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Non-marine carbon-isotope stratigraphy of the Triassic-Jurassic transition in the Polish Basin and its relationships to organic carbon preservation, pCO₂ and palaeotemperature

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Abstract

New carbon-isotope data obtained from homogenous organic material (separated microfossil wood; $\delta^{13}\text{C}_{\text{wood}}$) from the upper Rhaetian and entire Lower Jurassic permit chemostratigraphic correlation of these marginal/non-marine deposits with the biostratigraphically well-constrained Llanbedr (Mochras Farm) core in N Wales and other marine profiles, supported by sequence stratigraphic correlation and biostratigraphical markers. Statistically significant ($R_s = 0.61$) positive exponential correlation between $\delta^{13}\text{C}_{\text{wood}}$ values and continental TOC (TOC_{cont}) concentrations occurs and can be defined empirically by equation. Changes of $\delta^{13}\text{C}_{\text{wood}}$ observed in C3 plants depends on $\delta^{13}\text{CO}_2$ of atmosphere and can be modulated by other factors such as pCO₂ causing fractionation (enrichment in ¹²C) of C isotopes in source C3 plants and, to lesser extent, by soil moisture content. Floral remains occurring in the relatively stable palaeolatitude and climatic zone of the Polish Basin in the time interval studied lend no support for significant precipitation impact on the $\delta^{13}\text{C}$ fractionation, although enhanced precipitation could have had a limited impact during the Toarcian Oceanic Anoxic Event (T-OAE). We argue that the observed relation between $\delta^{13}\text{C}_{\text{wood}}$ values and TOC_{cont} reflects the global carbon cycle forcing. Such correlations may develop because fluxes of ¹²C-enriched methane, mobilized from near-surface carbon sources, lead to global warming, decreased $\delta^{13}\text{C}_{\text{wood}}$ and enhanced (usually fungally-mediated) decomposition of the terrestrial carbon pool, while subsequent massive burial of organic carbon results in higher $\delta^{13}\text{C}$ values in all carbon cycle reservoirs, and the attendant drawdown of atmospheric CO₂ leads to global cooling and promotes sequestration of soil organic matter. In turn, this relation can be used as an indirect indicator of atmospheric temperature trends, although organic carbon isotope records are potentially subject to many different influences. Based on the $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ relationship, an approximate qualitative estimation of general trends in air temperature is suggested for c. 40°N paleolatitude and the warm temperate climatic zone. The observed hypothetical trends in temperature are generally in

concordance with $p\text{CO}_2$ trends calculated from stomatal index. A weak $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} correlation in Rhaetian deposits is explained by local environmental factors (TOC concentration dependent on a more localized fluvial plain settings), while mostly deltaic – coastal deposits contain more representative, averaged material delivered from a large catchment area.

Key words: Chemostratigraphy, correlation, paralic facies, palaeoclimate, carbon isotopes

1. Introduction

Correlation of biostratigraphically-constrained marine sections with marginal-marine or continental deposits with poor biostratigraphical control is regarded as one of most complex and challenging, yet very important, problems in stratigraphy. As shown, for example by Hesselbo and Pieńkowski (2011), carbon-isotope ($\delta^{13}\text{C}$) chemostratigraphy provides a means of age correlation for strata deposited in diverse marine and non-marine depositional environments. However, such correlations are reliable only when appropriate profiles are accessible. In particular, long, cored borehole sections offer the opportunity to reconstruct Earth system evolution in the geological past and contain, for example, the records of tectonic, carbon cycle, climatic and biological cycles. Expanded core sections, providing a continuous record of the Lower Jurassic series – such as the Llanbedr (Mochras Farm) core recovered in Wales, UK (Woodland, 1971; Katz et al, 2005; Hesselbo et al, 2013; Ruhl et al, 2016; Xu et al, 2018; Storm et al, 2020), hereafter referred to as Mochras, and Kaszewy borehole drilled in central Poland (Figs. 1, 2), are exceptionally valuable. The isotope ratios of atmospheric CO_2 ($\delta^{13}\text{CO}_2$) to a certain degree reflect perturbations in atmospheric C fluxes (e.g. Pagani et al 2006 for the PETM case), and therefore estimates of $\delta^{13}\text{CO}_2$ are central to estimating past climate sensitivity to changes in atmospheric CO_2 pressure ($p\text{CO}_2$). While inputs of isotopically light carbon to the atmosphere-ocean system result in decreasing $\delta^{13}\text{CO}_2$ and increasing $p\text{CO}_2$ recorded as a negative carbon isotope excursion in both inorganic and organic carbon enhanced burial of organic carbon and enhanced silicate weathering leads to a fall in atmospheric $p\text{CO}_2$, and a positive excursion (Gröcke et al 1999; Kump and Arthur 1999). The $p\text{CO}_2$ and related temperature is a basic climate variable, yet its estimates in deep geological past are difficult and often controversial as the carbon cycle involves multiple sources and sinks in a dynamic rather than a static mass-balance equilibrium (Kump and Arthur 1999). The near surface carbon cycling, such as release of methane clathrates, permafrost destruction, decomposition of soil organic matter (acting as a source of ^{13}C -depleted carbon) and burial of organic matter and carbonate or silicate weathering (acting as a sink – Cohen et al 2004; Them et al 2017b; Kump 2018; Ullmann et al 2020) played a major role in modulating atmospheric carbon concentrations. Nevertheless, values of $\delta^{13}\text{C}_{\text{TOC}}$ which come from

sedimentary rocks (specifically, the values obtained from fossil plants) are widely used to estimate $\delta^{13}\text{C}$ of ancient plants and infer changes in $\delta^{13}\text{C}\text{CO}_2$. Additionally, $\delta^{13}\text{C}$ depends on pCO_2 - the higher pCO_2 , the stronger fractionation of $\delta^{13}\text{C}$ by plants towards light values. Thus the currently debated effect of CO_2 concentration on $^{13}\text{C}/^{12}\text{C}$ ratios ($\delta^{13}\text{C}$) is crucial to reconstructing ancient environments and quantifying the carbon cycle (Hare et al 2018; Ruebsam et al 2020).

Currently most of the temperature estimates for this time interval have been based principally on oxygen isotopes ($\delta^{18}\text{O}$) from calcareous macrofossils, such as oysters, brachiopods and belemnites, or calcareous nannofossils (Suan et al 2008, 2010; Korte and Hesselbo 2011; Dera et al 2011; Silva and Duarte 2015; Gómez et al 2016; Price et al, 2016; Peti and Thibault, 2017 – for recent comprehensive summary see Ruebsam et al 2020) from European marine sections. However, temperature interpretation based on $\delta^{18}\text{O}$ can be distorted by changes in the local source(s) of water and local/regional evaporation-precipitation dynamics as well as diagenesis, and therefore choosing the sites and samples unaffected by these processes is essential. Furthermore, the thermal perturbations are likely to have been controlled also by the silicate weathering flux, in the case of the Lower Jurassic extending these times of warmth by limitation of the global silicate weathering flux (e.g. Ullmann et al 2020). It should be noted that Os-isotope proxies from eastern and western Panthalassa show a modest decline in weathering intensity after the peak of the negative carbon-isotope excursion of the T-OAE (Them et al 2017b, Kemp et al 2020). Nevertheless, a broadly synchronous coupling between massive carbon release and enhanced global continental crust weathering during T-OAE is not controversial. Estimating palaeotemperatures based on $\delta^{18}\text{O}$ is also prone to problems such as the vital effects of the organism precipitating the carbonate (Price 2017). Herein, we discuss $\delta^{13}\text{C}_{\text{wood}}$ values and their relation to TOC_{cont} in context of the global carbon cycle and resulting interpretation of climate changes - including temperature trends – with particular reference to the Kaszewy core.

2. Geological setting

The Polish Basin is a large, now tectonically inverted, sedimentary basin covering most of modern-day Poland, and representing the eastern arm of the NE European epicontinental basin (Dadlez et al 1998; Dadlez, 2003) – Fig. 1. The upper Rhaetian strata and the whole Lower Jurassic series belong to the Kamienna Group composed of siliciclastic deposits (mudstones, sandstones) with subordinate conglomerate, coaly and siderite beds. Throughout the Mesozoic, regional subsidence patterns in the Polish Basin were dominated by the development of the NW–SE-trending Mid-Polish Trough, which was filled with up to 8000 m of Permian–Mesozoic sediments, of which c. 1200-1300 m belongs to the Kamienna Group (Pieńkowski, 2004). Intermittently, this long-term thermal subsidence was influenced by local modifications imposed mainly by lateral salt movements in its central and NW segments, creating salt pillows. The Kaszewy borehole is situated at a slope of one of these broad

and flat pillows, called Wojszyce structure (Dadlez 1998). In the latest Triassic – Early Jurassic times the Polish basin was located at a latitude about 40°N, within a warm temperate/winter-wet climate belt (e.g. Rees et al 2000; Dera et al, 2009). Sedimentology, lithofacies, ichnofacies, biofacies as well as sequence stratigraphy and palaeogeography of the NE European basin have been studied for decades and published in number of papers (Dadlez and Kopik 1972; Pieńkowski 2004, 2014, 2015; Pieńkowski, Schudack et al., 2008; Pieńkowski & Waksmundzka, 2009; Hesselbo & Pieńkowski, 2011; Pieńkowski et al, 2012, 2014, 2016; Barth et al., 2018 a, b).

The latest Rhaetian and Early Jurassic were times of extreme environmental change. Through this period there are well-documented examples of enhanced volcanic activity, rapid transitions from cold, or even glacial climates, through to super-greenhouse events, multiple large-magnitude isotopic anomalies, global sea-level changes, and mass extinctions. These events not only reflect changes in the global climate system but are also thought to have had significant influence on the evolution of Jurassic marine and terrestrial biota. However, our knowledge to date is fragmentary, largely because of the fragmentary and discontinuous nature of the existing datasets – particularly, with respect to atmospheric/terrestrial realm. Studies hitherto have largely focused on two events, connected to the development of Large Igneous Provinces (LIPs): Central Atlantic Magmatic Province (CAMP) at the Rhaetian-Hettangian transition, and early Toarcian Karoo-Ferrar Large Igneous Province, connected with the Toarcian Oceanic Anoxic Event (T-OAE – Jenkyns, 1988). While marine strata have been studied more extensively in terms of oceanographic, climatic and biological processes (Korte and Hesselbo 2011, Dera et al 2011; Lindström et al 2012, 2017; Harazim et al 2013; Suan et al 2015; Ruhl et al 2016; Them et al 2018; Van de Schootbrugge et al 2019; Storm et al 2020), reports from continental or marginal-marine materials remain relatively sparse (e.g. Pieńkowski 2004, 2014; McElwain et al 2005; Hesselbo and Pieńkowski 2011; Pieńkowski et al 2012, 2014, 2016; Them et al 2017 a,b; Baker et al 2017; Xu et al 2017; Ruebsam et al 2019; Liu et al 2020). Records in epicontinental seaways may potentially show a pronounced regional overprint on carbon isotope composition of sedimentary organic matter (McArthur et al 2008; Ruhl et al 2010), usually resulting from mixing of different organic components (Suan et al 2015), but results obtained from homogenous woody material ($\delta^{13}\text{C}_{\text{wood}}$) are more reliable in interpreting global changes more directly, as they reflect atmospheric (i.e. global) processes (Gröcke 2002) and can therefore be used more confidently for chemostratigraphic correlations (see for Lower Jurassic examples: Hesselbo and Pieńkowski 2011; Pieńkowski et al 2016; Them et al 2017 b; Ruebsam et al 2020; Storm et al., 2020).

3. Materials and Methods

3.1. Lithology and stratigraphy

A new and unique geological archive (2050.6 m through the Norian - Rhaetian- Lower Jurassic strata) comes from the Kaszewy 1 borehole (Fig. 1), drilled in central Poland (52° 12' 00.06" N; 19° 29' 35.38" E) by PGE (*Polish Energy Group*) in order to characterize the potential for carbon capture and storage (CCS) in that area. The entire core has been thoroughly logged and sampled. Samples for geochemical analyses have been taken from similar lithologies (mudstones) in order to avoid lithological bias. The length and continuity of the Kaszewy core (98 % core recovery) is essential in studying continental or marginal-marine deposits by sedimentological methods and allowing application of isotope chemostratigraphy of these facies, supported by sequence stratigraphy and some biostratigraphical markers (Fig. 2). For comparison to Kaszewy we use the new compilation from the biostratigraphically constrained Mochras core (Storm et al, 2020) which covers the entire Early Jurassic, reproducing large-amplitude $\delta^{13}\text{C}_{\text{TOC}}$ excursions ($>3\text{‰}$) at the Sinemurian–Pliensbachian transition and in the lower Toarcian *serpentinum* zone, as well as several previously identified medium-amplitude ($\sim 0.5\text{--}3\text{‰}$) shifts in the Hettangian to Pliensbachian. In addition, $\delta^{13}\text{C}_{\text{wood}}$ (Storm et al, 2020) and $\delta^{13}\text{C}_{\text{carb}}$ (Katz et al 2005) data was also obtained (Fig. 2).

3.2. Carbon isotopes

Phytoclast samples for analysis were manually picked from HF palynomacerals and subsequently dried, weighed and sealed in tin capsules. Phytoclast samples were run at two laboratories, depending on their mass (Supplementary data 1). At the Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, UK, larger samples were run on a Sercon Europa EA-GSL sample converter connected to a Sercon 20-22 stable isotope gas-ratio mass spectrometer running in continuous flow mode with a helium carrier gas with a flow rate of 70 ml per min. Carbon isotope ratios were measured against an internal alanine standard ($\delta^{13}\text{C}_{\text{alanine}} = -26.9 \pm 0.2\text{‰}$ V-PDB) using a single point calibration. The in-house RLAHA alanine standard is checked weekly against USGS40, USGS41 and IAEA-CH6 international reference materials. At the British Geological Survey, Nottingham, UK, smaller samples were analysed by combustion in a Costech Elemental Analyser (EA) on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with $\delta^{13}\text{C}_{\text{org}}$ values reported relative to V-PDB following a within-run laboratory standard calibration, with NBS-18, NBS-19 and NBS-22. Replicate analysis of well-mixed samples show a reproducibility of $\pm <0.1\text{‰}$ (1 SD).

3.3. Total Organic Carbon, Rock Eval 6 pyrolysis

Total Organic Carbon (TOC) analyses of 300 samples were performed using the chromatographic, coulometric method (procedure PB – 23) using an automated LECO analyser (Supplementary data 1). A total of 52 naturally carbonate-free mudstone samples (mostly those representing mixed environments – in order to evaluate which ones contain more marine kerogen) were analyzed in the

Rock Eval pyrolysis apparatus - model 6 Turbo (Vinci Technologies), in the laboratory of the Polish Geological Institute (Supplementary data 2). Crushed bulk rock material was thermally decomposed in a helium or nitrogen atmosphere. Every sample was heated to 650°C. The amount of free hydrocarbon (S1) thermally liberated from a rock sample at 300°C is measured using a Flame Ionization Detector (FID). Volatile components released during pyrolysis are separated into two streams. One of them passes through the FID and is registered as peak S2. Another volatile component released during pyrolysis, i.e., carbon dioxide generated from kerogen, is recorded by a thermal conductivity detector as the S3 peak. Repeat analyses of the parameters S1, S2, S3 and TOC agree within ± 0.05 . The Oxygen Index (OI, in mg CO₂/g TOC) is calculated according to the formula $(S3 \cdot 100) / \text{TOC}$. Hydrogen index (HI) = $S2 \text{ (mg/g)} / \text{TOC} \times 100$. Only mudstone was sampled, therefore some parts of profile are sampled more sparsely due to the high sandstone content and sample spacing is heterogeneous. Coals and coaly mudstones were avoided as non-representative. Parts containing marine kerogen were sampled more sparsely. Only samples paired with $\delta^{13}\text{C}_{\text{wood}}$ data and of clearly continental origin (dominating kerogen type III and IV, about 80% of all samples) were used for $\delta^{13}\text{C}_{\text{wood}}$, TOC_{cont} and temperature interpretation (Fig. 2, Supplementary data 1, 2).

3.4. Stomatal index (SI)

Fifty-one specimens containing fossil plant remains from the Kaszewy core interval 1936.5-1296 m were studied. Only few levels contained well preserved remains with preserved cuticle, belonging mostly to genera *Baiera* Braun *emend* Hieron and *Czekanowskia* Herr, on which the SI counting has been performed. Their determination was possible on a genus level only, but that is not a limitation for stomatal index study. *Baiera* and *Czekanowskia* are ginkgophytes, which means that all studied remains have the same nearest living equivalent species (NLEs), making ginkgophytes especially suitable for SI calculation (Eberling et al 1998; Xie et al 2006). The cuticles were prepared with standard methods in Schulz solution followed by 3% KOH. Only the surface of lower cuticle area within stomatal bands, was used for SI evaluation. The number of epidermal cells includes subsidiary cells. The investigated cuticle area was $300 \times 300 \mu\text{m} = 0.09 \text{ mm}^2$ (the minimum area for SI calculation is 0.03 mm^2 - Jones and Rowe 1999). This area was adapted to the width of average stomatal band). SI was calculated according to Salisbury's equation: $\text{SI} = [\text{SD}/(\text{ED}+\text{SD})] \times 100$, where SI – stomatal index, SD – stomatal density (number of stomata/area), ED – number of epidermal cells/area (Jones and Rowe 1999). SI was counted according to Kürschner (1996), using 40 microphotographs for *Baiera* and 13 microphotographs for *Czekanowskia* (totally for 21 leaf fragments). For those specimens, 8-19 measurements were carried out, depending on the state of preservation. The atmospheric CO₂ level was estimated as $600 \text{ ppm} \times \text{SR}$ where SR is the Stomatal Ratio, i.e. SI of the nearest living equivalent divided by SI of fossil plant: $\text{SR} = \text{SI of NLEs} / \text{SI fossil}$.

Standardization was applied after Berner and Kathavala (2001) and SI for the extant *Ginkgo biloba* was used according to Beerling and Royer (2002a), as 9.1 at 350 ppm. Based on this relationship, palaeoatmospheric CO₂ pressure (pCO₂) was estimated, using stomatal parameters of fossil plants – stomatal density (SD) and stomatal index (SI) in relation with parameters of their NLEs, defined as the stomatal ratio (SR) (Beerling and Royer 2002a; Beerling and Royer 2002b; Royer et al 2001). Plant reaction appears in leaf structure, especially in stomatal density, which is closely associated with fluctuations of atmospheric pCO₂ and displays an inverse correlation to pCO₂ (Woodward 1987; Beerling 1999; Pole and Kürschner 1999; Mosbrugger 1999; Royer et al 2001; Haworth and Raschi 2014). SI may be influenced by many factors that affect plants during their life, but, as has been discussed by many authors (Chen et al 2001; Erdei et al 2012), the estimated pCO₂ values are not invalidated (except very young, undeveloped leaves which are not appropriate to SI calculation).

4. Results

4.1. Stratigraphy

The sediments studied yielded very few animal body fossils. Of note is a single find of ammonite *Tragophylloceras cf. loscombi* (Sowerby) in a 1.5 m thick grey shale at a depth of 1281.5 m (Pieńkowski 2015). The stratigraphical range of this species is rather wide, ranging from upper lower Pliensbachian to lower upper Pliensbachian (from the upper part of the *ibex* Zone/ *centaurus* Subzone to the upper part of the *subnodosus* Subzone of the *margaritatus* Zone (Howarth and Donovan 1964). Other methods, such as sequence stratigraphy (Pieńkowski 2004; Barth et al 2018) and carbon isotope chemostratigraphy point to the uppermost part of this ammonite's range, i.e. *subnodosus* Subzone. Next, some palynomorphs provide constraints on the Triassic – Jurassic boundary. Of note are common appearances of *Ricciisporites tuberculatus* Lundblad, a pollen assigned to an enigmatic gymnosperm and known for its common occurrences in the Rhaetian (Lindström et al 2017), with a last occurrence of 1890.2 m. Slightly above (1879 m) there is also the last occurrence of *Brachysaccus neomundanus* (Leschik) Madler, which was previously described from Rhaetian deposits in NW Poland (Pieńkowski et al 2012, 2014). Above a barren sandstone interval, new taxa appear: *Dictyophyllidites mortoni* (de Jersey) Playford & Dettmann at 1830.7 m - a spore common in the Hettangian assemblage in NW Poland (Pieńkowski et al 2012) and, more importantly, pollen grain *Cerebropollenites thiergartii* Schulz (1822.8 m), the only post-Triassic miospore with the first occurrence (FO) close to the base of the Jurassic (Hillebrandt et al 2013). These finds allow placement of the Triassic/Jurassic boundary between 1830.7 and 1879 m, likely at the secondary $\delta^{13}\text{C}_{\text{wood}}$ negative peak, correlatable with the similar peak in the St Audries Bay profile, southern UK (Korte et al. 2009).

For chemostratigraphic correlation of the Lower Jurassic succession, the best prospect lies in carbon isotope values obtained from similar material ($\delta^{13}\text{C}_{\text{organic}}$, $\delta^{13}\text{C}_{\text{wood}}$) because, with the exception of purely pelagic carbonate palaeoenvironments, the carbon-isotope signature of any carbonate present is vulnerable to diagenesis, which is also borne out in the $\delta^{13}\text{C}_{\text{carb}}$ curve from Mochras presented by Katz et al (2005). However, comparison between the $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{wood}}$ and $\delta^{13}\text{C}_{\text{carb}}$ curves can still be useful in indicating the most reliable primary CIEs; therefore selected $\delta^{13}\text{C}_{\text{carb}}$ curves can also be used, particularly if $\delta^{13}\text{C}_{\text{org}}$ curves are not available (Fig. 3). Chemostratigraphical correlation of Mochras and Kaszewy is uniquely valuable, as these two profiles are the most expanded, continuous cored sections of the Lower Jurassic series. Occurrences of some palynomorph taxa and the single ammonite in the Kaszewy borehole allowed positioning of the Triassic-Jurassic boundary and confirmed Pliensbachian or Toarcian age of the respective intervals. Overall, biostratigraphical constraints are of poor resolution. In addition, sequence stratigraphic correlation of depositional sequences and parasequences within the Polish basin and the Central European basin (Pieńkowski 2004; Barth et al 2018) provided an effective complementary stratigraphic framework for the Kaszewy profile. For the Rhaetian, the section at St Audré's Bay (Hesselbo et al 2002; Ruhl et al 2010) is used for chemostratigraphic correlation with Kaszewy (Figs. 2, 3).

To interpret our Kaszewy $\delta^{13}\text{C}_{\text{wood}}$ curve, we compared it with Mochras and nine other published carbon isotope curves for the same time interval (Figs. 2, 3, 4). A continuous $\delta^{13}\text{C}_{\text{wood}}$ curve (Fig. 2) is constructed based on data obtained from homogenous terrestrial organic matter (phytostem separates), thus reflecting isotope changes in atmospheric carbon cycle (Hesselbo and Pieńkowski 2011; Pieńkowski et al 2016; Them et al 2017 a), although other factors such as kinetic isotope fractionations should be also considered as additional factors. The general pattern of the curve shows more negative values (mostly below -27‰ , with minimum of -28.3‰) in the strata assigned (based also on palynomorphs) to the Rhaetian (1905 – 1979 m) with three more prominent negative CIEs. Upwards from the Triassic/Jurassic boundary the $\delta^{13}\text{C}_{\text{wood}}$ values show a general, long-term trend towards heavier values, punctuated by five conspicuous negative CIEs (Figs. 1, 2). This trend is reversed at 1445.9 m and then again continuing upwards towards heavier values, with the heaviest value (-22.9‰) recorded in the upper Pliensbachian at 1266 m. A series of five prominent, step-wise CIEs (down to -30.6‰ at 1237.5 m, starting at 1247.3 m and ending at 1188.7 m) is assigned to the Toarcian Oceanic Anoxic Event/ T-OAE, called also Jenkyns Event) and can be clearly correlated with reference profiles of Mochras, Yorkshire, Peniche, and the composite reference profile by Ruebsam and Al-Husseini (2020) – Fig. 4. The major negative excursion of the T-OAE is unambiguous and has already been recognised in (with further biostratigraphic constraint) in many locations across the same basin (Hesselbo et al. 2000, Hesselbo and Pienkowski 2011). From 1188.7

m upwards the $\delta^{13}\text{C}_{\text{wood}}$ values stabilize at a level with a median c. -24‰ . The section above the T-OAE is a special case because it has already been demonstrated that the lower Toarcian is commonly truncated in the Polish Basin beneath younger Toarcian strata (Pieńkowski 2004, Hesselbo and Pieńkowski 2011).

All conspicuous negative CIEs can be correlated with the $\delta^{13}\text{C}$ curves from the Mochras borehole (Katz et al 2005; Storm et al 2020) and from the St Audrie's Bay section for the Rhaetian (Korte et al, 2009; Ruhl et al 2010); Fig. 2). $\delta^{13}\text{C}_{\text{wood}}$ values from Kaszewy are averagely and systematically heavier by about 1‰ than the corresponding values from $\delta^{13}\text{C}_{\text{TOC}}$ values from Mochras, likely due to contributions from marine organic matter to the Mochras curve (Storm et al., 2020), but what is important for chemostratigraphic correlation is concordance in general trends. This average $\delta^{13}\text{C}$ contrast disappears considering the results of $\delta^{13}\text{C}_{\text{wood}}$ from Mochras. The correlation presented shows also a general concordance with other biostratigraphically constrained $\delta^{13}\text{C}$ curves from marine sections in Europe and North America, e.g. almost complete Lower Jurassic section from Schandelah in Germany (Van de Schootbrugge et al 2019), Rhaetian-Hettangian in Danish Basin (Lindström et al 2012) and North America (Whiteside et al 2010; Bartolini et al 2012), Sinemurian-Pliensbachian in Yorkshire, UK (Korte and Hesselbo 2011), Hettangian to Pliensbachian in Dorset, UK (Schöllhorn et al 2020), Sinemurian-Pliensbachian in Spain (Gomez et al 2015), Sinemurian in the UK (Riding et al 2013; Hesselbo et al. 2020a), the Pliensbachian in the western US (De Lena et al. 2019), Pliensbachian and Toarcian in Portugal (Fantasia et al 2019) and France (Hermoso and Pellenard 2014) – Fig. 3, Supplementary data 3. In Mochras (Storm et al 2020) and Dorset (Schöllhorn et al 2020), there is a uncertainty with the placement of the upper Sinemurian CIE, labelled S2 in Figs 2, 3. In other reports, the conspicuous negative CIE occurs in the *oxynotum* zone, while in Mochras and Dorset the negative CIE occurs within the *obtusum* zone. The answer could be missing section (particularly in Dorset) or imprecise biostratigraphy. In the meantime, the stratigraphical position of this CIE in Mochras and Kaszewy remains open – it can be either of *obtusum* or *oxynotum* age. It should be noted, that some parts of the profile at Kaszewy represent reduced or condensed sections, particularly at the sequence boundaries (e.g. the Pliensbachian section). There are some reductions in thickness of Pliensbachian section observed between Kaszewy (located at the side of salt pillow) and Krośniewice borehole (located between salt structures 20 km to the NW – Dadlez 1973). Likely, these reductions can be attributed to salt movements and resulting hiatuses occurring at the sequence and parasequence boundaries. This could explain somewhat contrasting shapes of the Mochras ($\delta^{13}\text{C}_{\text{TOC}}$) and Kaszewy ($\delta^{13}\text{C}_{\text{wood}}$) carbon isotope curves in the uppermost Sinemurian-lower Pliensbachian interval. However, comparison of the $\delta^{13}\text{C}_{\text{wood}}$ curves is more compatible. Here we also provide an alternative correlation diagram for this interval, which

illustrates the more and the less likely scenario (Fig. 2). Nevertheless, correlation of this section is supported by sequence stratigraphy. The beginning of the Pliensbachian was connected with the major transgression in Polish basin, documented by ammonites in Pomerania and correlatable with NE European basins (Kopik and Dadlez 1972; Pieńkowski 2004; Barth et al. 2018). This widespread transgression is documented in Kaszewy by the appearance of marine kerogen and marine plankton (Pieńkowski 2015; Barth et al 2018). Concerning $\delta^{13}\text{C}$ correlations, sections of Yorkshire (Korte and Hesselbo 2011; Hesselbo et al. 2020a) and Dorset (Schöllhorn et al 2020) confirm the characteristic pattern of CIE excursions, with the lowermost Pliensbachian negative CIE preceded by a sharp positive CIE excursion in the uppermost Sinemurian. Such a pattern occurs also in Kaszewy between 1442 and 1450 m (Figs. 2, 3).

4.2. Total organic carbon (TOC), kerogen analyses

In the Rhaetian strata, TOC is usually below 1%, except for some darker mudstones interpreted to have been deposited in local ponds and lakes, where TOC content can reach 4% and more. The lowermost part of the Rhaetian strata is represented by red beds yielding very few or no palynomacerals (Supplementary data 1) and these strata are excluded from further considerations concerning TOC and $\delta^{13}\text{C}_{\text{wood}}$ as non-representative. In the Hettangian section TOC is in places abundant (Fig. 2), but most of these intervals contain marine kerogen (Supplementary data 2) occurring mostly in strata coeval with major transgressions of the *planorbis* and *liasicus* zones (Pieńkowski 2004; Barth et al 2018). In the upper Sinemurian – lower Pliensbachian section the studied samples usually contain more than 1% (1.14% in average). Moreover, a few beds have TOC up to 3-5 %, and the sample from the lowest part of Pliensbachian (depth of 1462.3 m) contains organic carbon as high as 15.2%. These samples contain marine kerogen associated with the *jamesoni-ibex* transgression and maximum flooding surface (Pieńkowski 2004; Barth et al 2018). In the upper Pliensbachian - Toarcian section TOC is usually in the range of 0 to 3% (1.0% on average). In contrast, most of the lower Toarcian is characterized by a low content of TOC (usually below 0.5%). In order to check the character of the kerogen, 52 mudstone samples from selected sections (based on sedimentological studies) were screened using RockEval 6 pyrolysis and interpreted using the Van Krevelen plot (Supplementary data 2). Kerogen was classified in classical types II, III and IV (type I has not been found), ranged in the order of H/C ratio obtained from the RockEval6 analyses. Type II originated in a shallow marine environment with phytoplanktonic input as the primary source. Type III and IV are found in deltaic/fluvial and coastal settings and derive from higher plant debris, commonly highly reworked and often degraded by fungi (Fig. 6). Type IV is considered as heavily altered Type III with very low H/C or Hydrogen Index and containing only the most resistant chemical

constituents of the terrestrial OM (inertinite). Type II is usually mixed with kerogen Type III. Samples containing only kerogen type III and IV (in total 224 samples) were taken for $\delta^{13}\text{C}_{\text{wood}}$ to TOC_{cont} interpretation (Figs. 2, 5; Supplementary data 1, 2).

4.3. Carbon isotope – total organic carbon ratio

The cross-plot of the $\delta^{13}\text{C}_{\text{wood}}$ to TOC_{cont} ratio (224 Rhaetian and Lower Jurassic samples: Fig. 5) shows significant positive correlation between the two variables with Pearson correlation coefficient $r = 0.53$ ($R^2=0.28$) for linear fit and $r=0.59$ and $R^2=0.59$ for exponential fit. In both cases the p-value is <0.5 . The result is statistically significant at $p<0.05$. The Spearman's Rank Correlation Coefficient (R_s) has been also applied, as it is more appropriate in the case of exponential correlation: $R_s = 0.61$; $p = 6.44 \cdot 10^{-24}$ (for all 224 samples), the result is significant with the significance threshold 0.001 (Supplementary data 4). Samples are shown with symbols representing their stratigraphical position (Fig. 5). $R_s = 0.61$ for all samples containing continental kerogen is satisfactory for demonstrating a statistically significant trend/correlation, classified (depending on literature) as a moderate or strong (Evans 1996), while the Rhaetian section (66 samples) is characterized by a weak linear positive correlation of $r = 0.16$, with a noticeable number of outliers. The correlation coefficients are highest when applying exponential law fits, and slightly degrade when using linear fits (with exception of the Rhaetian, where linear fit is slightly higher).

4.4. Stomatal index and $p\text{CO}_2$

The SI and $p\text{CO}_2$ could be calculated only in six levels, but four of them occurred in the relatively narrow upper Hettangian interval, and as they suggest marked fluctuations of $p\text{CO}_2$, they could be compared with results obtained from the corresponding $\delta^{13}\text{C}_{\text{wood}}$ results. SI and $p\text{CO}_2$ values were calculated from ginkgo leaves: *Czekanowskia* sp. 1 - upper Hettangian, 1694.2 m (1400 +/- 200 ppm CO_2); *Baiera* sp. 2 - upper Hettangian, 1688.9 m (1500 +/- 400 ppm CO_2); 1686.9 m (1200 ppm +/- 150 ppm CO_2); *Czekanowskia* sp. 1 - upper Hettangian, 1677.2 m (1300 +/- 100 ppm CO_2); *Baiera* sp. 1 (lower Sinemurian, 1624.9 m – 1500 +/- 100 ppm CO_2) and *Baiera* sp. 4 (upper Pliensbachian, 1276 m – 1200 +/- 150 ppm CO_2). The varied measurement error depends on the size and preservation quality of the measured cuticle surfaces. The difference between the two last samples shows a marked decrease of $p\text{CO}_2$, from a high value in the early Sinemurian to much lower value in the Late Pliensbachian (Fig. 7). For the Hettangian, our results fit the other results obtained in other studies, where $p\text{CO}_2$ varied from 1000 to 1500 ppm (Barbacka 2011), following high 2000-2500 ppm at the T/J boundary (Steinthorsdottir et al 2011). Similar values are given in the compilation of Foster et al. (2017), where CO_2 remains above 1000 ppm for Hettangian and Sinemurian. For the Late Pliensbachian, the single obtained value of c. 1200 $p\text{CO}_2$ from Kaszewy is the highest hitherto

reported. For this age there were values given by Xie et al (2006) of c. 940 ppm or c. 900 ppm, but these values were calculated from a different conifer species, which is discussed by Steinhorsdottir and Vajda (2015). More generally, the concentration of c 960 ppm pCO₂ for the Early Jurassic was interpreted also from Swedish (Beerling et al 1998), Danish (McElwain et al 2005 – of note is a wide range between 500 and 2500 ppm for lower Toarcian), Chinese (c. 800 ppm – Chen et al. 2001) and Australian (900 ppm based on araucarialean conifers) material (Steinhorsdottir and Vajda 2015) - see Fig. 7 and discussion by Barbacka (2011). Generally, the differences in SI and pCO₂ calculations are not outstanding: pCO₂ values oscillate within certain range and average values are given. Nevertheless, some inaccuracies are possible, for example pCO₂ can be also influenced by the Carboniferous standardization of NLE, with different authors making different assumptions. The SI and SD of the NLE are used as reference for counting these values for fossil plants. Calibration usually is made empirically in controlled values of CO₂ concentration. Different authors have calibrated *Ginkgo biloba* under different conditions from 300 to 560 ppm which results in fluctuations of calculated pCO₂ values ranging from c. 960 to c. 1500 ppm respectively, which is discussed by Barbacka (2011). Such deviations should appear if differently calibrated NLE are used in the pCO₂ calculation. The results from the Late Hettangian of Kaszewy, calculated from *Baiera* sp. 2, fit within general climatic trends given by Kürschner (2001). We observe that *Czekanowskia* and *Baiera* stomatal density (sensitive to pCO₂ and consequently temperature differences) is generally compatible with $\delta^{13}C_{wood}$, while these genera are not themselves specifically related to a strict range of temperature. Their deciduous character is connected with seasonal temperature and precipitation variations (Fig. 7). Both genera commonly occur together among dominant elements of Siberian-Canadian provinces and are known as mesotemperate plants, characteristic of flood plain/delta peat-forming assemblages (Rees et al. 2000). *Czekanowskia* is one of the commonest plants of coal bearing deposits of Siberia, forming wetland forests (Krassilov et al 2003). Commonly regarded as an indicator of temperate climate, in Poland it was found (apart from Kaszewy) in the northern margin of the Holy Cross Mountains (Barbacka et al 2014) together with other Siberian element *Pseudotorellia* Florin (Kürschner 2001). The genus *Baiera* in Poland has been reported from the Holy Cross Mountains and the Lublin Coal Basin (Barbacka et al 2014). In Mesozoic times, *Baiera*, together with other ginkgophytes of similar type (*Ginkgoites*, *Sphenobaiera*) were widespread and were connected with rather stable, warm to temperate climate and humid conditions (Barbacka 2011; Zhou 2009).

5. Carbon cycle and temperature interpretation

The interpretation of the relationship between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} must rely on some baseline assumptions. The carbon cycle includes many simultaneous processes with different time scales, involving very complex processes of carbon mass and isotopic fluxes to and out of the ocean–atmosphere system. Concerning the carbon cycle, in particular the fluxes into the atmospheric system, we focus here on processes registered in plant matter (Gröcke 2002). Experimental data from plant growth chambers obtained by Schubert and Jahren (2012), further developed by Cui and Schubert (2016) allowed formulation of a simple model (identified as the C3 proxy) in which plant carbon-isotope composition depends on changes in only two atmospheric variables, i.e. source isotopic composition of carbon dioxide ($\delta^{13}\text{C}_{\text{CO}_2}$) and the pCO_2 . However, for $\delta^{13}\text{C}$ to be used as an accurate and precise method to reconstruct pCO_2 the major requirement is to demonstrate that changes in CO_2 are the main driver of changes in $\delta^{13}\text{C}$. It should be emphasized that only those experiments which are based on C3 plants can be taken in account for the current study, as C4 plants (absent in Triassic - Early Jurassic times) show different fractionation pattern (Diefendorf et al 2010). Source isotopic composition of $\delta^{13}\text{C}_{\text{CO}_2}$ during the Early Jurassic epoch is a complex issue, as carbon released to the atmosphere can have multiple different sources with different $\delta^{13}\text{C}_{\text{CO}_2}$ values, anywhere from -70‰ (gas hydrate) through thermogenic methane (-50 to -7‰), oxic degradation of organic matter (-20 to -30‰) (Them et al 2017a), and volcanic CO_2 (-6±2‰) (Beerling & Brentnall 2007; Ruebsam et al 2019, 2020; Gales et al 2020). Thus, observed changes to $\delta^{13}\text{C}$ of the atmosphere (on the influx side) can be caused by widely varying flux changes of carbon depending on the source, which would have widely varying effects on changes in pCO_2 for the same change in $\delta^{13}\text{C}$ - and resulting temperature (one should bear in mind that changes to $\delta^{13}\text{C}$ can be caused by changes in carbon sink, such as decreasing organic carbon burial). However, negative carbon isotope excursions of an amplitude of about 3–4‰ observed in the latest Triassic and Early Jurassic can only be produced by emissions of ^{13}C -depleted carbon such as gas hydrates, thermogenic methane or oxic organic matter degradation (Them et al 2017a; Pieńkowski et al 2016; Ruebsam et al 2020) or a mixture of these sources (Pagani et al 2006), because unrealistically high amounts of volcanogenic CO_2 (released in short time – short carbon cycle) would be required to sufficiently affect the isotopic composition of the exchangeable carbon reservoir (Beerling and Brentnall 2007; Ruebsam et al 2020). For example, Heimdal et al (2020) postulate for the latest Rhaetian-earliest Hettangian case that thermogenic carbon generated from the contact aureoles around CAMP sills represented a credible source for the negative CIEs. Concerning short-term fluxes of carbon into the atmosphere–ocean system, volcanogenic emissions (usually prolonged over long periods of time) acted generally rather as a trigger for a cascade of surface carbon cycling processes, mobilizing methane and CO_2 characterized by a more negative $\delta^{13}\text{C}_{\text{CO}_2}$ signature. Thus, fluxes from the shallow sedimentary sources were a major contributor to the growth of pCO_2 with negative ^{13}C signature (e.g. Hesselbo et

al 2000, Them et al 2017 a, Ruebsam et al 2020). Additionally, increasing $p\text{CO}_2$ causes $\delta^{13}\text{C}$ negative fractionation by C3 plants and both caused the negative isotopic signal registered in fossil plants (Hare et al 2018). Similarly, enhanced decomposition of continental carbon pool caused by rising temperature has a short-term, strong feedback effect (Pieńkowski et al 2016). The rising $p\text{CO}_2$ was a major factor in raising temperature, and temperature growth led to depletion of TOC_{cont} .

On the other hand, increasing $p\text{CO}_2$, climate warming and enhanced hydrological cycle (causing enhanced delivery of nutrients to the oceans) lead to increased ocean productivity and increased rate of burial of organic carbon, resulting in drawdown and fall in atmospheric $p\text{CO}_2$, and positive excursions in both organic and inorganic carbon (Kump and Arthur 1999). The drawdown of atmospheric CO_2 led to global cooling and higher accumulation of TOC_{cont} .

Significant, moderate or strong (Evans 1996) correlation between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} ($r = 0.53 - 0.59$; $R_s = 0.61$; Fig. 5) could likely develop in response to the global carbon cycle (cf. Gröcke et al 1999). While the fluxes of CO_2 with negative $\delta^{13}\text{C}$ signature led to rising $p\text{CO}_2$, negative C isotopic signal registered in fossil plants and global warming, massive burial of ^{13}C -depleted organic carbon at a global scale resulted in higher $\delta^{13}\text{C}$ values in all carbon cycle reservoirs, and the attendant drawdown of atmospheric CO_2 led to global cooling. As noted by Pieńkowski et al (2016), the variability in TOC_{cont} contents in the Polish late Pliensbachian to early Toarcian successions is interpreted primarily as a reflection of the efficiency of terrestrial biodegradation, which depended particularly on temperature, creating favourable conditions for fungi (Fig. 6) that efficiently degraded the most common and otherwise resistant to degradation land palynomaceral, i.e. wood, composed mainly of lignin (Lopez-Mondelani et al 2018). Increased fungal activity was noted in other periods characterized by elevated temperature, such as Paleocene-Eocene thermal maximum (PETM) – Kender et al (2012). In contrast, lower temperatures slow down fungal-mediated decomposition rates (Feng et al 2008), enhancing terrestrial carbon accumulation. Similar processes connected with accumulation and destruction of soil organic matter are observed in recent experiments involving soil warming leading to decomposition of lignin in soil (Feng et al 2008). It should be noted that bacteria can play some role in wood degradation as well (Blanchette et al., 1990). However, bacterial degradation occurs at a slow rate compared with fungal decay and detritivore fungi are singled out as the only organisms which were able to degrade lignin tissues (Richardson et al 2012). The current study extends the $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} dataset for Poland to the whole Lower Jurassic series and the late Rhaetian (Figs. 2, 5, 7). If it is assumed that the temperature is the main factor of TOC_{cont} reduction, then we can link the observed relationship between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} to the temperature warming-cooling trends, associated with global carbon cycle. An important point is that

this correlation does not demonstrate $\delta^{13}\text{C}_{\text{wood}}$ – temperature direct causation. In this case, the $\delta^{13}\text{C}_{\text{wood}}$, temperature and TOC_{cont} would be responding to another forcing (CO_2 fluxes and C_{org} burial, i.e. carbon cycle – cf. Gröcke et al 1999). Additionally, possible influence of sedimentary and diagenetic factors, reflected also as palynofacies inversions (Pieńkowski and Waksmundzka 2009) could alter the TOC_{cont} content. On the other hand, extremely enhanced hydrological cycle at the peaks of T-OAE could have had some impact on the observed $\delta^{13}\text{C}_{\text{wood}}$ – TOC_{cont} relation, in that organic matter would have been rapidly removed and delivered to the receiving basin before the decomposition processes had fully taken effect. This could be responsible in slightly reversed $\delta^{13}\text{C}_{\text{wood}}$ – TOC_{cont} trend observed in four Toarcian samples with most negative $\delta^{13}\text{C}_{\text{wood}}$ values (Fig. 5).

Weaker correlation in the entirely continental Rhaetian section can be explained by much stronger impact of local environmental factors, influencing strongly differentiated TOC_{cont} sequestration that is facies specific in space and time, for example fluvial plain/lacustrine shifts of environments. In contrast, most of the Lower Jurassic strata were deposited in marginal-marine/deltaic environments, where the TOC_{cont} content was averaged in sedimentary processes. Thus, results obtained from these settings show fewer outliers.

Inferred latest Triassic-Early Jurassic temperature trends for the c. 40°N paleolatitude are shown in stratigraphical order in the Fig. 7. As shown by floral remains, the temperatures were generally temperate to warm, with a slight decreasing trend over time, punctuated by two marked hotter periods – in the Late Rhaetian and in particular in the early Toarcian, during the Toarcian Oceanic Anoxic Event Carbon Isotope Excursion (T-OAE CIE), when temperatures peaked. Several less marked periods of temperature rise were indicated in the Hettangian (*planorbis*, *liasicus*), Sinemurian (*turneri* – confirmed also by Schöllhorn et al 2020 and Hesselbo et al 2020a), *oxynotum* – see also Riding et al 2013) and Pliensbachian (*devonii*); the latter reported by several authors, e.g. Dera et al (2011); Gomez et al (2015); Price et al (2016); Peti and Thibault (2017). Lower temperatures occurred in the latest Rhaetian/earliest Hettangian, late Hettangian (periodically), early Pliensbachian (*jamesoni-brevispina*) and particularly in the Late Pliensbachian (*stokesi*, *gibbosus*, *spinatum*), which seems to be the coolest period in the Early Jurassic, confirmed in many papers (Price 1999; Korte and Hesselbo 2011; Dera et al, 2009, 2011). This cooler interval was punctuated by a short-lived warming episode at the *margaritatus/spinatum* boundary. Of note are relatively frequent inferred temperature shifts in the late Rhaetian and the late Hettangian, which can be attributed to the methane releases from clathrates or wetlands, triggered by peaks of volcanic activity of the Central Atlantic Magmatic Province (Palfy et al, 2001; Hesselbo et al 2002; Blackburn et al 2013) or by thermogenic carbon generated from the contact aureoles around CAMP sills (e.g., Heimdal et al 2020). Rapid climate shifts (inferred from clay mineral composition) in the late Rhaetian and possibly earliest Hettangian

with marked cool and dry episodes was postulated as one of the possible scenarios of the end-Triassic mass extinction on continents (Pieńkowski et al 2014). Similar contrasting temperature shifts are observed in the early Toarcian, when the T-OAE CIE and coeval greenhouse period might have been immediately preceded and followed by relatively cooler intervals (middle *tenuicostatum* and mid-*serpentinumfalciferum/serpentinum pessima*) – Mc Elwain et al (2009), although some reports point to continuity of warm conditions long after the T-OAE (Hermoso and Pellenard 2014). It should be pointed out, that the post-*falciferum* Toarcian sediments in Kaszewy and the whole Polish basin (Pieńkowski 2004; Hesselbo and Pieńkowski 2011) are poorly constrained in stratigraphic terms, as there is a major sequence boundary occurring somewhere in the upper *falciferum/serpentinum* zone with ensuing sedimentation of almost homogenous sandstone intervals. Generally, obtained temperature trends are broadly similar to the trends interpreted by Dera et al (2009, 2011). The inferred temperature trends are compared with independently obtained SI results, reflecting pCO₂ in the atmosphere, which should have reflected annual mean air temperature fluctuations in the atmosphere. Although only six pCO₂ measurement points were possible, four measurements came from relatively narrow upper Hettangian interval, enabling comparison with corresponding $\delta^{13}\text{C}_{\text{wood}}$ results. Additionally, more SI results come from McElwain et al (2005) and Steinthorsdottir et al. (2011) – Fig. 7. The general pCO₂/temperature trends inferred from SI correspond with the $\delta^{13}\text{C}_{\text{wood}}$ changes (Fig. 7).

6. Variables influencing $\delta^{13}\text{C}_{\text{wood}}$ and $\delta^{17}\text{O}_{\text{cont}}$ - discussion

The $\delta^{13}\text{C}_{\text{wood}}$ of plant matter in the geological record would be generally dependent on the $\delta^{13}\text{C}$ of the palaeoatmosphere (Hasegawa 1997; Hesselbo and Pieńkowski 2011; Schubert and Jahren 2012; Cui and Schubert 2016; Pieńkowski et al 2016; Them et al 2017b; Hare et al 2018; Ruebsam et al 2020). Moreover, a parallel stratigraphic evolution between terrestrial and marine organic matter- $\delta^{13}\text{C}$ (e.g. Hesselbo and Pieńkowski 2011; Them et al 2017b; Storm et al., 2020) strengthens the hypothesis that changes in the carbon isotope curve are a genuine feature reflecting the global carbon cycle and change in $\delta^{13}\text{C}$ of atmospheric CO₂. From an ecophysiological standpoint changes in $\delta^{13}\text{C}$ are also linked to changes in water use efficiency of the plants, therefore Lomax et al (2019) regarded that the model of Schubert and Jahren (2012) and Cui and Schubert (2016) is only operable over a limited climate space. Indeed, mean annual precipitation (MAP) can affect carbon isotope fractionation in plant materials, whereby $\delta^{13}\text{C}$ values are negatively correlated with MAP in extant and fossil C3 plant (Diefendorf et al 2010; Kohn, 2010; Hare et al, 2018). However, differences in fractionation caused by MAP are significant (over 2 ‰) only when the most contrasting plant habitats are compared - dry (< 600 mm/year) and very humid (> 2000 mm/year) MAP (Diefendorf et

al 2010; Kohn 2010). Moreover, Hare et al (2018) showed that the contributions from changing MAP are insignificant when compared to the effect of pCO₂ for C3 plants. Influence of mean annual precipitation (MAP) within a relatively stable climatic belt is regarded as generally insignificant (Hare et al 2018), although some intermittent increases of MAP (particularly during the Toarcian Oceanic Anoxic Event; Hesselbo et al 2007; Pieńkowski and Waksmundzka 2009; Hesselbo and Pieńkowski 2011; Pieńkowski et al 2016) might have had a minor impact on observed $\delta^{13}\text{C}_{\text{wood}}$ values. Rodriguez et al (2019) attributed the difference observed between $\delta^{13}\text{C}_{\text{cont}}$ in the Southern Tethyan and Iberian margin (semi-arid climate belt) and the Polish Basin (winter wet/warm climate belt) to the $\delta^{13}\text{C}$ fractionation caused by difference in MAP, but still this averaged difference does not exceed 1‰, even if this was a time of Toarcian Oceanic Anoxic Event characterized by much enhanced climatic contrasts. Studies on the Toarcian compound-specific carbon isotope data of land plant wax lipids have suggested that changes in $\delta^{13}\text{C}$ n-alkane vary as a function of changes in the atmospheric CO₂ concentration (Schouten et al 2000; Ruebsam et al 2020). Fractionation of $\delta^{13}\text{C}$ by C3 plants due to increasing pCO₂ would amplify the observed overall $\delta^{13}\text{C}_{\text{wood}}$ values, and increased pCO₂ would result in temperature rise and subsequent reduction of TOC_{cont}. Interestingly, there is also a direct positive feedback between elevated atmospheric CO₂ concentrations and soil organic matter decomposition (Wolf et al 2007). Fractionation by different plant organs related to different plant taxa or seasonal precipitation changes should also be considered. However, any sample of wood material analysed herein would also contain averaged isotopic signals spanning tens, hundreds or thousands of years – averaging out specific fractionation factors of the originating plant taxon, or the part of the plant from where the wood comes. This conclusion is supported by the common observation of parallel stratigraphic trends in $\delta^{13}\text{C}_{\text{wood}}$ values and $\delta^{13}\text{C}$ of bulk marine organic matter (e.g. example of Toarcian of Lusitanian Basin (Hesselbo et al. 2007, Fantasia et al. 2019). It should be also noted that only the Coniferales and Ginkgoophyta produced significant amounts of secondary xylem and most of our wood likely came from conifer trees (Morgans 1999; Philippe et al 2006; Pieńkowski et al 2016). The amount of TOC_{cont} could be also controlled by the rates of production, not only degradation. However, if production rate were the significant controlling factor, then we should expect maximum concentrations of TOC_{cont} during the periods characterized by highest humidity, pCO₂ and, consequently, productivity (e.g. T-OAE – Pieńkowski et al. 2016). However, the situation is exactly opposite and TOC_{cont} is very low during T-OAE, most likely due to a rapid decomposition (Figs. 2, 6). Another factor which could influence TOC concentration is the sedimentation rate – the higher it is, the lower TOC concentration should be. However, the highest overall sedimentation rate occurred in Hettangian, where the average TOC_{cont} content is highest (Fig. 2). Constraints on the late Rhaetian and Early Jurassic environment in Poland based on reconstruction of the hydrological cycle, standing vegetation and clay mineral analysis (Hesselbo and Pieńkowski 2011; Brański 2009, 2012; Pieńkowski

et al 2012, 2014, 2016) does not indicate the presence of dry or semi-dry habitats, except for short periods in the late Rhaetian (these samples were excluded from our $\delta^{13}\text{C}_{\text{wood-TOC}_{\text{cont}}}$ considerations). Macrophyte remains in Kaszewy (Fig. 7) and hitherto analysed palynomorphs in the late Rhaetian and Early Jurassic time interval (Pieńkowski and Waksmundzka 2009; Pieńkowski et al 2012; Pieńkowski et al 2016) point to generally stable climate zone and relatively stable mean annual precipitation (MAP). Annual sensitivity values for the Lower Jurassic woods from similar paleolatitude of Yorkshire, UK (Morgans 1999) generally fall into the 'complacent' field, suggesting little interannual perturbation and mostly uniform growing conditions, with weak to moderate seasonality. Our material comes from the same latitudinal zone of changing humidity, but not drastically enough to cause any significant $\delta^{13}\text{C}$ fractionation in C3 plants (Diefendorf et al 2010; Kohn 2010; Hare et al 2018).

Humidity-related fractionation effects could thus only slightly modulate the observed C isotope trends (for example during T-OAE, when floristic and palynological proxies indicate increased humidity; Pieńkowski et al 2016), rather than being the significant factor, or change systematically in conjunction with pCO_2 , thus indirectly amplifying rather than destroying the observed relationship. It should be noted that based on spore-pollen assemblages from marine strata of Yorkshire, UK, Slater et al (2019) postulated extreme seasonal conditions for the T-OAE time interval with an increase of warm- and even drought-adapted plants through the CIE interval. Notably, their palynodiagram (their fig. 2) shows lack or a minimum content of bryophyte and lycophyte spores through the Toarcian, in particular during the T-OAE. However, data from the Polish basin, located approximately at the same paleolatitude, show prominent and continuous share of spores and megaspores produced by extremely hydrophilic lycophyte (e.g. quill worts) through the T-OAE (Marcinkiewicz 1962, 1971; Pieńkowski and Waksmundzka 2009; Hesselbo and Pieńkowski 2011; Pieńkowski et al 2016). As the Polish material comes from coastal/deltaic sediments, it should better reflect standing vegetation in the hinterland than open marine settings in Yorkshire. Thus, it is still possible that the bryophyte and lycophyte spores (megaspores in particular) and much of fern spores were eliminated from the Yorkshire material by taphonomic processes. In our opinion, Slater's et al (2019) interpretation of extremely wet/dry seasons should be relaxed in favor of more humid conditions enabling the survival of extremely hydrophilic plants.

Plant chamber experiments have also revealed relationships between carbon isotope discrimination and changing pO_2 (Porter et al 2017), but this variable in the geological record is interpreted from reconstructions which vary widely, particularly for the Mesozoic and early Cenozoic eras (Glasspool and Scott 2010). In respect to the geological time interval studied herein, these low-

resolution models are often controversial, although they confirm a general rule that high rates of organic carbon burial results in subsequent oxygen production (Krause et al 2018).

The described herein $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ relationship is surprising. However, if the correlation is so significant, it follows that there is a natural reason for it. There is also a relationship between terrestrial TOC and temperature from actualistic experimental work. As we wrote above, decomposition of soil labile carbon is highly sensitive to temperature variation and elevated pCO_2 resulting in higher temperature could be conducive for enhanced soil organic matter decomposition (Fang et al 2005; Feng et al 2008; Pieńkowski et al 2016; López-Mondéjar 2018). The continental kerogen studied herein had likely been oxidized on land or in rivers and before delivery to the receiving basin – remineralization of TOC_{cont} in a marginal-marine basin was possible, but among different continental types of organic matter, the wood and charcoal was least affected by degradation in the basin (Pieńkowski and Waksmundzka 2009). Even the most critical approaches (Davidson and Janssens 2006) admit that despite controversies, the observational data are converging to demonstrate that irrespective of labile or recalcitrant character, the soil carbon pool decomposes with apparent detectable temperature sensitivity (Fang et al 2005; Feng et al 2008). Wood is known to react more to higher temperature changes (kinetic theory), which can explain why the population of samples with more diversified $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} values (e.g. Toarcian) shows relatively higher efficiency in $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ function (Fig. 5).

Considering the above argument, it should be noted that some emerging reports from Lower Jurassic marine sediments (Hesselbo et al 2020b; Ullmann et al 2020) demonstrate a lack of correlation between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{18}\text{O}$ (reflecting in general, although still debatably, sea-water temperature) in some sections, for example the lower Sinemurian in UK or the Toarcian in Iberia. However, Schöllhorn et al. (2020) show good convergence between these two variables in Sinemurian of Dorset (UK), while there are divergences in the lower Pliensbachian. Of note is also the fact that Hesselbo et al. (2020a,b) point to divergence in the lower Sinemurian, while the Hettangian part shows rather good convergence between the two variables. Similarly, Price et al. (2016) compared $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for the Sinemurian and Pliensbachian section in Dorset and there is a generally good convergence for most of the section, but in some parts of the profile one can observe some divergences as well. There is good convergence of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ both in the Rhaetian-Hettangian sections in SW UK (Korte et al. 2009) and in the uppermost Pliensbachian – lower Toarcian section in the Peniche GSSP profile in Portugal (Suan et al. 2008; Fantasia et al. 2019). Nevertheless, existing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ divergences tend to cast some doubts, at least on universality of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{18}\text{O}/\text{temperature}$ relations because one should expect even stronger relationship between these parameters in marine sediments than there is between $\delta^{13}\text{C}_{\text{wood}}$ and marine temperature, as the

relationship is more direct. However, there are some inherent uncertainties regarding $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ results from marine deposits and their interpretation. It is now well established that bulk organic C-isotope records need to be regarded with caution due to the mixing effects of different types of carbon, each with their own $\delta^{13}\text{C}$ signature (Van de Schootbrugge et al. 2008; Suan et al. 2015; Schöllhorn et al. 2020). In Kaszewy these problems are avoided, because the $\delta^{13}\text{C}_{\text{wood}}$ values comes from homogenous material. The other question is the possible influence of oceanographic processes, acting (at least partly) independently from global atmospheric pCO_2 and temperature changes. Opening of the Hispanic corridor in Sinemurian and its widening in Pliensbachian (Porter et al. 2013) impacted oceanic circulation, marine faunal exchange pattern and, very probably, also isotopic and temperature pattern in the Jurassic seaways of the European area.

The current paper supports and extends similar results obtained from the late Pliensbachian-early Toarcian deposits of the Polish basin (Pieńkowski et al. 2016) and this is a first attempt to infer a continuous record of air temperature trends through such a long period of geological time. Independently obtained trends of interpreted palaeotemperatures are juxtaposed with data from stomatal index which are thought to represent changes in pCO_2 . It seems that the proposed relationship works as a temperature signal only for a warm/winter-wet climatic zone. The $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ trend observed in the semi-arid climate belt seems to be different, at least during the Late Pliensbachian-early Toarcian interval in the Southern Tethyan and Iberian margin (Rodríguez et al 2019). It is possible that during the T-OAE the Southern Tethyan and Iberian margin was influenced by the adjacent tropical climatic zone, which caused the observed differences. Of note is also modeling of major carbon cycle perturbations around the Triassic-Jurassic boundary, showing coincidence between $\delta^{13}\text{C}$ and pCO_2 changes (Heimdal et al. 2020).

7. Conclusions

1. There is an observed highly significant relationship between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} in the Rhaetian/Lower Jurassic from Kaszewy that can be defined by an equation. The premise is that in mid-latitudes, a controlling factor on the relation between $\delta^{13}\text{C}_{\text{wood}}$ and preservation of continental total organic carbon (TOC_{cont}) is the efficiency of terrestrial biodegradation which is pCO_2 and temperature dependent, although there are several factors that control both $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} .
2. The $\delta^{13}\text{C}_{\text{CO}_2}$ of the Rhaetian and Early Jurassic was largely controlled by $\delta^{13}\text{C}$ -depleted fluxes in and out of the ocean-atmosphere system. Likely, there are non-causal correlations between $\delta^{13}\text{C}_{\text{wood}}$, TOC_{cont} and temperature trends. Such correlations may develop because massive fluxes into the ocean-atmosphere system and subsequent burial of ^{13}C -depleted organic carbon (flux out of the

ocean-atmosphere system), at a global scale results in global warming and cooling episodes, registered in the continental carbon pool as $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} fluctuations.

3. The relationship between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} can hypothetically be useful, even if non-causal, for ~25 Myr long latest Rhaetian and Early Jurassic air temperature interpretation at c. 40°N paleolatitude. However, its utility depends on how strong the carbon cycle signal is, and how many other influences have operated on the system.
4. Independently obtained trends of interpreted palaeotemperatures were juxtaposed with data from stomatal index which are thought to represent changes in pCO_2 , and results obtained from stomatal index calculations are compatible with the interpreted temperature trends.
5. In our material, deposits of coastal/deltaic environments are most suitable for studying the relationship between carbon-isotopes, continental TOC, and temperature, because these facies contain more representative, averaged material delivered from a large catchment areas – in contrast to alluvial plains where TOC is dependent on a more localized fluvial setting.
6. Unique, expanded and continuous cores from Kazewy and Mochras allowed reliable $\delta^{13}\text{C}$ chemostratigraphic correlation of marine and marginal/non-marine Lower Jurassic deposits.
7. While this study suggests an overall implication for Earth system studies and offers potentially independent means (registered in the continental carbon pool) to estimate latest Triassic to Early Jurassic atmospheric temperatures, the relationship between TOC_{cont} , $\delta^{13}\text{C}_{\text{wood}}$ and temperature should be further tested and treated as still hypothetical because in general organic carbon isotope records are potentially subject to many different influences.

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Figure captions

Fig. 1. A - Paleogeographical map of Europe in Early Jurassic showing positions of Kaszewy and Mochras boreholes (after Thierry et al. (2000)); B – Polish Lower Jurassic basin with location of Kaszewy borehole: 1 – inferred maximum range of the Lower Jurassic deposits, 2 – maximum thickness of the Lower Jurassic deposits – 500 and 1000 m isopachs (after Pieńkowski 2004).

Fig. 2. Stratigraphic correlation between Kaszewy ($\delta^{13}\text{C}_{\text{wood}}$ - black) and Mochras borehole (blue – $\delta^{13}\text{C}_{\text{TOC}}$, dashed red – $\delta^{13}\text{C}_{\text{carbonate}}$ and black dots – $\delta^{13}\text{C}_{\text{wood}}$), using carbon isotope chemostratigraphy, sequence stratigraphy and biostratigraphical proxies. Reference C isotope curves of the profile Mochras (biostratigraphically calibrated) are based on Storm et al. 2020 ($\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{13}\text{C}_{\text{wood}}$) and Katz et al. 2005 ($\delta^{13}\text{C}_{\text{carbonate}}$). For the Rhaetic section, the reference curve is based on Ruhl et al. (2010) (black). TOC content in Kaszewy is shown – marine (blue line) and continental (red line). Note two options of chemostratigraphic correlation of the upper Sinemurian – lower Pliensbachian transition. The first option (green bars) implies condensation and incomplete $\delta^{13}\text{C}_{\text{wood}}$ dataset in Kaszewy in the lowermost Pliensbachian, while the second correlation (pink bars) implies strong erosion at the sequence boundaries V and VI, resulting in absence of most of the lower Pliensbachian and atypical (for Polish basin) sedimentary development of both upper Sinemurian and lower Pliensbachian. Considering the above reasons, $\delta^{13}\text{C}_{\text{wood}}$ correlation and correlations with other profiles (Fig. 3), the first option was adopted as more likely, despite more similar general isotope trends when adopting the second option.

Fig. 3. Chemostratigraphic correlation of Kaszewy profile with other C isotope curves and major negative CIEs observed in reference sections and recognized in Kaszewy (see Supplementary data 3). All curves are based on $\delta^{13}\text{C}_{\text{organic}}$, except for Basque-Cantabrian Basin (Quesada et al, 2005) where

the $\delta^{13}\text{C}$ values are based on belemnites. The Toarcian Oceanic Anoxic Event (= Jenkyns Event) section is presented in detail in Fig. 4.

Fig. 4. Chemostratigraphic correlation of the lower Toarcian section and the Toarcian Oceanic Anoxic Event (= Jenkyns Event) of Kaszewy profile with selected C isotope curves, showing correlation of C isotope steps T. 1-5 (defined in other profiles in the Polish basin - Hesselbo and Pieńkowski 2011) with other C isotope curves and composite picture of T-OAE. Biostratigraphy: *P.sp.* – *Pleuroceras spinatum* zone (Pliensbachian), *D.Tenuicostaum* – *Dactylioceras tenuicostatum* zone (Toarcian), *H.falciferum* – *Harpoceras falciferum* zone (Toarcian). Note that positions of *Dactylioceras tenuicostatum*/*Harpoceras falciferum* boundary (sub-Boreal realm) and the *Dactylioceras polymorphum*/*Harpoceras levisoni* boundary (Mediterranean Realm) may slightly differ (Ruebsam and Al-Husseini 2020). $\delta^{13}\text{C}_{\text{org}}$ trends: r.l. – rising limb, pl. – plateau, vl – valley, f.l. – falling limb; A-O - $\delta^{13}\text{C}_{\text{org}}$ steps (after Ruebsam and Al-Husseini 2020). Kaszewy profile is much more expanded than coeval marine sections, while most of the section correspond to the falling limb of T-OAE (5 steps – T. 1-5) and rising limb is less complete, likely with condensations or hiatuses in the upper part (see Hesselbo and Pieńkowski 2011).

Fig. 5. Plot of $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ showing statistically significant positive correlation (Pearson) between the two variables in 224 samples, both for linear (lin) and exponential (exp) fit: $r = 0.59$ for exponential fit; $r = 0.53$ for linear fit. The p-value is <0.00001 . The result is statistically significant at $p < 0.05$. For the Rhaetian (66 samples) $r = 0.16$; for the Lower Jurassic (159 samples) $r = 0.57$; Spearman's Rank Correlation Coefficient (in 224 samples): $R_s = 0.61$, $p \text{ val} = 6.44 \cdot 10^{-24}$; the result is significant the significance threshold 0.001 (see Supplementary 4). The correlation is interpreted as a result of differentiated decomposition of terrestrial organic matter related to climate changes, but also other factors could have influenced the observed relationship.

Fig. 6. Four photographs from the lower Toarcian samples, showing wood strongly decomposed by fungi and fungal mycelia and spores: A – sample 1235.6 m: fungal mycelia; B – sample 1201.1 m: fungal mycelia and spores; C – sample 1201.1 m: fungal mycelia and spores; D – sample 1246.9 m: segmented fungal mycelia; E – sample 1201.1 m: fungal spore. Scale for A-E = 20 μ .

Fig. 7. Inferred temperature trends in Rhaetian and Early Jurassic in the Kaszewy profile based on stomatal index and macrofloral data and tentatively on the $\delta^{13}\text{C}_{\text{wood}}/\text{TOC}_{\text{cont}}$ plot (Fig. 5). Macroflora represents three general assemblages: *Czekanowskia-Pseudotorellia* (relatively drier-cooler conditions), *Baiera-Ginkgoites-Sphenobaiera* (relatively warmer and more humid) and *Neocalamites-Schizoneura* (humid). Climatic trends are indicated with their inferred stratigraphic age.

Supplementary data

Supplementary data 1: Kaszewy borehole, carbon isotope and TOC values

Supplementary data 2: Van Krevelen plot, Kaszewy borehole

Supplementary data 3: Chemostratigraphic correlation of major carbon isotope excursions

Supplementary data 4: Spearman's Rank Correlation Coefficient calculation (in 224 samples)

Journal Pre-proof

The authors declare no conflict of interest

Journal Pre-proof

*Significant relationship between $\delta^{13}\text{C}_{\text{wood}}$ and TOC_{cont} in the studied Rhaetian to Lower Jurassic strata

*Efficiency of terrestrial biodegradation is pCO_2 and temperature specific at northern mid palaeolatitudes

* $\delta^{13}\text{C}_{\text{wood}}$, TOC_{cont} and temperature respond to carbon cycle forcing

*Stomatal index results are compatible with the interpreted temperature trends

*Reliable $\delta^{13}\text{C}$ chemostratigraphic correlation of marine and marginal/non-marine deposits demonstrated

Journal Pre-proof

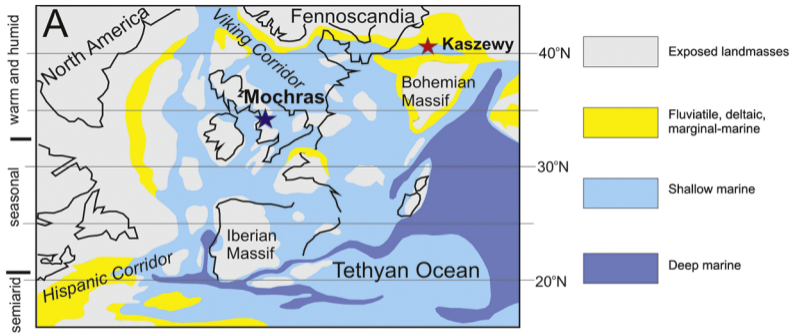


Figure 1

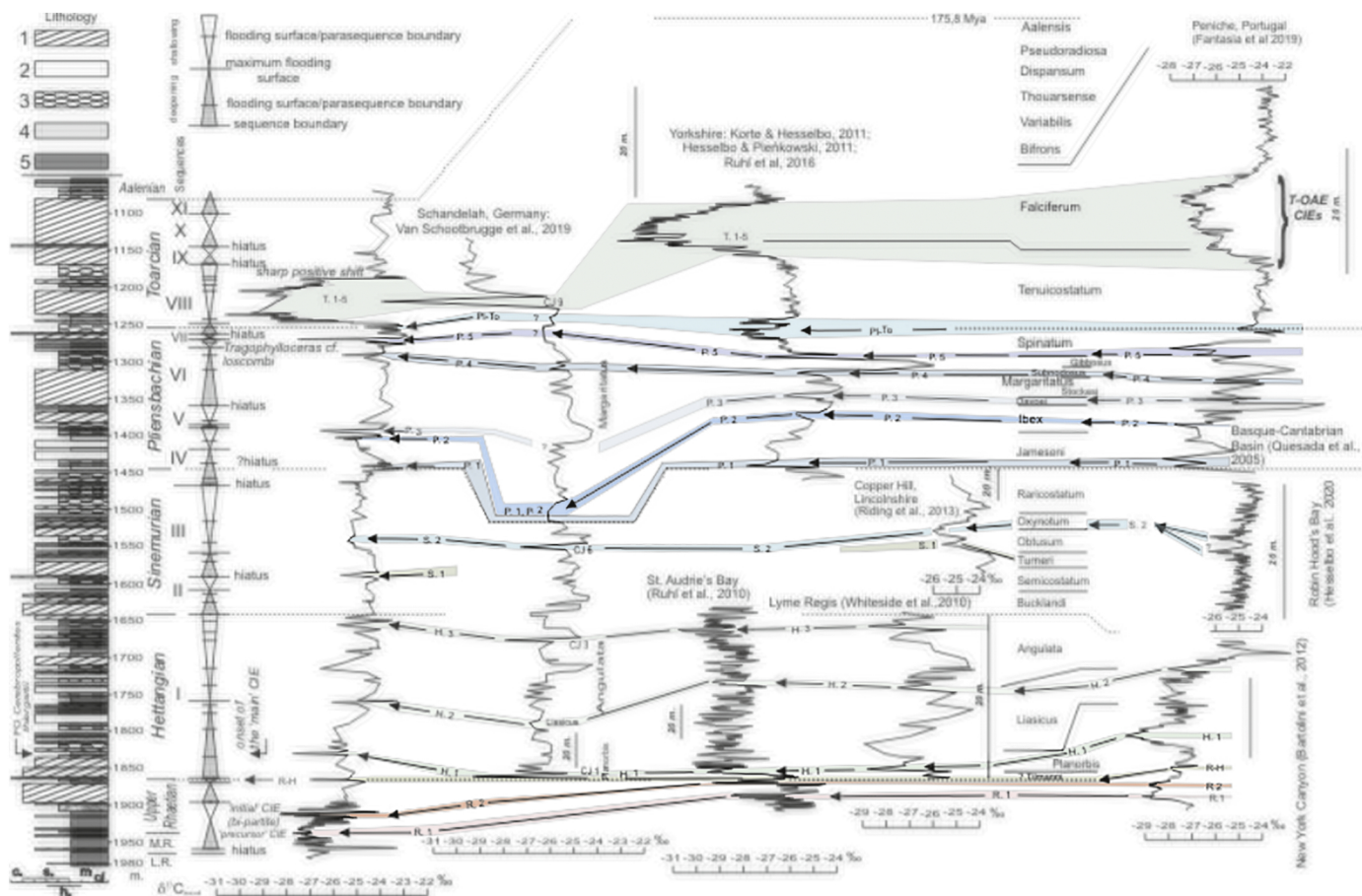


Figure 3

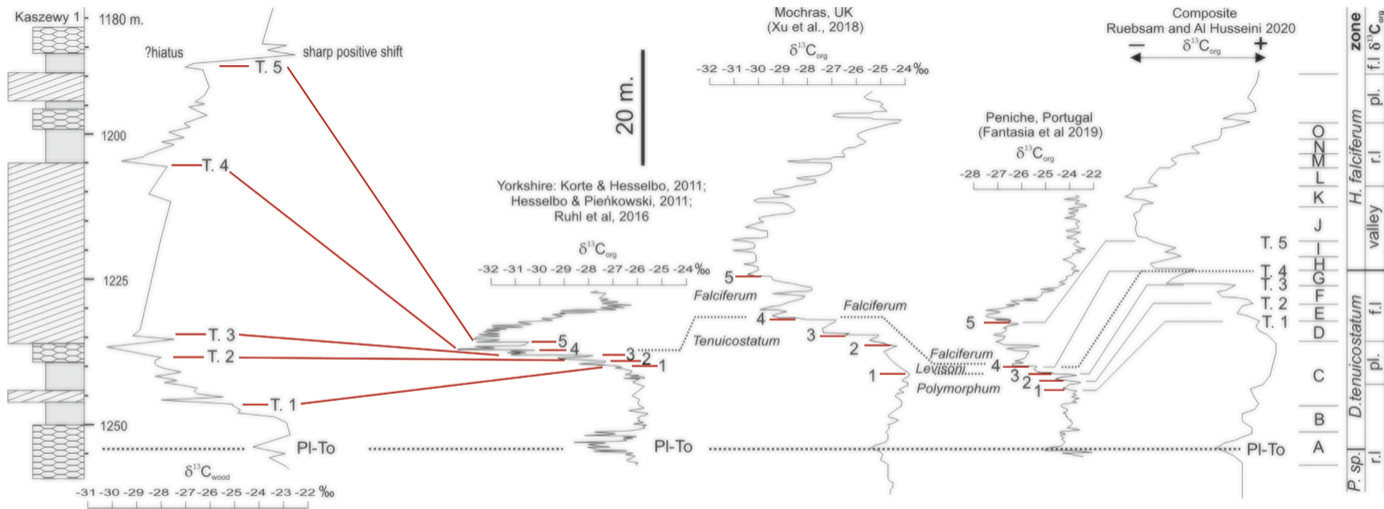


Figure 4

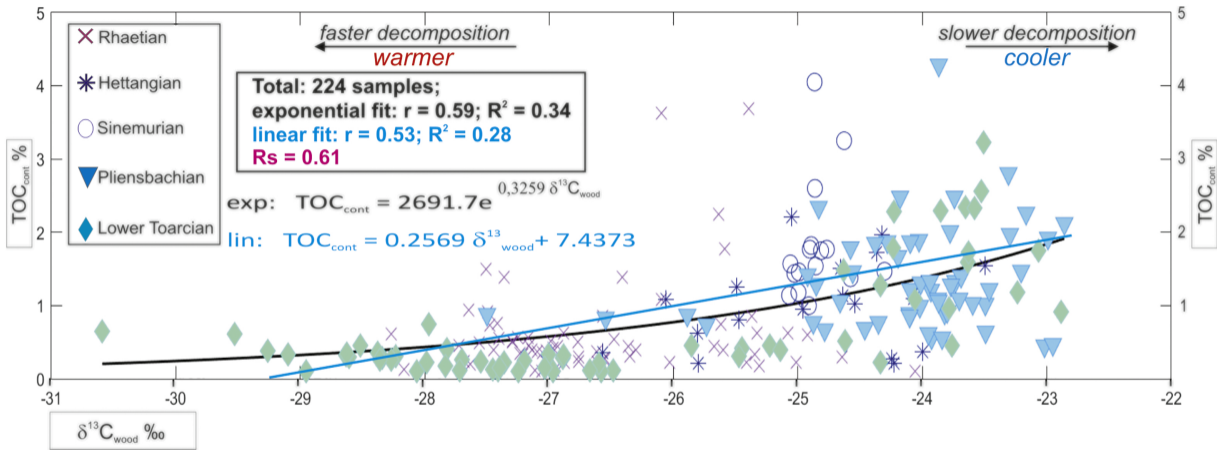


Figure 5

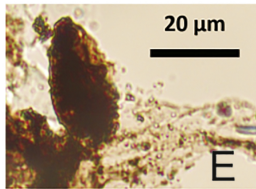
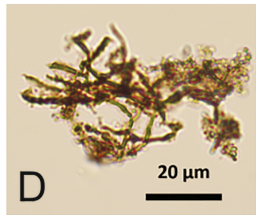
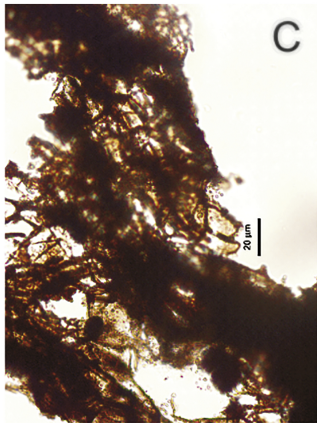
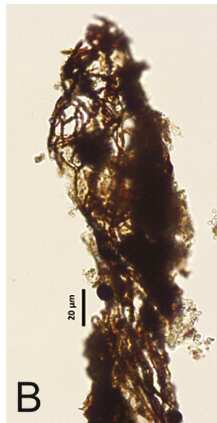
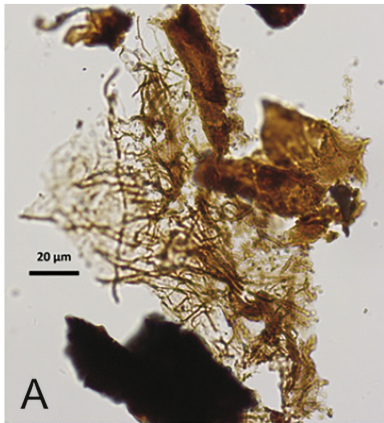


Figure 6

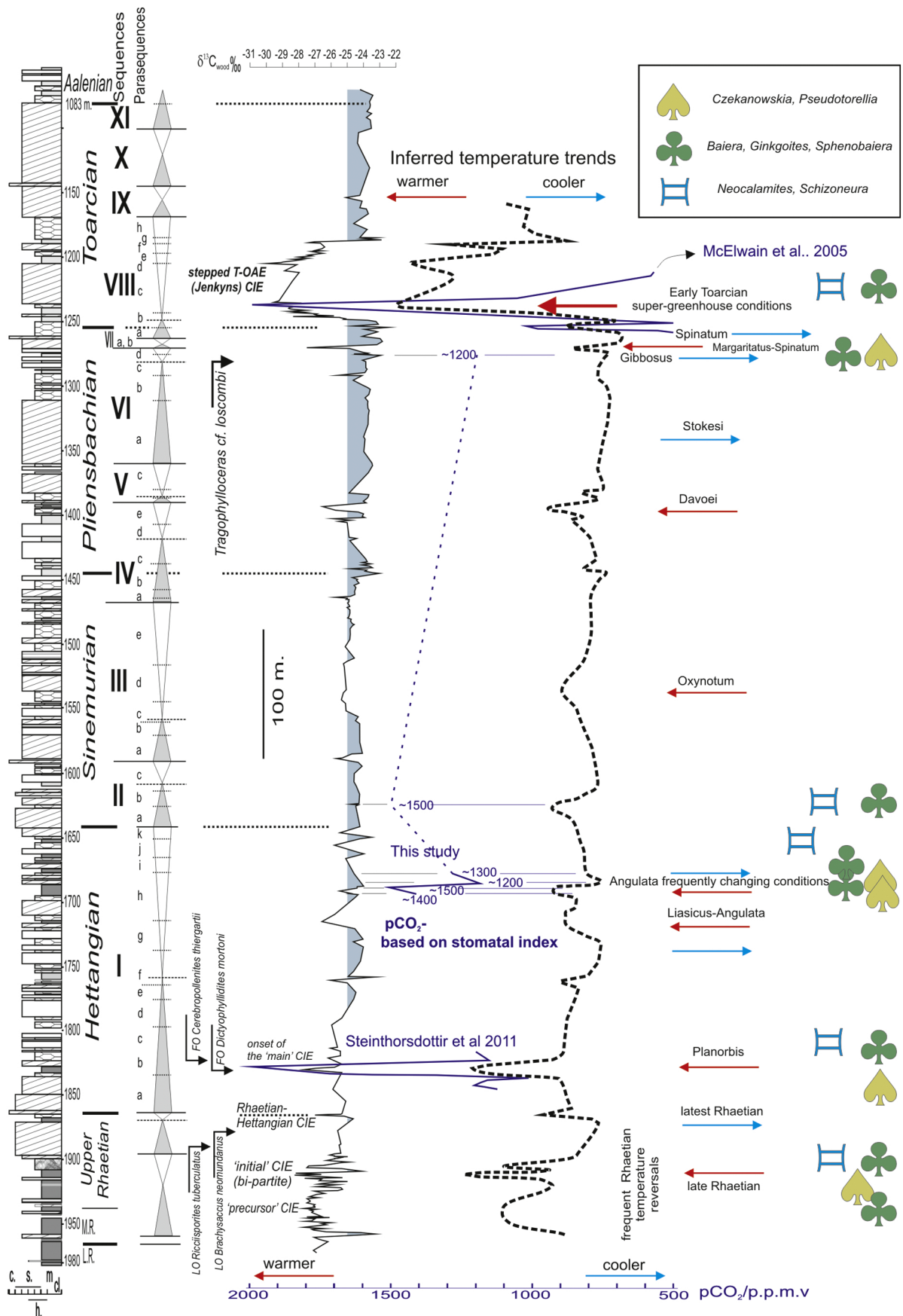


Figure 7