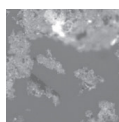


# Can biogeochemistry aid in the palaeoenvironmental/early diagenesis reconstruction of the ~187 Ma (Pliensbachian) organic-rich hemipelagic series of the Lusitanian Basin (Portugal)?

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Data on lipids, carbohydrates and proteins of the most expressive black shale (*s.l.*) intervals of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma) organic-rich hemipelagic series of the Lusitanian Basin (Portugal) were determined using a method that has been successfully applied over the last two decades in the characterization of biomass and very immature sediments. The goal of this paper is to test the applicability of these techniques to the ancient geological record. To our knowledge, this is the first time that this type of biogeochemical data from sedimentary series older than Oligocene is reported and tentatively used for palaeoenvironmental/diagenetic inferences. Carbohydrates and proteins are present in low concentrations, reaching up to 385.13 and 451.13 µg/g rock, respectively. The main variations are observed in the lipid contents, ranging from 197.67 to 8446.36 µg/g rock. The samples with the highest amounts of lipids seem to correlate with low [O<sub>2</sub>] time intervals determined by independent data, such as organic petrography, micropalaeontology and sedimentology. This was probably related with selective lipid preservation under oxygen and hydrogen sulfide-rich depleted environments. The good overall match between the determined lipid contents and specific depositional/early diagenetical conditions seem to favor the idea that the easy to perform and inexpensive method applied here has the potential to add useful information to the study of ancient organic-rich carbonate sedimentary series.

• Key words: biogeochemistry, black shale (*s.l.*) intervals, Pliensbachian, Early Jurassic, Lusitanian Basin.

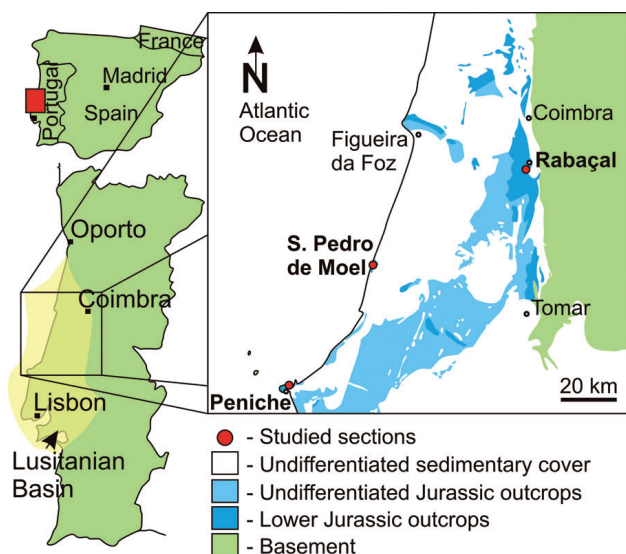
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The preservation of organic matter (OM) in the marine environment results from the interplay between a series of conditionals, mechanisms, triggers and feedbacks whose present knowledge, in spite of recent advances, is still incomplete (*e.g.* Keil & Hedges 1993, Parrish 1995, Tyson 1995, Peters *et al.* 2005, Vandenbroucke & Largeau 2007, Versteegh *et al.* 2010, Zonneveld *et al.* 2010, Balzano *et al.* 2011, Moodley *et al.* 2011, Ozaki *et al.* 2011, Pantoja *et al.* 2011). In ad-

dition, it is widely acknowledged that the fate of OM in the water column and during early diagenesis is of paramount importance in governing several of the global elemental cycles (Capone *et al.* 2008, Emerson & Hedges 2008).

The use of biochemical methods (*i.e.* the determination of lipid, protein and carbohydrate relative contents) is emerging as an important and valuable tool for the discrimination of several oceanographic parameters, for example,



**Figure 1.** Simplified geological map of the Lusitanian Basin and location of the studied sections.

as an indicator of trophic levels or in the distinction between autochthonous and allochthonous OM inputs (Dell’Anno *et al.* 2002, Pusceddu *et al.* 2010). However, this technique has been seldom applied to such research goals in the study of the geological record (Mendonça Filho *et al.* 2010a). On the other hand, lipid related biomarkers have been extensively used in the characterization of past depositional systems and palaeoenvironmental and diagenetic conditions (*e.g.* Breger 1966, Peters *et al.* 2005).

In the Jurassic sedimentary record of the Lusitanian Basin (LB, western central Portugal; Figs 1 and 2), several organic-rich intervals are recognized (Azerêdo *et al.* 2002, Duarte *et al.* 2010, Silva *et al.* 2011a). One of the oldest intervals is represented by the Marly limestones with organic-rich facies member (MLOF mb) of the Vale das Fontes Formation (Lower Jurassic; Fig. 2), which was proven to have a high potential for hydrocarbon generation (Oliveira *et al.* 2006, Ferreira *et al.* 2010) and includes numerous black shales (*s.l.*) (Duarte & Soares 2002, Duarte *et al.* 2010, Silva *et al.* 2011a). It has been suggested that part of this unit corresponds to a time interval characterized by a widespread organic matter preservation phase (Late Pliensbachian OMPI), which would have affected the global carbon cycle and was probably related to the complex chain of events that ultimately led to the Toarcian Oceanic Anoxic Event (*e.g.* Silva *et al.* 2011b). The aim of this work is to present the biogeochemical characterization (lipids, carbohydrates and proteins) of the main black shale intervals (*s.l.*) of the MLOF mb at a basinal scale, based on the detailed specific study of the black-shale levels supported by the integration of other data, namely from sedimentology, organic petrography, geochemistry and thermal maturation. To our knowledge, this is a novel

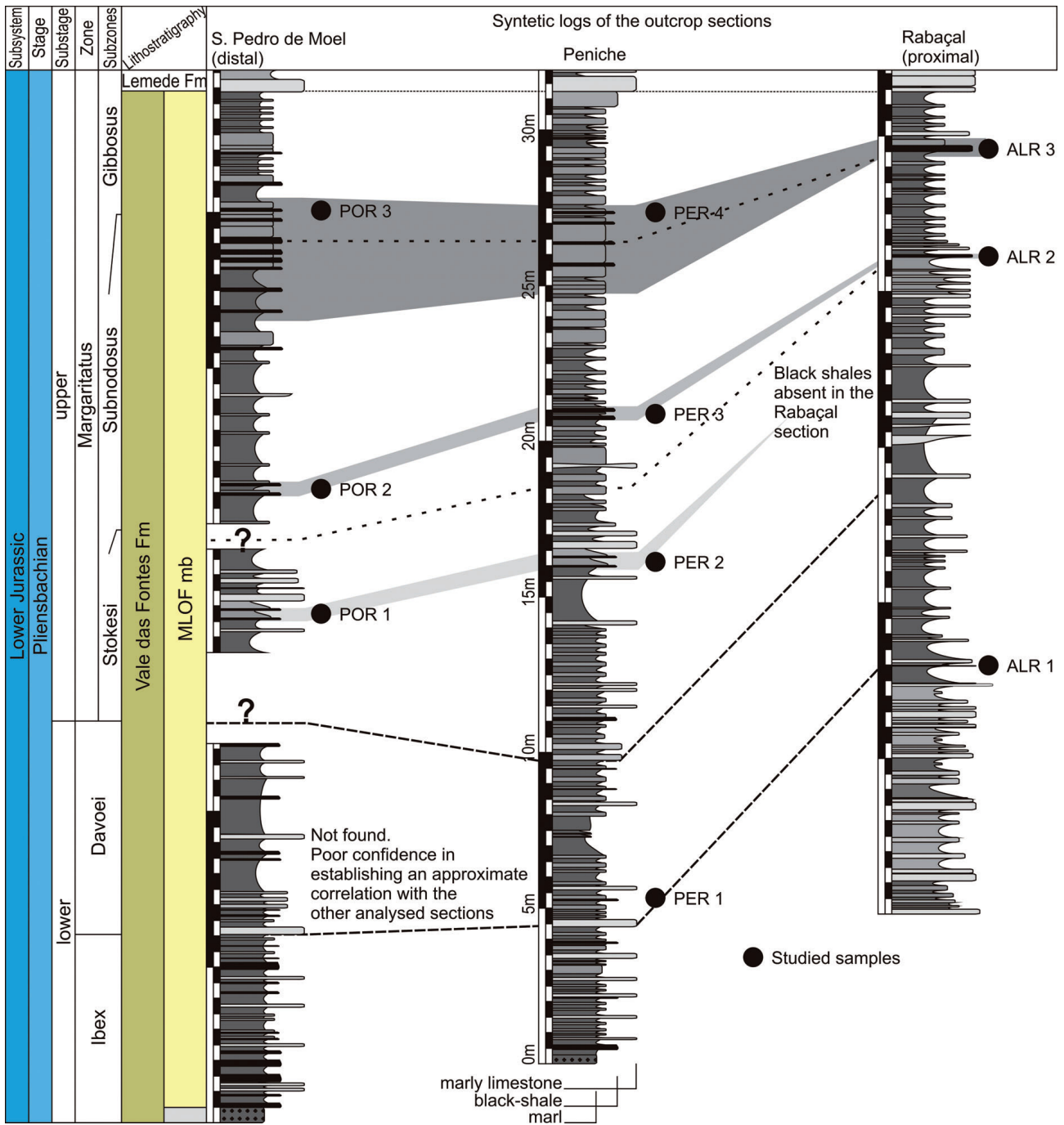
approach to the study of this type of sedimentary series and we hope that this work stimulates other research groups to develop this line of investigation and to present their results.

## Geological background

The studied hemipelagic series of Early–Late Pliensbachian [top of Ibex (Lurindum subzone)-Margaritatus zones] age corresponds to the Marly-limestones with organic-rich facies member (MLOF mb) of the Vale das Fontes Formation and is included in the Pliensbachian Transgressive–Regressive facies cycle, the first 2<sup>nd</sup>-order flooding event recognized at a basinal scale (Duarte *et al.* 2010). It consists of organic-rich marl–limestone hemipelagic alternations with abundant benthic and nektonic macrofauna (*e.g.* Mouterde *et al.* 2007, Duarte *et al.* 2010). During this time interval, deposition in the Lusitanian Basin took place on a north-westerly dipping, low-energy marine carbonate ramp (*e.g.* Duarte 2007), where the maximum depth of the water column should not have exceeded 200 m (N’Zaba-Makaya *et al.* 2003). The MLOF mb, when compared with the units under- and overlying, is characterized by an increase of the marly character of the series and by the occurrence of several organic-rich facies, which are particularly well developed in the western, distal hemipelagic sectors.

Based on sedimentological criteria, it is possible to distinguish three sedimentation domains in the LB during the Early–Late Pliensbachian interval (Figs 1 and 2). Westwards, corresponding to the Peniche, S. Pedro de Moel and Brenha (Figueira da Foz) sections, the MLOF mb main feature is the organic-matter richness, including several black shales (*s.l.*). Ammonites and belemnites are abundant and benthic macrofauna, mainly brachiopods and bivalves, are recorded. The central-eastern domain, corresponding to the Rabaçal sector, is distinguished by the significant increase of more proximal macrofauna and by a slight increase in the carbonate input. Locally, the organic-rich facies are observed, although these are not that relevant when compared with the western domain. The Tomar sector, in the south-eastern domain, represents the shallowest of the environments observable nowadays in the LB for this interval. It contrasts with the other two domains by the lack of organic-rich facies, the increased limestone and bioclastic character of the series and benthic macrofauna (brachiopods and bivalves) richness.

Macroscopically, the organic-rich facies correspond to grey and dark marls, locally showing marked lamination. The highest total organic carbon (TOC) values are recorded in the distal areas (western, at Peniche and S. Pedro de Moel), and gradually decrease towards the proximal locations of the basin (eastern, Rabaçal) (Duarte *et al.* 2010;



**Figure 2.** Synthetic stratigraphic logs of the Rabaçal, Peniche and S. Pedro de Moel outcrop sections, where are highlighted the main organic-rich intervals with black shales (*s.l.*) and its lateral extension. The S. Pedro de Moel section is incomplete due to intense tectonic disturbance, but ammonite data allow a confident correlation with the remaining sections.

Silva *et al.* 2011a, 2011b; Fig. 1). The palynofacies and source-related biomarkers from the Rabaçal, Peniche and São Pedro de Moel sections show that the organic content of this unit consists of a complex mixture of marine and continental components, preserved in a marine depositional environment and under variable redox conditions (Ferreira *et al.* 2010, Silva *et al.* 2010b).

## Materials and methods

Since our goal was to study the relation between relative contents of lipid, carbohydrate and protein and black shale paleodepositional/diagenetic conditions, the main organic-rich intervals with well defined black shales (*s.l.*), which can be traced at a basinal scale in the Rabaçal, Peniche and

**Table 1.** Temporal location, TOC, S, biogeochemistry and Pr/Ph results of the analyzed samples from the Rabaçal, Peniche and S. Pedro de Moel outcrop sections of the Lusitanian Basin (Portugal). (a) Total organic carbon. (b) Sulphur. (c) Lipids. (d) Carbohydrates. (e) Proteins. (f) Pristane/Phytane.

Samples	Time interval	TOC <sup>(a)</sup> (wt.%)	S <sup>(b)</sup> (wt.%)	Biogeochemistry (µg/g rock)				
				LIP <sup>(c)</sup>	CHO <sup>(d)</sup>	PTN <sup>(e)</sup>	Total	Pr/Ph <sup>(f)</sup>
<i>Rabaçal</i>								
ALR 3	base Gibbosus Subzone	2.00	0.11	236.45	385.13	333.92	955.50	1.93
ALR 2	Subnodosus? Subzone	1.71	0.03	197.67	268.67	63.49	529.83	1.69
ALR 1	Ibex/Davoei zones interval	22.30	1.49	2609.55	300.96	87.15	2997.65	1.19
<i>Peniche</i>								
PER 4	base Gibbosus Subzone	9.33	1.10	8446.36	63.88	394.14	8904.38	1.24
PER 3	Subnodosus Subzone	9.10	1.08	739.85	332.63	29.09	1101.56	1.95
PER 2	upper Stokesi Subzone	4.60	0.86	1651.97	302.63	58.12	2012.71	1.49
PER 1	Ibex/Davoei zones interval	26.30	3.40	5752.42	35.13	162.96	5950.51	1.97
<i>S. Pedro de Moel</i>								
POR 3	base Gibbosus Subzone	18.12	3.27	5513.03	40.13	451.13	6004.28	0.50
POR 2	Subnodosus Subzone	6.42	0.82	2115.61	285.13	93.06	2493.80	0.50
POR 1	upper Stokesi Subzone	20.70	12.50	5000.91	287.83	158.12	5446.86	0.74

S. Pedro de Moel outcrop sections were chosen. The selected intervals correspond to four time intervals: Ibex/Davoei zones boundary interval (Lower Pliensbachian) and upper Stokesi, Subnodosus and base of Gibbosus subzones of the Margaritatus Zone (Upper Pliensbachian; see Table 1 and Fig. 2). From these intervals, ten black shale levels (*s.l.*) were selected for organic petrography, palynofacies, TOC, sulphur (S), biomarkers and biochemical analysis (proteins, carbohydrates and lipids). These samples are black in colour and present a marked lamination to the sub-millimetric scale, making them easily recognizable at outcrop by the contrast with the framing lithofacies. Often, these levels present a sharp base and a gradational and bioturbated upper boundary into a more calcareous bed. Some of the selected samples have a significant amount of diagenetic pyrite nodules.

The TOC, S, organic petrography, palynofacies and biomarker analysis were made in the Palynofacies and Organic Facies Laboratory (LAFO) of the Rio de Janeiro Federal University (Rio de Janeiro, Brazil). The TOC and S contents were determined using a SC-144DR LECO analyzer, with an analytical precision of  $\pm 0.1$  wt.%. The organic petrography and palynofacies were performed by optic microscopy using transmitted white light and fluorescence mode and following the classification scheme for the organic matter groups and subgroups proposed by Tyson (1995) and later modified by Mendonça Filho (1999), Menezes *et al.* (2008) and Mendonça Filho *et al.* (2002, 2010c, 2011). The biomarkers analysis, namely the pristane/phytane ratio (Pr/Ph), were carried on the saturate fraction (after Soxhlet extraction with dichloromethane and liquid chromatography in a silica column using hexane) by gas chromatography-mass spectrometry (GC-MS) using Agilent Technologies instruments which includes one 7890 model gas chromatograph equipped with one

7673 auto sampler and coupled to one quadrupole 5973 MSD spectrometer. The injector temperature was 280 °C and the oven was programmed to 170 °C at 20 °C/min, then to 300 °C at 2 °C/min and held for 15 min at 300 °C.

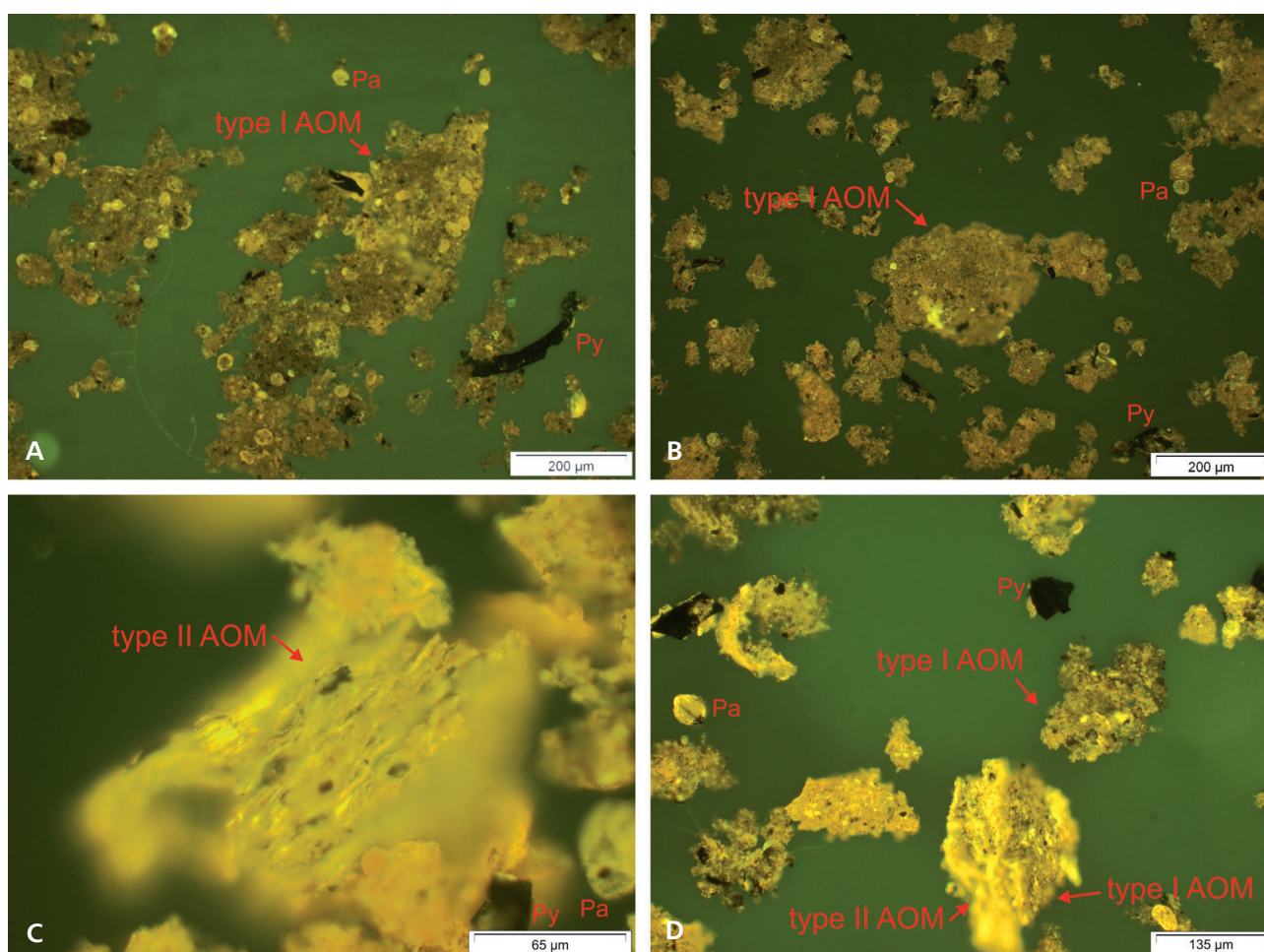
The biochemical analyses were conducted at the Marine Microbiology Laboratory of the Fluminense Federal University (Niterói, Brazil). The analytical procedure, applied over the last two decades in the characterization of biomass and very immature sediments, is the same as previously used in modern (*e.g.* Fabiano & Danovaro 1994, Dell'Anno *et al.* 2002, S. Silva *et al.* 2010) and older sediments (Oligocene, Mendonça Filho *et al.* 2010a), thus providing a common platform between analyses from different geological ages. In addition, these techniques are easy to perform by a trained laboratory technician and do not need expensive equipments. The standard methodology is as follows:

- Protein analysis: extraction by dilute alkaline hydrolysis (NaOH, 0.5 M) and the protein content determined following the Lowry method (Hartree 1972) later modified by Rice (1982) to compensate for phenol interference. Concentrations are reported as albumin equivalents.

- Carbohydrate analysis: extraction by phenol-sulfuric acid, following Gerchakov & Hatcher (1972). Concentrations are expressed as glucose equivalents.

- Lipid analysis: extraction by direct elution with chloroform and methanol and analyzed according to Marsh & Wenstein (1966) for nonspecific lipids by simple charring. Concentrations are reported as tripalmitine equivalents.

For each biochemical analysis, blanks were made with the same sediment samples which were previously treated in a muffle furnace (450 °C for 2 h). All analyses were carried out in 3–5 replicates following Fabiano & Danovaro (1994). Analytical precision is better than 6% for protein and carbohydrate determinations and 8% for the lipid determination.



**Figure 3.** Organic petrography aspects of the kerogen assemblages from the studied sections. A – PER 3; B – POR 2; C – ALR 1; D – PER 4. All photos were taken in fluorescence mode. Abbreviations: Py – phytoclasts; Pa – palynomorphs.

## Results and discussion

### TOC, sulphur and organic petrography characterization

TOC and S data from the studied sections vary between 1.71 to 26.30 wt.% and 0.03 to 12.50 wt.%, respectively (Table 1). The highest TOC and S values from the Rabaçal and Peniche sections are observed in the Ibez/Davoei zones boundary interval samples ALR1 and PER 1; at S. Pedro de Moel the highest values are found in the sample from the upper Stokesi Subzone sample POR 1 (see Duarte *et al.* 2010 for more details about TOC basinal variation of the MLOF mb).

The organic petrography observations show that kerogen assemblages of the studied samples are composed of phytoclasts, marine and continental palynomorphs and Amorphous Organic Matter (AOM). The latter is the dominant group, ranging from 44% to more than 80%.

The AOM corresponds to two main types. The type I AOM (AOM *s.s.* in Mendonça Filho *et al.* 2011) presents a

variable fluorescence and a highly heterogeneous “clotted” fabric (Fig. 3A, B, D). This AOM corresponds to mucilaginous aggregates (Decho & Herndl 1995, Tyson 1995), build up by the interaction of abiotic (*e.g.* transparent exopolymer particles, TEP) and biotic (*e.g.* microbial or algal exopolymeric substances, EPS) gels (*e.g.* Alldredge *et al.* 1993, Verdugo *et al.* 2004). Modern examples show that the biological composition of these aggregates is highly diverse. They include phytoplankton (*s.l.*), bacteria, viruses, organic and inorganic debris embedded in an organic matrix formed by four major structural constituents: polysaccharides; aliphatic components; organic molecules bearing functional groups, such as esters and amides; and organo-elemental compounds (*e.g.* Kovac *et al.* 2002, Simon *et al.* 2002). During transit through the water column, deposition and burial by sediments, these organic aggregates can be modified, for example by heterotrophic microbial reworking (Tissot & Welte 1978; Mendonça Filho *et al.* 2010a, 2010c). The type II AOM (amorphous products of bacteria and microbial mats subgroups of Mendonça Filho *et al.* 2011) occurs as a highly fluorescent homogenous AOM

(pelicular AOM *sensu* Combaz 1980, Fig. 3C, D) and it is suggested that it corresponds to microbial biofilms. However, whether they were produced in the water column or correspond to an established benthic community is yet to be determined. In some samples, especially those from the Ibex/Davoei zones boundary interval, these biofilms appear to have been intensively reworked by heterotrophic bacteria, resulting in a dense, moderate fluorescent AOM with a more regular outline (see Mendonça Filho *et al.* 2010a, 2010c, 2011).

### Biogeochemistry: high lipid content as indicative of oxygen depleted marine palaeoenvironments/early diagenesis

Since our samples are from outcrops we have to assume that thermal and exposure related degradation have taken place. This hampers the use of absolute concentrations to palaeoenvironmental/depositional interpretations (*e.g.* Dell'Anno *et al.* 2002). Another possible source of concern is contamination by modern organisms. In living organisms carbohydrates are dominant so, the very low contents of this parameter in the analyzed samples allow discarding contamination. In the following discussion we assume that the observed relationship between the contents of lipids, proteins and carbohydrates reflects an interplay of several processes during sedimentation and diagenesis and may be indicative of palaeoenvironmental/diagenetical conditions.

Lipids are dominant in most of the studied samples, with only small amounts of carbohydrates and proteins (Table 1). This suggests that lipids were selectively preserved (relative to proteins and carbohydrates) since this relative proportion is not observed in modern marine environments. For example, marine plankton is roughly characterized by  $65 \pm 9$ ,  $19 \pm 4$  and  $16 \pm 6$  wt.% of proteins, carbohydrates and lipids, respectively (Hedges *et al.* 2002).

In the upper layers of the oceans, the chemistry of the organic matter is relatively well characterized; after early diagenesis, carbohydrates, proteins and lipids usually contribute with less than 10% to the total organic carbon in sediments. Two main mechanisms are accepted for OM transformation and preservation during diagenesis, catagenesis and metagenesis: degradation/recondensation (Tissot & Welte 1978) and selective preservation (Tegelaar *et al.* 1989) (the discussion on the merits of each one is beyond the purpose of this work; see Largeau & Derenne 1993, Tyson 1995 for a discussion about this subject). Carbohydrates and proteins are regarded as components with low diagenetic preservation potential (although a fraction of these macromolecules can be preserved in sediments, see Nguyen & Harvey 2001, Jensen *et al.* 2005 and references therein). Lipids, on the other hand, are thought to be more resistant. Several mechanisms and properties have

been suggested to explain the selective preservation of lipids in sediments (*e.g.* Kohnen *et al.* 1990, Schouten *et al.* 1994, Harvey *et al.* 1995, Sinninghe Damsté *et al.* 1995, Sun *et al.* 2002, Farrimond *et al.* 2003, Lee *et al.* 2004, Farrimond *et al.* 2003, Bowden *et al.* 2006, Lü *et al.* 2010) but it has been shown that it mainly depends on O<sub>2</sub> availability and its variation over time controlling, for example, grazing pressure, bacterial remineralization and OM reactivity efficiency. The most efficient environments are those characterized by low and stable O<sub>2</sub> contents (Kohnen *et al.* 1990, 1992; Harvey *et al.* 1995; Sun *et al.* 2002; Ding & Sun 2005; Zonneveld *et al.* 2010).

For the case under study, an independent checking of the likely environmental oxygen levels may be made using data from Brunel *et al.* (1998), based on foraminifera, and N'Zaba-Makaya *et al.* (2003), based on ostracoda. These studies show that the O<sub>2</sub> content of bottom waters during the Late Pliensbachian decreases from the proximal to the most distal sectors, *i.e.* from Rabaçal to S. Pedro de Moel (the Peniche section was not considered in these studies). When a lateral-equivalence comparison is made for each time interval, it is possible to conclude that lipid contents increase from the proximal (Rabaçal) to the distal (Peniche and S. Pedro de Moel) sections (Table 1 and Figs 2 and 4), following the referred microfossil trend and defining a regional pattern. However, it is observed that the lipid content of the sample PER 4 (Peniche) is distinctively higher than the time equivalent sample POR 3 (S. Pedro de Moel), even though the latter has much higher TOC and S contents (Table 1). The organic petrography observations of these samples show that AOM mostly corresponds to heterotrophically reworked type II AOM in sample POR 3 whereas in sample PER 4 is made up of a mixture of type I and type II AOM, with some evidences of heterotrophic reworking. The Lower Pliensbachian samples from Rabaçal and Peniche (Ibex/Davoei zones interval) also tend to present the lipid enrichment pattern, but micropalaeontological data are not available for this time interval. Pr/Ph ratios (see Peters *et al.* 2005 for a discussion about this ratio) also tend to show the same regional trend outlined by the micropalaeontological data. Although the Pr/Ph ratio from Rabaçal and Peniche shows a reversed trend for the Ibex/Davoei zones boundary interval and the Subnodosus Zone samples, they are always higher than the values from S. Pedro de Moel, suggesting more reducing conditions in the latter location (Table 1 and Fig. 4).

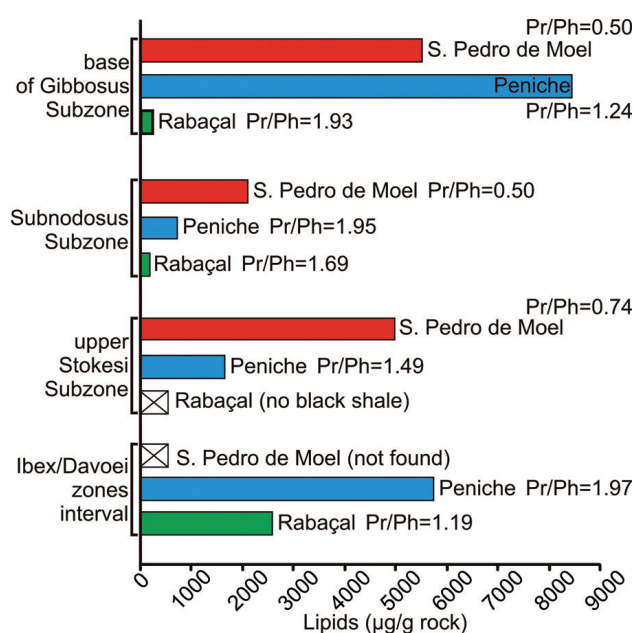
Brunel *et al.* (1998) and N'Zaba-Makaya *et al.* (2003) also demonstrate the existence of a major temporal trend of increasing hypoxia in the section representing the distal areas of the basin (namely S. Pedro de Moel), with the highest oxygen depletion conditions inferred to have occurred at the base of the Gibbosus Subzone. At Peniche and S. Pedro de Moel, and solely regarding the three analyzed Upper Pliensbachian organic-rich intervals (Fig. 2), the

samples from the Gibbosus Subzone present the highest lipid contents, whereas those from the Subnodosus Subzone present the lowest ones (Fig. 4). The fact that the highest lipid contents are determined in samples from the Gibbosus Subzone is in good agreement with the micropalaeontological data given by Brunel et al (1998) and by N'Zaba-Makaya *et al.* (2003) from S. Pedro de Moel and the interpretation that this interval corresponds to the maximum flooding interval of the 2<sup>nd</sup>-order Pliensbachian transgressive-regressive facies cycle (Duarte *et al.* 2010). Also, comparing the samples PER 3 (Subnodosus Subzone) and 4 (Gibbosus subzone) from the Peniche section it is observed that they have virtually the same TOC, S (Table 1) and AOM contents (80% and 84%, respectively) but are markedly different with respect to AOM typology (Table 1). While AOM from sample PER 3 mostly corresponds to the type I (mucilaginous aggregates, Fig. 3A), in sample PER 4 it is composed of both types (mucilaginous aggregates and microbial biofilms, Fig. 3D). The presence of microbial biofilms suggests low sedimentation rates and/or environmental restriction linked to the maximum flooding interval of the 2<sup>nd</sup>-order Pliensbachian transgressive-regressive facies cycle (Duarte *et al.* 2010). The latter kerogen association and its impact on lipids preservation is not yet fully understood, although it has been suggested that biofilm EPS may play an important role in OM preservation (Pacton *et al.* 2007).

The lowest lipid contents were found in samples from the Subnodosus Subzone. However, following the aforementioned temporal trend it would be expected that the lowest lipid contents were observed in samples from the Stokesi Subzone. Taking into account all the available information (*e.g.* N'Zaba-Makaya *et al.* 2003, Ferreira *et al.* 2010, Silva *et al.* 2010a, in preparation), it is likely that this discrepancy is linked to lower order/higher frequency palaeoceanographic changes that control, for example, OM dilution by sediments, kerogen composition and O<sub>2</sub> levels of the oceans.

At Rabaçal, the lipid contents of the Upper Pliensbachian samples is extremely low, suggesting the lack of lipid preservation. The sedimentological and micropalaeontological data (see references above) suggest that sedimentation rates in this part of the basin were greatly reduced during the Late Pliensbachian, hence, prolonged exposure of OM on the ocean floor or to molecular oxygen in sediment pore waters and its depletion by benthic consumption is expected to have occurred. This inference is supported by low TOC and S contents, high Pr/Ph (Table 1) and lack of visual evidence of strong benthic heterotrophic reworking, which is known to largely depend on the amount of metabolizable OM incorporated into sediments (see Tyson 1995 and references therein).

The generic agreement between sedimentological, micropalaeontological and biomarker information, coupled with the lateral and temporal variation of our data, favour the



**Figure 4.** Lateral and temporal variation of the lipids content and the Pr/Ph ratio in the Rabaçal, Peniche and S. Pedro de Moel outcrop sections.

idea that the lipid content of the studied material can be used as a proxy to bottom water/early diagenesis O<sub>2</sub> availability during the Late Pliensbachian in the LB. However, studies from other sedimentary basins and time series following the same approach are necessary to validate our findings.

## Diagenetic bias

In the studied samples, incorporation into kerogen and clay mineral adsorption may affect the observed lipid contents, as they can be released and migrate later in the diagenetic history. For example, it is well known that lipids may be incorporated into kerogen via sulphur-bonds during early diagenesis (Sinninghe Damsté *et al.* 1995 and references therein) and can be released during late diagenesis/early catagenesis due to cleavage of carbon-sulphur bonds (Sinninghe Damsté *et al.* 1995, Pan *et al.* 2008). For the Kimmeridge clays, Murray *et al.* (1998) observed that the ratio of free to kerogen-bound aliphatic biomarkers extracted after hydrolysis markedly increase at approximately 0.45–0.50% of vitrinite reflectance, although the total concentration of these components only start to decrease at vitrinite reflectance values around 0.55%. In the case under study, the available thermal-maturity related data (Spore Coloration Index, Vitrinite Reflectance, thermal maturation related biomarkers and Rock-Eval pyrolysis) indicate that the studied successions are immature; the MLOF mb in Peniche, for example, presents vitrinite reflectance values of % R<sub>0</sub> = 0.47 and T<sub>max</sub> (Rock Eval) always below 440 °C (Oliveira *et al.* 2006, Ferreira *et al.* 2010, Mendonça Filho

et al. 2010b). It is suggested that in these thermally immature sediments, hydrocarbon migration may not be a major factor in controlling the determined lipid contents within a given section. However, the possibility that it may play a role in the regional variations cannot be discarded.

## Conclusions

In the organic-rich Pliensbachian hemipelagic series of the LB protein, carbohydrate and lipid relative contents were determined and correlated with organic petrography, micropalaeontological and sedimentological data. The preservation of lipids, relatively to carbohydrates and proteins, seems to be related to palaeoenvironments/early diagenesis where O<sub>2</sub> concentrations are low. It has been demonstrated that [O<sub>2</sub>] vary as a response to depositional, palaeoceanographic and palaeoenvironmental changes, favouring the idea that determination of relative contents of proteins, carbohydrates and lipids may be a viable work tool in the characterization of ancient sedimentary environments. We hope that this work stimulates other research groups to develop this line of investigation and to present their results.

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