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Changes in organic matter composition during the Toarcian Oceanic Anoxic Event (T-OAE) in the Posidonia Shale Formation from Dormettingen (SW-Germany)

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ABSTRACT

During the Early Toarcian, deposition of organic carbon-rich-shales occurred throughout the epicontinental sea across Europe. Climate instability and high extinction rates in the marine realm were associated with profound environmental changes. The Toarcian Oceanic Anoxic Event (T-OAE) has been linked to the injection of greenhouse gases (e.g. oceanic methane) into the atmosphere triggered by the emplacement of the Karoo-Ferrar large igneous province (LIP) volcanism. The data presented are obtained from the Posidonia Shale Formation in Dormettingen (southwestern Germany), ~2 km from the well-known Dotternhausen section. Despite the intense palaeontological and geochemical research, studies on the particulate organic matter (POM) across the T-OAE are scarce. Here, we provide a detailed study of POM of the Dormettingen section as a tool to evaluate changes in the depositional environment. Integrated POM (i.e. amorphous organic matter, marine and terrestrial palynomorphs) and geochemical (i.e. carbon isotope $\delta^{13}C$) analyses reveal different episodes of palaeoecological upheavals during the studied time interval. In this study, we will integrate new palynofacies data and combine it with the existing sedimentological and palaeoecological data of Dotternhausen in order to interpret relative sea-level fluctuations and climatic changes at the local palaeogeographic setting.

1. Introduction

During the Early Jurassic, organic carbon-rich black shales, associated with the Toarcian Oceanic Anoxic Event (T-OAE, ~183 Ma) were deposited in wide-ranging areas (Fig. 1a). The deposition of black shales is documented in two main palaeogeographic regions with characteristic micro-and macrofauna (Stevens, 1971; Bucefalo Palliani and Riding, 2003). These are: (1) the Tethyan continental margins (Tethyan Realm) encompassing Italy and southern Europe (Stevens, 1971; Jenkyns and Clayton, 1997) and (2) the European epicontinental seas (Boreal Realm) comprising Germany, UK and northern Europe. In the Tethyan records the black shales reach organic matter contents of <3 wt%, while in the Boreal Realm they reach up to ~17 wt% (Küspert, 1982; Jenkyns, 1985, 1988; Jenkyns et al., 2001; Röhl et al., 2001; Hesselbo et al., 2007; Jenkyns, 2010; Remírez and Algeo, 2020a). In the third intermediate sub-Boreal region, including France, Spain, Portugal and Hungary, sediments have an intermediate and mixed floral and faunal composition between the two aforementioned regions (Bucefalo Palliani et al., 1997; Bucefalo Palliani and Riding, 2003) with a TOC < 3 wt% (Remírez and Algeo, 2020a; Rodrigues et al., 2020).

The Central European Basin (CEB) was located between 20° and 40° N palaeolatitude during the Early Jurassic when the organic-rich black shales were deposited. This W-E trending shallow shelf sea basin was subdivided into several sub-basins (Ziegler et al., 1983; Röhl and Schmid-Röhl, 2005; van Acken et al., 2019). The basin was periodically connected to the Proto-North Atlantic to the north and the Tethys Ocean

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to the south (Ziegler, 1982; Ziegler et al., 1983) (Fig. 1a).

Due to its high organic matter content, the Lower Toarcian deposits of the Posidonia Shale Formation in Germany were the focus of early geochemical studies with the purpose of oil exploration and preliminary studies on the depositional environment (von Gaertner et al., 1968; Küspert, 1982; Jenkyns, 1985, 1988; Moldowan et al., 1986; Seilacher, 1990). A negative excursion followed by a positive shift in carbonate and organic $\delta^{13}C$ values has been documented that is possibly caused by

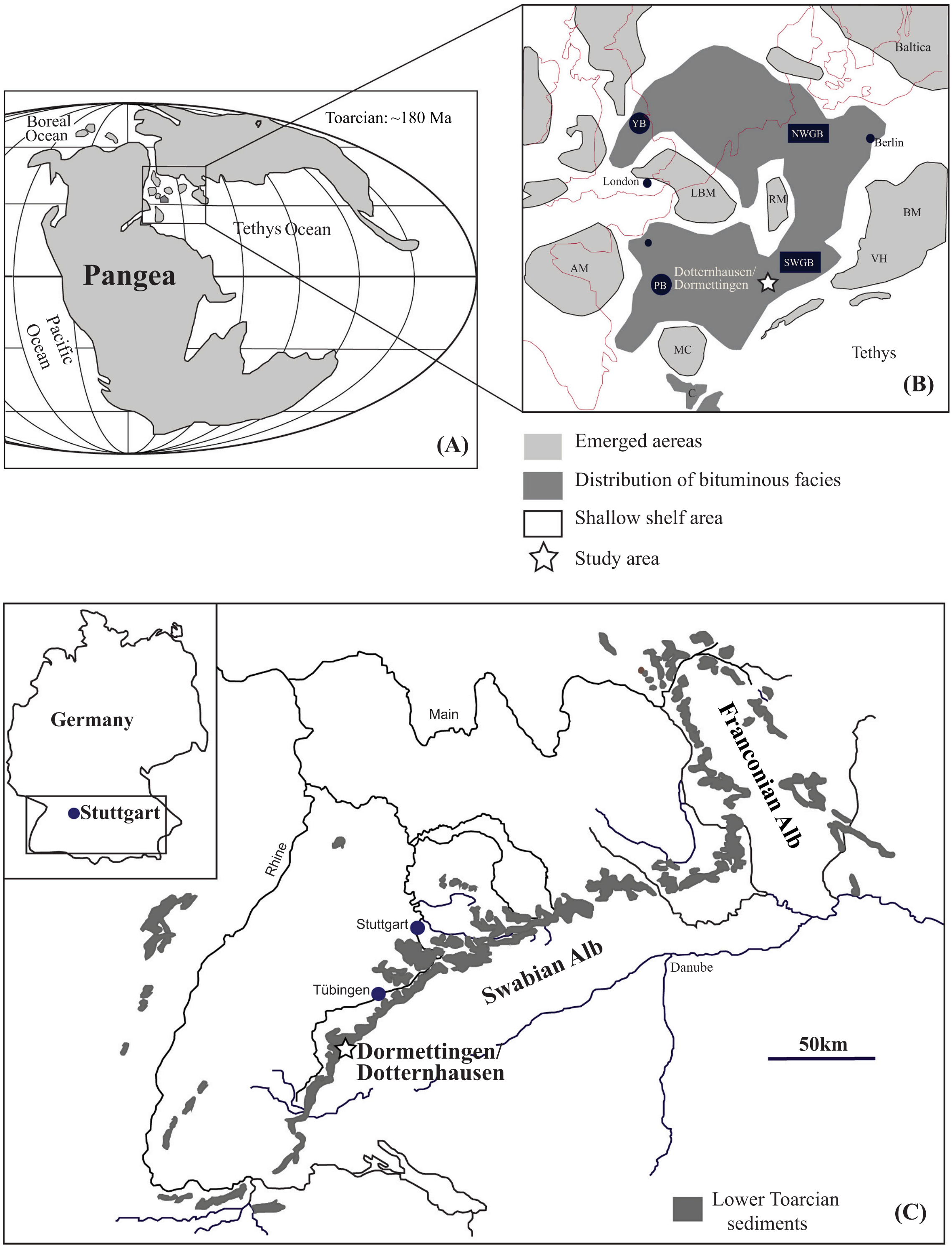

Fig. 1. (A) Palaeogeography, (B) location map of the Early Toarcian and (C) locality map of southern Germany showing the outcrop of Early Toarcian sediments (**in dark grey**) along the Swabian and Franconian Alb. (B) In the Early Jurassic a shallow shelf sea spread over most parts of Central Europe and caused the deposition of dark bituminous shales in the epicontinental basin. Distribution of the Lower Toarcian black shale facies (**in dark grey**). The Central European Basin (CEB) was subdivided into several sub-basins; YB: Yorkshire Basin, NWGB: NW-German Basin, SWGB: SW-German Basin, PB: Paris Basin. Emerged areas (**in light grey**), AM: Armorican Massif, BM: Bohemian Massif, LBM: London-Brabant-Massif, MC: Massif Central, RM: Rhenish Massif, VS: Vindelician Swell (modified after Röhl et al., 2001; Röhl and Schmid-Röhl, 2005; Hesselbo et al., 2007).

organic matter recycling or large-scale introduction of CO_2 into the atmosphere-ocean system (Küspert, 1982; Jenkyns and Clayton, 1997). Since then, geochemical, sedimentological, and palaeontological studies have been conducted to understand the palaeoenvironmental conditions leading to the deposition of the black shales, especially in SW Germany (e.g. Schouten et al., 2000; Röhl et al., 2001; Schmid-Röhl et al., 2002; Mattioli et al., 2004; Röhl and Schmid-Röhl, 2005; van de Schootbrugge et al., 2005; Bour et al., 2007; Correia et al., 2017; van Acken et al., 2019).

The T-OAE was associated not only with oceanic anoxia but also with sea surface temperature increase (Rosales et al., 2004; van de Schootbrugge et al., 2005) and mass extinction in the marine realm (Raup and Sepkoski, 1982; Dera et al., 2010; Guex et al., 2012; Caruthers et al., 2013; Vörös et al., 2019). The biotic turnover has been linked to environmental upheavals associated with the emplacement of the Karoo-Ferrar large igneous provinces (LIPs). Today the remnants of the Karoo-Ferrar LIPs are located in southern Africa, Antarctica, and Tasmania (Remírez and Algeo, 2020a and reference therein).

The Dotternhausen section (formerly Rohrbach Zement quarry, since 2005 Holcim, Süddeutschland, GmbH, SW-Germany) is considered one of the key sections for the T-OAE. Stable isotope studies of organic and inorganic carbon, coupled to Rock-Eval analysis, were carried out by Röhl et al. (2001) and Röhl and Schmid-Röhl (2005). In contrast to the overwhelming quantity of published geochemical and palaeontological data, studies on the characterisation and composition of the particulate organic matter (POM) in the Posidonia Shale Formation are rather scarce (except for Prauss et al., 1991). Since the nature of the organic matter is extremely sensitive to changes in sea level and associated water column stratification, the organic facies analysis provides a complementary method for re-interpreting those fluctuations. The analysis of changes in the POM, coupled with bulk organic carbon isotope data, are used to improve our understanding on the depositional environment and re-investigate the nature of the carbon isotope excursion at the Toarcian OAE sedimentary succession of Dormettingen (SW Germany).

2. Materials and methods

2.1. Geographical and geological setting

The German Basin is located at the SW border of the European epicontinental seaway, which connected the NW Tethys Ocean and the Boreal sea during the Early Jurassic (Ziegler, 1988) (Fig. 1b, c). Several models have been proposed to explain the exceptional preservation of fossils in the Posidonia Shale (Posidonienschiefer in German). It is generally agreed that it results from anoxic conditions caused by stratification of the water column, which in turn was controlled by sea-level changes and the climate variations that promoted the changes in the deep-water redox condition. Restricted water circulation during sea-level lowstand led to long-term anoxic conditions excluding benthic fauna. This has been described as the restricted “silled basin model” introduced by Pompeckj (1901) and further developed by Küspert (1982), Röhl et al. (2001), Schmid-Röhl et al. (2002), Röhl and Schmid-Röhl (2005), van de Schootbrugge et al. (2005).

The Lower Jurassic succession at Dormettingen (48°14′34.8”N, 8°45′54.0″E), located ~2 km NW of the classical Dotternhausen section, offers excellent outcrop conditions. The Dormettingen section is ca. 12 m thick encompassing the uppermost part of the Amaltheenton Formation (latest Pliensbachian) and the Posidonia Shale Formation (Early Toarcian). The section is well dated litho- and biostratigraphically and subdivided in four ammonite zones (Spinatum, Tenuicostatum, Falciferum and Bifrons Zones) and associated subzones (Fig. 2) (Riegraf, 1985; Röhl et al., 2001; Röhl and Schmid-Röhl, 2005).

The Amaltheenton Formation in the basal part of the section is composed of marly limestones of Pliensbachian age (Spinatum Zone) with the Costatenkalk limestone bed at the top. The bioturbated marls contain different benthic faunas suggesting sufficient oxygen availability (Riegraf et al., 1984; Riegraf, 1985; Röhl and Schmid-Röhl, 2005) up to the Paltus Subzone of Tenuicostatum Zone, implying a continuous sedimentation across the Late Pliensbachian–Early Toarcian boundary (Riegraf et al., 1984; Riegraf, 1985; Röhl and Schmid-Röhl, 2005).

Overlying is the Posidonia Shale Formation (Tenuicostatum to

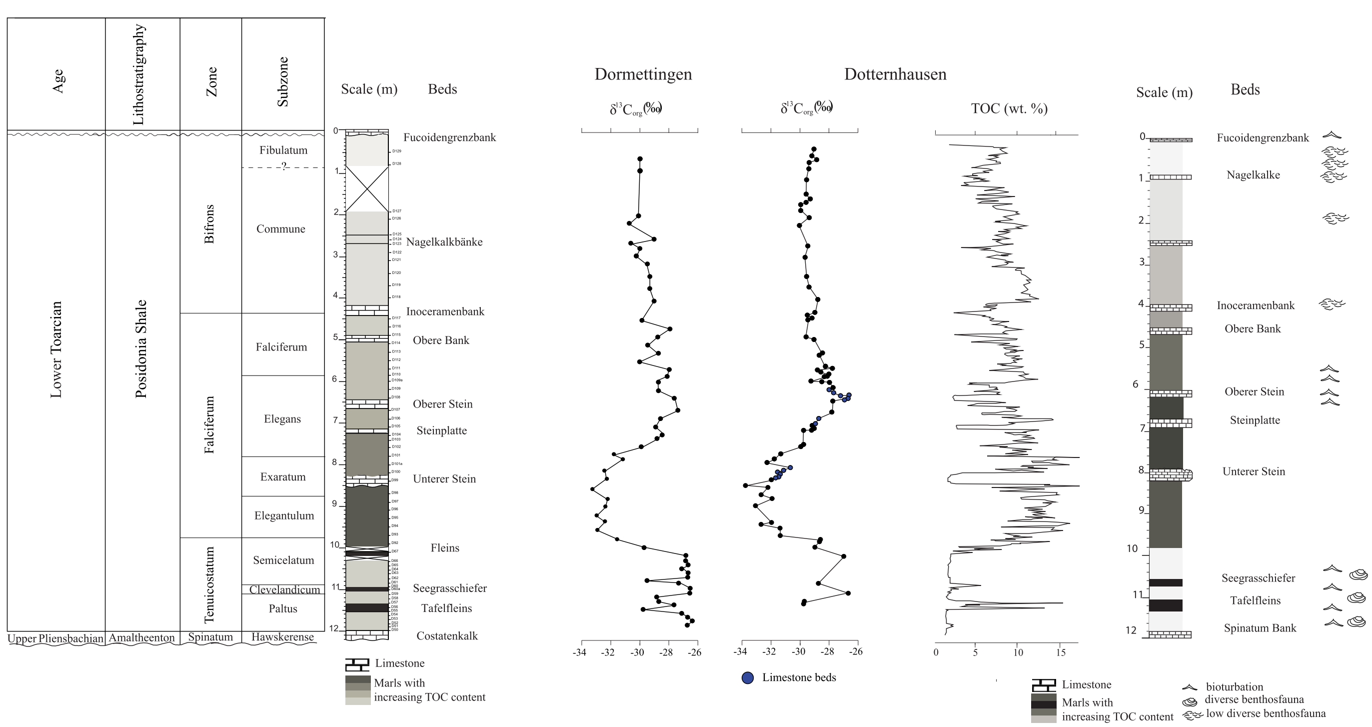

Fig. 2. Stratigraphy of the Dormettingen section with ammonite zones and subzones, modified from Röhl and Schmid-Röhl (2005). Bulk organic carbon isotope curves of the Dormettingen section compared to the Dotternhausen section (Röhl et al., 2001) and TOC curve of Dotternhausen (after Röhl and Schmid-Röhl, 2005).

Bifrons Zones). The basal part of it is characterised by grey marls with two carbon-rich shale layers intercalated, the Tafelfleins and the Seegrasschiefer beds (Tenuicostatum Zone, Paltus, and Clevelandicum Subzones, respectively). The Tafelfleins Bed is a black organic carbon-rich shale layer with indistinct lamination, which is bioturbated in the upper part. The Seegrasschiefer Bed is also a black organic-rich shale showing indistinct lamination and bioturbation structures which were erroneously interpreted as seaweed leading to its traditional German name (seaweed = Seegras). Continuous black shale deposition commenced in the latest Tenuicostatum Zone (Semicelatum Subzone) from the Fleins Bed onward associated with wavy and lenticular laminations. Intercalated in the black shales is a series of characteristic limestone marker beds named in ascending order "Unterer Stein" (20–30 cm thick), "Steinplatte" (~10 cm thick), "Oberer Stein" (~20 cm thick) and "Obere Bank" (~10 cm thick) (Fig. 3). They all belong to the Falciferum Zone. The thickest of these limestone beds, the Unterer Stein Bed (Exaratum Subzone), is used as a stratigraphic marker within the Posidonia Shale Formation and its equivalents in the European epicontinental basin (van de Schootbrugge et al., 2005). Further up section, the Inoceramenbank Bed, another limestone bed of ~10 cm thickness, marks the transition from Falciferum to Bifrons Zone. An indistinct type of lamination characterizes the dark shales of the Bifrons Zone (Commune and Fibulatum Subzones). The boundary between the two subzones is obscured in the Dormettingen section.

2.2. Sampling and laboratory analysis

Fifty-nine outcrop samples, evenly distributed over 12 m succession, were collected, with a sample size of 0.5 to 2 cm thickness to minimize time-averaging effects. Palynological processing of the rock samples has been carried out by Palynological Laboratory Service Ltd. (PLS, Holyhead, Anglesey, LL65 4RJ, UK). The standard procedure was applied to process the samples, using concentrated HCl and HF, followed by a modified multi-step oxidation. The residues were treated with fuming nitric acid, Schulze's solution, detergent and/or ultrasonic vibration. The residues were sieved over a 15 μm mesh screen and mounted for the analysis of POM. For the present study, unoxidised kerogen slides were analysed and a minimum of 300 particles per sample was counted.

The samples were analysed for organic carbon isotope composition ($\delta^{13}C_{org}$) at ETH Zürich. Samples were ground in a ceramic mortar and treated with 6 N HCl for at least one day to dissolve all the carbonates. The residue was homogenised and analysed with a ThermoFisher Flash-EA1112 elemental analyser coupled with a Conflo IV interface to a ThermoFisher Delta V isotope ratio mass spectrometer.

Isotope ratios are reported in the conventional δ-notation in parts per million (‰) with respect to V-PDB (Vienna Pee Dee Belemnite) isotope standard. The system was calibrated with NBS22 ($\delta^{13}C = -30.03‰$) and IAEA CH-6 ($\delta^{13}C = -10.46‰$). Reproducibility of the measurements is better than ±0.15‰.

2.3. Palynofacies analysis

Palynofacies is a term commonly used to describe the total particulate organic matter (POM) assemblage contained in a body of sediment thought to reflect a specific set of environmental conditions or to be associated with a characteristic range of hydrocarbon-generating potential (Tyson, 1995). Palynofacies has been successfully applied to interpret sequence stratigraphic changes (e.g. Tyson, 1995; Pittet and Gorin, 1997; Bombardiere and Gorin, 2000; Oboh-Ikuenobe et al., 2005; Götz et al., 2008). Organic facies analysis provides a complementary method for integrating and eventually improving standard sedimentological observations in both shallow- and deep-water deposits (Bombardiere and Gorin, 2000 and reference therein). The spatial and stratigraphic variations in the distribution and composition (i.e. relative abundance of terrestrial and marine POM fractions) of sedimentary organic matter reflect changes in the depositional system related to relative sea-level fluctuations (e.g. Tyson, 1995; Bombardiere and Gorin, 2000; Götz et al., 2008).

Fig. 3. Photographs of the Dormettingen sedimentary section. Dormettingen Toarcian CIE black shale facies intercalated by five limestone beds (Unterer Stein, Steinplatte, Oberer Stein, Obere Bank and Inoceramenbank).

The classification of particulate organic matter (POM) used in this study is illustrated in Fig. 4. The classification is based on similar schemes provided by previous authors (Steffen and Gorin, 1993; Tyson, 1995; Pittet and Gorin, 1997) and has been modified and adapted to the present purpose.

3. Results

3.1. Particulate organic matter (POM)

For POM analysis, we distinguished two main categories: marine and terrestrial organic particles (OM). The terrestrial organic matter was subdivided in two sub-groups: the phytoclasts and palynomorphs sub-group. Phytoclasts consist of translucent and opaque wood fragments, cuticles, and membranes, while the palynomorphs sub-group contains bisaccate pollen, Circumpolles, other non-saccate pollen grains and spores. The marine organic matter was subdivided into amorphous organic matter (AOM), a marine phytoplankton sub-group and foraminifera. AOM consists of structureless organic aggregates, derived from dissolution and partial biochemical degradation of organic compounds. The marine phytoplankton includes dinoflagellate cysts, acritarchs and prasinophytes. Foraminifera are represented in palynological samples by the inner organic test linings of benthic foraminifera. Examples of the palynofacies components are illustrated in photomicrographs in Figs. 5 and 6.

3.2. Palynofacies intervals

Based on changes in the relative abundance of the different POM constituents described above, five palynofacies intervals are distinguished (Fig. 7).

3.2.1. Palynofacies interval A (samples D50 to D66, from 12.0 m to 10.3 m, uppermost Spinatum Zone and most of Tenuicostatum Zone)

Opaque phytoclasts are present in relatively low quantities in the lower half of the interval (~15%) but become abundant towards the top within Semicelatum Subzone (~48%). Translucent phytoclasts show the opposite trend with high percentages at the base of the interval reaching ~40% and a subsequent decline in Semicelatum Subzone with relative abundances of less than 10%. Spores, bisaccate pollen and Circumpolles are present in almost equal percentages of ~2–3%. Most abundant taxa are *Classopollis* spp. and *Chasmatosporites* spp. Smooth trilete spores are frequent while ornamented spores are rare. Fungal remains are sporadic and occur only in a few samples. Marine organic matter composition is characterised by the dominance of AOM (30–80%). The majority of the samples contain an elevated number of dinoflagellate cysts and show relatively high species diversity, with the highest abundances of ~10% in sample D59 (Clevelandicum Subzone). *Nannoceratopsis* spp. and *Luehndea spinosa* are the most abundant dinoflagellate cysts occurring in high percentages at the base of Tenuicostatum Zone. Foraminiferal test linings were recorded infrequently and in low abundance at the base of the interval. Acritarchs are frequent (ca. 5%), especially the genus *Micrhystridium* (Figs. 5 A-E, 7).

3.2.2. Palynofacies interval B (samples D67 to D102, from 10.3 m to 7.6 m, uppermost Tenuicostatum Zone and lower part of Falciferum Zone)

Translucent and opaque phytoclasts are reduced to ~20% and ~10%, respectively. Smooth spores exhibit comparable abundances as in palynofacies interval A (~1–2%). Bisaccate pollen grains are entirely absent in this interval. AOM is the most dominant component (~75% on average) in these assemblages. Dinoflagellate cysts and acritarchs are extremely rare or absent. Prasinophytes (e.g. *Tasmanites* spp.) are recorded in almost all the samples. Sample D99 (Exaratum Subzone) sticks out by its slightly different organic matter composition compared to the rest of the assemblages with high percentages of opaque phytoclasts (28%) and few translucent phytoclasts (3%) (Figs. 6 H-I, 7).

3.2.3. Palynofacies interval C (samples D103 to D117, from 7.6 m to 4.5 m, upper half of Falciferum Zone)

Translucent phytoclasts are well-represented (≤20%) and opaque phytoclasts occur in low abundances (≤10%). Spores are present in relatively low abundances as previously mentioned for intervals A and B with ~1–2%, while bisaccate pollen grains are absent. With relatively constant percentages of ~79%, AOM is the most prominent fraction of

Particulate organic matter (P.O.M.)					
Origin		Group		Constituent	Interpretation
terrestrial organic matter	Higher plant debris	Phytoclasts		opaque phytoclasts	Is interpreted as charcoal (signal for wildfires). Is the result of terrestrial post-depositional alteration, reflecting seasonal fluctuations in the water column
terrestrial organic matter	Higher plant debris	Phytoclasts		translucent phytoclasts	Mostly related to proximal depositional conditions. The limiting factors is the availability of wood, other plant material, and transport conditions
terrestrial organic matter	Terrestrial fungi			fungal remains	Oxigenated environment transported by rivers
terrestrial organic matter	Pollen	sporomorphs	palyno-morphs	bisaccate pollen	High relative abundance in oxigenated environments with relatively low 'AOM' preservation potential AND Moderate proximity to fluvio-deltaic source(s), but without dilution by phytoclasts
terrestrial organic matter	Spores	sporomorphs	palyno-morphs	non saccate pollen and spores	
marine organic matter	Degraded plant debris	Amorphous organic matter (A.O.M.)		non-fluorescent AOM	Reducing (i.e. at least temporarily dysoxic to anoxic) environments with high preservation potential of autochthonous planktonic organic matter AND Distal depositional environments
marine organic matter	Marine phytoplankton		palyno-morphs	dinoflagellate cysts and acritarchs	High relative abundance in oxigenated environments with low 'AOM' preservation potential but high productivity AND/OR Distal shelf areas removed from river inputs, with adjacent land areas poorly vegetated (e.g. arid)
marine organic matter	Marine phytoplankton		palyno-morphs	prasinophytes	
marine organic matter	Foraminifera			foraminiferal test linings	Oxigenated conditions at the sediment surface

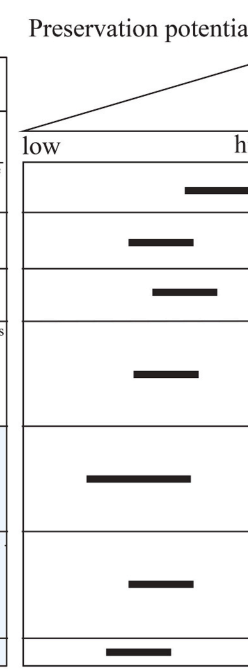

Fig. 4. Origin and classifications of particulate organic matter (POM) for observations in transmitted light microscopy as used in this study. The approximate preservation potential of each palynofacies constituent is illustrated on the right-hand side (modified from Steffen and Gorin, 1993; Tyson, 1995; Pittet and Gorin, 1997).

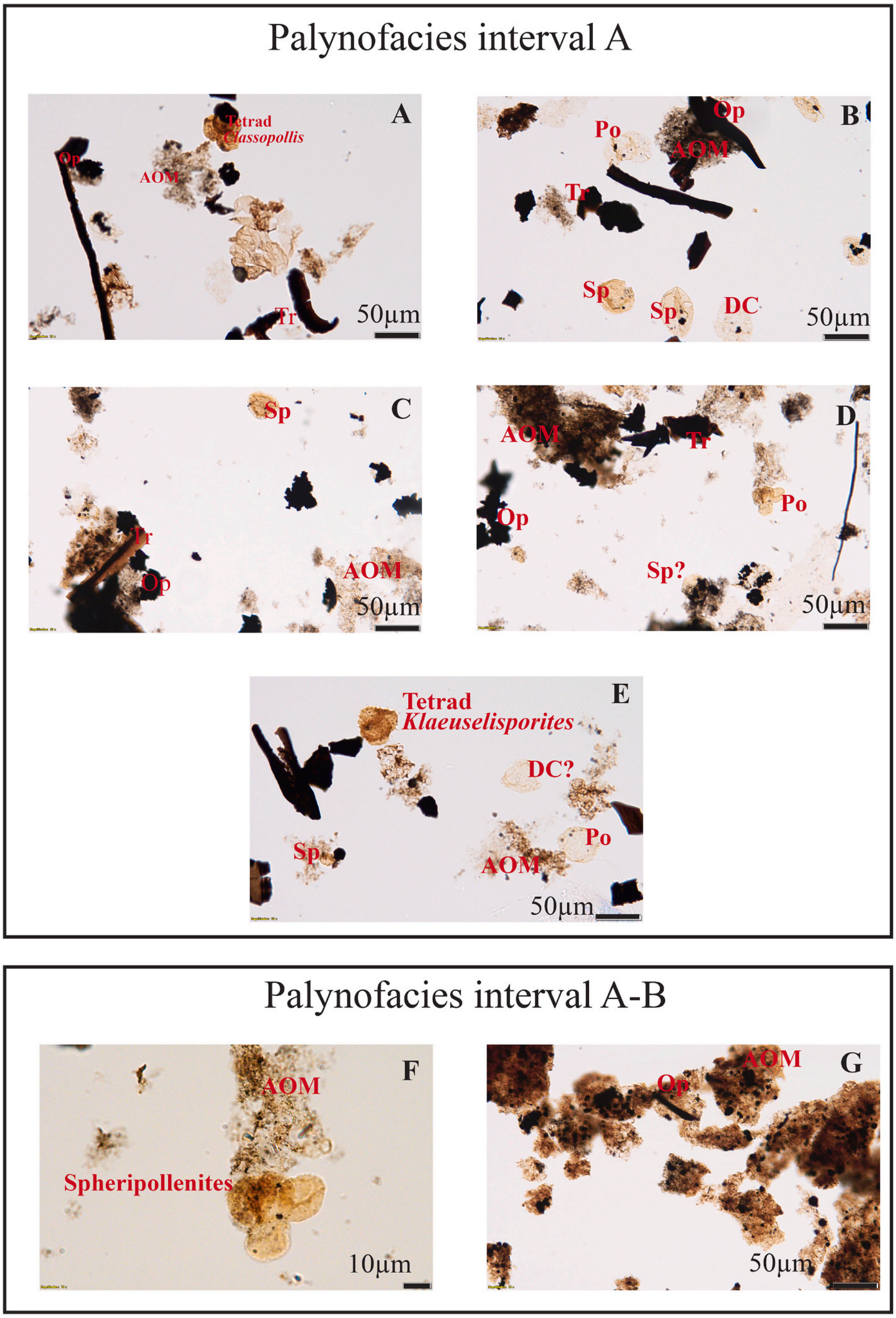

Fig. 5. Photomicrographs of the organic matter components from the Dotternhausen section (SW Germany). (Op): opaque phytoclasts, (Tr): translucent phytoclasts, (Sp): spores, (Po): pollen, (AOM): Amorphous organic matter, (DC): dinoflagellate cysts. A, B, C, D, E - Palynofacies interval A (Spinatum to Tenuicostatum Zones) (samples D50, D53, D56, D62, and D65, respectively); F, G – Transition from palynofacies interval A to B, (topmost of Tenuicostatum Zone) (sample D67) with *Spheripollenites*.

this interval. Most striking in this phase is the re-appearance of dinoflagellate cysts, although low in abundances (≤1%) and in low diversity. Acritarchs, on the other hand, are extremely rare or absent. Prasinophytes (e.g. *Tasmanites* spp.) are present with percentages of ~2–3% (Figs. 6 J-K, 7).

3.2.4. ***Palynofacies interval D*** *(samples D118 to D127, from 4.5 to 1.9 m, lower Bifrons Zone)*

At the base of this interval terrestrial woody plant remains (opaque and translucent phytoclasts) account for ~15% increasing to about 30% in the upper part of the interval. Despite the low percentages in pteridophyte spores, the re-introduction of gymnosperm pollen grains, although in low quantity (<1%) and diversity, is recorded. Abundance of AOM is relatively high (~70%) and slightly decreases towards the top. Dinoflagellate cysts are present in low numbers (<1%), their diversity increases towards the top. Noteworthy is the first occurrence of phallocystean dinoflagellate cysts, which will be subject of a separate paper. Acritarchs are absent and prasinophytes (e.g. *Tasmanites* spp.) show the same abundance as in palynofacies interval C (Figs. 6 L-M, 7).

3.2.5. ***Palynofacies interval E*** *(samples D128 and D129, 0.8 and 0.5 m, upper Bifrons Zone)*

The terrestrial phytoclasts, both opaque and translucent, are less abundant with percentages of ~10% on average, each. Sporomorphs are extremely rare or absent, obscured by high amounts of AOM. A high relative abundance of AOM (80%) is recorded. The base of this interval is characterised by a change in composition of the palynomorph assemblage. Dinoflagellate cysts, prasinophytes and acritarchs account for similar percentages as in palynofacies interval D (Figs. 6 N-O, 7).

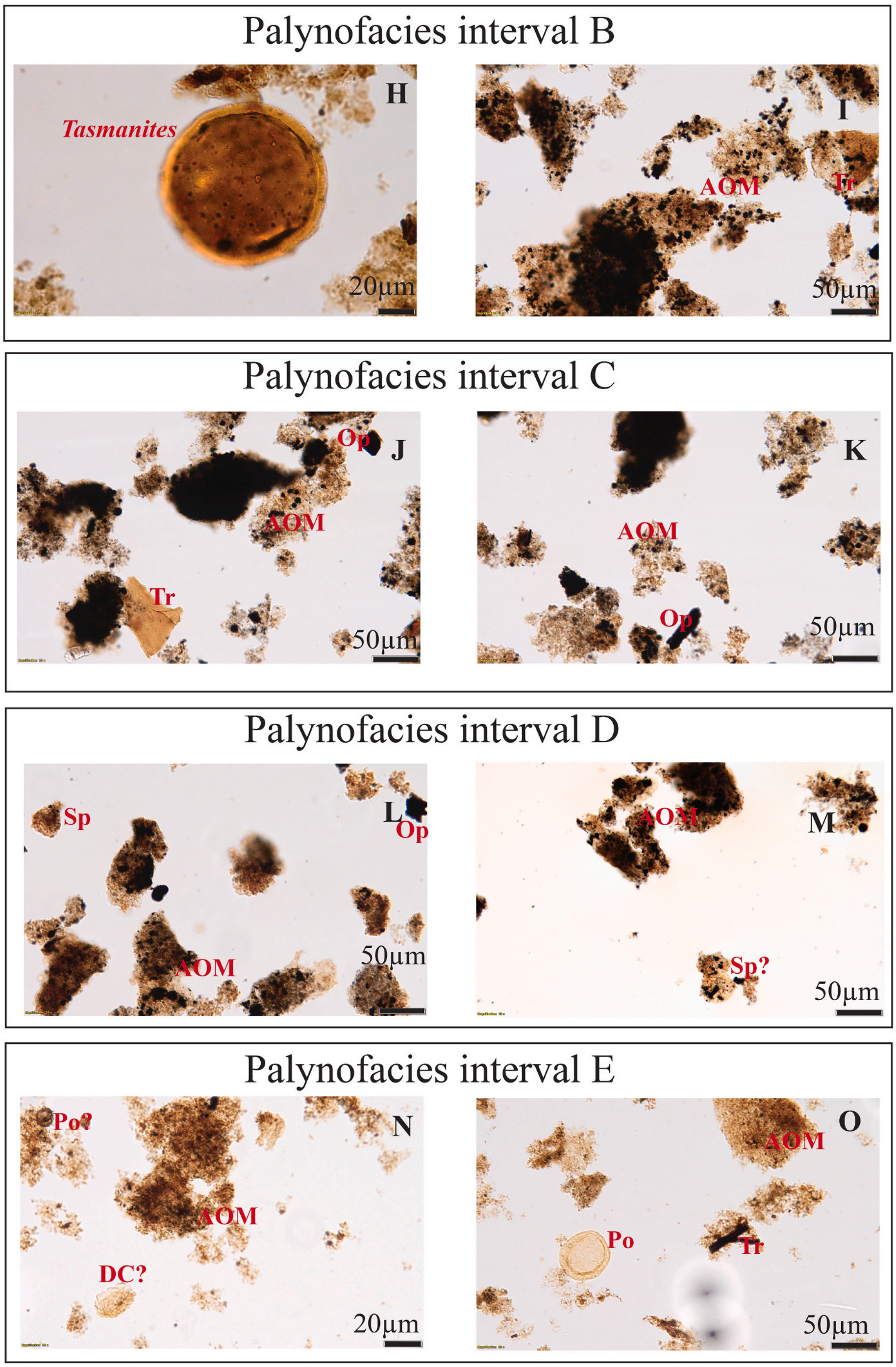

Fig. 6. Photomicrographs of the organic matter components from the Dotternhausen section (SW Germany). (Op): opaque phytoclasts, (Tr): translucent phytoclasts, (Sp): spores, (Po): pollen, (AOM): Amorphous organic matter, (DC): dinoflagellate cysts. H, I – Palynofacies interval B (lower Falciferum Zone) (samples D95 and D98) with *Tasmanites*; J, K – Palynofacies interval C (upper Falciferum Zone) (samples D114 and D116); L, M – Palynofacies interval D (lower Bifrons Zone) (samples D124, and D125); N, O – Palynofacies interval E (upper Bifrons Zone) (samples D128 and D129).

3.3. Bulk organic carbon isotope composition

The bulk organic carbon isotope values range from −33.49‰ to −26.36‰ (V-PDB), showing the characteristic negative excursion at the T-OAE (Figs. 2, 7).

Three bituminous shale layers are recognised at the base of Tenuicostatum Zone (palynofacies interval A), in ascending order, the Tafelfleins Bed, Seegrasschiefer Bed and Fleins Bed.

These three bituminous beds are associated with minor negative carbon isotope shifts (Fig. 2).

The first peak (sample D54) commences in the Paltus Subzone with $\delta^{13}C$ values of −29.68‰ just below the Tafelfleins Bed and continuous throughout this bed. Above, average values are −27.63‰, followed by a second negative peak in the Clevelandicum Subzone, right above the Seegrasschiefer Bed with a value of −29.61‰ (sample D60). In the following layers above, average values of −26.79‰ are followed by a third drop in $\delta^{13}C_{org}$ to −29.79‰ at the top of the Fleins Bed in Semicelatum Subzone. This negative trend continues into the Falciferum Zone (palynofacies interval B) and represents the main negative carbon isotope excursion typical for the T-OAE at the base of Falciferum Zone. The interval of the main negative carbon isotope excursion is marked by $\delta^{13}C_{org}$ values of ∼ − 32.01‰. A positive shift in $\delta^{13}C_{org}$ values is observed from the Exaratum into the Elegans Subzone (palynofacies intervals B to C). Samples from the upper part of Falciferum Zone (palynofacies interval C) show $\delta^{13}C_{org}$ values ranging around −30.12‰ (sample D112) to −27.40‰ (sample D107) with an average of

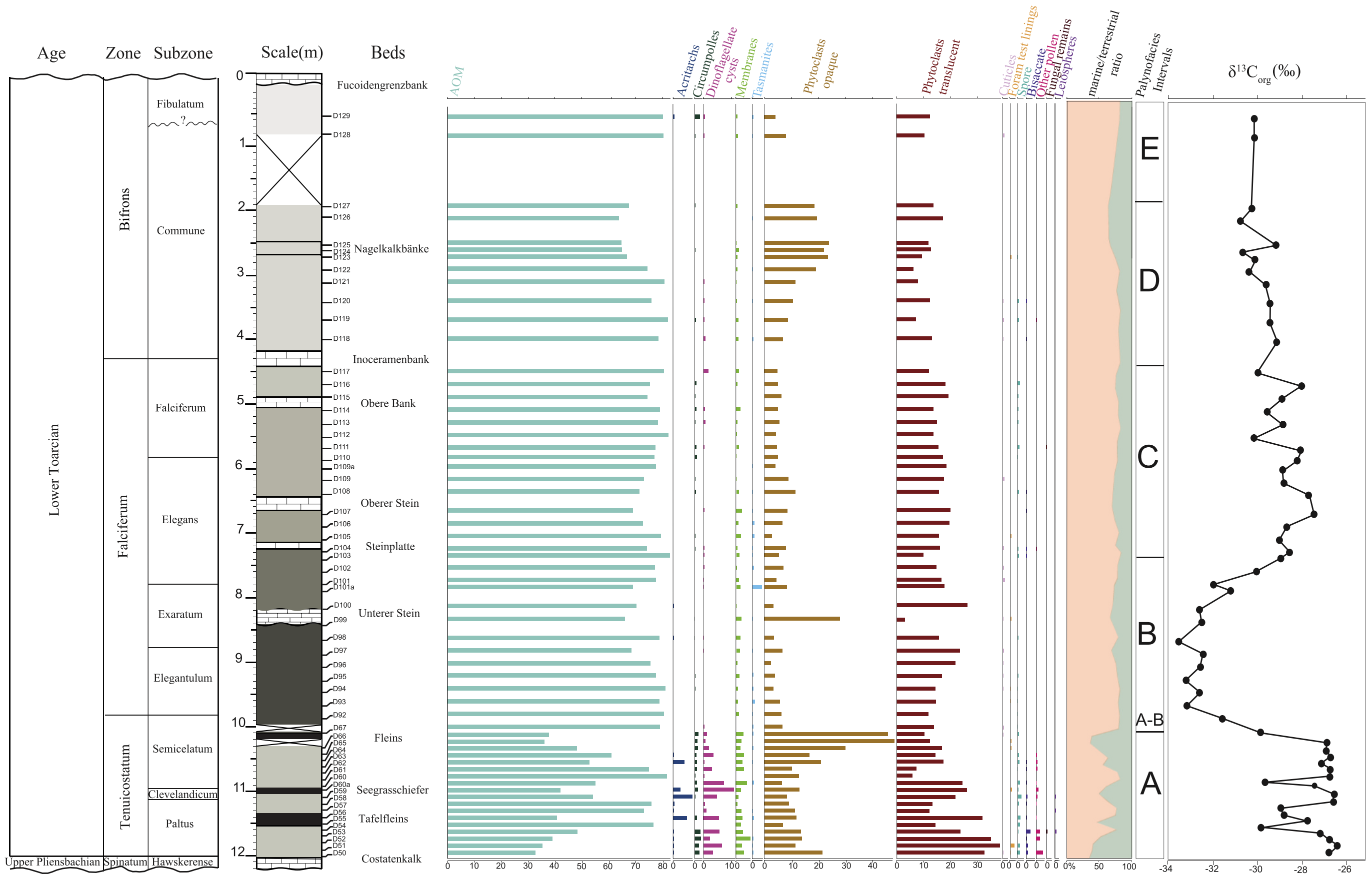

Fig. 7. From left to right: Ammonite zonation, stratigraphy, relative abundance of the POM, marine(orange)/terrestrial(green) ratio, palynofacies intervals (A to E) and carbon isotope curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

−28.41‰. In Bifrons Zone (Commune Subzone) $\delta^{13}C$ values are rather stable ranging from −30.72‰ (sample D126) to −29.09‰ (samples D118-D125). Both samples, D128 and D129, covering the Fibulatum Subzone of Bifrons Zone (palynofacies interval E) show a bulk carbon isotope value of −30.07‰.

4. Discussion

4.1. Source of the organic components

The use of palynofacies, combined with other approaches, can provide useful information on sedimentary processes and on the chemical and ecological parameters of the depositional environment in terms of salinity, oxygenation and redox conditions, productivity and water column stability (e.g. Steffen and Gorin, 1993; Tyson, 1995; Batten and Stead, 2005). A summary of the POM constituents, their origin/source and meaning for palaeoenvironmental interpretations is illustrated in Fig. 4. The study of marine and terrestrial palynomorphs is an excellent tool for interpreting palaeoclimatic variations (Dale, 1996; Riding et al., 1999), therefore some significant taxa are especially mentioned. In addition, changes in the composition of terrestrial particles can be indicative of ecological disturbances on land (Slater et al., 2019).

4.2. Palaeoenvironmental interpretation of palynofacies data

The palynofacies of Dormettingen have been subdivided into five intervals according to the characteristic POM assemblages.

4.2.1. *Palynofacies interval A (uppermost Spinatum Zone and most of Tenuicostatum Zone)*

At Dormettingen during the majority of the Tenuicostatum Zone, the accumulation and preservation of organic matter (OM) was low with a paucity of marine OM and significant contributions of terrestrial OM (Fig. 7). The relatively high percentages of (specific) marine and terrestrial palynomorphs and the elevated influx of siliciclastics components reflect shallow marine conditions. Bioturbation, the well-diversified benthic fauna and a TOC generally below 1 wt% suggest a well oxygenated depositional environment (Röhl et al., 2001; Schmid-Röhl et al., 2002; Frimmel et al., 2004). These organic-lean deposits show low TOC/P ratios and low contents of metals that are indicators of reducing environment (e.g. Mo, S, V, Cu), which is consistent with oxic bottom water conditions (Dickson et al., 2017; Baroni et al., 2018). The relatively high abundance of marine phytoplankton offers information on salinity levels, transgression and even on specific nutrient conditions (Tyson, 1995; Feist-Burkhardt et al., 2008 and references therein). *Nannoceratopsis* spp. and *Luehndea spinosa* are the most abundant dinoflagellate cysts in the basal part of the section. These opportunistic species may have favoured elevated nutrient levels related to high terrigenous input (Bucefalo Palliani et al., 1997; Bucefalo Palliani and Riding, 1999). Furthermore, the presence of *Micrhystridium* spp. (an acanthomorph acritarch) may reflect shallow-water conditions in a high energy environment (Lei et al., 2012; van Soelen and Kürschner, 2018). Triangular smooth spores are generally abundant throughout this interval, especially those deriving from hygrophytic mother plants (e.g. lycopsids, ferns). Presence of these spores are likely to reflect humid and warm environments (e.g. Bek, 2012). According to Vakhrameyev (1982), the abundance of *Classopollis*-producing cheirolepidiacean plants displays a climate-controlled increase towards lower latitudes.

The frequent occurrence of *Classopollis* pollen produced by thermophilic plants and the relatively more positive $\delta^{13}C$ of terrestrial kerogen suggest that the OM was mostly sourced from an area characterised by semi-arid climate with pronounced arid periods.

The oxic conditions in the earliest Toarcian were later interrupted by two anoxic phases, represented by the bituminous shales of the Tafelfleins and Seegrasschiefer beds (Paltus and Clevelandicum Subzones, respectively). The lack of benthic fauna in these two-organic carbon-rich shale layers imply a reduced oceanic circulation and oxygen-depleted conditions in the benthic environment (Röhl et al., 2001; Schmid-Röhl et al., 2002). These bottom conditions have fostered OM preservation as is illustrated by the presence of AOM, as well as the good preservation of terrestrial and marine palynomorphs (Fig. 5A-E). In concert with elevated levels of productivity, as stimulated by the terrestrial nutrient influx, the increased preservation potential of OM caused the formation of these initial bituminous layers. These periods were interrupted by short oxygenation events (weeks to tens of year) favouring benthic colonization within the Seegrasschiefer facies (Röhl and Schmid-Röhl, 2005).

4.2.2. *Transition from palynofacies interval A to B*

Large-scale black shale deposition started at the end of Tenuicostatum Zone as indicated by the sudden and strong increase in total organic carbon (TOC) and the negative $\delta^{13}C_{org}$ values (Fig. 2). The onset of a sharp transgression is accompanied by a change from shallow marine to deeper marine deposits with the marine OM suddenly becoming dominant (Figs. 5 F-G and 7, sample D67 onwards). The accompanying lack of bioturbation and the near absence of benthic biota, except for the local occurrence of the opportunistic pseudoplanktonic bivalve *Pseudomytiloides dubius,* indicates anoxic conditions at the beginning of the continuous black shale deposition (Röhl et al., 2001; Röhl and Schmid-Röhl, 2005; Ruebsam et al., 2018). Thus, from the palynofacies perspective, the black shale deposition occurred under higher sea-level conditions associated with water stratification induced by freshwater influx (Röhl and Schmid-Röhl, 2005). Freshwater-driven salinity stratification has been proposed as a driver for shelf sea anoxia and OM accumulation (Röhl et al., 2001; Röhl and Schmid-Röhl, 2005; McArthur et al., 2008; Remírez and Algeo, 2020b).

4.2.3. ***Palynofacies interval B*** *(uppermost Tenuicostatum Zone and lower part of Falciferum Zone)*

An abrupt increase in AOM coupled with common pyrite (FeS_2) framboids indicates a dysoxic-anoxic environment (Schouten et al., 2000; Röhl and Schmid-Röhl, 2005; Montero-Serrano et al., 2015; Xu et al., 2018). Well-laminated shales rich in organic carbon with intermittent limestone beds (not sampled in this study) are completely devoid of benthic fossils, thus indicative of anoxic bottom water environments lacking any significant wave or storm activity. The anoxia was extreme causing the oxygen-minimum zone reaching into the photic zone. This is illustrated by elevated concentrations of biomarkers for photosynthetic sulphide-oxidising bacteria (Schouten et al., 2000; Frimmel et al., 2004; Schwark and Frimmel, 2004; French et al., 2014). The increasing anoxic conditions resulted in a marine turnover with the complete disappearance of dinoflagellate cysts replaced by a surge of prasinophytes and *Spheripollenites*. Green algae (prasinophytes) have a high tolerance to adverse conditions and can survive in situations with significant fresh-water input, as well as periodic anoxia/dysoxia in the photic zone (Tappan, 1980; Riegel et al., 1986; Prauss et al., 1991; van de Schootbrugge et al., 2013). Their relative abundance was not impacted by nutrient depletion in the photic zone, caused by the sinking of OM and limited nutrient recycling back into the photic zone (Wall et al., 1977; Prauss et al., 1991; Feist-Burkhardt and Wille, 1992; Bucefalo Palliani et al., 2002; Prauss, 2007; van de Schootbrugge et al., 2007; Correia et al., 2017). *Spheripollenites* are small originally spherical bodies of ambiguous biological affinity widely observed throughout Europe in the anoxic facies of Lower Toarcian sediments (Bucefalo Palliani et al., 2002 and reference therein). They are strikingly abundant with highest abundance in layers with the highest contents of AOM and abundant prasinophytes, therefore suggesting rather a green algae affinity than being related to gymnosperms or bacteria. This turnover was further enhanced by reduced salinity ($<$ 2.5 ppt based on $\delta^{18}O$ data from belemnites) and oligotrophic conditions in the photic zone (Prauss et al., 1991; Bailey et al., 2003; Prauss, 2007). In SW Germany, the depletion in $\delta\ ^{18}O$ coupled with detrital proxies (Ti/Al and Zr/Rb ratios), the increase of kaolinite and the highest influx of siliciclastics, as verified in coeval successions elsewhere, suggest warmer and more humid conditions in the hinterland with increased continental weathering (e.g. Suan et al., 2008; Dera et al., 2010; Xu et al., 2018; Korte et al., 2015; van Acken et al., 2019). Os- and Ca-isotope studies have suggested an increase in continental weathering by at least 200% as a consequence of an enhanced global hydrological cycle (Cohen et al., 2004; Percival et al., 2016; Them II et al., 2017). The enhanced hydrological cycle was verified also in the Tethyan and Panthalassic locations (Brazier et al., 2015; Krencker et al., 2015; Izumi et al., 2018) resulting in storminess and tempestites in tropical latitudes (Kemp et al., 2019).

Despite the decrease in opaque phytoclasts (sample D92 and onwards), terrestrial particles are still relatively abundant (average of $\sim$20%). This might be explained by increased delivery of land plant material by rivers (Tyson, 1995 and reference therein) and/or by a decrease in the supply of opaque particles from continental areas due to generally wetter climate conditions and thus less frequent fires (McArthur et al., 2008). The increased transportation of nutrients to the shelf seas would have stimulated marine primary productivity, resulting in high amounts of marine OM. The increase in surface runoff (thus freshwater-driven stratification) in combination with restriction of the basin, would have led to the formation of a stable pycnocline and thus decreasing vertical mixing (Röhl et al., 2001; McArthur et al., 2008; Remírez and Algeo, 2020b). This combined with an increased input of marine OM would lead to more oxygen-depleted deep-water conditions. At Dotternhausen the Mo/TOC ratio yields 1.7% (Dickson et al., 2017) which implies a more severe basin restriction than the modern Black Sea (Algeo and Lyons, 2006; McArthur et al., 2008; Baroni et al., 2018) and indicates that the sediments were deposited under euxinic conditions.

The water-mass circulation was reconstructed in the coeval Cleveland Basin by McArthur et al. (2008) who suggested that Mo-depletion was associated with isolation of deep watermasses with low salinity levels from an enhanced hydrological cycle. This was recently confirmed using Cd/Mo and Co*Mn proxies (McArthur, 2019). Despite still being subject of debate (Hesselbo et al., 2020), recently, Remírez and Algeo (2020b) have interpreted palaeo-salinities using B/Ga, Sr/Ba and S/TOC ratios indicating a major salinity reduction throughout the NW European Basin caused by enhanced freshwater run-off during the T-OAE.

4.2.4. ***Palynofacies interval C*** *(upper half of Falciferum Zone)*

Recovery in marine and terrestrial palynobiota was commencing likely as a result of reconnection of the German Basin to the open ocean. The moderate number of dinoflagellates cysts recovered are low in diversity implying persistent adverse environmental conditions (e.g. low mixing of the water column persisted). Dinoflagellate cysts that had occurred in Tenuicostatum Zone re-appear in palynofacies interval C after the main anoxic period as Lazarus taxa (e.g. *Nannoceratopsis*). Pollen grains and spores on the other hand were still in upturn although in both low abundance and diversity. The slow recovery led to a second but moderate phase of hydrological basin restriction. Through the upper Falciferum Zone phases of short, oxygenated events with a shallower pycnocline were alternating with anoxic periods due to phases of reduced run-off (McArthur et al., 2008). The appearance of bioturbated horizons together with the uncommon and sporadic occurrence of bivalves in the German and coeval basins confirm that the anoxia was not continuous but likely was interrupted by short periods of re-oxygenation (e.g. Röhl et al., 2001; van de Schootbrugge et al., 2005). The less frequent water exchange with the oceans and the better oxygen availability would have favoured marine communities (McArthur et al., 2008). Simultaneously, the general stability in terms of sea level (i.e. absence of major transgressive-regressive cycles) and thus an absence of continued disturbances, would have favoured the recovery of the terrestrial ecosystem through secondary succession.

4.2.5. ***Palynofacies intervals D and E*** *(Bifrons Zone)*

Marine conditions and well-developed exchange with the surrounding oceans were re-established and the anoxic event came to an end (McArthur et al., 2008 and references therein). Abiotic factors (e.g. salinity, temperature, nutrients) were returning to "normal conditions" (Bucefalo Palliani et al., 2002; Ruebsam et al., 2020a). The indistinct, faint lamination and the gradual increase in abundance and diversity of benthic fauna, presumably in a seasonal pattern, indicate enhanced water column and seafloor oxygenation (Röhl et al., 2001; Schmid-Röhl et al., 2002; Frimmel et al., 2004). Sample D112, associated with a slightly elevated level of marine OM, shows a minor negative carbon excursion coinciding with a temporary lack of benthic activity as described by Röhl et al. (2001). The same holds for a period of increased benthic activity and a positive excursion in sample D125. A slight decrease in marine OM especially in the upper part of Bifrons Zone, suggests a possible (minor) regression in the late Early Toarcian.

4.3. *Bulk organic carbon isotopes and OM composition*

Bulk organic carbon isotope values can vary in response to changes in the isotopic composition of the atmosphere and ocean, in biological isotope fractionation processes and in the source of the organic matter (e.g. terrestrial vs marine, leafy vs woody, etc.) (Tyson, 1995; Köhler et al., 2010; Suan et al., 2015). The $\delta^{13}C_{org}$ values in Jurassic marine palynomorphs (i.e. dinoflagellate cysts, acritarchs and prasinophyte algae) varies between −34.5‰ and − 30.7‰ whereas modern marine OM ranges between −22‰ and − 18‰ (Remírez and Algeo, 2020a). Terrestrially derived woody fragments have $\delta^{13}C_{org}$ values of between −28‰ and − 26‰ (Suan et al., 2015; Remírez and Algeo, 2020a). The isotopic composition of the organic matter accumulated in sediments is directly impacted by abundance and isotopic composition of dissolved CO_2 in the ocean (marine organic matter) or atmospheric CO_2 (terrestrial organic matter). Since marine and terrestrial organic matter have different ranges of carbon isotope values, changes in relative abundance of these isotopic end-members may significantly influence the carbon isotope curve (van de Schootbrugge et al., 2013; Suan et al., 2015). Variation in temperature, pCO_2, moisture, and generally climate effects, might have altered the carbon isotope signature of land plant-derived continental OM (Gröcke, 2002; Suan et al., 2015; Ruebsam et al., 2020b).

Hence, changes in POM type could affect $\delta^{13}C_{org}$ values. To highlight this possible effect on the carbon isotope curve, POM is plotted next to $\delta^{13}C_{org}$ (Fig. 7). In order to detect palaeoecological changes in the water column and at the sediment-water interface, TOC values of the Dotternhausen section were extracted from Röhl et al. (2001) and correlated with the section at Dormettingen (Fig. 2).

4.3.1. *Pre-T-OAE*

At Dormettingen, the first and minor negative shift is recorded ca. 1.5 m below the main anoxic event (palynofacies interval A, Fig. 7). It is noteworthy that, while the majority of the Tenuicostatum Zone is characterised by relatively low TOC values, likely being a result of well-oxygenated bottom waters, two minor and rapid negative carbon isotope excursions are observed in the Paltus and Clevelandicum Subzones, respectively. Although presumably present in the Dotternhausen section, the higher resolution sampling in Dormettingen provides a more detailed image of the specific isotopic changes during Tenuicostatum Zone. The minor excursions produce $\delta^{13}C_{org}$ values of around −29.23‰ and correlate with high TOC contents up to 15% and higher percentages in marine OM. This is interpreted as a short period of bottom water anoxia/euxinia and increased marine productivity. The carbon isotope curve is partially influenced by this increase in marine OM that contributes to a more pronounced negative shift (Figs. 2, 7).

4.3.2. *Main phase of T-OAE*

In the Dormettingen and Dotternhausen sections, as well as in other sections in the Northwest European Province, the main carbon isotope excursion (CIE) of several per mill in magnitude starts in the latest Tenuicostatum Zone (Röhl et al., 2001; Remírez and Algeo, 2020a and reference therein). The organic-rich facies that formed under generally reducing conditions have shown a prominent negative CIE with an amplitude of < -8‰ on the bulk organic matter (Hermoso et al., 2012) and wood (Hesselbo et al., 2007; Hesselbo and Pieńkowski, 2011). However, compound-specific biomarkers studies suggest an absolute global magnitude of the CIE as only ~3–4‰ (French et al., 2014; Suan et al., 2015).

The rapid increase in TOC co-occurs with the negative $\delta^{13}C_{org}$ excursion, high content of marine OM and a major floral turnover. Dinoflagellate cysts are replaced by prasinophyte algae and *Spheripollenites* indicating long term photic zone suboxia/anoxia.

Although the onset of the negative shift coincides with a change in POM (palynofacies interval B) no further significant changes in the POM can be observed (Fig. 7). Therefore, the large negative carbon excursion reflects a major perturbation in the global carbon cycle rather than solely changes in the type of the OM source.

The eruptive phase of the Karoo and Ferrar flood basalt volcanism which is approximately synchronous to the T-OAE (Pálfy and Smith, 2000) released a huge amount of CO_2 and leading to a subsequent rise in global temperatures (Retallack, 2001, 2009; McElwain et al., 2005; Ruebsam and Al-Husseini, 2020). In this period, greenhouse conditions with high atmospheric pCO_2 levels prevailed, as derived from a stomatal index study (McElwain et al., 2005) and compound-specific carbon isotope data of land plant (Hermoso et al., 2012; Ruebsam et al., 2020b). The subsequent increase in temperature caused a significant stress on the vegetation (e.g. McElwain et al., 2005; Slater et al., 2019; Ruebsam et al., 2020b). The elevated pCO_2 levels affected both, terrestrial and marine carbon pools, and influenced the rapid carbon isotope excursion at the end of Tenuicostatum Zone. Recently, $\delta^{13}C_{n\text{-alkane}}$ records from the Cleveland and Sichuan Basins have shown values more depleted in ^{13}C by about 4 to 5‰ compared to lower latitudinal sites (Ruebsam et al., 2020b). This offset has been associated with latitudinal climate gradients linked to different floral assemblages and precipitation rates impacting on the $\delta^{13}C$ of land plants (Ruebsam et al., 2020b and references therein). During the Early Jurassic, the German Basin was in the same, winter-wet temperate climate belt as Cleveland and Sichuan Basins suggesting a similar effect on $\delta^{13}C$ of terrestrial vegetation. The enhanced humidity, resulting from the elevated global temperatures, caused by the global carbon release to the atmosphere, coeval with isotopically light $\delta^{13}C$ values in the atmosphere and the increased CO_2 could have led to an intensification of the hydrological cycle (e.g. Percival et al., 2016; Them II et al., 2017; Izumi et al., 2018). This would have strengthened stratification and marine eutrophication (Bucefalo Palliani et al., 2002). Global warming additionally would have had a negative impact on the oceanic carbonate production (Bucefalo Palliani et al., 2002; Mattioli et al., 2009) in shallow basins and on carbonate platforms during the CIE (Suan et al., 2008). In addition to the elevated sea surface temperature, the extreme ocean acidification coupled with elevated pCO_2 could have caused a biocalcification crisis in marine organism (Bucefalo Palliani et al., 2002; Mattioli et al., 2004).

4.3.3. *Recovery phase*

The main positive carbon isotope shift occurs in the Exaratum Subzone to early Elegans Subzone and, from a palynofacies perspective, it is not accompanied by any changes in OM composition (Fig. 7). This positive excursion has been recorded in most European sections, whether in bulk rock or belemnite carbonates, in marine organic matter, and in wood (van de Schootbrugge et al., 2005; Hesselbo et al., 2007; Hermoso et al., 2012). The recovery of carbon isotopes to more positive values is interpreted as the response of the carbon cycle to increased and rapid burial of large amounts of ^{13}C-depleted organic carbon that led to an enrichment in ^{13}C of the atmosphere-ocean system (Jenkyns and Clayton, 1997; Schouten et al., 2000). Although palynofacies intervals D and E (Bifrons Zone) show relatively unvarying isotopic values, the isotope curve in palynofacies interval C (base Elegans to top half Falciferum Subzone) is marked by more positive $\delta^{13}C_{org}$ spikes comparable to those in Tenuicostatum Zone, followed by a minor negative excursion in $\delta^{13}C_{org}$ (samples D112 and D117) (Fig. 7). These more positive (single data points) spikes are not linked to any significant POM changes. Despite the higher sampling resolution at Dotternhausen (Röhl and Schmid-Röhl, 2005) in the upper part of the section compared to Dormettingen no further significant excursions were recorded.

4.4. Sea-level trends in the region Dotternhausen-Dormettingen

In Dotternhausen sedimentological, geochemical, and fossil content indicate a third order transgression from the Clevelandicum Subzone up to the Falciferum Subzone culminating in maximum flooding around the boundary of Falciferum to Bifrons Zone in the Inoceramenbank Bed (Röhl and Schmid-Röhl, 2005). This bed represents a condensed interval rich in calcareous shell and fish debris and the highest C27/C29 sterane ratios (Frimmel et al., 2004; Röhl and Schmid-Röhl, 2005). Röhl and Schmid-Röhl (2005) correlated this interval with the third-order maximum flooding zone proposed by Haq et al. (1988).

The POM dataset from Dormettingen does not clearly reflect this transgression from the Clevelandicum to the Falciferum Subzone as proposed by Röhl and Schmid-Röhl (2005). The sharp contrast between palynofacies interval A and B (samples D67-D92) where a predominance of terrestrial OM is replaced by a sudden increase in marine OM indicates a rather abrupt transgression (Fig. 8). The strong transgressive signal as indicates by our POM analysis finds a good correlation with sea-level interpretation in some other European Basins. For example, in the Lorraine Sub-Basin (Fr-210-78 Core) the Pliensbachian-Toarcian boundary black shale was accompanied by a rapid but short-lived transgressive phase (Pl8-Toa1 transgression) with elevated concentrations of Mn and Mg as an indicator of high sea level (Ruebsam et al., 2014; Ruebsam et al., 2019). Prauss (1996) described the Early Toarcian sea-level changes at Grimmen, NE Germany, based on the ratio between marine and terrestrial palynomorphs (t/m index). He described a strong increase in organic carbon contents and the occurrence of pyrite followed by a sudden change in the t/m index. As a result, he suggested a strong transgressive event in the Tenuicostatum Zone in contrast to the sea-level curve proposed by Haq et al. (1988) who suggested a continuous transgression into the Falciferum Zone (Fig. 8). The data from Dormettingen show the same characteristics as observed in NE Germany, if we exclude the phytoclasts, and only consider the palynomorphs (e.g. acritarchs, dinoflagellate cyst, pollen grains and spores). Thus, the palynofacies and TOC data from Dormettingen show a strong transgressive signal at the beginning of the Toarcian sea-level rise (Fig. 8). This does not indicate different sea-level histories in these close-by localities but is due to the nature of the organic matter records, which is very sensitive to changes in sea level and associated water column stratification. Thus, we see a strong signal at the beginning of the sea-level rise. In Dotternhausen, the transgressive phase starts in the middle Clevelandicum Subzone and lasts to the latest Falciferum Subzone while in Dormettingen the transgression is documented by increasing AOM contents from the Semicelatum Subzone up to Elegantulum Subzone (Fig. 8). The transgression in Dormettingen from a palynofacies perspective seems to be abrupt; however, further sea-level changes as documented in Dotternhausen are concealed by continued high relative abundance of AOM. After the significant sea-level rise in the upper Semicelatum Subzone based on POM analysis in Dormettingen, evidence for sea-level fall is only found in the Commune Subzone where higher contribution of terrestrial organic matter in POM assemblage is documented (Fig. 8).

5. Conclusions

In this study, particulate organic matter (POM) and bulk organic

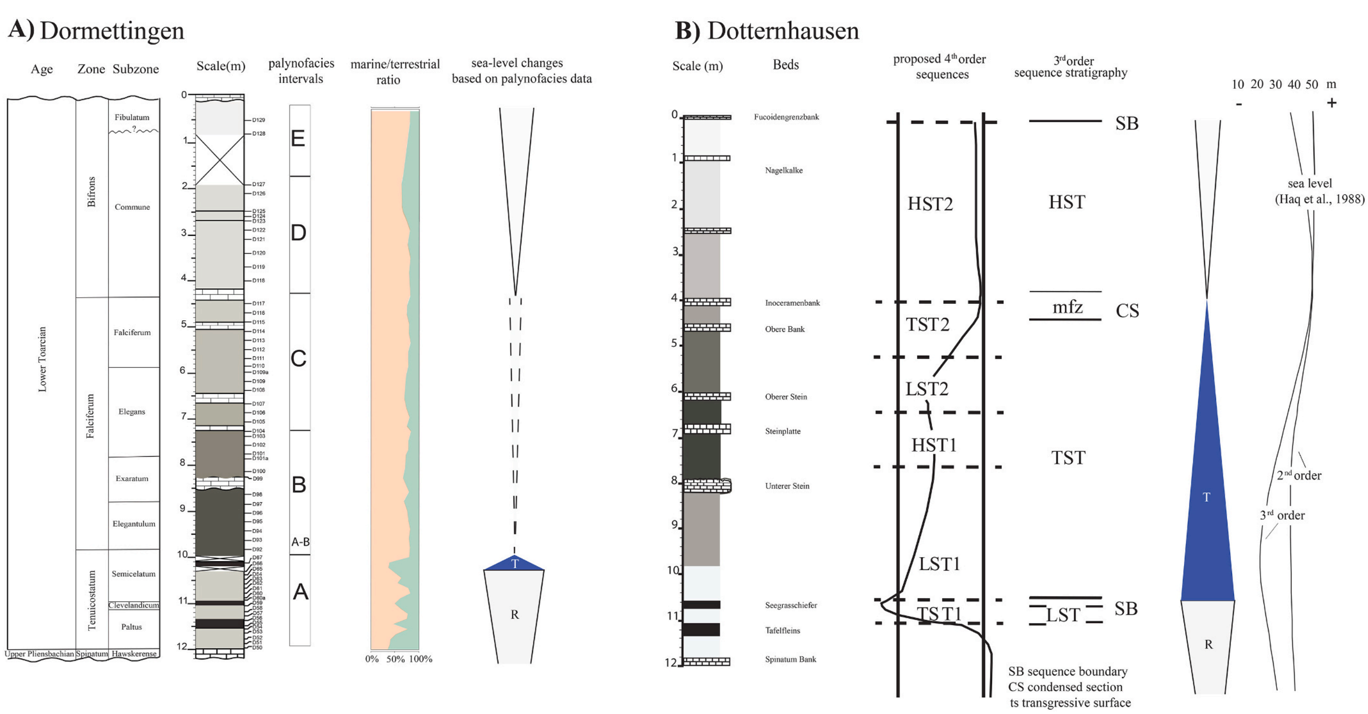

Fig. 8. Comparison of the sea-level trends in the region Dormettingen-Dotternhausen sections. A) In Dormettingen section the sea-level changes are based on palynofacies data. The dashed line indicates that in the palynofacies no major changes are observed in the AOM. B) Interpretation and sea-level curve of Dotternhausen section (modified after Röhl and Schmid-Röhl, 2005).

carbon isotope data are used to re-interpret the depositional environment of the Posidonia Shale Formation at Dormettingen, SW Germany (Late Pliensbachian to Early Toarcian).

- At the base of the Posidonia Shale Formation, two negative carbon isotope excursions were recorded in correspondence of two bituminous shales of the Tafelfleins and Seegrasschiefer beds (Paltus and Clevelandicum Subzones, respectively). The oxic conditions in the earliest Toarcian were interrupted by these anoxic phases, which are not only marked by changes in the lithology, changes in the microfacies and elevated TOC but also by strong variations in POM composition and bulk organic carbon isotope values.
- POM analysis shows an abrupt transgression that occurs in the latest Tenuicostatum Zone where the terrestrial OM is replaced by marine AOM. This was accompanied by a major marine turnover during which dinoflagellate cysts and acritarchs were replaced by prasinophytes and by a major negative shift in bulk organic carbon isotope values.
- The bulk organic carbon isotope and POM data provide a clear evidence that the pronounced ~8‰ negative CIE recorded in the SW German Basin during the onset of the T-OAE, reflects a major perturbation in the global carbon cycle, likely being induced by a massive injection of ^{13}C-depleted carbon into the atmosphere-ocean carbon reservoir, rather than changes in the OM source.
- The restricted silled-basin model previously proposed for SW Germany and other coeval basins from the European epicontinental seaway is supported by the POM data obtained in Dormettingen section.

In this study, the combined approaches of bulk organic carbon isotopes and POM analysis was fundamental to describe environmental changes in the Toarcian in SW Germany; however, with those approaches alone it is not possible to identify minor sea-level changes in this restricted basin.

Data availability

Rock samples, palynological slides and residues used in this study are stored at the Palaeontological Institute and Museum (PIM), University of Zurich (Switzerland). Reference numbers A/VI 155, A/VI 156, A/VI 157 and A/VI 158.

Declaration of Competing Interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.palaeo.2021.110327.

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