembourg; Ruebsam et al. 2019). The Schandelah core is located about 8 km to the southeast of the Hondelage section. Accordingly, ammonite zones and  $\delta^{13}\text{C}_{\text{org}}$  trends are comparable to those seen in Hondelage. At both sites, the *D. tenuicostatum* Zone is extremely condensed and only represented by the *D. semicelatum* subzone (Fig. 6). The abrupt decline in  $\delta^{13}\text{C}_{\text{org}}$  values, marking the onset of the negative T-CIE, directly starts in the interval above the Pliensbachian/Toarcian boundary. This pattern of carbon isotope trends indicates that most of the lower *D. tenuicostatum* Zone and most likely the Pliensbachian/Toarcian boundary interval is missing in Hondelage and Schandelah. A comparable pattern is seen in the Rietheim Core from the South-German Basin, where the Pliensbachian/Toarcian boundary is directly followed by the negative T-CIE, whereby the *D. tenuicostatum* Zone is condensed. Moreover, in the Rietheim succession, the Pliensbachian/Toarcian boundary is marked by an erosive horizon (Montero-Serrano et al. 2015). At these three sites, the *D. tenuicostatum* Zone is condensed and lithological data attest to the presence of a major hiatus. Moreover, a P/T-CIE is not clearly expressed in the  $\delta^{13}\text{C}_{\text{org}}$  data. Accordingly, the Pliensbachian/Toarcian boundary interval is most likely not preserved at Hondelage, Schandelah and Rietheim (Fig. 6).

In contrast, the *D. tenuicostatum* zone is more expanded in core FR-210.078 (Luxembourg) and the Pliensbachian/Toarcian boundary is indicated by the P/T-CIE (Ruebsam et al. 2019). This suggests that basin morphology in combination with sea-level fluctuations controls the deposition and stratigraphic completeness as indicated by previous works (Pittet et al. 2014; Ruebsam et al. 2019, 2020b, 2024; Ruebsam and Al-Husseini 2020; Ruebsam and Schwark 2024). Stratigraphic gaps are most pronounced at the Pliensbachian/Toarcian boundary interval and in the *D. tenuicostatum* Zone. This interval corresponds to marked sea-level lowstands, which at shallow sites led to erosion and the development of hiatuses (Hallam 1997; Morard et al. 2003; Wignall 2005; Pittet et al. 2014; Krencker et al. 2019; Ruebsam et al. 2020b, 2024; Bodin et al. 2023). The preservation of the P/T-CIE in Luxembourg suggests that this basin was deeper and, hence, not affected by erosion during sea-level lowstand in the early *D. tenuicostatum* Zone (Ruebsam et al. 2019). Accordingly, the sites Hondelage, Schandelah, and Rietheim may represent more shallow depositional settings that were prone to erosion or winnowing by contour currents upon sea-level lowstands. The onset of the negative T-CIE is very abrupt in Rietheim and in Luxembourg, which points to sediment starvation and stratigraphic condensation upon the early Toarcian transgression (Ruebsam et al. 2019). On

the contrary, a more gradual decline in the  $\delta^{13}\text{C}_{\text{org}}$  values is seen at Hondelage and Schandelah (Fig. 6).

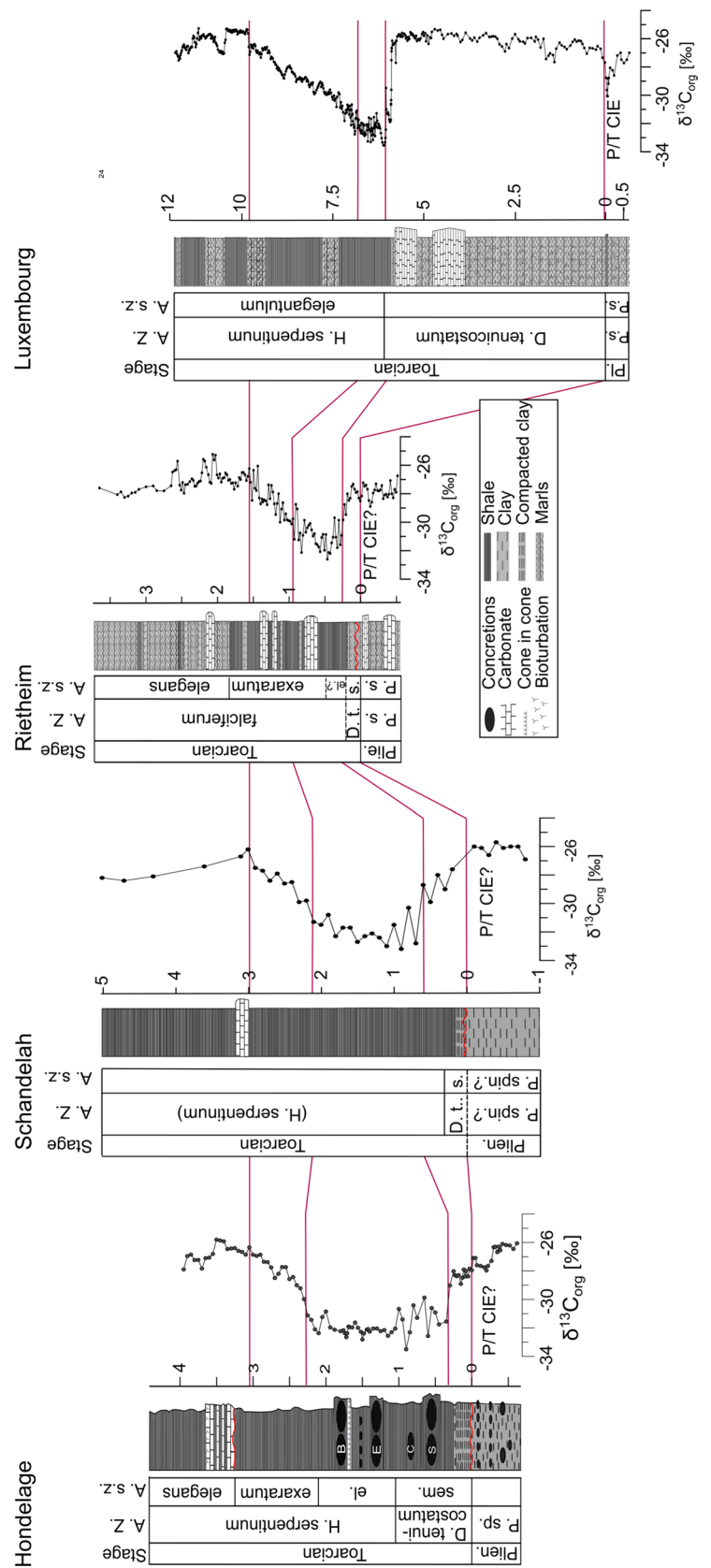
Data from the Hondelage succession and comparison with coeval strata from adjacent basins highlight the role of sea-level fluctuations and basin morphology as a major factor controlling the stratigraphic completeness of Early Toarcian sediment archives. Data indicate a major sea-level lowstand immediately prior to the T-CIE, while the T-CIE coincides with a major transgression and a sea-level highstand. Moreover, at Hondelage, a sea-level fall is indicated for the post T-CIE interval by an erosive horizon at the base of the Lower Elegans Bed (Fig. 2c). Evidence for erosive events at coeval stratigraphic intervals were documented for the Paris Basin (Hermoso et al. 2013; Thibault et al. 2018), or the Lusitanian Basin (Pittet et al. 2014). Data thereby attest to dynamic sea-level changes, not only prior to the T-CIE, but also after the T-CIE (Ruebsam et al. 2020b; Schwark and Ruebsam 2024).

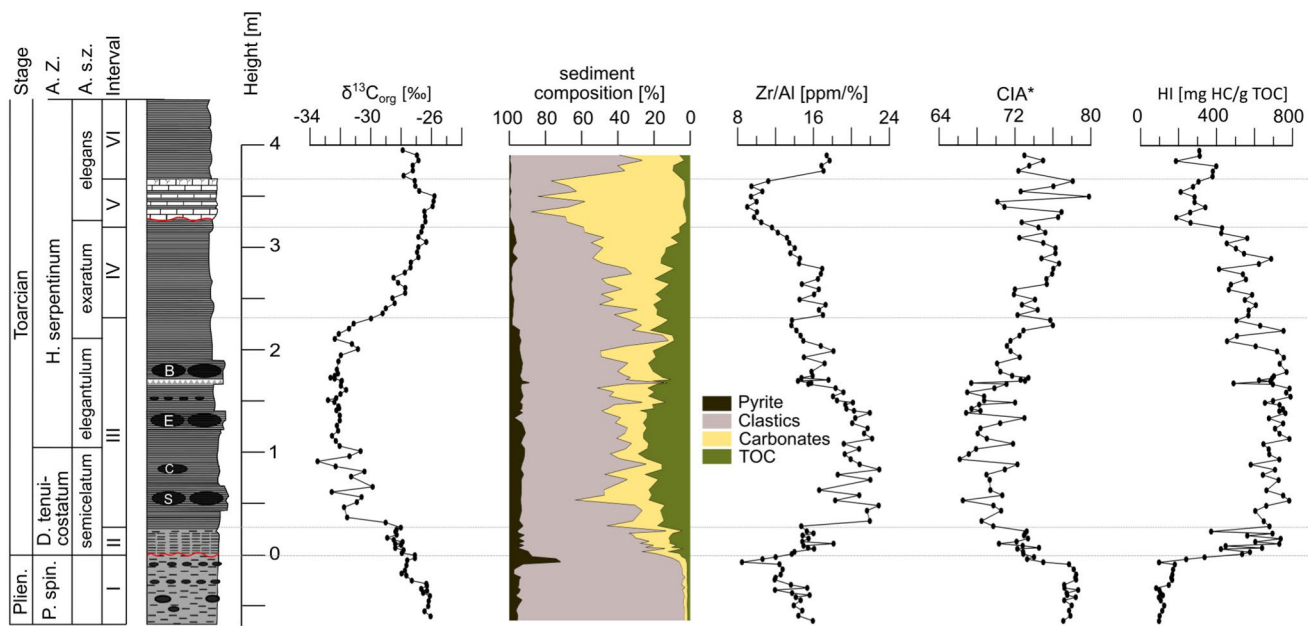
### Sediment composition and evolution of the depositional setting

The sediment composition of marine basins is controlled by the interplay of sea-level fluctuations, climate, primary productivity, depositional conditions, weathering in the catchment area, runoff, and the position of river mouths. The general composition of marine sediments can be described as four-component system, composed of siliciclastics [= 100%—carbonate (%)—organic matter (%)—pyrite (%)], carbonates, organic matter (= TOC  $\times$  1.3) and pyrite (= TS  $\times$  1.7) (e.g., Ricken 1993; Röhl et al. 2001; Burnaz et al. 2024). A major change in the sediment composition occurred throughout interval II that records an increase in the relative abundance of carbonate and organic matter (Fig. 7). A minor increase in pyrite is seen as well, whereby the interval I/II boundary records a marked pyrite spike.

Overall low carbonate abundances in interval I (Pliensbachian) are explained by a low-productive, shallow marine environment, in which marine biocalcifiers, such as calcareous nannoplankton, were scarce (Mutterlose et al. 2022; Visentin et al. 2022). Therefore, the Pliensbachian Amaltheenton strata is strongly dominated by clastic sedimentation. In intervals II–VI, increased carbonate abundances can be linked to enhanced contributions from calcareous nannoplankton, a major source of the sedimentary carbonate fraction (e.g., Mattioli et al. 2008; Mutterlose et al. 2022; Visentin et al. 2022). During deposition of intervals II–VI, a higher sea level favored higher abundances of calcareous nannoplankton, even though these organisms experienced a marked crisis during the T-OAE or “Jenkyns Event” (e.g., Mattioli et al. 2008; Ruebsam et al. 2022c). This biocalcification crisis might be expressed by moderate carbonate abundances

**Fig. 6** Bio- and chemostratigraphic correlation of Late Pliensbachian–Early Toarcian sediment archives from the NGB, South-German Basin (SGB), and Paris Basin. NGB, Hondelage: This study and Mutterlose et al. (2022). NGB, Schandelah: Ruvalcaba Baroni et al. (2018); Van de Schootbrugge et al. (2019), Visentin et al. (2022). SGB, Rietheim; Montero-Serrano et al. (2015). Paris Basin, Lorraine Sub-Basin, Luxembourg: Ruebsam et al. (2019). Due to the lack of age diagnostic macrofossils, the ammonite biostratigraphy for Schandelah above the *D. tenuicostatum* Zone remains uncertain (see van de Schootbrugge et al. (2019) and Fig. 2)





**Fig. 7** Stratigraphic trends in  $\delta^{13}\text{C}_{\text{org}}$ , four-component gross sediment composition for pyrite, clastics, carbonates, and TOC, Zr/Al ratios, CIA\* (modified Chemical Index of Alteration), hydrogen index (HI) from programmed pyrolysis

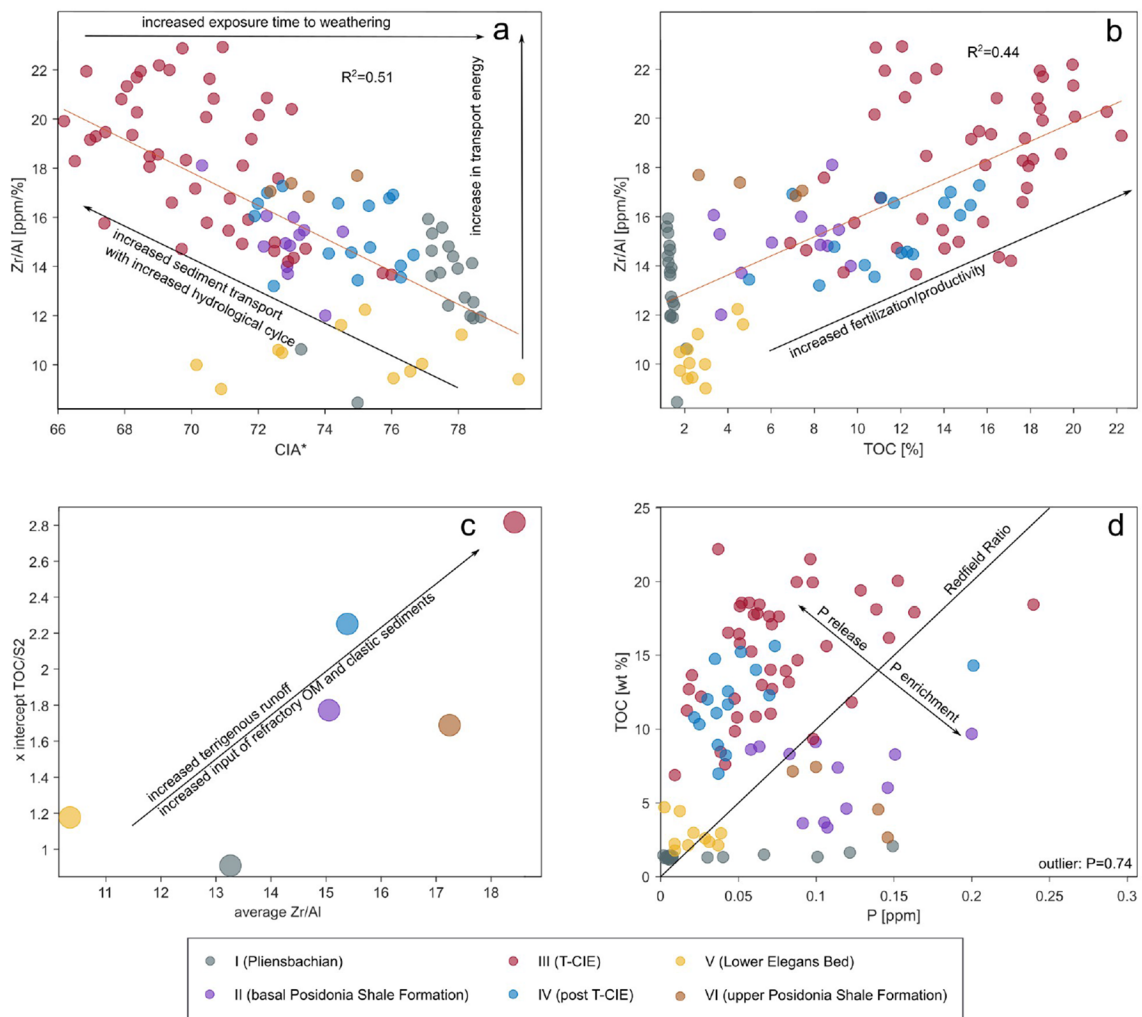
in interval III (Fig. 7). Carbonate abundances increase in interval IV and maximize in interval V (Lower Elegans Bed), indicative of a recovery of calcareous nanoplankton subsequent to the Jenynks Event (Mattioli et al. 2008, 2009; Hermoso et al. 2009; Ruebsam et al. 2022c). Marked fluctuations occur in carbonate contents of interval III. Caution must be taken here as syn-/post-depositional growth of carbonate concretions, abundant in this interval, was most likely associated with the redistribution of bulk sedimentary carbonate.

In interval I, low organic matter (and TOC) abundances accompanied by low HI and moderate OI values attest to a well-oxygenated shallow marine depositional setting unfavorable for the preservation of labile marine organic matter. Increased organic matter abundances, high HI and low OI values occur in intervals II–IV, which indicates the presence of well-preserved labile marine organic matter deposited in a low-energetic setting, below the wave/storm base, under preferentially oxygen-deficient conditions (Fig. 7). Changes in redox regime, but in the Hondelage outcrop also weathering controlled trends in pyrite abundances. The pyrite spike at the interval I/II boundary may reflect post-depositional diagenetic pyrite formation in strata underlying the Posidonia Shale Formation. Lowered organic matter abundances in interval V are best explained by carbonate dilution (Fig. 7). In intervals V and VI, lowered organic matter and pyrite abundances may be affected by outcrop weathering.

### Interplay of sea level, continental weathering, and fluvial discharge

Changes in the composition of the siliciclastic sediment fraction, in terms of its grain-size (sand, silt, clay) and clay assemblages (e.g., kaolinite, smectite, illite, chlorite), will vary as function of sea level and associated shifts in the shoreline, as well as clastic influx via fluvial discharge and continental weathering (Nesbitt and Young 1982; Taylor and McLennan 1985; Ganeshram et al. 1999; Dypvik and Harris 2001; Dera et al. 2009; Govin et al. 2012; Hermoso et al. 2013).

In intervals II–IV, an increase in the Zr/Al ratio (and Si/Al, Ti/Al), accompanied by a decline in the CIA\* (Figs. 7, 8a, and Fig. S3), reflects an increase in grain size of the clastic fraction and the presence of less-hydrolyzed clay mineral assemblages (Nesbitt and Young 1982; Taylor and McLennan 1985). The coarser grain size is explained by higher transport energy via enhanced riverine runoff during an intensified Toarcian hydrological cycle (e.g., Cohen et al. 2004; Brazier et al. 2015; Izumi et al. 2018; Krencker et al. 2020). At Hondelage, grain-size variation of the clastic sediment fraction was primarily driven by changes in riverine runoff, counterbalancing a fining upward trend associated with the early Toarcian transgression (Ruebsam et al. 2019). The complex interplay of continental runoff and sea-level change is expressed by the heterogeneity of grain-size proxies seen in coeval strata elsewhere (e.g., Dera et al. 2009;



**Fig. 8** **a** Positive correlation of Zr/Al ratio vs. CIA\* indicates increased transport efficiency of clastic material via an enhanced hydrological cycle. **b** Zr/Al ratio vs. TOC shows a positive correlation suggesting nutrient delivery via terrestrial runoff. **c** x-axis intercept of TOC/S<sub>2</sub> regression line vs. Zr/Al ratios averaged for the respective intervals (I–VI) indicating increased erosion of refractory organic

matter from terrestrial sources (presumably soils) via an increased hydrological cycle. **d** TOC vs. P indicating P release from the sediment under reducing conditions for values above the Redfield ratio (Redfield 1958). Samples plotting below the line indicate P enrichment either by precipitation of authigenic apatite (Jarvis et al. 1994; Reimers et al. 1996) or fish debris (Delaney 1998)

Hermoso et al. 2013; Montero-Serrano et al. 2015; Xu et al. 2018; Fantasia et al. 2019; Ruebsam et al. 2019).

The decline of the CIA\* seems to contradict the widely accepted model of an accelerated hydrological cycle and increased chemical weathering during the T-CIE (e.g., Cohen et al. 2004; Dera et al. 2009; Hermoso et al. 2013; Brazier et al. 2015; Xu et al. 2018; Kemp et al. 2020). Data from coeval strata show an increase in the relative abundance of chemically altered clay mineral assemblages dominated by smectite and illite (Dera et al. 2009; Montero-Serrano et al. 2015; Xu et al. 2018; Burnaz et al. 2024).

At Hondelage, the relative increase in abundance of less-hydrolyzed clay minerals and coarse-clastics might point to a proximal source area from which coastal-plain

bedrock sediment was rapidly eroded and transported to adjacent marine areas. Either, erosion of freshly exposed bedrock occurred rapidly prohibiting intensive hydrolysis of the transported material (Figs. 7, 8a) and/or coastal-plain sediments contained weathering residues rich in quartz and heavy minerals. Such a scenario is in agreement with an intensified hydrological cycle and substantial strengthening of riverine discharge to the EEBS (e.g., Cohen et al. 2004; Montero-Serrano et al. 2015; Xu et al. 2018; Kemp et al. 2020), although changes in catchment area and, hence, source region cannot be excluded. This scenario is further supported by the palaeogeographic setting of the study site located in the Oberaller Through in close proximity to exposed land masses, such as the Bohemian Massif to the

east, the Calvörde and Altmark Swells/Islands to the north and the Fallstein Swell/Island to the south (Fig. 2b). Thus, short transport distances facilitated proximal marine deposition of both fine and coarse-grained terrigenous clastics.

The clastic input and grain size decline in the T-CIE recovery interval (interval IV) toward the Lower Elegans Bed (interval V), which may mark a weakening of the hydrological cycle and longer sediment exposure times to chemical weathering, might have caused a slightly increased CIA\* (e.g., Cohen et al. 2004; Montero-Serrano et al. 2015; Kemp et al. 2020). This presumably was related to colder temperatures (Ruebsam et al. 2020a). In interval VI, an increase in Zr/Al ratios is not accompanied by changes in the CIA\* and may reflect the increase in transport energy during a lowered sea level, changes in river mouth or delta system position (Figs. 7, 8a).

## Organofacies and organic matter accumulation

### Organofacies characterization

Organofacies characterization is based on programmed pyrolysis-derived proxies (HI, OI,  $T_{\max}$ ). Low to moderate  $T_{\max}$  values (<430 °C; 415 °C on average) attest to an overall low thermal maturity of the sedimentary organic matter. The variability of the  $T_{\max}$  reflects differences in the stability of the kerogen toward thermal breakdown and, thus, differences in the kerogen composition. Low HI (<200 mgHC/gTOC) and slightly increased OI (20–45 mgCO<sub>2</sub>/gTOC) values in TOC-lean samples from interval I indicate the presence of mainly degraded marine organic matter, as well as minor contributions from land plants. Moreover, increased  $T_{\max}$  values suggest the presence of recalcitrant kerogen in sediment of interval I, the destruction of which requires higher temperatures (Espitalie et al. 1985; Bordenave et al. 1993; Stock et al. 2017). In interval I, mainly low Zr/Al ratio argues for a low influx of clastic material from adjacent land masses, suggesting that organic matter contributions from land plant sources were low as well. Low HI values could indicate that relative contributions of terrigenous organic matter may have been elevated by even more diminished flux of marine organic matter. Enhanced terrigenous wax lipid fluxes during deposition of the Amaltheenton Fm. was proposed by Burnaz et al. (2024) based on a dominance of long-chain *n*-alkanes found in sediments of the Hils syncline.

Increased HI values (mainly >500 mgHC/gTOC) and low OI values (<20 mgCO<sub>2</sub>/gTOC), as seen in the TOC-rich intervals II–IV, indicate the presence of high abundances of labile marine organic matter originating from algae and bacteria. The lowest  $T_{\max}$  values were observed in intervals II–IV supporting this interpretation and indicating

the presence of labile kerogen, whose thermal breakdown requires less energy (Espitalie et al. 1985; Stock et al. 2017). Moderate HI, accompanied by increased OI and  $T_{\max}$  values, is seen in samples from intervals V and VI. In particular, high OI and  $T_{\max}$  values point to the alteration of sedimentary organic matter by outcrop weathering. Thus, a reliable organo-facies assessment is hampered for these intervals.

### Primary productivity

In marginal marine environments, such as in epicontinental seas, marine primary productivity will be maintained by the nutrient supply from adjacent land masses (van Helmond et al. 2015). In particular, areas in proximity to estuaries and deltas can be considered being highly productive (Bianchi and Allison 2009). The evolution of clastic proxies (Zr/Al, CIA\*) indicate that the setting of Hondelage, located in proximity to the north-western wedge of the Bohemian Massif and also close to some smaller islands (Fig. 2b), presumably was strongly affected by changes in the continental runoff, clastic influx and weathering intensity. Samples from the Pliensbachian (interval I) are characterized by low TOC abundances, Zr/Al ratios, and high CIA\* values. In contrast, highest TOC abundances accompanied by increased Zr/Al ratios (and decreased CIA\*) are seen in intervals II–IV (Fig. 8a, 8b), corresponding to the T-CIE (interval III). During the Jenkyns Event, intensified hydrological cycling led to enhanced mobilization of nutrients that were transported to marginal marine settings and maintained a high primary productivity. The positive relationship of TOC and Zr/Al ratios indicates that at this marginal marine setting, changes in continental runoff and nutrient supply directly impacted marine primary productivity and organic matter burial (Fig. 8b). This interpretation is supported by the pattern seen in Zr/Al ratios and the x-axis intercept of the TOC/S<sub>2</sub> binary diagram (see supplement Figs. S4 and S5) averaged for the different intervals (Fig. 8c). Hereby, the TOC-axis intercept value indicates the proportion of refractory organic carbon derived from reworked terrigenous biomass (Fig. 8c, Fig. S4). Highest x-axis intercepts of the TOC/S<sub>2</sub> regression line, along with increased average Zr/Al ratios, occur for intervals II–IV (Fig. 8c), and indicate that the refractory organic matter originated from terrigenous sources and became remobilized via surface weathering and erosion. The enhanced delivery of terrigenous soil organic matter and associated nutrients presumably fostered primary productivity at marginal marine areas.

Additionally, the establishment of reducing conditions might have caused phosphorous release from the sediments (Tyson and Pearson 1991; Ingall et al. 1993; van Cappellen and Ingall 1994). Phosphorous often is a limiting nutrient that is sequestered in the sediments under oxic conditions (Jarvis et al. 1994; Reimers et al. 1996). A release of

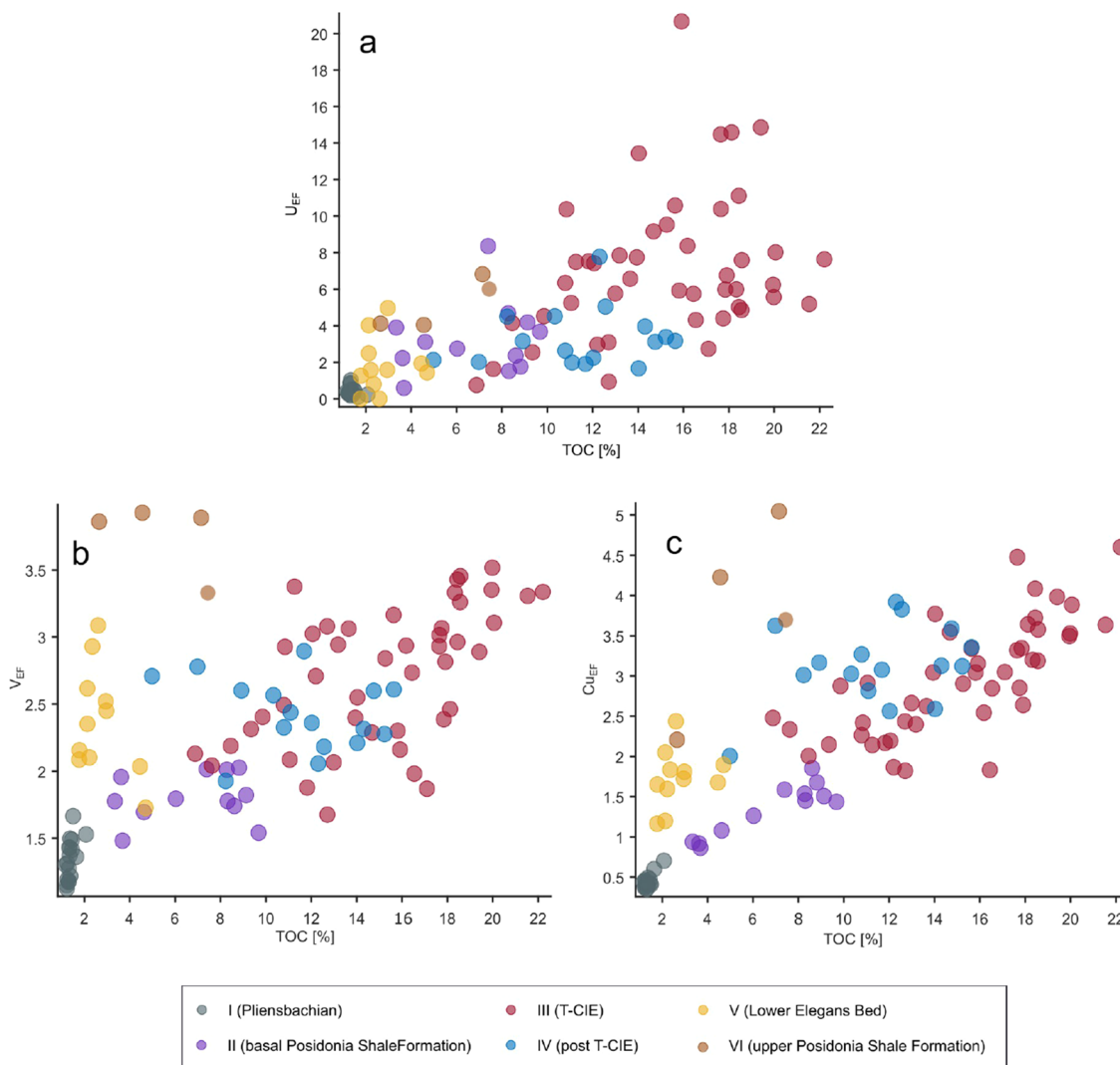
P becomes evident from TOC/P ratios. A strong deviation from the Redfield ratio (106:16:1, C:N:P (Redfield 1958)) toward higher values indicates the release of P from the sediments. The proposed elevated frequency of cyclones with the establishment of green/hothouse conditions during the onset of the T-CIE (Korty et al. 2008; Krencker et al. 2015) and also in the period thereafter (Schwark and Ruebsam 2024) might have induced upwelling of deep P- and nutrient-enriched waters further promoting surface water productivity (Fig. 8d).

### Redox regime

The T-OAE caused the expansion of oxygen-deficient conditions in shelf seas, epicontinental seas and potentially in deep oceanic settings (e.g., Jenkyns 1988, 2010; Kemp

et al. 2022). Redox conditions prevailing in pore and bottom-waters can be inferred from sedimentological characteristics (e.g., Wignall 1991), the enrichment pattern of redox-sensitive elements, such as U, Mo, Cu, or V (e.g., Algeo and Maynard 2004; Tribouillard et al. 2006), from TOC-TS-Fe systematics (Bernier and Raiswell 1983) or from fossil assemblages (Röhl et al. 2001), including trace fossil associations (Savrda and Bottjer 1986) and coupled biomarker and fossil indicators (Frimmel et al. 2004).

The TOC-lean Pliensbachian (interval I) samples lack an enrichment of redox-sensitive element (Figs. 5, 9). Moreover, organic matter in samples from this interval was subjected to intense aerobic degradation, as indicated by low HI and increased OI values. Data attest to a well-oxygenated shallow marine depositional environment not favorable for the preservation of labile marine organic matter. This



**Fig. 9** Binary diagrams of redox-sensitive trace elements vs. TOC. **a**  $U_{EF}$  vs. TOC, intervals IV–VI are affected by the loss of U due to outcrop weathering. **b**  $V_{EF}$  vs. TOC, **c**  $Cu_{EF}$  vs. TOC

interpretation is consistent with data from coeval strata from the wider EEBS, which commonly lack evidence for reducing conditions (e.g., Hermoso et al. 2013; Montero-Serrano et al. 2015; Ruvalcaba Baroni et al. 2018). Under these conditions, the chemocline was predominantly localized within the sediment and no oxygen-deficient conditions could develop at the sediment–water interface or in the water column.

An initial increase in TOC and redox-sensitive elements is seen in the Toarcian interval II. In particular, an increase is seen in  $\text{Cu}_{\text{EF}}$  and  $\text{U}_{\text{EF}}$ , while  $\text{V}_{\text{EF}}$  and  $\text{Mo}_{\text{EF}}$  show a minor increase only (Figs. 5, 9). The increase in  $\text{Cu}_{\text{EF}}$  and  $\text{U}_{\text{EF}}$  attest to an enhanced organic matter flux to the sediment and the expansion of suboxic-anoxic conditions. Low enrichment factors seen for the elements Mo and V indicate that anoxic–euxinic conditions may not have developed over longer periods of time (Algeo and Maynard 2004; Tribouillard et al. 2006). Toarcian interval II corresponds to the onset of the T-CIE and the early-stage T-OAE marked by an initial sea-level rise and an increase in marine primary productivity, as indicated by clastic proxies and calcareous nanofossil evidence (Mutterlose et al. 2022). Highest TOC abundances along with high HI values and a substantial enrichment of Cu and V are noted for samples from intervals III and IV. An enrichment of U is lacking in interval IV, but this may be affected by outcrop weathering. Data argue for a substantial increase in marine organic matter flux and establishment of prolonged anoxic–euxinic conditions in the intervals marking the T-OAE climax. During this time, high temperatures, intensified hydrological cycling and increased runoff provided substantial amounts of nutrients to marginal marine areas, thus maintaining a high primary productivity that subsequently favored the development of oxygen-deficient conditions in pore- and bottom-waters (Cohen et al. 2004; Brazier et al. 2015; Izumi et al. 2018). Moreover, increased runoff will have promoted freshwater stratification limiting the vertical ventilation of the water column (Riegel et al. 1986; Brumsack 1991; Saalen et al. 1996; Röhl et al. 2001; Schwark and Frimmel 2004), thus initiating oxygen-deficiency in pore- and bottom-waters. The sea-level highstand during the T-CIE initiated a basinwide expansion of low-energy depositional settings favoring the preservation and accumulation of TOC-rich strata (Wignall 1991; Röhl et al. 2001).

Enrichment factors for Cu and V, as well as TOC abundances decline in interval V (Lower Elegans Bed) (Figs. 5, 9). Here, evidence of sediment reworking, erosion, and bioturbation, which indicate sea-floor ventilation suggest a lowered sea level (Mutterlose et al. 2022). In the Sancerre Core (southern Paris Basin), sea-floor re-oxygenation events have been documented from a comparable stratigraphic position (Hermoso et al. 2013). A return to predominantly anoxic/euxinic conditions in the interval VI can be inferred from

increasing TOC,  $\text{Mo}_{\text{EF}}$ ,  $\text{Cu}_{\text{EF}}$ , and  $\text{V}_{\text{EF}}$  (Fig. 5, 9). This interval corresponds to a sea-level rise, which impacted on the depositional and redox conditions (Röhl et al. 2001; Frimmel et al. 2004; Hermoso et al. 2013; Ruebsam et al. 2019). Data from Hondelage thereby highlight the role of sea-level change as a major process modulating the redox environment during the late Pliensbachian to early Toarcian times.

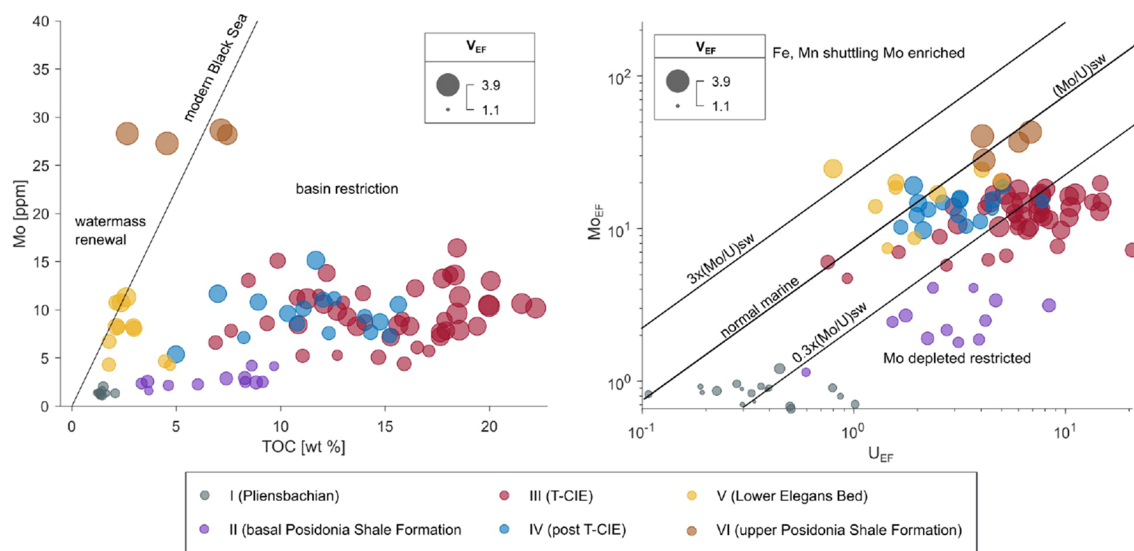
### Basinal restriction and hydrology

Molybdenum is a conservative element in the modern ocean with an average concentration of 105 nmol/kg and a residence time of 800 ka (Emerson and Husted 1991). Under anoxic/euxinic conditions, Mo is efficiently scavenged from the water column in the form of thiomolybdate complexes leading to an accumulation of Mo in the sediment (Helz et al. 1996). In restricted basins, where Mo scavenging exceeds the resupply, Mo can become depleted in seawater over time (Algeo and Maynard 2004; Algeo and Lyons 2006). Under such conditions, anoxic/euxinic sediments can lack a Mo-enrichment.

For the EEBS, widespread anoxic–euxinic conditions occur in the T-CIE interval marking the peak T-OAE (e.g., Röhl et al. 2001; Schwark and Frimmel 2004; McArthur et al. 2008; Burnaz et al. 2024) and were confirmed for the Hondelage succession in this study. Sediments corresponding to the Jenkyns Event are characterized by low to moderate Mo-enrichment, which has been interpreted to reflect the Mo drawdown in the restricted EEBS under prolonged euxinic conditions (e.g., McArthur et al. 2008). A comparable pattern was observed at Hondelage with lowest  $\text{Mo}_{\text{EF}}$  seen in samples from the Pliensbachian (interval I) explained by a well-oxygenated depositional setting in which Mo is not efficiently transferred from the water column to the sediment. Sediments of the Toarcian Interval II show a significant enrichment in TOC, Cu, and U, while only minor enrichments are seen in V and Mo. This pattern attests to rather suboxic-anoxic conditions that favored organic matter preservation, but not the enrichment of elements with euxinic affinity, such as V and Mo (Algeo and Maynard 2004). High  $\text{Mo}_{\text{EF}}$  are seen in interval III that corresponds to the core of the T-CIE, for which prolonged euxinic conditions have been inferred. Throughout the intervals IV–VI,  $\text{Mo}_{\text{EF}}$  mainly follows trends seen in the enrichment of V, indicating that Mo-enrichment was controlled by changes in the redox conditions and replenishment through water mass renewal. Hence, the highest observed Mo concentrations in interval VI could be explained by increased water mass exchange.

The cross-plots of Mo versus TOC and  $\text{U}_{\text{EF}}$  versus  $\text{Mo}_{\text{EF}}$  attest to significant changes in the Mo burial in the anoxic–euxinic strata of the Posidonia Shale (intervals II–VI). In the cross-plot of TOC vs. Mo (Fig. 10a), samples from intervals II–IV plot below the Black Sea





**Fig. 10** Left: TOC (%) vs. Mo (ppm) with the black line indicating the modern Black Sea ratio (Algeo and Lyons 2006): Samples plotting below the Black Sea line indicate a more severe restriction than evident for the Black Sea. Right: Increases in the ratio indicate enhanced water mass enrichment of Mo ( $Mo_{EF}$ ) vs. U ( $U_{EF}$ ). Black

lines represent the ratio of Mo/U in sea water under normal marine conditions, Mo-depleted (basin restriction) and Mo-enriched conditions (Fe, Mn shuttling) adapted from Algeo and Tribouillard (2009). The size of data symbols represents  $V_{EF}$

trend, which characterizes highly restricted and Mo-depleted basins (Algeo and Lyons 2006). This pattern is in agreement with data from coeval strata that also lack a significant Mo-enrichment, although they were deposited under euxinic conditions (e.g., McArthur et al. 2008; Hermoso et al. 2013; Fernández-Martínez et al. 2023). For these intervals, the cross-plot of  $U_{EF}$  with  $Mo_{EF}$  indicates a rather low aqueous Mo inventory (Fig. 10b), which is best explained by the establishment of prolonged euxinia in a hydrologically restricted basin with limited water exchange with the open ocean. In addition, the global scale expansion of anoxic/euxinic sinks during the climax of the T-OAE (T-CIE interval) led to a decline in the Ocean Mo inventory (Dickson et al. 2017; Them et al. 2022).

An increase in the  $Mo_{EF}$  is seen in the post-Lower Elegans Bed interval VI (Fig. 5). A comparable pattern of increasing sedimentary Mo-enrichment is apparent in coeval strata from other basins and is best explained by a replenishment of  $Mo_{sw}$  via the enhanced connectivity of the EEBS with the Tethyan and Arctic Oceans (McArthur et al. 2008). In post T-CIE intervals, increased Mo-enrichment in anoxic/euxinic basins may also be related to a replenishment of the global Ocean Mo inventory, due to an overall decline of anoxic/euxinic sinks (Dickson et al. 2017; Them et al. 2022).

## Conclusion

Although the North-German Basin (NGB) has been studied for its depositional environment during the Pliensbachian/Toarcian transition before, comparably few studies exploiting the potential of complementary application of organic, elemental and isotope proxies embedded in a detailed biostratigraphic framework exist. The succession from Hordelage in the NGB covers the latest Pliensbachian to Early Toarcian interval including the Toarcian Carbon Isotope Excursion (T-CIE). Bio- and chemostratigraphic data suggest that the Pliensbachian Toarcian boundary and parts of the lower *D. tenuicostum* Zone are missing.

High-resolution geochemical data show that in the NGB changes in sedimentation, terrestrial input, redox conditions and organic matter accumulation are closely linked to sea-level fluctuations mediated by continental ice sheet volume and the climate-dependent hydrological cycle. The positive correlation of Zr/Al and TOC suggests fluvial input as main driver of soil-derived nutrient supply, which promoted high primary productivity during the Toarcian. This is supported by evidence for enhanced soil erosion leading to an increased input of refractory organic matter, as seen in the increased x-intercept of the regression line in a TOC vs. S<sub>2</sub> cross-plot. In contrast, low marine productivity and poor organic matter preservation under oxic to suboxic conditions prevailed during the Pliensbachian. An enhanced hydrological cycle during the T-CIE counter-intuitively led to a decreased chemical index of alteration,

presumably due to shorter residence times and faster transport of sediments from terrestrial sources to the marine basin. The source regions supplying sediment likely were proximal islands (Calvörde Island, Altmark Swell) as well as the Bohemian Massif hosting a large delta system with a sediment focusing toward the Oberaller Trough. The lowered sea level during the Pliensbachian coldhouse climate likely caused better bottom water ventilation with oxic to suboxic conditions and low accumulation of redox-sensitive trace elements. With increasing sea level, freshwater stratification, and export productivity, the oxygen levels decreased and anoxic to euxinic conditions established, reaching a maximum during the T-CIE. However, severe basin restriction prohibited further trace element enrichment in the sediments due to their drawdown in ocean waters. A sea-level drop toward the Lower Elegans Bed reduced anoxic conditions and coincided with increased carbonate precipitation, reduced terrestrial input and primary productivity, presumably due to reduced nutrient and freshwater input as well as a recovery of the carbonate factory. A presumed sea-level rise in uppermost part of the succession likely led to increased water mass exchange causing trace element replenishment leading to highest trace element abundances, coinciding with increased primary productivity and terrigenous nutrient supply.

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**Data availability** Data is available as supplementary information.

## Declarations

**Conflict of interests** The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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