Optical and geochemical characterization of Upper Sinemurian (Lower Jurassic) fossil wood from the Lusitanian Basin (Portugal)

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It is hypothesized that carbon and nitrogen isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of fossil wood fragments will provide useful information regarding conditions prior, during, and after deposition. Eleven fossil wood samples were collected from the Sinemurian–lowermost Pliensbachian marly hemipelagic deposits of the Água de Madeiros Formation at S. Pedro de Moel (Lusitanian Basin, Portugal), and analyzed using optical and geochemical methods to confidently determine their use in palaeoenvironmental studies.

Organic petrography observations show that the fossil wood samples contain a wide variety of particles mostly related to the phytoclast group, but also include resin impregnations, palynomorphs, and/or marine amorphous organic matter. A significant positive correlation between total carbon content and $\delta^{13}\text{C}$ is observed (defined by 8 out of 11 samples), and most samples have high $\delta^{15}\text{N}$. These data suggest that isotopic compositions of the studied samples were severely affected by sedimentary and diagenetic processes (biological or related to early diagenesis and coalification). It is evident that various processes of alteration either acted on different samples of the studied stratigraphic interval, or occurred with different magnitudes. It is considered that future stable isotopic studies on fossil wood should involve detailed screening as presented in this study, to ensure a proper understanding of the biological (mostly biodegradation) or diagenetic processes affecting samples and their impact on the determined chemical properties.

Keywords: fossil wood, carbon and nitrogen stable isotopes, Sinemurian, Lusitanian Basin, Portugal

INTRODUCTION

It is often assumed that C and N isotopic composition of fossil wood can provide important information to enable the discrimination of certain environmental parameters, (such as $p\text{CO}_2$, and water availability), or to distinguish between C_3 and C_4 precursors in post-Cretaceous sediments. Numerous studies conducted over the recent years have investigated $\delta^{13}\text{C}$ of fossil wood and its significance in palaeoenvironmental studies (e.g., Gröcke, 2002; van Bergen and Poole, 2002; Robinson and Hesselbo, 2004; Bechtel *et al.*, 2007, 2008; Diefendorf *et al.*, 2010). The emerging use for this kind of data is related to differentiating between discrete, short-lived geological intervals at a time when the carbon cycle was globally perturbed and affected both the atmospheric and oceanic carbon reservoirs (e.g., Hasegawa, 1997; Gröcke *et al.*, 1999a; Hesselbo *et al.*, 2007; Hesselbo and

Pieńkowski, 2011). It is assumed that when the $\delta^{13}\text{C}$ record of both marine carbonates and fossil wood show a coupled trend, (reflecting the oceanic and atmospheric carbon reservoirs), it is an indication that there was a global perturbation of the carbon cycle.

However, the use of fossil wood isotopic data are related to two main assumptions: 1) that the $\delta^{13}\text{C}$ of fossil wood reflects, to some extent, the $\delta^{13}\text{C}$ of the atmosphere at the moment of tree growth; 2) although diagenesis has altered the original $\delta^{13}\text{C}$ values, it is likely that through a given section all samples have undergone similar diagenetic changes. Although the first assumption may seem fairly reasonable, the second assumption raises concerns as it tends to ignore lithological constraints (e.g., Gröcke, 1998), the process of degradation associated with residence time in the continental and marine environments prior to deposition (e.g., Tyson, 1995), the early diagenetic/coalification processes (e.g., Suárez-Ruiz and Crelling, 2008), a shift in composition due to severe oxidation (including burning) (e.g., Czimeczik *et al.*, 2002) and the impact of these processes on the isotopic composition of fossil wood (e.g., Rimmer *et al.*, 2006). In con-

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trast, $\delta^{15}\text{N}$ has been seldom used in fossil wood studies (e.g., Boudou *et al.*, 1984; Gröcke *et al.*, 1999b; Gröcke, 2002; Kanduč *et al.*, 2005; Rimmer *et al.*, 2006) and its application is mostly related to the discrimination of diagenetic and coalification processes.

The uppermost Sinemurian record of the western sector of the Lusitanian Basin (Portugal) is characterized by the presence of marine, organic-rich marl–limestone alternations rich in benthonic and nektonic macro- and microfauna (Duarte and Soares, 2002; Duarte *et al.*, 2010, 2012) (Fig. 1). In addition, the series occasionally includes fossil wood remains, up to 1 m in length (Fig. 2). The

aim of this work is to determine whether fossil wood samples from the Sinemurian–lowermost Pliensbachian Água de Madeiros Formation at S. Pedro de Moel can be confidently used in palaeoenvironmental studies. The methods used in this study were visual observation under transmitted white light (TWL) and using a fluorescence mode (FM), and elemental (carbon and nitrogen) and isotopic [$\delta^{13}\text{C}_{(\text{PDB})}$ and $\delta^{15}\text{N}_{(\text{Air})}$] geochemistry.

GEOLOGICAL BACKGROUND

S. Pedro de Moel is located on the Portuguese coast,

Fig. 1. a) Geological map of the main carbonate Jurassic outcrops in the Lusitanian Basin (modified from Duarte *et al.*, 2010); b) synthetic composite log from the Polvoeira and Água de Madeiros reference sections of Sinemurian age at S. Pedro de Moel, Lusitanian Basin, Portugal (modified from Duarte *et al.*, 2008; Azerêdo *et al.*, 2010; chronostratigraphy from Comas-Rengifo *et al.*, 2013). Detailed log based on Duarte *et al.* (2012).

about 110 km north of Lisbon. The Lower Jurassic outcrops correspond to a thick succession of carbonate units belonging to the Coimbra, Água de Madeiros, Vale das Fontes, Lemede, and S. Gião formations (e.g., Duarte *et al.*, 2008, 2012). This study focuses on the Polvoeira Member of the Água de Madeiros Formation, which crops out in two main locations south of S. Pedro de Moel; the Polvoeira and Água de Madeiros sections (Fig. 1). At this point, the Polvoeira Member corresponds to a marl-dominated unit, composed of marl–limestone alternations with the inclusion of several horizons of black shale (see Duarte *et al.*, 2012 for a detailed description of this section). Detailed total organic carbon (TOC) and palynofacies studies have been conducted in the Água de Madeiros Formation of the S. Pedro de Moel region (e.g., Duarte *et al.*, 2012; Poças Ribeiro *et al.*, 2013), and ac-

cording to such studies the kerogen assemblages of the Água de Madeiros Formation are dominated by amorphous organic matter (AOM), with some levels richer in palynomorphs or phytoclasts. According to Poças Ribeiro *et al.* (2013), the percentage of huminite reflectance in dispersed organic matter of the S. Pedro de Moel sections is around 0.45% (R_o), suggesting that the studied section reached the final stages of humification and gelification (Sýkorová *et al.*, 2005), in agreement with the T_{max} data from Duarte *et al.* (2012).

MATERIALS AND METHODS

Based on detailed field work, 11 fossil wood samples were collected (Figs. 1(b) and 2) and prepared for organic petrography and elemental and isotopic analysis. Every effort was made to avoid contamination from the sedimentary matrix (rock). During sampling, a lustrous, black material resembling jet was discarded. The samples were inspected and any visibly altered parts were mechanically removed, along with the remaining sedimentary matrix.

After initial crushing, each sample was reacted with HCl (37%) to remove the carbonate fraction, then with HF (40%) to remove the siliceous fraction. The sample was then divided into two subsets, one to be prepared according to the standard methodology for Palynofacies (Tyson, 1995) and the other to be analysed for total carbon (TC) and total nitrogen (TN) contents (wt. %) and $\delta^{13}C_{(PDB)}$ and $\delta^{15}N_{(Air)}$ (‰).

Organic petrographic observations were performed by optical microscopy using transmitted white light (TWL) and a fluorescence mode (FM), at the Palynofacies and Organic Facies Laboratory (LAFO) located at the Federal University of Rio de Janeiro (Brazil).

TC and TN contents and $\delta^{13}C_{(PDB)}$ and $\delta^{15}N_{(Air)}$ were determined at the IMAR-CMA (at Coimbra University),

Fig. 2. Field view of the fossil wood sample V-OU224+0.3 of the Polvoeira Member, Água de Madeiros Formation at S. Pedro de Moel (Lusitanian Basin, Portugal).

Table 1. Lithology, total carbon and nitrogen and stable isotopic data of fossil wood from the Upper Sinemurian Polvoeira Member (Água de Madeiros Formation) at S. Pedro de Moel

Sample	Stratigraphic distance (cm)	Lithological matrix	TN (wt. %)	TC (wt. %)	$\delta^{15}N_{(Air)}$ (‰)	$\delta^{13}C_{(PDB)}$ (‰)	C/N
V-GP38	1949	Marl	1.4	67.7	4.5	−25.4	50
V-GP 26B	1670	Black shale	1.0	68.9	4.6	−23.9	68
V-GP23T	1565	Limestone	1.1	71.3	3.3	−24.7	66
V-GP18T	1446	Black shale	1.0	71.5	3.5	−24.5	75
V-GP 7B	1210	Black shale	0.9	66.7	4.8	−22.6	74
V-GP2T	1112	Marl	0.3	87.6	0.9	−22.8	280
V-OU224+0.3	1025	Marl	0.9	73.4	4.2	−24.1	81
V-OU215B	798	Marl	0.9	72.9	5.2	−24.1	77
V-OU208B	592	Marly limestone	0.9	72.8	4.5	−24.4	78
V-OU201	449	Marly limestone	1.3	68.8	3.7	−25.3	51
V-OU176	0	Marly limestone	1.3	73.8	4.7	−22.9	57

Note: TN, total nitrogen; TC, total carbon; C/N, total carbon/total nitrogen.

Fig. 3. Fossil wood characteristics in transmitted white light (a1, b1, c1, d1, e1, f1, g1, h1); and fluorescent mode (a2, b2, c2, d2, e2, f2, g2, h2); and isotopic and elemental data from the Polvoeira Member (Late Sinemurian) of S. Pedro de Moel.

using dynamic flash combustion. Around 0.5 mg of previously dried (at room temperature) and ground material was placed in tin cups and analysed using a Flash EA, coupled with a Thermo Electron Delta V Advantage mass

spectrometer. Internal precision is better than 0.1‰ for $\delta^{13}\text{C}$ and 0.3‰ for $\delta^{15}\text{N}$ (Acetanilide Standard from Thermo Electron Corporation was used for external precision). The fossil wood sample preparation for determi-

Fig. 3. (continued).

nation of TC and TN data was not performed according ASTM or ISO standards for a sample preparation for ultimate coal analysis; hence, a comparison with previously published data is difficult. However, as our samples were

air-dried and the inorganic matter (minerals) was removed prior to analysis, we consider that our data is comparable to those of coal ultimate analyses reported as being air dry-ash free.

Fig. 4. Cross plots for $\delta^{13}\text{C}$ vs. TC, TN vs. TC, and $\delta^{15}\text{N}$ vs. TN of the fossil wood samples from the Polvoeira Member (Late Sinemurian) at S. Pedro de Moel (Lusitanian Basin, Portugal). The samples represented in red were not included in the regression line calculation.

RESULTS

The stratigraphic position, lithological matrix, and geochemical data of the studied samples are presented in Table 1. The hand-specimen samples are all black in color, dull, and tend to break in blocks. Lamination and striates are poorly marked, but are sometimes observed. In terms of general macroscopic aspects, sample V-GP38 exhibits the most differences as it tends to be more lustrous and breaks in a more brittle way compared to others.

Observations using TWL and FM reveal the detection of large compositional variations (palynofacies descriptions) and the preservation of fossil wood (Fig. 3). Using TWL, the specimens of fossil wood varies from opaque

to translucent, although with different degrees of opacity. The optical data shows that particles are similar to those termed as phytoclasts (Bostick, 1971) in palynofacies studies (e.g., Mendonça Filho *et al.*, 2011) which, according to Tyson (1995), are derived from the lignified parts of terrestrial plants. In samples V-OU224+0.3 (Fig. 2) and V-GP2T, although particles of fossil wood are visible, the particle assemblages include high amounts of AOM, interpreted as probably being of a wood origin (Figs. 3(b) and (c)). In a few samples, palynomorphs or the AOM of marine origin are observed (e.g., Figs. 3(a), (b), (c) and (g)) (see, for example, Tyson, 1995; Mendonça Filho *et al.*, 2011; Sawada *et al.*, 2012 for a detailed description). It is possible to observe that the wood particles present both fluorescent and non-fluorescent particles in all the samples (e.g., Fig. 3(d)) using FM. Fluorescence intensity varies between orange-brown (Fig. 3(f1)) and dark brown (Fig. 3(h1)). Sample V-GP23T presents a high amount of resins (Fig. 3(f)). Most of these features are also seen in kerogen from rock samples of the same stratigraphic interval (e.g., Poças Ribeiro *et al.*, 2013).

TC and TN contents vary from 66.7 to 87.6 and 0.3 to 1.4 wt. %, respectively (Table 1). The C/N ratio (determined from wt. % data in Table 1) varies from 50 to 280, with an average of 87. The $\delta^{13}\text{C}$ ranges from -25.4 to -22.6 ‰, which is in good agreement with previously published data for terrestrial organic material (e.g., Gröcke, 2002) (Table 1). The $\delta^{15}\text{N}$ varies from 0.9 to 5.2‰ (Table 1). Although the entire dataset presents a large scatter ($r^2 = 0.20$, linear correlation), if we exclude three apparent outliers (red circles), r^2 of the TC vs. $\delta^{13}\text{C}$ increases to 0.89 (linear correlation). Therefore, 8 out of the 11 samples present a significant positive correlation between TC content and $\delta^{13}\text{C}$ (Fig. 4).

DISCUSSION

Optical observation of fossil wood composition and preservation bias

The original composition of the fossil wood samples is dominated by lignin, cellulose, tannins, colloidal humic gels, proteins, and lipid substances (Sýkorová *et al.*, 2005), and is chemically and physically modified by biological activity, compaction, and thermal alteration during its geological evolution (e.g., ICCP, 1998, Suárez-Ruiz and Crelling, 2008).

The analysis of the fossil wood under TWL and FM allowed the discrimination of different preservation states of the particles, even within the same sample (Fig. 3). This is expressed in the wide range of components that were observed in each sample (see also, for example, Tyson, 1995; Mendonça Filho *et al.*, 2011). Some of the main features noted using the optical observation of fos-

sil wood, are the occurrences of apparently well preserved fossil wood (related to humification and gelification), opaque phytoclasts (oxidized and/or charcoalfied) and AOM (of probable flora origin related to microbiological remineralization).

It is therefore evident that an assumption of a similar diagenetic (and even syngenetic) condition throughout the studied stratigraphic interval is not true for this case study (see Fig. 3). We found one of the main difficulties was to discover where the physical and chemical alteration processes took place, (i.e., in a terrestrial or marine environment). One of the key features of the palynofacies analyses from this study and that of Duarte *et al.* (2012) and Poças Ribeiro *et al.* (2013) is the occurrence of zygospores (Fig. 3(b1), an oval and slightly reticulated yellow fluorescence particle of about 200 μm located in the center of the microphotography), which are interpreted as being derived from fresh-water green algae (e.g., Grenfell, 1995; Mendonça Filho *et al.*, 2011). This suggests that at least a part of the diagenetic evolution of some of the studied fossil wood may have occurred in fluvial/swap/lacustrine/lagoonal environments, and then remobilized to be incorporated in the nearby hemipelagic depositional setting.

Elemental and isotopic data

Carbon and nitrogen elemental data are usually expressed as a C/N ratio, and are regarded as an indicator of source, nutritional value or the degree of organic matter alteration (e.g., Tyson, 1995). It has been observed that buried plant material has a lower C/N ratio than fresh material, and that aerobic or anaerobic conditions cause an increase or decrease of this ratio, respectively (Gröcke, 2002 and references therein). Compared to modern fresh wood (C/N ratios from 250 to 1340), our data have lower C/N ratios. Although we are aware of the many problems involved in the use of C/N dating (including the possible methodological bias referred to above in Section “Materials and Methods” regarding sample preparation and ultimate coal analysis), our ratios obtained are perfectly compatible with those from ancient (buried) terrestrial organic matter presented in other studies (see Tyson, 1995, table 22.1).

The main factors controlling the amount of $\delta^{13}\text{C}$ in fossil wood are the types of preserved plant tissues, taxonomic affinity, growing environment and chemical composition (e.g., Feng and Epstein, 1995; Loader *et al.*, 2003; Poole *et al.*, 2004, 2006; Preston *et al.*, 2006; Harlow *et al.*, 2006; Bechtel *et al.*, 2007; Galle *et al.*, 2010). Such factors pose many considerations when interpreting obtained data (e.g., Yans *et al.*, 2010). For example, Gröcke (1998) suggested that wood diagenesis in different lithological contexts would lead to a negative correlation of $\delta^{13}\text{C}$ with C, whereas Schleser *et al.* (1999) suggested that in more advanced stages of thermal degradation, the

initial depletion of ^{13}C is overprinted by the loss of certain compounds (e.g., volatiles). During microbial activity, thermal degradation and coalification $\delta^{13}\text{C}$ is expected to increase (Teichmüller and Teichmüller, 1979; Bechtel *et al.*, 2001). In addition, Brodie *et al.* (2011) demonstrated that different acid pre-treatments, residual inorganic carbon contents and the organic matter state and composition can affect the C/N, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ values of organic matter.

The fossil wood fragments are of Jurassic age and are derived from C_3 plants. The $\delta^{13}\text{C}$ of C_3 plants range between -23 and -34‰ , with an average of approximately -27‰ (e.g., Gröcke, 2002). However, based on extensive literature survey, Konh (2010) has shown that this variation can actually be much larger, and that the assumed average might be overestimated by as much as 2‰ . We found that the observed natural variation of $\delta^{13}\text{C}$ posed many problems when analyzing our data because of a similar range of variation detected in our dataset, making it impossible to predict the direction of change (i.e., increasing or decreasing) of measured $\delta^{13}\text{C}$ relative to the original wood carbon isotopic composition. The apparent dissimilarity of the obtained fossil wood record with contemporaneous data obtained from shells and fossil wood (Korte and Hesselbo, 2011) suggests that the $\delta^{13}\text{C}$ of the studied samples does not reflect the $\delta^{13}\text{C}$ of the paleoatmosphere. The organic petrographic observations and the positive correlation between TC and $\delta^{13}\text{C}$ (Figs. 3 and 4) indicate that the main processes affecting $\delta^{13}\text{C}$ are those linked with biological alteration or related to early diagenesis and coalification (see the aforementioned references and discussion below). In addition, our results suggest that these processes were different through the studied stratigraphic interval or if similar, acted with different magnitudes.

The obtained $\delta^{15}\text{N}$ data is in good agreement with similar studies (e.g., Boudou *et al.*, 1984; Gröcke *et al.*, 1999b; Gröcke, 2002; Kanduč *et al.*, 2005; Rimmer *et al.*, 2006) and is characterized by high values of $\delta^{15}\text{N}$ when compared to data from modern plants. If it is true that the $\delta^{15}\text{N}$ of the atmosphere during the Jurassic was not significantly different from modern day values ($\delta^{15}\text{N}$ approximately 0‰), the fossil wood samples are therefore enriched in ^{15}N . It is generally assumed that assimilation and uptake of nitrogen by plants does not exert a major fractionation effect, thus reflecting the isotopic signal of the atmosphere (Ostrom and Macko, 1992). However, recent studies on modern flora (e.g., Evans, 2001; Hietz *et al.*, 2010 and references therein) show that the $\delta^{15}\text{N}$ of wood can vary, for example, due to the presence of fungal symbiotic associations, fractionation between NH_4^+ and NO_3^- during uptake and assimilation, N availability in soil and “open vs. closed” N cycle. The increase of $\delta^{15}\text{N}$ in wood has been associated to N fertilization and/

or changes in drainage patterns, which are known to increase soil N dynamics and thereby increase soil, leaf, and wood $\delta^{15}\text{N}$. In addition, diagenesis and coalification also have the capability to change the original $\delta^{15}\text{N}$ of fossil wood. During the initial stages of wood decomposition, the processes of mineralization (*sensu* Kanduč *et al.*, 2005) and anaerobic bacteria decomposition following fungi aerobic activity are expected to occur (e.g., Bechtel *et al.*, 2001, 2003), leaving the residual organic matter depleted in ^{14}N (Rimmer *et al.*, 2006). The isotopic composition is then expected to remain stable until the onset of the bituminous stage (Boudou *et al.*, 1984). From the above, it seems most likely that the high $\delta^{15}\text{N}$ of fossil wood samples was the result of microbial activity (see Rimmer *et al.*, 2006) during the initial stages of wood decomposition and burial. It has been suggested that gelification and humification may be microbiologically mediated (Bechtel *et al.*, 2001, 2003; Rimmer *et al.*, 2006).

In summary, several samples present clear evidence of being affected by several processes (e.g., microbial degradation, atmospheric oxidation) or include “exotic” compounds (e.g., resin), known to modify the isotopic signal of fossil wood. However, the comparison of the (limited) isotopic dataset with the organic petrography observations does not allow the inference of a predictable variation trend of $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ (Fig. 3).

CONCLUDING REMARKS

The main results concerning the use of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of fossil wood from the Água de Madeiros Formation at S. Pedro de Moel are summarized below:

- Organic petrography observations show that fossil wood samples include a wide variety of particles mostly related to the phytoclast group, but also including resin impregnations, palynomorphs, and/or marine amorphous organic matter. A significant positive correlation between total carbon content and $\delta^{13}\text{C}$ (defined by 8 out of 11 samples) is observed, and most samples present high $\delta^{15}\text{N}$.

- Optical observation of fossil wood samples and the positive correlation between TOC and $\delta^{13}\text{C}$ and the high $\delta^{15}\text{N}$, suggests that the main processes affecting values of $\delta^{13}\text{C}$ are linked with diagenesis (either biological or related with early diagenesis and coalification).

- The data also suggest that the processes of alteration were not similar throughout all the studied samples, invalidating one of the main assumptions when using wood isotopic data for palaeoenvironmental interpretation, (i.e., that although diagenesis has altered the original $\delta^{13}\text{C}$ values, it is likely that throughout a given section all samples will have undergone similar diagenetic changes).

- Our findings warrant caution on the stable carbon isotopic studies on fossil wood. It is clear that the issues raised in this work need to be taken into account in future studies, and a more detailed diagenetic screening needs to be implemented, (for example observation under TWL and FM, determination of carbon and nitrogen and $\delta^{15}\text{N}$), to ensure that results produced are not biased.

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