Ricardo Ferreira Louro Silva

Séries carbonatadas ricas em matéria orgânica do Jurássico da Bacia Lusitânica (Portugal): Sedimentologia, Geoquímica e interpretação paleoambiental

Jurassic organic-rich carbonate series of the Lusitanian Basin (Portugal): sedimentology, geochemistry and palaeoenvironmental interpretation

2013

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Universidade de Coimbra

Faculdade de Ciências e Tecnologia
Universidade de Coimbra

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Tipo de trabalho	Tese de Doutoramento
Título	Séries carbonatadas ricas em matéria orgânica do Jurássico da Bacia Lusitânica (Portugal): Sedimentologia, Geoquímica e interpretação paleoambiental
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Orientador	Professor Doutor Luís Vítor da Fonseca Pinto Duarte (Universidade de Coimbra)
Coorientador	Professora Doutora Ana Cristina Costa Neves dos Santos Azerêdo (Universidade de Lisboa)
Identificação do Curso	Doutoramento em Geologia (Pré-Bolonha)
Área científica	Geologia
Especialidade	Estratigrafia e Paleontologia
Data da defesa	2013

· U C ·

UNIVERSIDADE DE COIMBRA

Financiado pela Fundação para a Ciência e Tecnologia (SFRH/BD/47362/2008)

QREN - POPH - Tipologia 4.1 - Formação Avançada, comparticipado pelo Fundo Social Europeu e por fundos nacionais do Ministério da Educação e Ciência

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
PORTUGAL 2007.2013

Capa: afloramento do membro Margo-calcários com níveis betuminosos (Formação de Vale das Fontes) na praia do Portinho da Areia do Norte, Peniche

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Agradecimentos

Gostaria de expressar os meus sinceros agradecimentos às seguintes pessoas e instituições que contribuíram para a execução desta tese (em cada capítulo encontram-se os agradecimentos individuais respeitantes a cada temática):

-Professor Doutor Luís Vítor Duarte (Universidade de Coimbra), orientador, mentor e amigo, e que me introduziu nestas investigações jurássicas há quase 8 anos. É impossível traduzir por palavras a minha gratidão por tudo o que me proporcionou – encorajamento, bons conselhos, companhia e imensas boas ideias – mas de qualquer das formas fica aqui uma tentativa. Muito obrigado;

-Professora Doutora Ana Cristina Azerêdo (Universidade de Lisboa) pela sua amável disponibilidade em coorientar este projeto de tese de Doutoramento e pela sua participação ativa na produção científica;

-Professora Doutora María José Comas-Rengifo (Universidad Complutense de Madrid) por me *enseñar los bichos* e pelas extensas discussões de cariz paleo-bio-geo-local-regional-mundo mundial que tivemos tanto no gabinete como nos afloramentos;

-Professor Doutor João Graciano Mendonça Filho (Universidade Federal do Rio de Janeiro) pela sua calorosa receção durante as minhas estadias no laboratório de que é responsável (LAFO-UFRJ).

-Dr. Selma Sofia Martins Lima, pela sua disponibilidade em participar nos trabalhos de campo, colaboração científica e dedicada atenção na revisão dos trabalhos aqui apresentados;

-Professor V. Paul Wright for receiving me at the University of Cardiff and for his kind amiability during my stays at the Cardiff University;

-Mestres Rui Ferreira, Nadi Poças Ribeiro, Gil Correia, Ricardo Paredes, António Santos, Elsa Rodrigues e todos os colegas que, pela sua amabilidade em partilhar dias de campo e/ou de gabinete, também contribuíram para que esta tese fosse uma realidade;

-Laboratório de Palinofácies e Facies Orgânica (LAFO) e aos seus colaboradores pela excelente receção e partilha de conhecimento que me proporcionaram durante as minhas estadias no Rio de Janeiro;

- Sr. Armando, Sra. Aurora, Sr. Carlos, Sra. Conceição, Sra. Manuela e Sr. Moura, por todo o apoio prestado durante quase uma década no Departamento de Ciências da Terra da Universidade de Coimbra;

-Departamento de Ciências da Terra (Universidade de Coimbra), Departamento de Geologia (Universidade de Lisboa) e *School of Earth and Ocean Sciences* (*University of Cardiff*), instituições de acolhimento;

Por último, agradeço, do fundo do meu coração à Selma, Mãe e manos pela sua dedicação e paciência em me aturar; em boa verdade é a eles que dedico esta tese.

Resumo/Abstract

Resumo

As bacias sedimentares *on-* e *offshore* pertencentes às margens conjugadas do oceano Norte Atlântico são atualmente foco de intensa investigação, tendo como um dos principais objetivos a avaliação do seu potencial para exploração de petróleo. A Bacia Lusitânica é considerada como um potencial alvo de exploração, devido à excelente exposição e elevada qualidade dos seus afloramentos, ou como um ponto de partida para a compreensão das pouco conhecidas bacias *offshore* das margens Norte Atlânticas. Uma das principais razões que motiva o continuado investimento no território nacional é o reconhecimento (em afloramento e em sondagens) de vários intervalos ricos em matéria orgânica no registo sedimentar da Bacia Lusitânica, nomeadamente no Sinemuriano (Membro de Polvoeira da Formação de Água de Madeiros), Pliensbaquiano (membro Margo-calcários com níveis betuminosos da Formação de Vale das Fontes) e Oxfordiano (formação de Cabaços).

Nesta tese é apresentada a caracterização geológica destes intervalos, singulares pela ocorrência de quantidades significativas de matéria orgânica à escala da bacia, recorrendo a técnicas *clássicas* da Sedimentologia, Estratigrafia e Paleontologia em conjunção com *modernas* ferramentas derivadas da Geoquímica, Palinofácies e Biogeoquímica. O objetivo é o de contribuir para a reconstituição das condições sedimentológicas, biológicas e hidro-atmosféricas correlativas da sedimentação e para a interpretação de detalhe e discussão dos possíveis eventos, regionais ou globais que, em última análise, condicionaram a produção, deposição e preservação da matéria orgânica nesta área do futuro Oceano Atlântico.

A interpretação dos dados obtidos e a sua interseção com a informação preexistente permitiu refinar os quadros estratigráficos e modelos paleoambientais estabelecidos para as referidas séries da Bacia Lusitânica. Estes dados também possibilitaram a construção de um quadro de evolução sequencial de 2ª- e 3ª-ordem para o Sinemuriano Superior–Pliensbaquiano, enquadrado pela evolução lateral, temporal, geoquímica e palinofaciológica dos principais intervalos ricos em matéria orgânica. Observa-se, no intervalo de idade pliensbaquiana, que as principais ocorrências deste tipo de fácies são refletidas na variação temporal do $\delta^{13}C$ e no registo lateral e vertical das suas quantidades em lípidos, hidratos de carbono e proteínas. Os trabalhos desenvolvidos no limite Jurássico Médio-Superior (especialmente a Formação de Cabaços) mostram, através das variações laterais e temporais dos teores de Carbono Orgânico Total e do estudo da Palinofácies, a elevada dinâmica biológica associada a variações de alta frequência dos ambientes deposicionais.

Palavras-chave: Matéria orgânica; Sedimentologia; Estratigrafia; Palinofácies; Geoquímica; Interpretação paleoambiental; Membro de Polvoeira da Formação de Água de Madeiros (Sinemuriano Superior); membro Margo-calcários com níveis betuminosos da Formação de Vale das Fontes (Pliensbaquiano); Formação de Cabaços (Oxfordiano); Jurássico; Bacia Lusitânica; Portugal.

Abstract

The on- and offshore sedimentary basins belonging to the North Atlantic conjugate margins are currently the focus of intense research having, as one of the main objectives, the assessment of their potential for petroleum exploration. The Lusitanian Basin (Portugal) is regarded as a potential target for exploration, due to the remarkable exposure and high quality of its outcrops, or as a starting point to the comprehension of the less known offshore basins of the North Atlantic margin. One of the key reasons that motivates the continuous investment in national territory is the recognition (in outcrop or borewhole data) of several organic-rich intervals in the sedimentary record of the Lusitanian Basin, namely in the Sinemurian (Polvoeira Member from the Água de Madeiros Formation), Pliensbachian (Marly-Limestones with organic-rich facies member from the Vale das Fontes Formation) and Oxfordian (Cabaços Formation).

Here is presented the geological characterization of these intervals, unique by the basin-wide occurrence of organic matter in significant amounts, using *classical* techniques from the Sedimentology, Stratigraphy and Paleontology with modern tools derived from Geochemistry, Palynofacies and Biogeochemistry. The objective is to contribute to the reconstruction of the sedimentological, biological and hydro-atmospheric conditions correlative of sedimentation and to the detailed interpretation and discussion of possible events, regional or global, that ultimately conditioned the production, deposition and preservation of organic matter in this region of the future Atlantic Ocean.

The interpretation of the obtained data and its interception with the pre-existing information, allowed the refinement of the established stratigraphic charts and palaeoenvironmental models. These data have also allowed the construction of a 2^{nd}- and 3^{rd}-order sequential model for the Upper Sinemurian–Pliensbachian, supported by the lateral, temporal, geochemical and palynofaciological evolution of the main organic-rich intervals. In the Pliensbachian interval, it is observed that the main occurrences of this kind of facies are reflected in the temporal variation of $\delta^{13}C$ and in the lateral and vertical record in the amounts of lipids, carbohydrates and proteins. The works developed in the Middle–Upper Jurassic boundary (Cabo Mondego and Cabaços formations) show, trough the lateral and temporal variations of Total Organic Carbon and Palynofacies, the high biological dynamic associated with high frequency variations of these depositional environments.

Keywords: Organic matter; Sedimentology; Stratigraphy; Palynofacies; Geochemistry; Paleoenvironmental interpretation; Polvoeira Member from the Água de Madeiros Formation (Upper Sinemurian); Marly-Limestones with organic-rich facies member from the Vale das Fontes Formation (Pliensbachian); Cabaços Formation (Oxfordian); Jurassic; Lusitanian Basin; Portugal.

Capítulo 1 | Introdução

1.1. Rationale

1.1.1. Introdução

A valorização de qualquer recurso contido no território nacional é imperativa no atual contexto económico. Desde há mais de um século que se prospetam hidrocarbonetos em território nacional, muito embora e até ao momento, os resultados não sejam os mais animadores. Uma das principais razões que motiva o continuado investimento nacional e estrangeiro no território Português é o reconhecimento, em afloramento, de um dos principais elementos estruturais dos possíveis sistemas petrolíferos, a rocha-mãe ou rocha geradora.

A prospeção de hidrocarbonetos assenta num vasto conjunto de ferramentas, sendo uma delas a elaboração de um modelo evolutivo da bacia que permita a dedução das mais diversas propriedades dos corpos rochosos presentes numa determinada área de interesse. No entanto, a conceção de modelos relativos aos sistemas sedimentares carbonatados com significado geológico é problemática, uma vez que estes implicam um conhecimento alargado dos vários fatores físicos, químicos, geológicos e biológicos que governam a sedimentação nestes ambientes de deposição. Assim, e atendendo à realidade do panorama nacional e internacional, parece-nos oportuno abordar as questões temáticas que possam, por num lado, aumentar o conhecimento científico destes intervalos singulares do registo geológico português e, por outro, contribuir para mitigar o risco associado à elaboração dos modelos usados na indústria, sobretudo a dedicada à exploração de hidrocarbonetos.

Uma das áreas de especial interesse de pesquisa no território nacional é a que compreende os afloramentos de idade mesozoica que se estendem desde a Serra da Arrábida até ao Norte de Aveiro ao longo da costa, e limitada a Este pela faixa de cisalhamento Porto-Tomar. Estes são os testemunhos geológicos do desenvolvimento de uma pequena bacia marginal Peri-Atlântica, denominada Bacia Lusitânica.

No registo jurássico da Bacia Lusitânica são reconhecidos vários intervalos ricos em matéria orgânica. Destes, apenas dois têm distribuição bacinal e são reconhecidos como rochas potencialmente geradoras de petróleo. O primeiro corresponde ao membro Margo-calcários com níveis betuminosos da Formação de Vale das Fontes (Pliensbaquiano) (abordado no capítulo 4) e o segundo à Formação de Cabaços (Oxfordiano inferior?/médio) (abordado no capítulo 5). Ainda no Jurássico Inferior é observado um potencial intervalo gerador correspondente ao Membro de Polvoeira da Formação de Água de Madeiros, embora a sua distribuição espacial seja bastante restrita (capítulo 3).

1.1.2. Organização da tese e objetivos

De acordo com o conhecimento científico público e acessível à data do início dos trabalhos, foram identificadas 3 linhas principais de investigação relativas ao estudo dos principais intervalos estratigráficos ricos em matéria orgânica da Bacia Lusitânica: a) caracterização sedimentar das unidades em estudo, correlação dos perfis e melhoramento dos quadros estratigráficos e sequenciais; b) caracterização da matéria orgânica (geoquímica orgânica e inorgânica, Palinofácies e Biogeoquímica); c) cronologia relativa, amplitude, causas e consequências dos eventos que conduziram à preservação da matéria orgânica.

Destas três linhas de investigação resultaram diversas publicações, desde apresentações em congressos a trabalhos publicados em revistas internacionais da especialidade. Os principais trabalhos, publicados ou submetidos em revistas do *Thomson Reuters Journal Citation Reports* com fator de impacto, são aqui apresentados e formam o corpo principal desta tese de doutoramento, organizada em 6 capítulos principais. Os subcapítulos 2.1, 3.1, 4.2, 4.3 e 5.1. correspondem a trabalhos já publicados na *Geologica Acta* (Ricardo L. Silva é 2° coautor), *Journal of Petroleum Geology* (Ricardo L. Silva é 2° coautor), *Chemical Geology* (Ricardo L. Silva é 1° coautor), *Bulletin of Geosciences* (Ricardo L. Silva é 1° coautor), *Facies* (Ricardo L. Silva é 1° coautor), respetivamente. O subcapítulo 3.2 corresponde a um trabalho que, à data da entrega desta tese, se encontra em revisão na revista *Geochemical Journal* (Ricardo L. Silva é 1° coautor). A secção 4.1. será o tema de uma submissão a realizar (Ricardo L. Silva é 1° coautor).

1.1.2.1. Caracterização sedimentar das unidades em estudo, correlação dos perfis e melhoramento dos quadros estratigráficos e sequenciais

Os primeiros trabalhos, essencialmente de campo, foram dirigidos para a caracterização sedimentar detalhada das unidades ricas em matéria orgânica do Jurássico Inferior e melhoramento dos quadros estratigráficos e sequenciais. Estas questões são abordadas nos subcapítulos 3.1. e 4.1. Nestes são apresentados os perfis estratigráficos de alta resolução de S. Pedro de Moel, Peniche, Rabaçal e Tomar. Em relação à Formação de Cabaços foram estudados os perfis de Cabo Mondego, Pedrogão e Vale de Ventos (subcapítulo 5.1). Os trabalhos previamente efetuados por Azerêdo e colaboradores, complementada por novas observações de campo, serviram de base para a amostragem.

1.1.2.2. Caracterização geoquímica dos sedimentos e da matéria orgânica (incluindo Palinofácies e Biogeoquímica)

Esta segunda etapa teve como finalidade a caracterização dos sedimentos e da matéria orgânica através de determinações de Carbono orgânico Total (subcapítulos 2.1., 3.1., 4.2., 4.3. e 5.1.), geoquímica isotópica (isótopos estáveis de carbono, oxigénio e nitrogénio, subcapítulos 3.2. e 4.2.), pirólise *Rock-Eval* (subcapítulo 3.1.), Palinofácies (subcapítulos 3.1., 3.2., 4.3. e 5.1.) e Biogeoquímica (subcapítulo 4.3.). Nestes trabalhos é apresentada a caracterização ótica e geoquímica de detalhe das séries em estudo, onde são também discutidos os parâmetros ambientais contemporâneos da sedimentação.

1.1.2.3. Cronologia relativa, amplitude, causas e consequências dos eventos que conduziram à preservação da matéria orgânica

Esta discussão está presente em todas as secções que compõem o corpo principal desta tese, sustentada pela abordagem multidisciplinar que orientou a sua realização. O cumprimento deste objetivo depende claramente da compreensão das condições paleoambientais e paleoceanográficas correlativas da sedimentação do Jurássico a num nível local-regional-global (subcapítulos 3.1., 4.1., 4.2., 4.3. e 5.1.) ou dos processos condicionantes dos ciclos biogeoquímicos de alguns elementos, como o carbono (subcapítulos 3.2. e 4.1.).

Capítulo 2 | Uma introdução ao Jurássico Inferior e os intervalos ricos em matéria orgânica

2.1. Organic-rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total Organic Carbon distribution and relation to transgressive regressive facies cycles

Luís V. Duarte, Ricardo L. Silva, Luiz C.V. Oliveira, María J. Comas-Rengifo, Francisco Silva, 2010, Geologica Acta, 8 (3), 325–340

Abstract

The upper Sinemurian to Pliensbachian series of the Lusitanian Basin (Portugal) correspond to marly limestone sediments rich in benthic and nektonic macrofauna. This sedimentary record includes several intervals of organic-rich facies, which are particularly well developed in the western sectors of the basin. They correspond to grey and dark marls locally showing strong lamination (black shale type) and are recognized as one of the most important potential oil source rocks. This study shows the vertical and lateral distribution of these organic-rich intervals, supported by over 550 total organic carbon (TOC) determinations. The results presented reveal two important intervals, with several black shale occurrences, in the Oxynotum(?)–Raricostatum (Polvoeira Member of Água de Madeiros Formation) and at the top of the Ibex-upper part of Margaritatus zones (top of the Vale das Fontes Formation), showing in the distal (western) sectors up to 22% and 15% TOC, respectively. TOC values decrease progressively towards the proximal sectors, the youngest organic-rich interval being the most expressive at the basin scale. This lateral TOC distribution, the facies stacking patterns and the decrease observed in benthic macrofauna confirm that these intervals are related to 2nd-order transgressive phases. 2nd-order regressive phases, developed during the uppermost Raricostatum and Spinatum zones respectively, show lower TOC values. TOC distribution combined with other stratigraphic and sedimentological parameters enabled seven facies maps to be created for the time interval studied. At the regional scale, this study shows for the first time the good similarity between the upper Sinemurian-Pliensbachian sedimentary successions of the Lusitanian and Basque-Cantabrian basins.

Keywords: Lusitanian Basin, Portugal, Early Jurassic, Água de Madeiros Formation, marly limestones, black shales, source rock

2.1.1. Introduction

In Portugal, the Lower Jurassic sedimentary record is particularly well represented in the western margin (Lusitanian Basin, hereinafter called LB) of the Variscan Iberian Massif. It corresponds to a thick carbonate succession, comprising up to 550 m of mostly marl-limestone alternations, characterizing much of the upper Sinemurian–Toarcian series of the basin (Soares et al., 1993; Duarte and Soares, 2002; Duarte et al., 2004b). These facies, comprising abundant nektonic and benthic macrofauna, are included in the Upper Triassic–Callovian 1st-order cycle (Wilson et al., 1989; Soares et al., 1993; Duarte, 1997; Azerêdo et al., 2002, 2003; Duarte et al., 2004b) and are associated with a palaeogeography controlled by an epicontinental sea, sustained by a low-gradient carbonate ramp dipping towards the northwest (Duarte, 1997, 2007; Duarte et al., 2004b). In this geological context, the upper Sinemurian–Pliensbachian interval is characterized by the occurrence of organic-rich facies regarded as a potential oil source rock (Oliveira et al., 2006).

The first aim of this paper, through the study of several key-sections of the LB (Tomar, Rabaçal, Coimbra, Anadia, Montemor-o-Velho, Figueira da Foz, S. Pedro de Moel and Peniche; Fig. 2.1.1), involves characterizing the marly units with accompanying organic-rich levels, based on a detailed ammonite biostratigraphy and other biotic and abiotic parameters.

The second objective is to quantify the total organic carbon (TOC) in these facies, showing its basin wide vertical and lateral variation. This procedure has allowed the creation of several facies maps based on organic facies and TOC distribution. Apart from constituting a key stratigraphic marker and a tool in the intrabasinal correlation of the several studied sections, TOC is also useful in terms of sequence stratigraphy interpretation of the series, particularly in the identification of 2nd-order transgressive-regressive sequences or the equivalent transgressive-regressive facies cycles (T-R facies cycles *sensu* de Graciansky et al., 1998; Jacquin and de Graciansky, 1998a, 1998b). Thus, we compared the sequential scheme already presented for the LB (e.g. Duarte et al., 2004b; Duarte, 2007) with others from neighbouring basins, emphasizing the main similarities in terms of regional transgressive and regressive events.

2.1.2. Geological setting and lithostratigraphy

During the Early Jurassic, the LB was characterized by carbonate sedimentation (Soares et al., 1993; Azerêdo et al., 2003; Duarte et al., 2004b). The Sinemurian-

Pliensbachian series show important changes in the depositional system, from lower-upper Sinemurian peritidal facies (Coimbra Formation; Azerêdo et al., 2008; subsequently denominated as Fm.) to Pliensbachian hemipelagic deposits (including the Vale das Fontes and Lemede formations; Duarte and Soares, 2002) (Fig. 2.1.2). However, in the western sectors of the basin, such as Peniche, S. Pedro de Moel, Figueira da Foz and Montemor-o-Velho, hemipelagic deposition started earlier during the late Sinemurian (Oxynotum-Raricostatum zones; Água de Madeiros Fm.; Duarte and Soares, 2002; Duarte et al., 2004b, 2006) (Fig. 2.1.2).

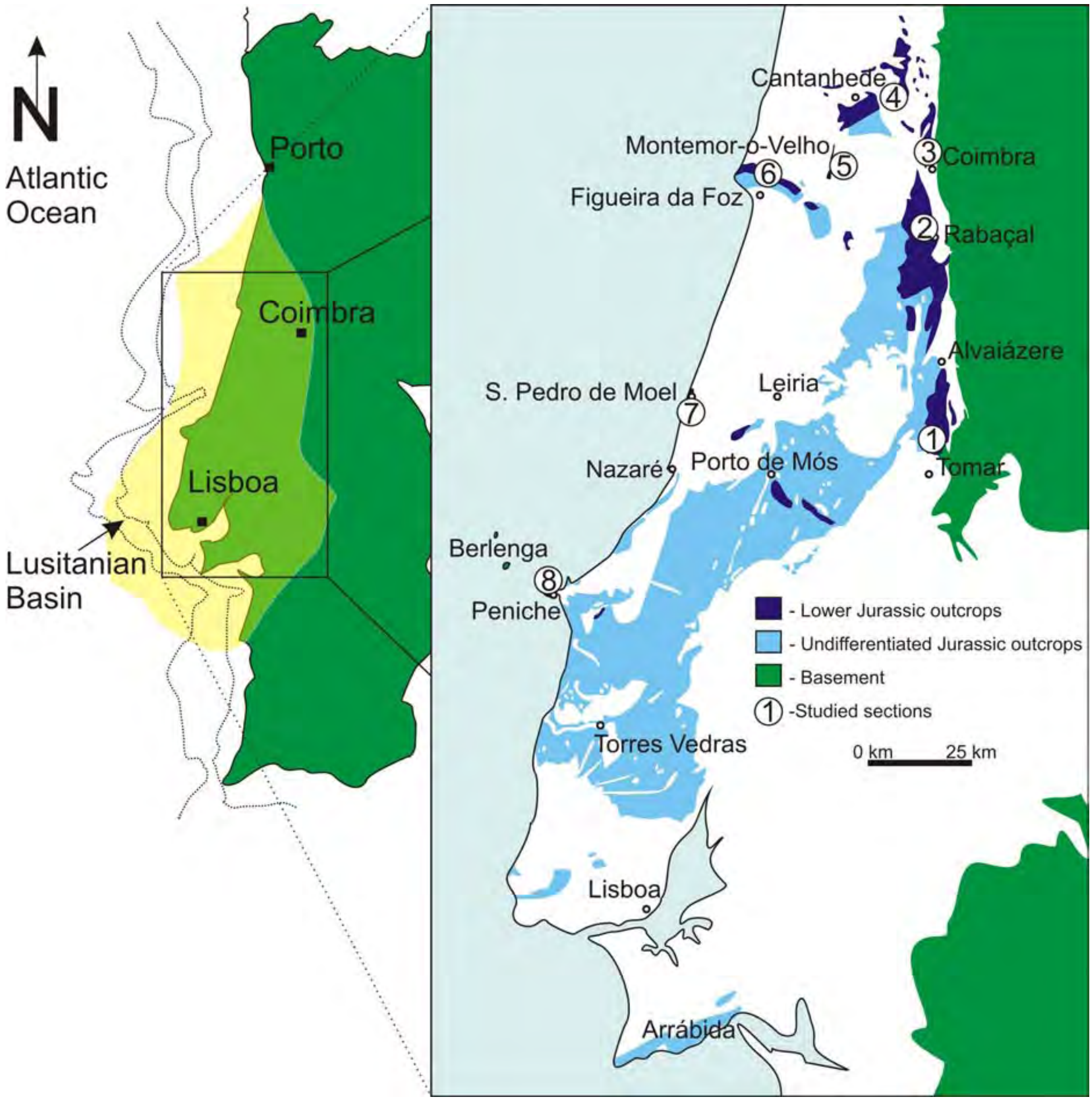


Fig. 2.1.1. Geological map of Jurassic in the Lusitanian Basin. Location of the main studied Sinemurian–Pliensbachian outcrops: 1) Tomar; 2) Rabaçal; 3) Coimbra; 4) Anadia-Cantanhede; 5) Montemor-o-Velho; 6) Figueira da Foz; 7) S. Pedro de Moel; 8) Peniche.

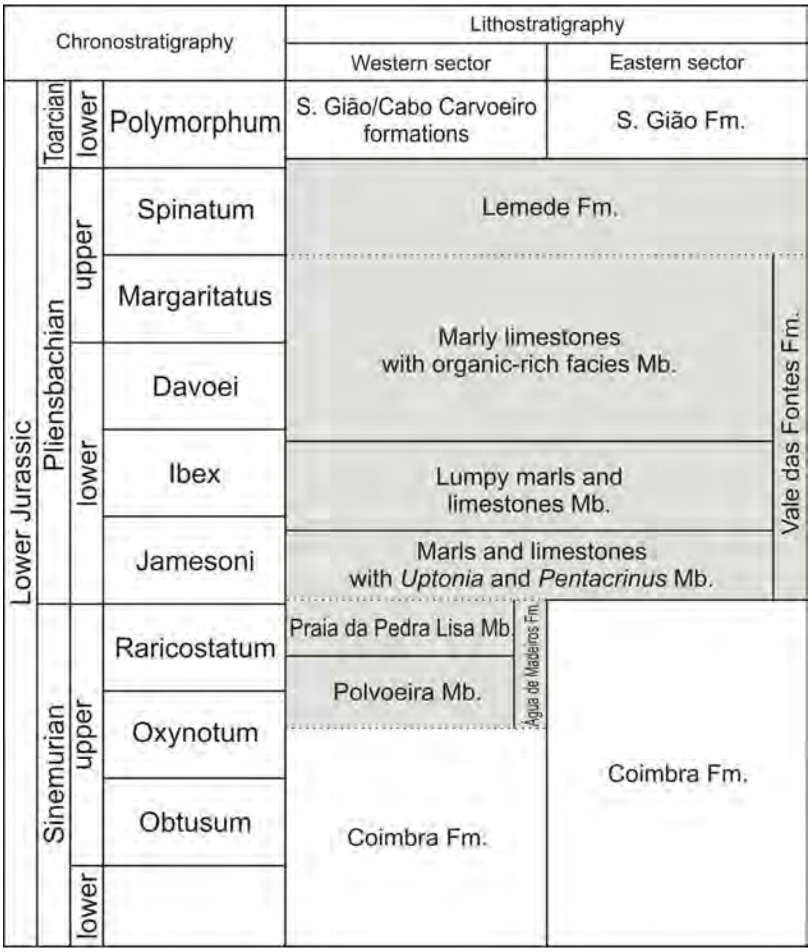


Fig. 2.1.2. Lithostratigraphic chart for the Sinemurian–lowermost Toarcian series of the Lusitanian Basin (Duarte and Soares, 2002). Light grey corresponds to the studied units.

All these units are characterized by different marl/limestone relations, organic matter content and specific benthic/nektonic macrofauna and microfauna. As a result of the ramp morphology, controlled by regional tectonics and relative sea level changes, the thickness of these series increases in the western sectors, which are biostratigraphically well constrained by ammonites and calcareous nannofossils (e.g. Mouterde, 1955, 1967; Antunes et al., 1981; Phelps, 1985; Dommergues, 1987; Dommergues et al., 2004; Mouterde et al., 2007; Oliveira et al., 2007).

2.1.2.1. Água de Madeiros Formation

This unit, belonging to the Oxynotum-Raricostatum zone interval, rests over the inner-shelf Coimbra Fm., which is composed of dolomitic and calcareous facies, more or less bioclastic/fossiliferous (Azerêdo et al., 2008). The Água de Madeiros Fm. has been subdivided into two members: the Polvoeira Member (Member henceforth known as Mb.) at the base and the Praia da Pedra Lisa Mb. at the top (Figs. 2.1.2, 2.1.3). These two units are particularly well exposed along the coastal sections of S. Pedro de Moel (Água de Madeiros-Polvoeira area), where their type-sections are defined (Duarte and Soares, 2002; Duarte et al., 2004b, 2006) (Fig. 2.1.4). Here, the base of Polvoeira Mb. consists of marl-limestone alternations that become progressively more argillaceous, presenting several organic-rich facies horizons. The middle-upper part of this member is a rhythmic succession with marl/limestone ratios around 1.5 to 2.

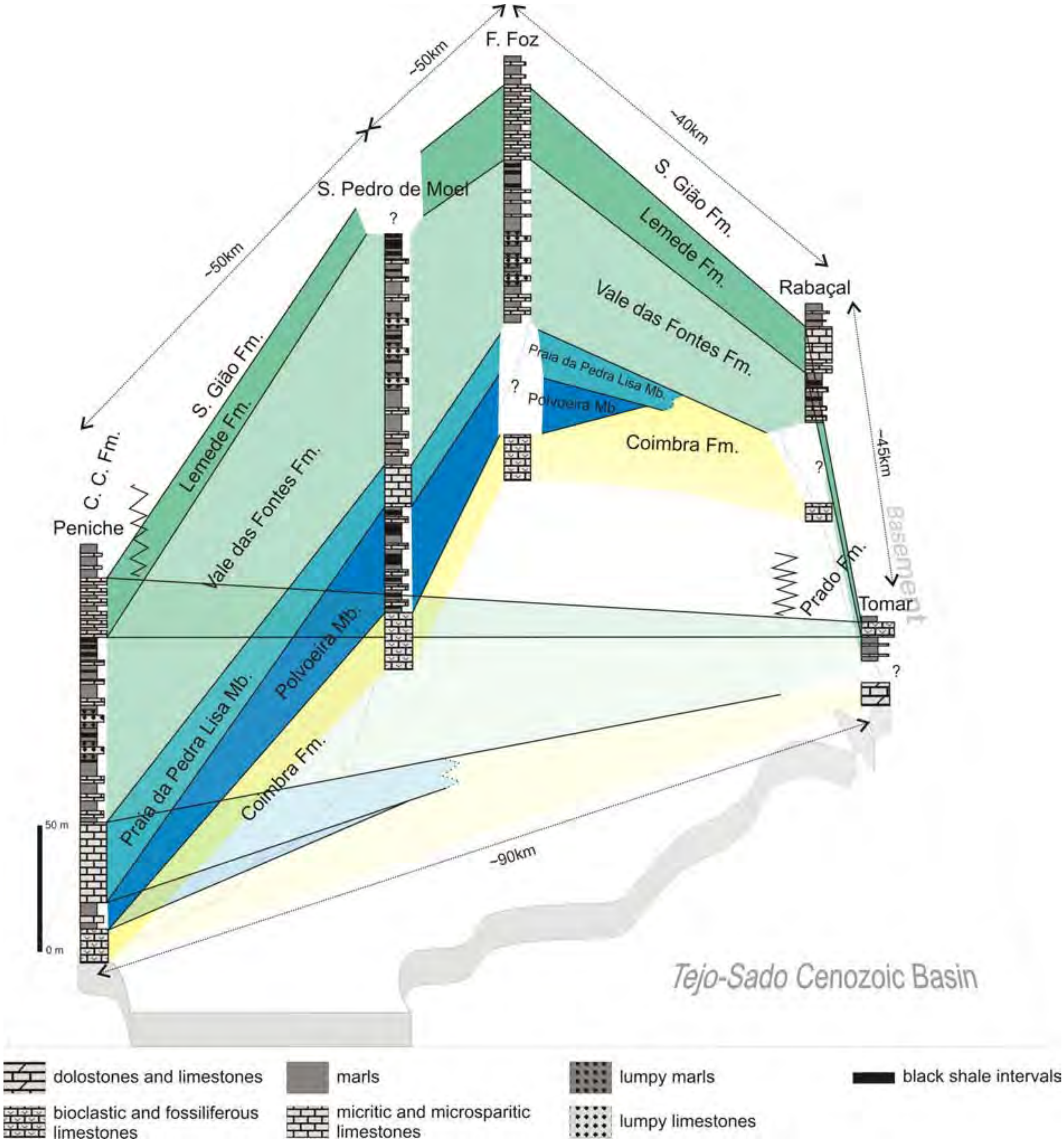


Fig. 2.1.3. Lateral and vertical sedimentary variation of the uppermost Sinemurian–lowermost Toarcian marly limestone series in the Lusitanian Basin. Synthetic logs of Tomar, Rabaçal, Figueira da Foz, S. Pedro de Moel and Peniche.

This member is rich in benthic (bivalves, brachiopods) and nektonic (ammonites and belemnites) macrofauna, with a clear inverse distribution of these two groups across the unit: abundant benthic fauna at the base (*Pholadomya*, *Gryphaea, Pleuromya, Zeilleria, Cincta, Piarorhynchia*, *Spiriferina*, etc); nektonic fauna increasing in abundance towards the top. Some horizons (mainly laminated limestones) are rich in ammonites (Echioceratids and Oxynoticeratids).

Limestones generally correspond to fossiliferous wackestones that are sometimes rich in ostracods, molluscs and organic matter. At S. Pedro de Moel the thickness of this member is approximately 42 m (Fig. 2.1.4), decreasing to 10 m in Peniche and Montemor-o-Velho. The Praia da Pedra Lisa Mb. is predominantly calcareous (wackestones to grainstones). Thickness and vertical facies arrangements are very different at several points of the basin, such as Peniche (around 30 m thick) and S. Pedro de Moel (around 16 m thick). In its type-section, located in the Praia de Água de Madeiros (Fig. 2.1.4), 2km south of S. Pedro de Moel, the Praia da Pedra Lisa Mb. is included in the uppermost Raricostatum-lowermost Jamesoni zone interval (Duarte and Soares, 2002). Here, this member begins (around 9 m) by decimetre- to centimetre-thick microspar limestones (wackestones very rich in ostracods and radiolarians), with planar lamination, *Rhizocorallium* and *Thalassinoides*. Some surfaces at the top of the unit are rich in tiny ammonites (*Gemmellaroceras* sp.), but benthic macrofauna is very scarce. The upper part, approximately 7 m thick, is marked by a gradual increase in interbedded centimetre-scale grey to dark marls and a sharp thickening of the limestone beds. These limestones consist of fossiliferous micrites to biomicrites/wackestones with molluscs and ostracods. Nektonic macrofauna is common, comprising belemnites and large Apoderoceratids, such as *Apoderoceras subtriangulare* (YOUNG and BIRD) among others, and which have been attributed by Edmunds et al. (2003) to the Jamesoni Zone, Taylori Subzone.

2.1.2.2. Vale das Fontes Formation

The Vale das Fontes Fm., ranging in age from the lowermost Jamesoni to the uppermost Margaritatus zone interval, represents the return to a marly sedimentation, widespread across the whole basin. It is particularly well exposed in the western part of the basin, where it is approximately 75-90 m thick (namely in Peniche; Fig. 2.1.4) and is subdivided into three informal members: Marls and limestones with *Uptonia* and *Pentacrinus*

(MLUP) Mb., Lumpy marls and limestones (LML) Mb. and Marly limestones with organic-rich facies (MLOF) Mb.

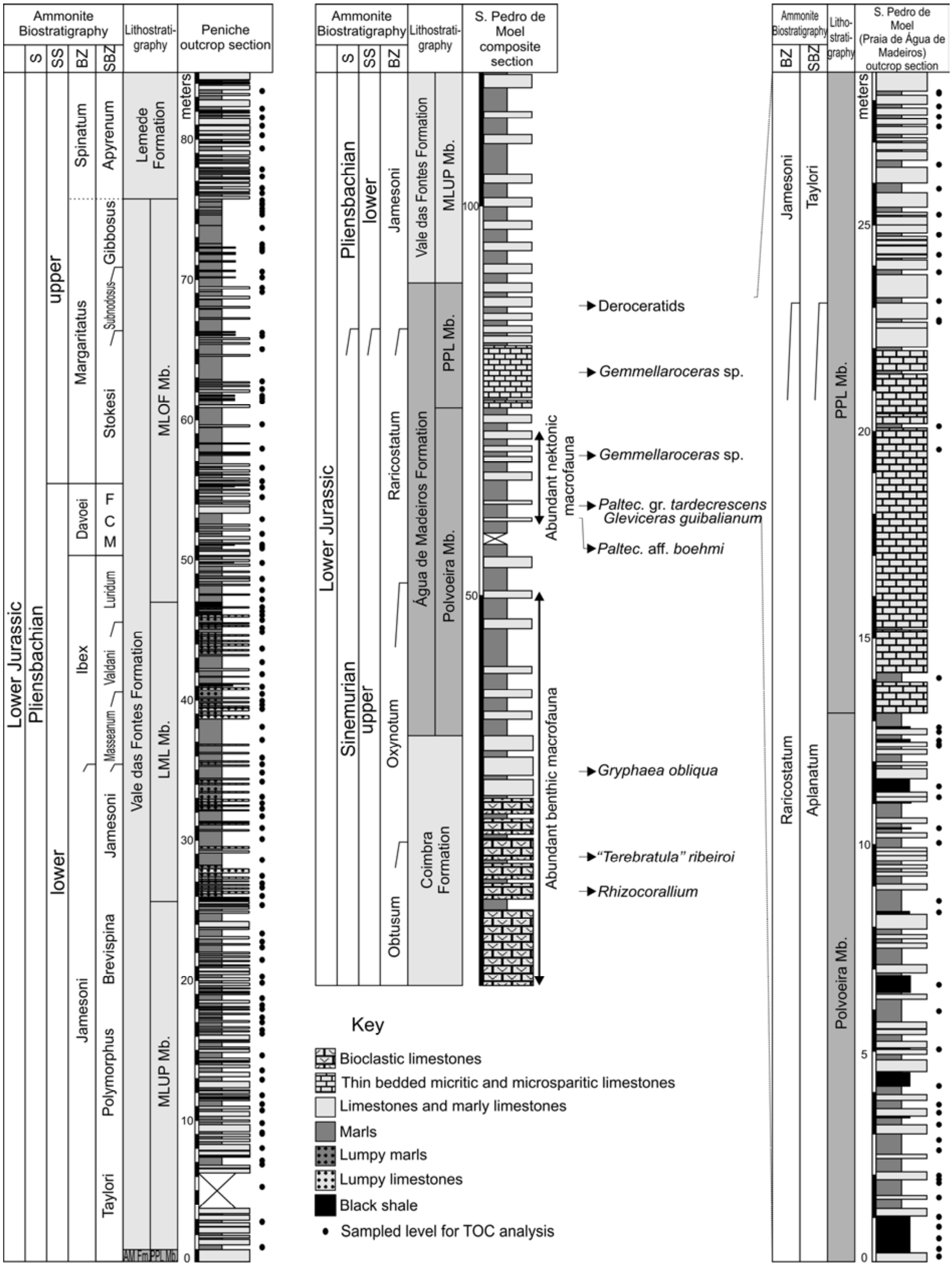


Fig. 2.1.4. Type-sections of the Água de Madeiros (S. Pedro de Moel area) and Vale das Fontes (Peniche) formations in the Lusitanian Basin.

MLUP Mb. This unit is characterized by bioturbated decimetre marl/centimetre-thick marly limestone alternations, with nektonic and benthic macrofauna, comprising crinoids, brachiopods and bivalves. The microfacies consist of fossiliferous micrites to biomicrites/wackestone. Across the basin, an increase is observed in the marly character from the proximal to the distal sectors, where this unit is dated as Jamesoni Zone, involving the Taylori-Jamesoni subzone interval. This member reaches approximately 35 m in Montemor-o-Velho and 25 m in Peniche, two points of the basin where the entire member can be observed.

LML Mb. This unit is defined by the occurrence of lumpy facies (Hallam, 1971; Dromart and Elmi, 1986; Elmi et al., 1988; Fernández-López et al., 2000), interbedded in a marl-limestone succession. The lumps consist of micritic grumose concretions, generally subspherical-shaped and reaching several centimeters (up to 3 cm) in size. The composition of these concretions appears to be a microbial origin, showing some cryptalgal oncolite structures (Dromart and Elmi 1986; Elmi et al. 1988). Interbedded in these facies, metricscale grey to dark marls occur. In this member, benthic macrofauna is scarce but ammonites and belemnites are always present. This unit, with about 21 m at Peniche and 22 m at Figueira da Foz, ranges from the Jamesoni to the Luridum subzone interval.

MLOF Mb. This unit is characterized by an increase of the marly terms of the series, alternating with centimeter thick limestone facies, locally with diverse and abundant tiny benthic macrofauna (ostreids, crinoids and brachiopods), ammonites and belemnites. In the distal regions, such as the Peniche, S. Pedro de Moel and Figueira da Foz sectors, organic-rich sediments are particularly abundant. This member comprises the Luridum Subzone (topmost of Ibex Zone) to the uppermost Margaritatus Zone interval and ranges from 10 m at Tomar to around 20 m at Rabaçal and 28/29 m at Figueira da Foz and Peniche.

2.1.2.3. Lemede Formation

This unit generally comprises centimetre marl/decimeter limestone bioturbated alternations, very rich in belemnites, ammonites, bivalves and brachiopods. In the southeastern part of the LB, such as Tomar, facies are much more bioclastic (packstone to grainstone) and locally dolomitic, with a diversified benthic macrofaunal component (large bivalves and brachiopods). This unit ranges in age from the Spinatum Zone to the lowermost part of Polymorphum Zone, reaching a thickness of approximately 30 m to the northwest.

2.1.3. Studied sections and methods

For this contribution we have revised all the important and classic sections characterizing the upper Sinemurian and Pliensbachian hemipelagic deposits of the LB (Duarte and Soares, 2002; Duarte et al., 2004b, 2006; Oliveira et al., 2006; Silva et al., 2007). TOC content was analyzed in approximately 550 samples from eight key-sections (Fig. 2.1.1), chosen due to the occurrence of organic-rich facies, good biostratigraphic control and other stratigraphic and sedimentological (e.g. petrographic and mineralogical data) criteria. The intervals richer in organic matter were analyzed in greater detail, as in the cases of the Rabaçal (Upper Sinemurian and Davoei-Spinatum zone interval), Coimbra (Jamesoni-Margaritatus zone interval), Montemor-o-Velho (Raricostatum-Jamesoni zone interval), Figueira da Foz (Jamesoni-Margaritatus zone interval), S. Pedro de Moel (Oxynotum-Jamesoni and Davoei-Margaritatus zone intervals; Fig. 2.1.4) and Peniche (Raricostatum-Spinatum zone interval; Fig. 2.1.4) sections. Despite the good biostratigraphic data available for most of the sections (see references above), new ammonite data enabled stratigraphic boundaries to be improved, particularly in the case of the Raricostatum and Davoei-Margaritatus zone interval.

TOC content was determined with a Leco SC-444 analyzer in the Universidade do Estado do Rio de Janeiro and Cenpes-Petrobras (Brazil), with an analytical precision of ± 0.1%. The results are presented in weight percent (wt %) and in every ten samples analyzed a duplicated analysis was performed. The equipment was calibrated daily with standards, before analyses were initiated.

2.1.4. Organic-rich facies: age calibration and TOC values

The organic-rich facies are quite similar in all the studied series and are characterized by a grey to dark colour, generally with a net lamination and, locally, abundant pyrite. These facies include black shales, dark grey marls and laminated limestones. In the whole upper Sinemurian-Pliensbachian succession, the black shales are generally thin (a few cm) but in the uppermost Sinemurian (middle part of Polvoeira Mb.) of S. Pedro de Moel area they are thicker, locally reaching 50 cm. Generally, black shales are not bioturbated but, in a few organic-rich facies, the ichnogenus *Chondrites* occurs. In addition, the main inorganic components include carbonate (practically limited to calcite), clay minerals (mainly illite and 10-14 mixed layer minerals; small amounts of kaolinite, chlorite and vermiculite) and some quartz (e.g. Duarte et al., 2007b).

In terms of stratigraphic distribution, organic-rich facies occur in the latest Sinemurian to the earliest part of the late Pliensbachian, involving the Água de Madeiros and Vale das Fontes formations. Black shales occur in all members of these two formations and are recognized in all ammonite biostratigraphic zones. According to Fig. 2.1.5, which summarizes the vertical and lateral distribution of TOC in several studied sections, two intervals particularly rich in organic-rich facies and with high TOC values are observed: top of the Oxynotum-Raricostatum (Polvoeira Mb.) and top of the Ibex-Margaritatus (MLOF Mb.) zones.

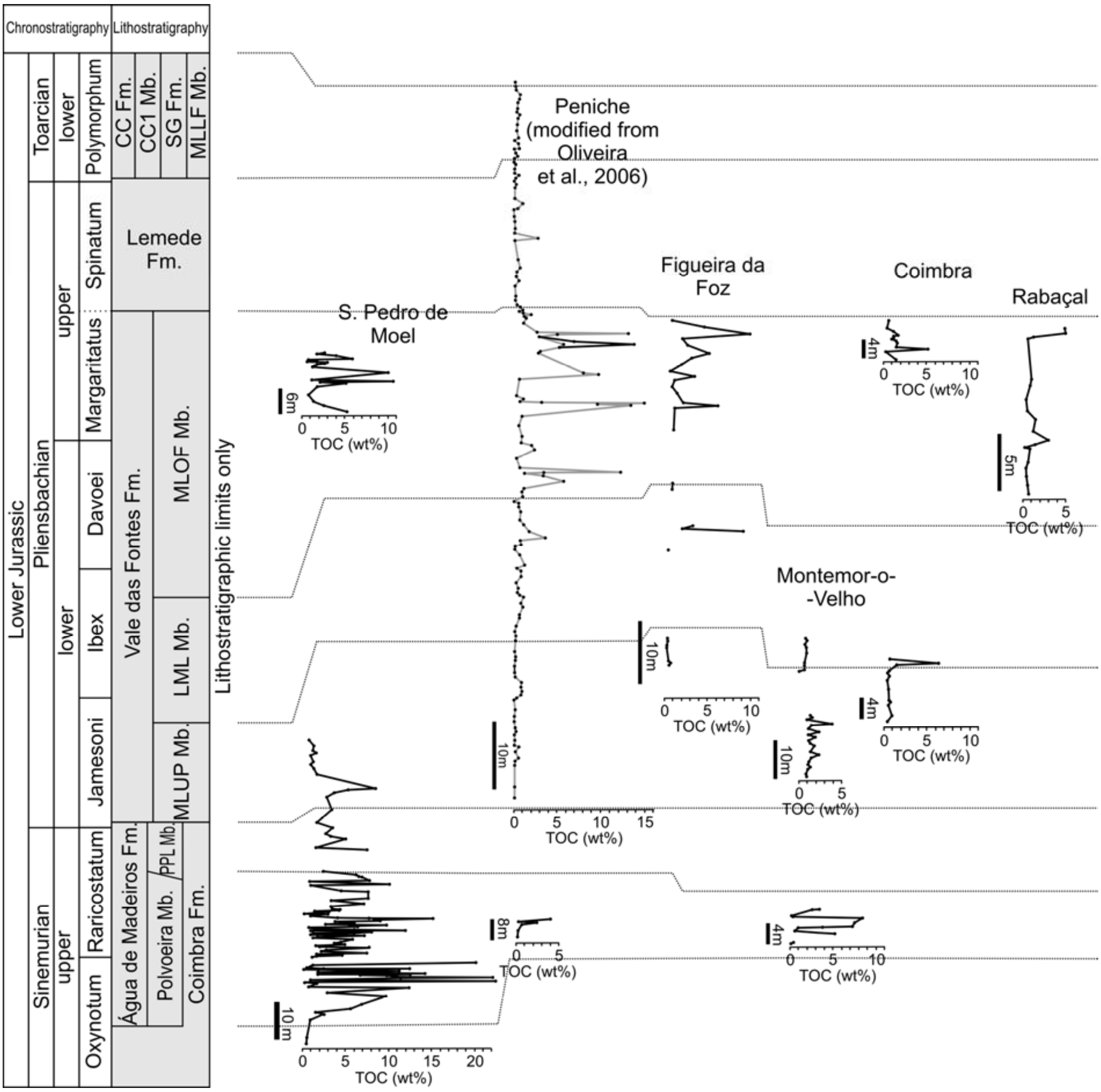


Fig. 2.1.5. TOC distribution in the uppermost Sinemurian–Pliensbachian of the Lusitanian Basin (abbreviations as explained in text except for Cabo Carvoeiro Fm.: CC Fm., Cabo Carvoeiro 1 Mb.: CC1 Mb., S. Gião Fm.: SG Fm. and Marly-limestones with *Leptaena* Facies Mb.: MLLF Mb.).

2.1.4.1. Oxynotum-Raricostatum zone interval

The highest and major number of levels with high TOC values of the LB, are observed in this first stratigraphic interval, but lateral distribution of organic-rich facies in the basin is restricted to the western sectors. In the particular case of S. Pedro de Moel, where the succession is thicker, TOC values reach up to 22% in two horizons (Oxynotum(?)-base of Raricostatum Zone). Here, the TOC background values of the Polvoeira Mb. is generally above 1%, and 50% of the samples analyzed show TOC values higher than 5-6% (Fig. 2.1.5). Aside from these two peaks, several values above 10% can be found in the upper part of the Raricostatum Zone. This Zone is well constrained by an abundant ammonite record [levels with *Paltechioceras boehmi* (Hug), *Leptechioceras meigeni* (Hug), *Paltechioceras tardecrescens* (Hauer), *Gleviceras guibalianum* (D'Orbigny) and *Paltechioceras romanicum* (Uhlig)], belonging to the Raricostatum, Macdonnelli and Aplanatum subzones which, to date, have only been recognized in S. Pedro de Moel (Fig. 2.1.4). The top of the Oxynotum Zone (?), particularly rich in benthic macrofauna (bivalves and brachiopods) and very poor in ammonites, shows the first organic-rich facies, which reaches the maximum TOC value of 7.4 %.

Laterally, like the thickness of the marly facies, TOC values decrease abruptly towards the north and south of S. Pedro de Moel, reaching the maximum values of 8% In Montemor-o-Velho, black shales are well recognized in some levels, generally with TOC values above 2.5%.

According to new ammonite data (unpublished) collected in these two sectors, the highest TOC values are located at levels that appear to be laterally correlative and dated from the Macdonnelli and Aplanatum subzones.

2.1.4.2. Top of Ibex-Margaritatus zone interval

This interval corresponds to the MLOF Mb. (Figs. 2.1.2-5), which constitutes the most organic-rich part of the Vale das Fontes Fm.. TOC contents of the studied samples in the basin show the maximum value of 15% in both the Peniche and S. Pedro de Moel sectors. Laterally, high values of this parameter are distributed widespread, reaching up to 9.8% in Figueira da Foz, 5.2% in Coimbra and 4.8% in Rabaçal. Detailed analysis of the vertical variation of TOC in distal sectors of the basin (Fig. 2.1.5) enables three intervals rich in organic facies to be defined that, in Peniche, present values of 12, 15 and 15%, respectively. These intervals are dated as Davoei (levels with Aegoceras and Liparoceras), the basal part of Margaritatus [Stokesi Subzone, levels with Protogrammoceras cf. celebratum (Fucini)] and the upper part of the Margaritatus (between Subnodosus and Gibbosus subzones) zones, respectively. The latter interval is clearly the thickest and laterally the richest in TOC values, even in the proximal parts of the basin, such as Coimbra and Rabaçal (around 5%).

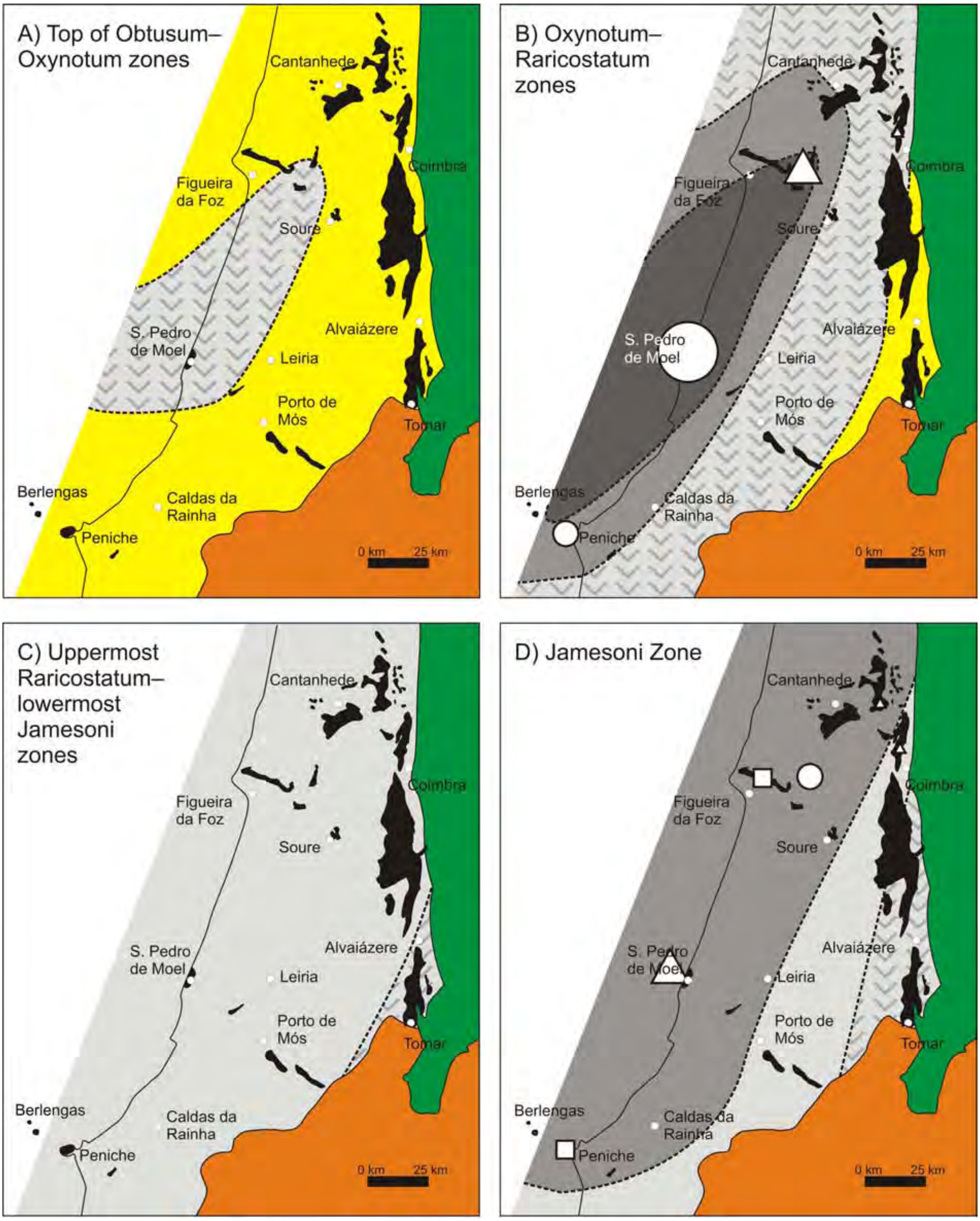
2.1.4.3. Other intervals

According to Fig. 2.1.5, TOC values are generally low in the other marly units of the basin. There are, however, some other interesting stratigraphic reference points. In the Jamesoni Zone, the TOC content is generally below 1%, but at S. Pedro de Moel can reach 5-8% in several thin black shales. In the Ibex Zone, and in spite of the low TOC background values, a thin organic-rich horizon is observed throughout the basin, showing values of 9.1% in Figueira da Foz, 7.3% in Cantanhede, 6.5% in Coimbra, and 4% in Peniche.

2.1.5. Areal distribution of the organic-rich facies

As presented above, in the LB the Sinemurian marks an important sedimentary transition, from shallow-water dolomites and limestones (Coimbra Fm.) to hemipelagic deposits. The high-resolution stratigraphy and TOC data obtained in this study allow, for the first time, the construction of detailed spatial facies maps, showing the different stages of development (Obtusum Biochron) and the top of the Pliensbachian (Spinatum Biochron). These maps correspond to the following time intervals (Figs. 2.1.6A to 2.1.6G): Top of Obtusum-Oxynotum(?) biochrons (top of Coimbra Fm.), Oxynotum(?)-Raricostatum biochrons (Polvoeira Mb.), uppermost Raricostatum-base of Jamesoni biochrons (Praia da Pedra Lisa Mb.), Jamesoni Biochron (MLUP Mb.), Jamesoni-upper Ibex biochrons (LML Mb.), uppermost Ibex-top of Margaritatus biochrons (MLOF Mb.) and Spinatum-extreme base of Polymorphum biochrons (Lemede Fm.).

According to Fig. 2.1.3, the thickness of the different units increases from the southeastern proximal part of the basin (Tomar region) towards the northwest sector (Figueira da Foz region; distal region), following the direction of the dipping ramp. Well-developed organic-rich facies, where TOC values are always very high throughout the whole succession, are practically restricted to the western part of the basin. During the late Sinemurian, these facies were centred in the distal sectors, whereas in the Pliensbachian, black shales with higher TOC values reach several eastern sectors of the basin, such as Coimbra and Rabaçal (Figs. 2.1.6B and 2.1.6F).


A) Top of Obtusum–Oxynotum zones
B) Oxynotum–Raricostatum zones
C) Uppermost Raricostatum–lowermost Jamesoni zones
D) Jamesoni Zone
Cantanhede
Coimbra
Figueira da Foz
Soure
Alvaiázere
S. Pedro de Moel
Leiria
Porto de Mós
Tomar
Berlengas
Caldas da Rainha
Peniche
0 km
25 km

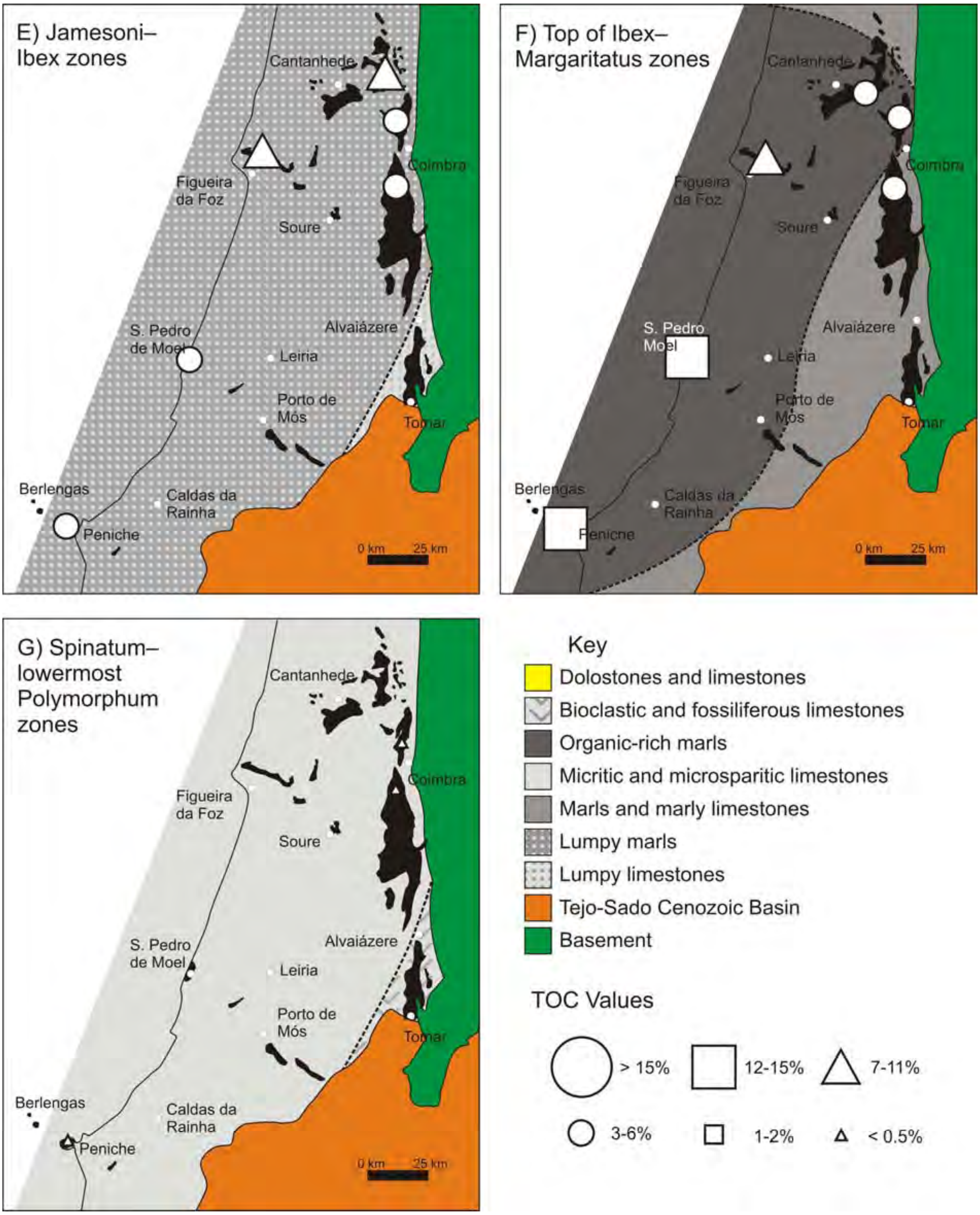


Fig. 2.1.6. (includes the previous page) Facies maps and TOC distribution for the studied interval. A) top of Obtusum-Oxynotum zones (top of Coimbra Fm.); B) Oxynotum–Raricostatum zones (Polvoeira Mb.); C) uppermost Raricostatum–lowermost Jamesoni zones (Praia da Pedra Lisa Mb.); D) Jamesoni Zone (MLUP Mb.); E) Jamesoni–Ibex zones (LML Mb.); F) top of Ibex–Margaritatus zones (MLOF Mb.); G) Spinatum–lowermost Polymorphum zones (Lemede Fm.).

2.1.6. TOC variation related to T-R facies cycles

Apart from the importance of TOC as palaeoenvironmental and palaeogeographic markers in the studied series, this parameter is also decisive in sequence stratigraphic analysis and in the recognition of T-R facies cycles (e.g. Quesada et al., 2005). Indeed, the marly accumulation of the Polvoeira and MLOF members, the TOC-richer units of the whole Early Jurassic of the LB, are correlated with maximum flooding intervals, associated with 2nd-order transgressive phases in the Sinemurian (Sequence SS) and Pliensbachian (Sequence SP) (see Duarte et al., 2004b; Duarte, 2007). On the other hand, absence of black shales and low TOC values, observed in the base of Praia da Pedra Lisa Mb. and Lemede Fm., are both related with 2nd-order regressive phases (Fig. 2.1.7).

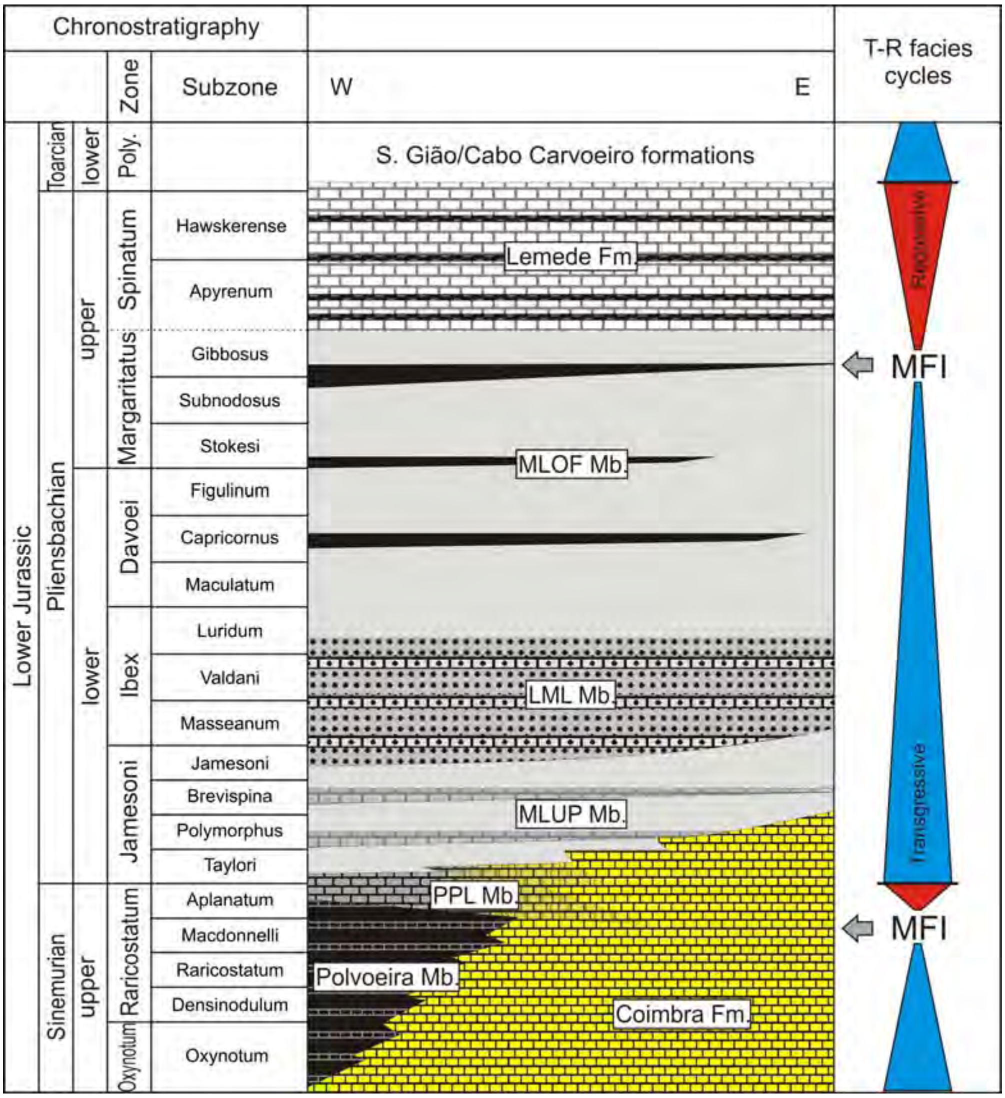


Fig. 2.1.7. General facies stratigraphic chart and 2nd-order transgressive–regressive facies cycles for the uppermost Sinemurian–lowermost Toarcian of the Lusitanian Basin. Arrow: major black-shale intervals; MFI: maximum flooding interval (abbreviations as explained in text).

2.1.6.1. Sinemurian 2nd-Order T-R Facies Cycle

Despite the limited observational conditions (few and discontinuous outcrops), dolomitization, lack of biostratigraphic control and other sedimentary features, knowledge of Sinemurian carbonates in the eastern part of the basin (Coimbra Fm.; Figs. 2.1.1, 2.1.3, 2.1.7) does not allow a good sequential scheme to be constrained. However, the study of some sections located in the western part, allows interpretation of the sequential evolution (2nd-order) for the Early to Late Sinemurian. In a recent study, Azerêdo et al. (2008) demonstrated that the lower carbonate facies of the Coimbra Fm. in Praia da Concha (North of S. Pedro de Moel), correspond to the onset of a large transgressive event, with the occurrence of several microbial structures and stromatolitic mounds, which possibly marks the basal limit of the Sinemurian T-R facies cycle. The middle-top of the Oxynotum Zone (?), which marks the base of the Água de Madeiros Fm. in S. Pedro de Moel (Duarte and Soares, 2002; Duarte et al., 2004b), is represented by the first occurrence of marl/limestone alternations of the LB, very rich in benthic macrofauna (mainly brachiopods and bivalves). This lutitic sedimentation is also coupled with an increase in organic matter content and TOC values (marls generally above 1%). Despite the high TOC values (maximum of 22%) observed at some levels (Fig. 2.1.5), organicrich facies are restricted to the S. Pedro de Moel area, which confirms a local hemipelagic deposition (Figs. 2.1.6A-B, 2.1.7). During the Raricostatum Zone (upper part of the Polvoeira Mb.), the great abundance of ammonites and calcareous nannofossils (Duarte et al., 2006), the sharp decrease in benthic macrofauna and the spreading of black shales to other parts of the basin (maximum TOC values of 15% in S. Pedro de Moel, 8.4% in Montemor-o-Velho and 4.1% in Peniche) are criteria to mark the maximum flooding interval of this T-R facies cycle. Occurrences of *Paltechioceras* gr. *Tardecrescens* (Hauer) and *Gleviceras guibalianum* (D'Orbigny) date this event in the Aplanatum Subzone.

The regressive phase of this cycle corresponds almost fully to the lower part of the Praia da Pedra Lisa Mb. However, in S. Pedro de Moel, this progradational phase appears to begin in the middle-upper part of the Polvoeira Mb. (Fig. 2.1.7), marked by a slight decrease in TOC values (Fig. 2.1.5 and an increase of limestone (Fig. 2.1.4). The above mentioned facies of the Praia da Pedra Lisa Mb. (thin bedded micritic and microsparitic limestones in Fig. 2.1.4), clearly indicate an evolution towards a shallow-marine palaeoenvironment. The last level with this kind of facies, recorded at the Água de Madeiros beach (e.g. Duarte and Soares, 2002; Duarte et al., 2006), marks the top of the Sinemurian T-R facies cycle. This limit is overlain by decimetre-thick argillaceous limestones, interbedded with centimetre-thick grey shales, and shows a gradual upward increase in the clay and macrofossil contents (base of SP in Duarte et al., 2004b). Laterally, the top of the Sinemurian T-R facies cycle is composed by bioclastic/packstones-grainstones.

2.1.6.2. Pliensbachian 2nd-order T-R facies cycle

The basal limit of the Pliensbachian T-R facies cycle, dated roughly from the Sinemurian/Pliensbachian boundary, is well observed in the S. Pedro de Moel area (Água de Madeiros beach) and at Peniche, and represents the first 2nd-order flooding event recognized at a basinal scale (Fig. 2.1.6D; see Duarte et al., 2004b; Duarte, 2007). The Pliensbachian succession shows a typical 2nd-order sequence, with dominant marly deposition at the base (lower Pliensbachian to lower upper Pliensbachian) and a calcareous dominant facies at the top (uppermost Pliensbachian to extreme base of early Toarcian).

The Pliensbachian series shows a large transgressive phase that includes marlstones, argillaceous and lumpy limestones, grey to dark marls and thin (millimetre-thick) black shales, ranging from the Jamesoni to Margaritatus zones (Figs. 2.1.6D-F). In the LML Mb., the interplay of these lithofacies (lumpy marls and limestones and grey marls) has been well observed and studied at Peniche and Figueira da Foz (Elmi et al. 1988; Fernández-López et al. 2000). According to Fernández- López et al. (2000) the series is organized into sets (4^{th}-order sequences) of elementary sequences (5th-order sequences), each one comprising at the base a grey marly interval (sometimes with TOC above 1%) and end by an increase of calcareous and lumpy facies. Thus, TOC variation in LML Mb. seems to be coupled with this short-term cyclicity.

This 2^{nd}-order transgressive phase is characterized by an increase in marly deposits observed in the basin (excepting Arrábida). In distal regions, facies show a marly dominance, with the development of several black-shale intervals, particularly abundant in the Davoei Zone and at the base and top of the Margaritatus Zone (Stokesi Subzone and top of Subnodosus-base of Gibbosus subzones respectively) (Figs. 2.1.5 and 2.1.7). With the exception of Arrábida and Tomar, the last black-shale interval is widespread in the basin, and corresponds to the peak transgression of the Pliensbachian T-R facies cycle (SP maximum flooding interval in Oliveira et al., 2006; Duarte, 2007)

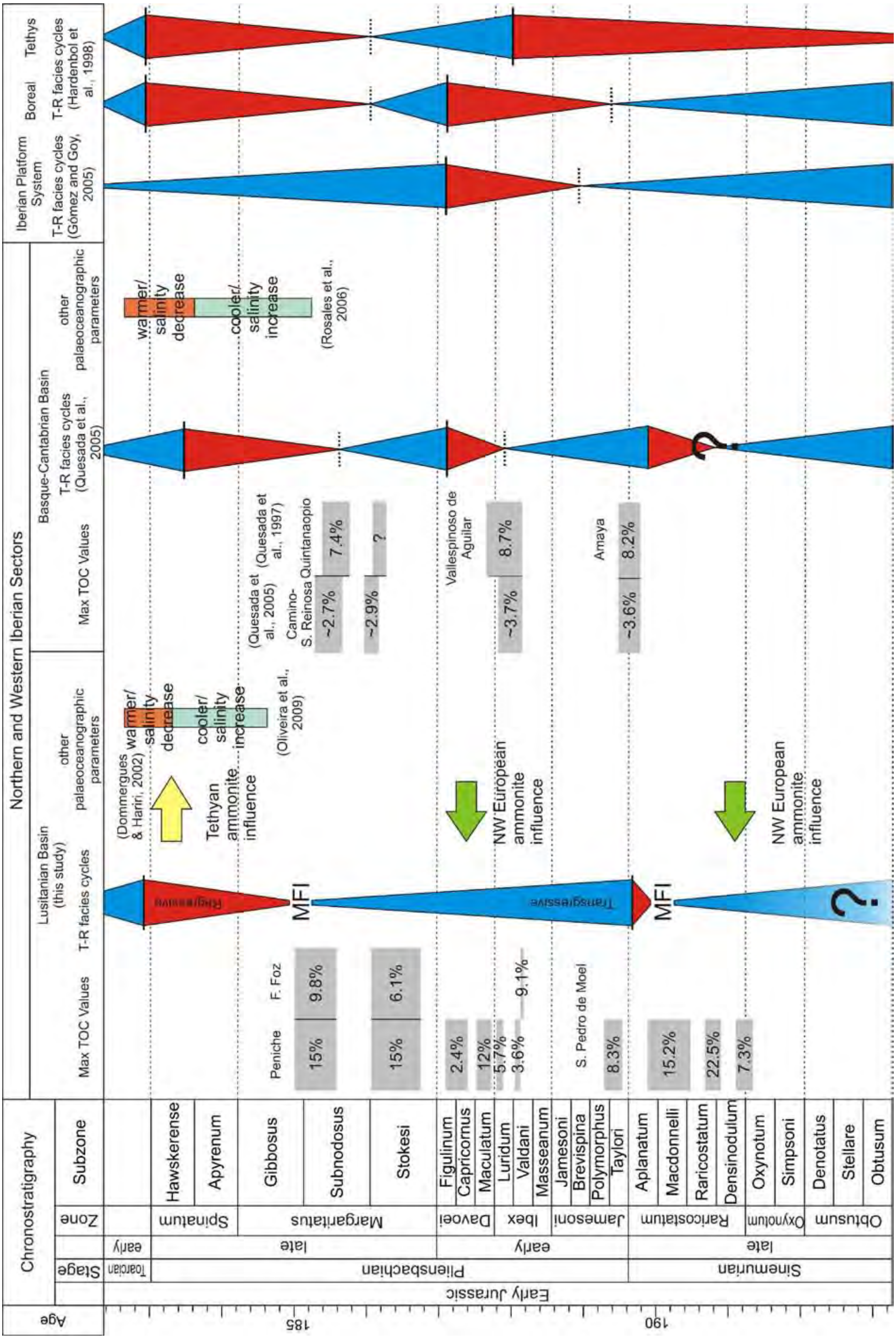
During the Spinatum Zone (Lemede Fm.) the sedimentation returned to a calcareous regime (Figs. 2.1.6G and 2.1.7), with low TOC values and very rich in benthic macrofauna. In the southeastern sectors of the basin, this regressive phase is represented by shallow-water bioclastic/grainstone facies. The upper limit of this 2nd-order cycle, clearly observed throughout the basin (DT1 *in* Duarte, 1997; SBT1 *in* Duarte et al. 2007a), is dated from the lowermost Polymorphum Zone.

2.1.7. Discussion: comparison to other western European basins

As demonstrated above, the organic sedimentation that occurred during the late Sinemurian-Pliensbachian of the LB is associated with marine peak transgressions (mainly of 2nd-order scale), which probably caused significant oxygen oscillations in the marine botto water. The transgressive phases that culminate during the Raricostatum and Margaritatus Biochrons appear to have favoured a restricted circulation on the sea bottom, probably as a result of water mass stratification (Hallam and Bradshaw, 1979; Wignall, 1991). Although this discussion is not the central goal of this paper, this palaeoenvironmental interpretation of oxygen-deficient conditions is particularly well supported by benthic macro- and microfauna distribution in the basin. Indeed, brachiopods (mainly terebratulids and rhynchonellids), bivalves (mainly ostreids) and gastropods, locally very abundant in several parts of the succession, are absent in the black shales and in the horizons with the highest TOC values. In addition, this relation between fauna and aerobic conditions is confirmed by three previous studies on benthic microfauna. Brunel et al. (1998) and N'zaba-Makaya et al. (2003) show for the Margaritatus Zone of the LB a clear decrease in foraminifera and ostracods from the eastern sectors towards S. Pedro de Moel. This idea tallies well with that of Duarte et al. (2006) who, in a preliminary study on the Sinemurian-Pliensbachian boundary of S. Pedro de Moel, show that ostracods are totally absent in the organic-rich facies (with TOC values above 1%) of the Raricostatum Zone. These microfossils are particularly abundant in the intercalated limestones, a fact that seems to confirm oxygen depletion on the sea floor during organic accumulation. These oxygen-deficient conditions may also be inferred by the occurrence of *Chondrites* in some organic-rich levels (see Bromley and Ekdale, 1984; Savrda et al., 1991).

In the Lower Jurassic, organic-rich marine facies are geographically widespread, associated with the Early Toarcian Oceanic Anoxic Event (T-OAE; Jenkyns, 1988; Jenkyns et al., 2002). In spite of this large organic matter sedimentation, which presents a significant record in Central and Western Europe (e.g. Jenkyns et al., 2002; among others), black shales are practically absent in the Portuguese Lower Toarcian (Duarte et al., 2004a, 2007a), probably as a consequence of the siliciclastic deposition that occurred during the base of the Levisoni Biochron (see Wright and Wilson, 1984; Duarte, 1997; Duarte et al., 2004b, 2007a; Suan et al., 2008). However, this OAE is well recognized in the LB, through the negative carbon isotopic signatures in both carbonates and wood, as confirmed by several authors (Duarte, 1998; Duarte et al., 2007a; Hesselbo et al., 2007). In this context, the organic-rich facies occurring in the late Sinemurian-Pliensbachian interval constitute the main reference of deposition and preservation of marine organic matter in the LB. These deposits correspond to an important hydrocarbon source rock (Oliveira et al., 2006).

In terms of Tethyan and Boreal realms, organic-rich marine facies of the late Sinemurian-Pliensbachian time interval are very rare (Jenkyns et al., 2002). Although these facies are absent in the Iberian Range (e.g. Gómez and Goy, 2005), Betic Cordillera (e.g. Ruiz-Ortiz et al., 2004) and Algarve Basin (Azerêdo et al., 2003; Ribeiro and Terrinha, 2007), they are well developed in northern Iberia, in the Asturian and Basque-Cantabrian basins, as confirmed by several authors (e.g. Borrego et al., 1996; Herrero, 1998; Quesada et al., 1997, 2005; Perilli and Comas-Rengifo, 2002; Rosales et al. 2006; Bádenas et al., 2009). The sedimentary context of the latter occurrence is very similar to that of the LB, which constitutes an interesting palaeogeographic and palaeoceanographic feature, considering the relative proximity of these two basins. However, comparison of the studied stratigraphic parameters in each basin shows several differences between these two sectors of the Iberia Peninsula. According to Fig. 2.1.8, high-resolution stratigraphic control shows clear discrepancies in the distribution of black shales in these two basins and TOC values are notably higher in the western Iberian margin. As a consequence of this facies record, the sequence stratigraphic interpretation is also different between them (Quesada et al., 2005; Rosales et al., 2006). They also differ from the sequential schemes proposed for other Iberian basins (Aurell et al., 2003; Gómez and Goy, 2005; Quesada et al., 2005), Morocco (Souhel et al., 1998) and from the sequential (transgressive-regressive facies cycles) general schemes presented for the Boreal and Tethyan realms by Hardenbol et al. (1998) (Fig. 2.1.8). However, according to the same figure, and despite the different number and length of sequences, some interesting correspondences are evidenced. 2nd-order maximum flooding events recognized in the LB are practically synchronous in the Basque-Cantabrian Basin. The connection between western and northern Iberia is also confirmed by the ammonite palaeobiogeographic distribution.


Chronostratigraphy
Age
Stage
Zone
Subzone
Early Jurassic
Toarcian
Pliensbachian
Sinemurian
early
late
early
late
Spinatum
Margaritatus
Davoei
Ibex
Jamesoni
Raricostatum
Oxynotum
Obtusum
Hawskerense
Apyrenum
Gibbosus
Subnodosus
Stokesi
Figulinum
Capricornus
Maculatum
Luridum
Valdani
Masseanum
Jamesoni
Brevispina
Polymorphus
Taylori
Aplanatum
Macdonnelli
Raricostatum
Densinodulum
Oxynotum
Simpsoni
Denotatus
Stellare
Obtusum
185
190
Northern and Western Iberian Sectors
Lusitanian Basin (this study)
Max TOC Values
Peniche
F. Foz
15%
9.8%
15%
6.1%
2.4%
12%
5.7%
3.6%
9.1%
S. Pedro de Moel
8.3%
15.2%
22.5%
7.3%
T-R facies cycles
Regressive
MFI
Transgressive
MFI
?
other palaeoceanographic parameters
(Dommergues & Hariri, 2002)
Tethyan ammonite influence
NW European ammonite influence
NW European ammonite influence
warmer/ salinity decrease
cooler/ salinity increase
(Oliveira et al., 2009)
Basque-Cantabrian Basin
Max TOC Values
(Quesada et al., 2005)
(Quesada et al., 1997)
Camino-S. Reinosa
Quintanaopio
~2.7%
7.4%
~2.9%
?
Vallespinoso de Aguilar
~3.7%
8.7%
Amaya
~3.6%
8.2%
T-R facies cycles (Quesada et al., 2005)
?
other palaeoceanographic parameters
warmer/ salinity decrease
cooler/ salinity increase
(Rosales et al., 2006)
Iberian Platform System
T-R facies cycles (Gómez and Goy, 2005)
Boreal
Tethys
T-R facies cycles (Hardenbol et al., 1998)

According to Dommergues and El Hariri (2002), the ammonite fauna of the latest Sinemurian and of much of the Pliensbachian of the LB shows a clear influence of NW Europe, with the occurrence of some endemic species. This boreal palaeobiological influence ended definitively in the Spinatum Zone, after which Tethyan ammonites dominated. The latter palaeobiogeographic evidence is significant, correlated with the 2nd-order regressive phase observed in the LB, and is effectively common to both Boreal and Tethyan realms (Hardenbol et al., 1998). This phase is also justified by a cooling effect (Morard et al., 2003), as documented by recent published data on oxygen isotopes from the Basque-Cantabrian and Lusitanian basins (Rosales et al., 2004, 2006; Oliveira et al., 2009) (Fig. 2.1.8). Thus, with all these stratigraphical and geochemical data, we demonstrate that, during the late Sinemurian-Pliensbachian, the LB shows more palaeoceanographic affinities with the Basque-Cantabrian basin than with any other palaeogeographic domain.

2.1.8. Conclusions

The upper Sinemurian-Pliensbachian (Água de Madeiros and Vale das Fontes formations) series of the LB is mainly composed of marly limestone sediments, deposited in a homoclinal carbonate ramp system. This sedimentary record, controlled by an accurate ammonite biostratigraphic resolution, includes organic-rich facies with several black shale levels. The stratigraphical, sedimentological and geochemical TOC study of the uppermost Sinemurian-Pliensbachian classical sections of the western Iberian margin, shows that these organic-rich facies occur practically throughout the whole succession (Oxynotum-Margaritatus zone interval), with the exception of the uppermost Pliensbachian (Spinatum Zone). The vertical and lateral distributions of TOC values show that these facies are essentially restricted to the western side of the basin and are particularly well developed I the Oxynotum-Raricostatum and the top of Ibex-Margaritatus zone intervals. Apart from the significance of these results with regard to palaeogeographical interpretation of the basin, the temporal and spatial distribution of these organic-rich facies is decisive in sequence stratigraphic interpretation of the studied series.

Previous page: Fig. 2.1.8. Correlation of black-shale (and its highest TOC values) intervals between the Lusitanian and Basque-Cantabrian basins, and comparison of the sequence stratigraphic interpretations for several domains of Iberia with the general schemes of Hardenbol et al. (1998). This chart shows the good correspondence between northern and western Iberia margins.

The observed persistence of black shales in the Oxynotum-Raricostatum and Margaritatus zones, where TOC values reach 22% and 15%, respectively, are both associated with 2nd-order transgressive phases. In addition, the density of high TOC values observed throughout the basin, associated with other sedimentological arguments, confirm the Aplanatum Subzone and the Subnodosus-Gibbosus subzone boundary as the 2nd-order maximum flooding intervals. In spite of the differences between the sequence stratigraphic schemes presented by several authors for Western Europe, these phenomena recognized in the LB are very similar to those recorded in the neighbouring Basque-Cantabrian Basin.

References

ANTUNES, M.T., ROCHA, R.B. and WENZ, S., 1981. Faunule ichtyologique du Lias inférieur de São Pedro de Moel, Portugal. Ciências da Terra, 6, 101-116.

AURELL, M., ROBLES, S., BÁDENAS, B., ROSALES, I., QUESADA, S., MELÉNDEZ, G. and GARCÍA-RAMOS, J.C., 2003. Transgressive–regressive cycles and Jurassic palaeogeography of northeast Iberia. Sedimentary Geology, 162, 239–271.

AZERÊDO, A.C., DUARTE, L.V., HENRIQUES, M.H. and MANUPPELLA, G., 2003. Da dinâmica continental no Triásico aos mares do Jurássico Inferior e Médio. Cadernos de Geologia de Portugal. Instituto Geológico e Mineiro, Lisboa, 43 pp.

AZERÊDO, A.C., SILVA, R.L. and DUARTE, L.V., 2008. Stromatolites as event signs of earliest steps of the Sinemurian marine transgression in the Lusitanian Basin, Portugal. In: 26th Regional Meeting of the International association of Sedimentologists (IAS). Abstracts Volume, Schriftenreihe der Deutschen Gesellschaft für Geowissenschaften (German Geological Society), Bochum (Alemanha), Heft 58, 39.

AZERÊDO, A.C., WRIGHT, V.P. and RAMALHO, M., 2002. The Middle–Late Jurassic forced regression and disconformity in central Portugal: eustatic, tectonic and climatic effects on a carbonate ramp system. Sedimentology, 49, 1339–1370.

BÁDENAS, B., AURELL, M., GARCIA-RAMOS, J.C., GONZÁLEZ, B. and PIÑUELA, L., 2009. Sedimentary vs. diagenetic control on rhythmic calcareous successions (Pliensbachian of Asturias, Spain). Terra Nova, 21, 162-170.

BORREGO, A.G., HAGEMANW, H.W., BLANCO, C.G., VALENZUELA, M. and SUAREZ DE CENTI, C., 1996. The Pliensbachian (Early Jurassic) "anoxic" event in Asturias, northern Spain: Santa Mera Member, Rodiles Formation. Organic Geochemistry, 25, 295-309.

BROMLEY, R.G. and EDKALE, A.A., 1984. Chondrites: a trace fossil indicator of anoxia in sediments. Science, 224, 872–874.

BRUNEL, F., BONNET, L., RUGET, C., REY, J., MOUTERDE, R. and ROCHA, R., 1998. Variations des associations de Foraminifères dans le Domérien du bassin lusitanien en relation avec les flutuations de l'environment. Comunicações do Instituto Geológico e Mineiro, 84, A49-A52.

DE GRACIANSKY, P.C., JACQUIN, T. and HESSELBO, S.P., 1998. The Ligurian Cycle: an overview of Lower Jurassic 2nd-order transgressive/regressive facies cycles in western Europe. In: de GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P.R. (eds.). Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication 60, 467–479.

DOMMERGUES, J-L., 1987. L'évolution chez les Ammonitina du Lias Moyen (Carixien, Domerien basal) en Europe occidentale. Documents des Laboratoires de Géologie Lyon, 98, 1-297.

DOMMERGUES, J-L. and EL HARIRI, K., 2002. Endemism as a palaeobiogeographic parameter of basin history illustrated by early- and mid-Liassic peri-Tethyan ammonite faunas. Palaeogeography, Palaeoclimatology, Palaeoecology, 184, 407-418.

DOMMERGUES, J-L., MEISTER, C., NEIGE, P. and ROCHA, R. B., 2004. Endemic Sinemurian (Early Jurassic) ammonites from the Lusitanian Basin (Portugal). Revue de Paléobiologie, 23, 529-549.

DROMART, G. and ELMI, S., 1986. Développement de structures cryptalgaires en domaine pélagique au cours de l'ouverture des bassins jurassiques (Atlantique central, Téthys occidentale). Comptes rendus de l'Académie des sciences de Paris, Série 2, 303(4), 311-316.

DUARTE, L.V., 1997. Facies analysis and sequential evolution of the Toarcian-Lower Aalenian series in the Lusitanian Basin (Portugal). Comunicações do Instituto Geológico e Mineiro, 83, 65-94.

DUARTE, L.V., 1998. Clay minerals and geochemical evolution in the Toarcian-Lower Aalenian of the Lusitanian Basin. Cuadernos de Geología Ibérica, 24, 69-98.

DUARTE, L.V., 2007. Lithostratigraphy, sequence stratigraphy and depositional setting of the Pliensbachian and Toarcian series in the Lusitanian Basin (Portugal). In R. B. Rocha (ed.). The Peniche section (Portugal). Contributions to the definition of the Toarcian GSSP. International Subcommission on Jurassic Stratigraphy, 17-23.

DUARTE, L.V., OLIVEIRA, L.C., and RODRIGUES, R., 2007a. Carbon isotopes as a sequence stratigraphic tool: examples from the Lower and Middle Toarcian marly limestones of Portugal. Boletín Geológico y Minero, 118, 3-18.

DUARTE, L.V., OLIVEIRA, L.C., SILVA, F., ROCHA, F. and RODRIGUES, R., 2007b. TOC, carbon isotopes and clay minerals signatures across the Upper Sinemurian carbonate deposits of Western Iberia Margin. Patras (Greece), Abstract Volume of the 25th Regional Meeting of the International Association of Sedimentologists (IAS), 228.

DUARTE, L.V., PERILLI, N., ANTONIOLI, L., RODRIGUES, R., CABRAL, M.C., DINO, R. and AZERÊDO, A. C., 2006. Evidências sedimentológicas, geoquímicas (COT) e micropaleontológicas nas fácies betuminosas do Sinemuriano terminal de Água de Madeiros (Portugal). In: Mirão, J., Balbino, A. (eds.). Proceedings of VII Congresso Nacional de Geologia, Évora, 2, 633-636.

DUARTE, L.V., PERILLI, N., DINO, R., RODRIGUES, R. and PAREDES, R., 2004a. Lower to Middle Toarcian from the Coimbra region (Lusitanian Basin, Portugal): sequence stratigraphy, calcareous nannofossils and stable-isotope evolution. Rivista Italiana di Paleontologia e Stratigrafia, 110 (1), 115-127.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das series margo-calcárias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicaçoes do Instituto Geológico e Mineiro, 89, 135-154.

DUARTE, L.V., WRIGHT, V.P., LÓPEZ, S.F., ELMI, S., KRAUTTER, M., AZERÊDO, A.C., HENRIQUES, M.H., RODRIGUES, R. and PERILLI, N., 2004b. Early Jurassic carbonate evolution in the Lusitanian Basin (Portugal): facies, sequence stratigraphy and cyclicity. In*:* Duarte, L.V. and Henriques, M.H. (eds.).

Carboniferous and Jurassic Carbonate Platforms of Iberia. 23rd IAS Meeting of Sedimentology, Field Trip Guide Book, Coimbra, 1, 45-71.

EDMUNDS, M., VARAH, M. and BENTLEY, A., 2003. The ammonite biostratigraphy of the Lower Lias 'Armatum Bed' (Upper Sinemurian-Lower Pliensbachian) at St Peter's Field, Radstock, Somerset. Proceedings of the Geologists' Association, 114, 65-96.

ELMI, S., ROCHA, R.B. and MOUTERDE, R., 1988. Sediméntation pelagique et encroutements crytalgaires: les calcaires grumuleux du Carixien portugais. Ciências da Terra (UNL), 9, 69-90.

FERNÁNDEZ-LÓPEZ, S., DUARTE, L.V. and HENRIQUES, M.H., 2000. Ammonites from lumpy limestones in the Lower Pliensbachian of Portugal: taphonomic analysis and paleoambiental implications. Revista de la Sociedad Geológica de España, 13, 3-15.

GÓMEZ, J.J. and GOY, A., 2005. Late Triassic and Early Jurassic palaeogeographic evolution and depositional cycles of theWestern Tethys Iberian platform system (Eastern Spain). Palaeogeography, Palaeoclimatology, Palaeoecology, 222, 77–94.

HALLAM, A., 1971. Facies analysis of the Lias in West Central Portugal. Neues Jahrbuch für Geologie und Paläontologie, Abhandlungen, 139, 226-265.

HALLAM, A. and BRADSHAW, M.J., 1979. Bituminous shales and oolitic ironstones as indicators of trangressions and regressions. Journal of the Geological Society of London, 136, 157–164.

HARDENBOL, J., THIERRY, J., FARLEY, M.B., JACQUIN, TH., DE GRACIANSKY, P.C. and VAIL, P.R., 1998. Mesozoic and Cenozoic sequence chronostratigraphy framework of European Basins. Jurassic chronostratigraphy. In: de Graciansky, P.C., Hardenbol, J., Jacquin, Th., Vail, P. (eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60, 3–13.

HERRERO, C., 1998. Foraminíferos del Pliensbachiense en la sección de Camino (Cuenca Vasco-Cantábrica, España). Cuadernos de Geología Ibérica, 24, 121-139.

HESSELBO, S., JENKYNS, H., DUARTE, L.V. and OLIVEIRA, L.C., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth and Planetary Science Letters, 253, 455-470.

JACQUIN, T. and de GRACIANSKY, P.C., 1998a. Major transgressive/regressive cycles: the stratigraphic signature of European basin development. In: de GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P. (eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60, 15-30.

JACQUIN, T. and DE GRACIANSKY, P.C., 1998b. Transgressive-regressive (second order) facies cycles: the effects of tectonoeustacy. In: de GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P. (eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60, 445-466.

JENKYNS, H.C., 1988. The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. American Journal of Science, 288, 101–151.

JENKYNS, H.C., JONES, C.E., GRÖCKE, D.R., HESSELBO, S.P. and PARKINSON, D.N., 2002. Chemostratigraphy of the Jurassic System: application, limitations and implications for palaeoceanography. Journal of the Geological Society of London, 159, 351–378.

MORARD, A. GUEX, J. BARTOLINI. A., MORETTINI, E. and DE WEVER, P., 2003. A new scenario for the Domerian - Toarcian transition. Bulletin de la Societé Géologique, France, 174(4), 351-356

MOUTERDE, R., 1955. Le Lias de Peniche. Comunicações dos Serviços Geológicos de Portugal, 36, 5-33.

MOUTERDE, R., 1967. Le Lias du Portugal. Vue d'ensemble et division en Zones. Comunicações dos Serviços Geológicos de Portugal, 52, 209-226.

MOUTERDE, R., DOMMERGUES, J-L., MEISTER, C. and ROCHA, R.B., 2007. Atlas des fossiles caractéristiques du Lias portugais. III a) Domérien (Ammonites). Ciências da Terra, 16, 67-111.

N'ZABA-MAKAYA, O., ANDREU, B., BRUNEL, F., MOUTERDE, R., REY, J. and ROCHA, R., 2003. Biostratigraphie et paléoécologie des puplements d'ostracodes dans le Domérien du Bassin Lusitanien, Portugal. Ciências da Terra, 15, 21-44.

OLIVEIRA, L.C.V., DUARTE, L.V., LEMOS, V.B., COMAS-RENGIFO, M.J. and PERILLI, N., 2007. Bioestratigrafia de nanofósseis calcários e correlação com as zonas de amonites do Pliensbaquiano-Toarciano basal (Jurássico inferior) de Peniche (Bacia Lusitânica, Portugal). In: CARVALHO, I.S., CASSAB, R.C.T., SCHWANKE, C., CARVALHO, M.A., FERNANDES, A.C.S., RODRIGUES, M.A.C., CARVALHO, M.S.S., ARAI, M. and OLIVEIRA, M.E.Q. (eds.). Paleontologia: Cenários de Vida, Proceedings of XIX Congresso Brasileiro de Paleontologia, Búzios (Brazil), Editora Interciência, 411-420.

OLIVEIRA, L.C.V., RODRIGUES, R., DUARTE, L.V. and LEMOS, V., 2006. Avaliação do potencial gerador de petróleo e interpretação paleoambiental com base em biomarcadores e isótopos estáveis do carbono da seção Pliensbaquiano-Toarciano inferior (Jurássico inferior) da região de Peniche (Bacia Lusitânica, Portugal). Boletim de Geociências da Petrobras, 14(2), 207-234.

OLIVEIRA, L.C., DUARTE L.V., SILVA R.L. and RODRIGUES R. (2009). Belemnite $\delta^{18}O$ and $\delta^{13}C$ record of the Lusitanian Basin Pliensbachian carbonate series (Portugal). Geochimica and Cosmochimica Acta, 73 (13S), A969.

PERILLI, N. and COMAS-RENGIFO, M.J., 2002. Calibration of Pliensbachian calcareous nannofossils events in two ammonite-controled sections from Northern Spain. Rivista Italiana di Paleontologia e Stratigrafia, 108(1), 133-152.

PHELPS, M., 1985. A refined ammonite biostratigraphy for the Middle and Upper Carixian (Ibex and Davoei zones, Lower Jurassic) in North-West Europe and stratigraphical details of the Carixian-Domerian boundary. Geobios, 18, 321-362.

QUESADA, S., DORRONSORO, C., ROBLES, S., CHALER, R. and GRIMALT, J.O., 1997. Geochemical correlation of oil from the Ayoluengo field to Liassic black shale units in the southwestern Basque–Cantabrian Basin (northern Spain). Organic Geochemistry, 27, 25–40.

QUESADA, S., ROBLES, S. and ROSALES, I., 2005. Depositional architecture and transgressive–regressive cycles within Liassic backstepping carbonate ramps in the Basque–Cantabrian Basin, northern Spain. Journal of the Geological Society of London, 162, 531–548.

RIBEIRO, C. and TERRINHA, P. 2007 Formation, deformation and chertification of systematic clastic dykes in a differentially lithified carbonate multilayer. SW Iberia, Algarve Basin, Lower Jurassic. Sedimentary Geology, 196, 201-215.

ROSALES, I., QUESADA, S. and ROBLES, S. 2004. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque–Cantabrian basin, northern Spain. Palaeogeography, Palaeoclimatology, Palaeoecology, 203, 253-275.

ROSALES, I., QUESADA, S. and ROBLES, S. 2006. Geochemical arguments for identifying second-order sea-level changes in hemipelagic carbonate ramp deposits. Terra Nova, 18 (4), 233-240.

RUIZ-ORTIZ, P. A., BOSENCE, D. W. J., REY, J., NIETO , L. M., CASTRO, J. M. and MOLINA, J. M., 2004. Tectonic control of facies architecture, sequence stratigraphy and drowning of a Liassic carbonate platform (Betic Cordillera, Southern Spain). Basin Research, 16, 235–257

SAVRDA, C.E., BOTTJER, D.J. and SEILACHER, A., 1991. Redox-related benthic event. In: EINSELE, G., RICKEN,W. and SEILACHER, A. (eds.), Cycles and Events in Stratigraphy. Springer-Verlag, Berlin, 524–541.

SILVA, F., DUARTE, L.V., OLIVEIRA, L. C., RODRIGUES, R. and COMAS-RENGIFO, M. J., 2007. Caracterização do Carbono Orgânico Total e pirólise *Rock-Eval* no intervalo Sinemuriano superior – Pliensbaquiano do sector norte da Bacia Lusitânica (Portugal). In: GOMES, E.P. and ALENCOÃO, A.M. (Coords). Proceedings of VI Congresso Ibérico de Geoquímica, Vila Real, 564-567.

SOARES, A.F., ROCHA, R.B., ELMI, S., HENRIQUES, M.H., MOUTERDE, R., ALMERAS, Y., RUGET, C., MARQUES, J., DUARTE, L.V., CARAPITO, C. and KULLBERG, J.C., 1993. Le sous-bassin nord-lusitanien (Portugal) du Trias au Jurassique moyen: histoire d'un "rift avorté". Comptes rendus de l'Académie des sciences de Paris, 317, 1659-1666.

SOUHEL, A., EL HARIRI, K., CHAFIKI, D. and CANEROT, J., 1998. Stratigraphie séquentielle et évolution géodynamique du Lias (Sinémurien terminal-Toarcien moyen) de l'Atlas de Béni-Mellal (Haut Atlas central, Maroc). France, Bulletin de la Société Géologique, 169, 527-536.

SUAN, G., PITTET, B., BOUR, I., MATTIOLI, E., DUARTE, L.V. and MAILLOT, S., 2008. Duration of the Early Toarcian carbon isotope excursion deduced from spectral analysis: consequence for its possible causes. Earth and Planetary Science Letters, 267, 666-679.

WIGNALL, P.B., 1991. Model for transgressive black shales?. Geology, 19, 167–170.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. and GRADSTEIN, F.M., 1989. The Lusitanian basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphy, and subsidence history. American Association of Petroleum Geologists, 46 (Memoir), 341-361.

WRIGHT, V.P. and WILSON, R.C.L., 1984. A carbonate submarine-fan sequence from the Jurassic of Portugal. Journal of Sedimentary Petrology, 54, 394-412.

Acknowledgements

We wish to thank René Rodrigues from the Universidade do Estado do Rio de Janeiro (Brazil) and Cenpes-Petrobras for technical support in the TOC analysis. We also thank M. Aurell, H. Jenkyns, I. Rosales and the editor L. Cabrera for constructive comments that greatly improved the manuscript. This research is a contribution to the Projects PDCTE/CTA/44907/2002 (Foundation for Science and Technology, Portuguese Government) and CGL2008-03112/BTE (Ministry of Science and Technology, Spanish Government).

Capítulo 3 | Sinemuriano: Formação de Água de Madeiros

3.1. High-resolution stratigraphy, Palynofacies and source-rock potential of the Água de Madeiros Formation (Lower Jurassic), Lusitanian Basin, Portugal

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Journal of Petroleum Geology, 35 (2), 105–126

Abstract

In the Lusitanian Basin (central-western Portugal), the Lower Jurassic carbonate-dominated succession is thought to have significant source rock potential. One of the most important units is the Água de Madeiros Formation (Upper Sinemurian–lowermost Pliensbachian) which is composed of alternating organic-rich marls and limestones including black shale horizons. This paper is based on a study of this formation at its type locality at S. Pedro de Moel in western Portugal. Data includes Total Organic Carbon (TOC) measurements, palynofacies analyses and results of Rock-Eval pyrolysis presented within a high-resolution lithostratigraphic framework.

TOC contents were measured in some 200 samples from the Água de Madeiros Formation covering a stratigraphic interval of 58 m, and vary widely up to a maximum of about 22 wt%. Kerogen assemblages are dominated by marine amorphous organic matter with varying contributions by phytoclasts and palynomorphs. A majority of the 85 samples analyzed by Rock-Eval pyrolysis have S_2 values above 10 mg HC/g rock, reaching a maximum of 78 mg HC/g rock. These high S_2 values are correlative with maximum values of the Hydrogen Index which averages 355 mg HC/g TOC (maximum of 637 mg HC/g TOC). However in spite of these indicators of source-rock potential, the Água de Madeiros Formation in the study area is thermally immature or very early mature, as indicated by T_{max} values below 437 °C and average vitrinite reflectance values of 0,43 % R_o.

Keywords: Lusitanian Basin, Portugal, Early Jurassic, Água de Madeiros Formation, marly limestones, black shales, source rock

3.1.1. Introduction

The Mesozoic Lusitanian Basin, central-western Portugal, is located between the Atlantic and Tethyan realms (e.g. Hiscott et al., 1990; Thierry et al., 2000). The stratigraphic column is well exposed at the surface and the basin includes international reference sections for the study of the Jurassic in terms of basin evolution (e.g. Azerêdo et al., 2003; Duarte, 2004; Leinfelder and Wilson, 1998; Pena dos Reis et al., 1999; Soares et al., 1993), the Early Toarcian Oceanic Anoxic Event (e.g. Hesselbo et al., 2007; Suan et al., 2010) and large-scale perturbations of the carbon cycle.

Source rock potential is highest in two stratigraphic intervals: the latest Sinemurian–late Pliensbachian, and the Oxfordian (e.g. Beicip-Franlab, 1996; Duarte et al., 2010, 2011b; GPEP, 1986; Oliveira et al., 2006; F. Silva et al., 2010; Silva et al., 2011a; Uphoff, 2005). The Sinemurian – Pliensbachian interval is composed of fully-marine organic-rich marls and limestones (e.g. Duarte et al., 2004, 2010; Silva et al., 2011a; 2011b), whereas the Oxfordian is composed of lacustrine, lagoonal and shallow-marine deposits (e.g. Azerêdo et al., 2002; Silva et al., 2011a). These two intervals are probably responsible for several surface oil seepages (e.g. DPEP, 2011; Spigolon et al., 2010) and subsurface oil shows which have been recorded in various parts of the western Lusitanian Basin (see DPEP, 2011). According to GPEP (1986) and DPEP (2011), diverse carbonate and siliciclastic units of Jurassic and Cretaceous age have been identified as reservoirs and possible seals.

In this paper, we present a detailed characterization of the latest Sinemurian – earliest Pliensbachian Água de Madeiros Formation (Duarte and Soares, 2002; Duarte et al., 2010), focusing on its organic matter (OM) content and source rock potential. Data include the results of Total Organic Carbon (TOC) measurements, palynofacies analysis and Rock-Eval pyrolysis. The formation was studied at outcrops near S. Pedro de Moel (Fig. 3.1.1) (Duarte and Soares, 2002; Duarte et al., 2010). The results will contribute to a better understanding of the petroleum systems in the Lusitanian Basin and the sedimentary record of the neighbouring offshore Peniche and Alentejo Basins (e.g. Alves et al., 2006; 2009; Pereira and Alves, 2011) (see locations in Fig. 3.1.1) which are currently the sites of hydrocarbon exploration (see for example DPEP, 2011).

3.1.2. Geological setting and stratigraphy

Located on the western Iberian margin (Fig. 3.1.1), the Lusitanian Basin has a sedimentary fill more than 5 km thick which spans the Triassic to end-Cretaceous (e.g. Alves et al., 2002; Pinheiro et al., 1996; Rasmussen et al., 1998; Stapel et al., 1996; Wilson et al., 1989). This succession has been divided into a number of first-order cycles bounded by intra-basinal discontinuities (e.g. Alves et al., 2002; Pinheiro et al., 1996; Wilson et al., 1989). The first of these cycles, which is the focus of the present paper, is more than 1800 m thick and comprises the interval between the Middle (?) Triassic and the top – Middle Jurassic (e.g. Alves et al., 2002; Azerêdo et al., 2003; Soares et al., 1993).

At the base are coarse-grained red siliciclastics of Triassic age which rest on Precambrian metamorphics and locally on Upper Carboniferous/Lower Permian siliciclastics (Palain, 1976).

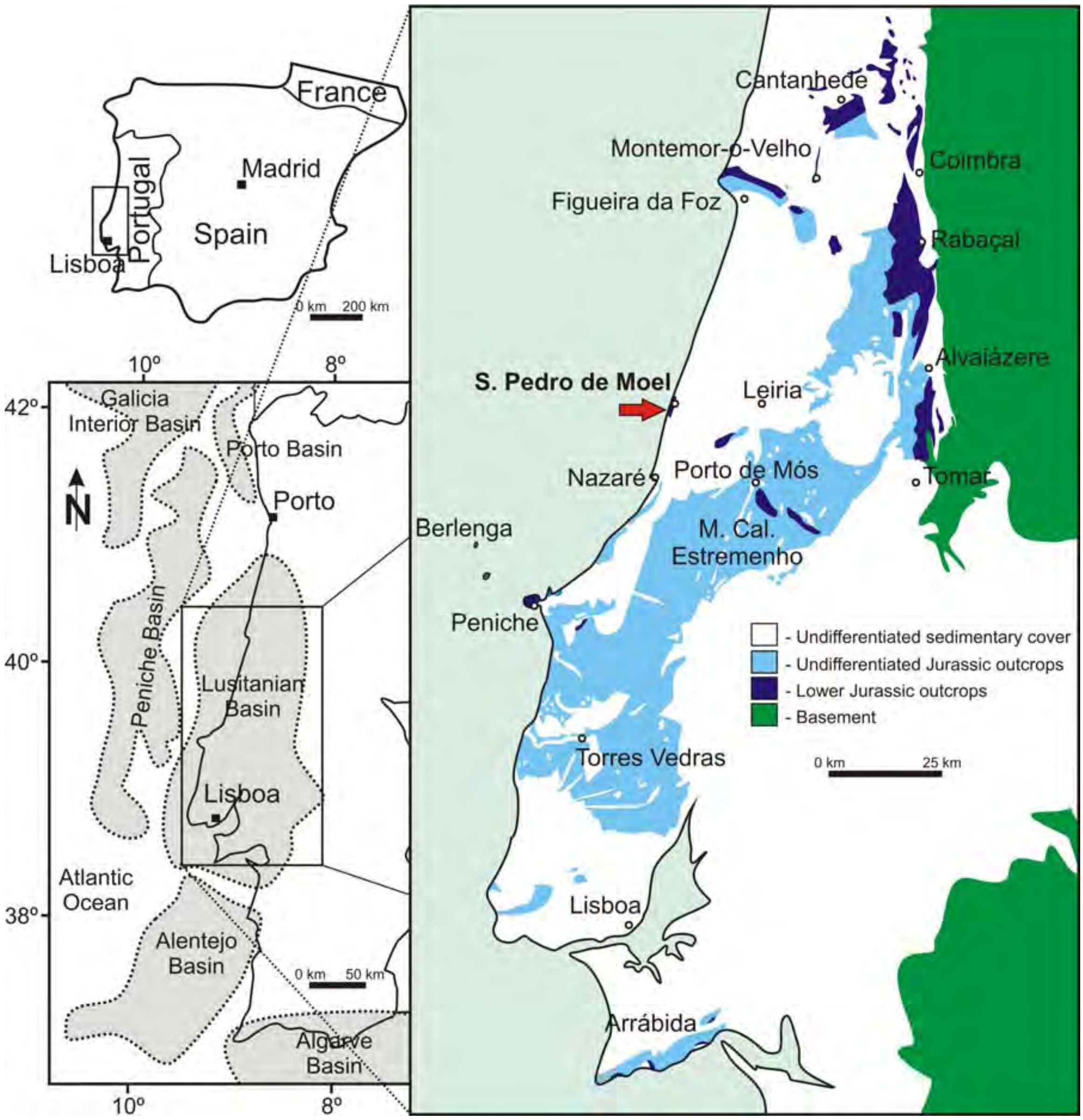


Fig. 3.1.1. Simplified geological map of the central-northern part of the Lusitanian Basin location of the studied area (modified from Duarte et al., 2010).

A major part of the overlying Lower and Middle Jurassic succession (Hettangian-Sinemurian – Callovian: Fig. 3.1.2) is composed of carbonates deposited on a NW-dipping ramp; these have been recorded in several onshore areas (e.g. Azerêdo et al., 2003; Duarte, 2007; Duarte et al., 2010; Soares et al.,1993), and correspond in the offshore part of the basin to the J20 seismic sequence of Alves et al. (2002). The boundary between the top-Callovian and the base of the overlying Upper Jurassic succession (in the second cycle) is marked by a regional hiatus associated with an important phase of emergence and sub-aerial exposure (Azerêdo et al., 2002).

At the base of the Jurassic section in the Lusitanian Basin are the fine-grained siliciclastics with dolomitic and evaporitic intercalations of the Hettangian Dagorda Formation (top of seismic sequence J10 of Alves et al., 2002) (Fig. 3.1.2).

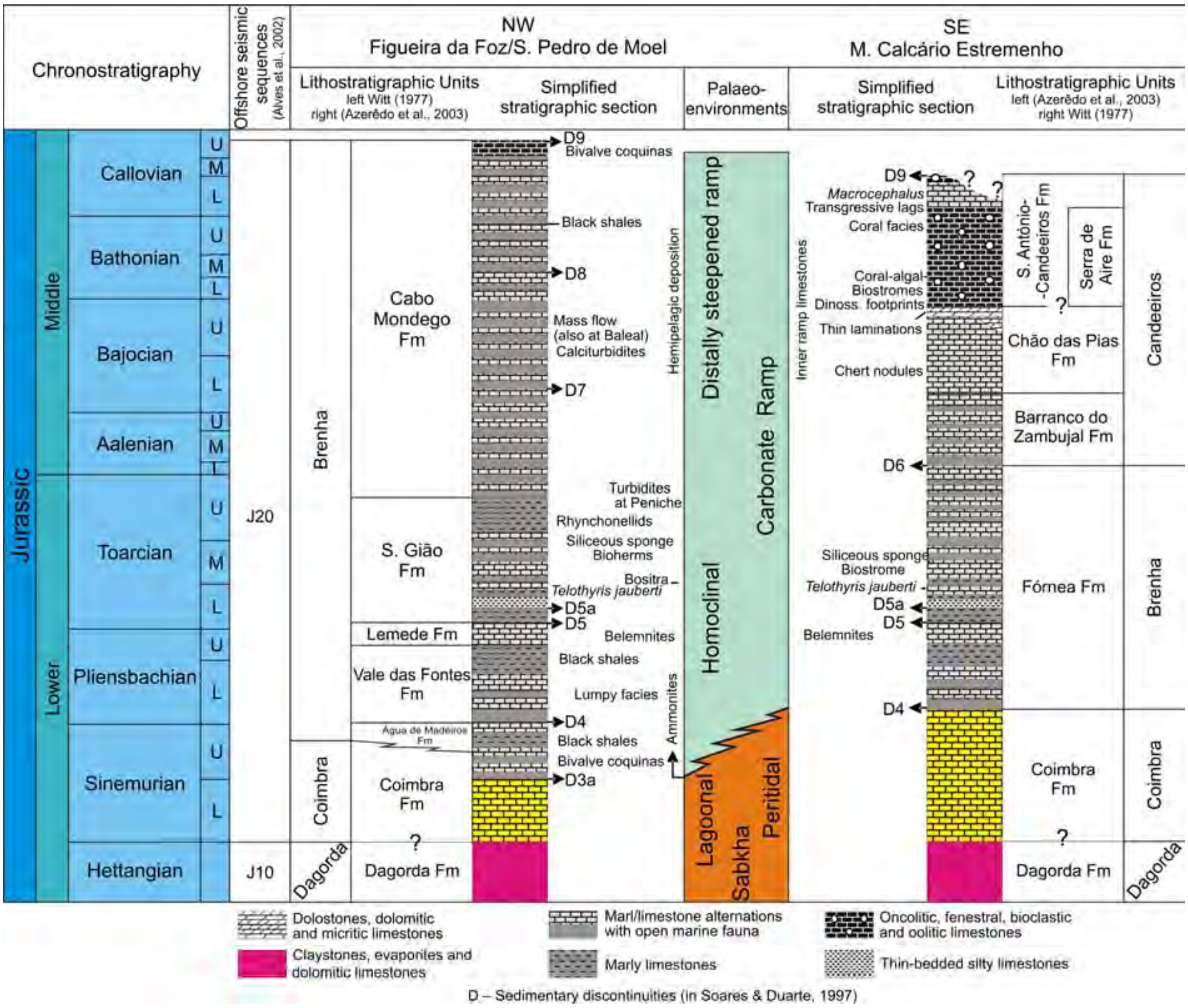


Fig. 3.1.2. Stratigraphic units and main sedimentological features of the Lower and Middle Jurassic succession at two locations in the NW and SE of the Lusitanian Basin (modified from Azerêdo et al., 2003). Locations in Fig. 3.1.1.

This formation is interpreted to have been deposited in a lagoonal environment under arid climatic conditions (Azerêdo et al., 2003; Soares et al., 1993). The Dagorda formation is overlain by the Sinemurian Coimbra Formation (seismic facies J20.a of Alves et al., 2002), which is dominated by dolostones and dolomitic and bioclastic limestones (e.g. Azerêdo et al., 2003, 2010). The dolomitic facies is diachronous and reaches up to the base of the Pliensbachian in the eastern part of the Lusitanian Basin (Fig. 3.1.3). The dolomitic character of the facies declines progressively to the west in the upper Sinemurian, and the formation passes into organic-rich alternating marls and limestone with an abundant nektonic fauna. This facies corresponds to the base of the "Brenha Formation" of previous studies and is now included in the Água de Madeiros Formation which is divided into the Polvoeira and Praia da Pedra Lisa members (Duarte and Soares, 2002). Ammonites provide good biostratigraphic control and date this unit to the oxynotum-jamesoni chronozones, as well as marking the onset of open-marine conditions in the basin (Duarte et al., 2010, 2011a). The overlying Vale das Fontes Formation (Pliensbachian) is dominated by marlstones and shows little lateral facies variations compared to the Água de Madeiros Formation (Fig. 3.1.3) (e.g. Duarte et al., 2010; Silva et al., 2011b).

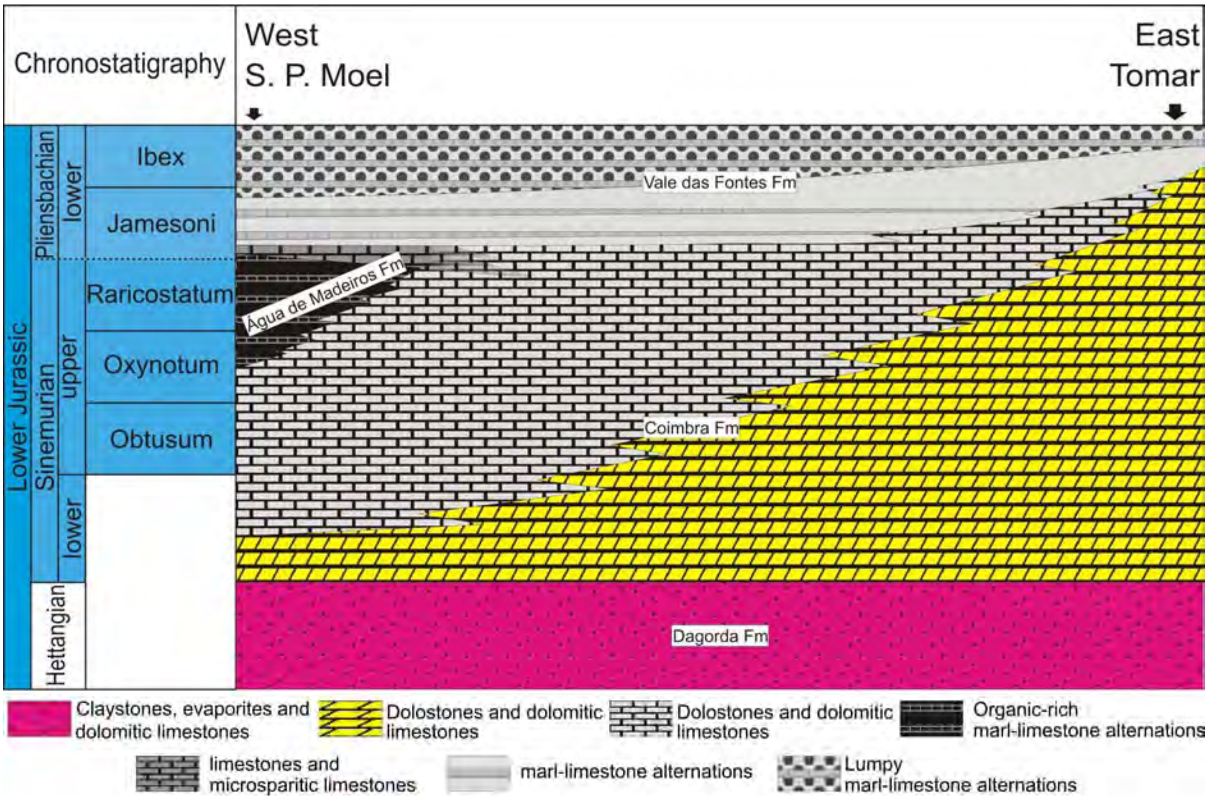


Fig. 3.1.3. Generic facies and stratigraphic chart for the Hettangian – Lower Pliensbachian Lusitanian Basin (adapted from Duarte et al., 2010).

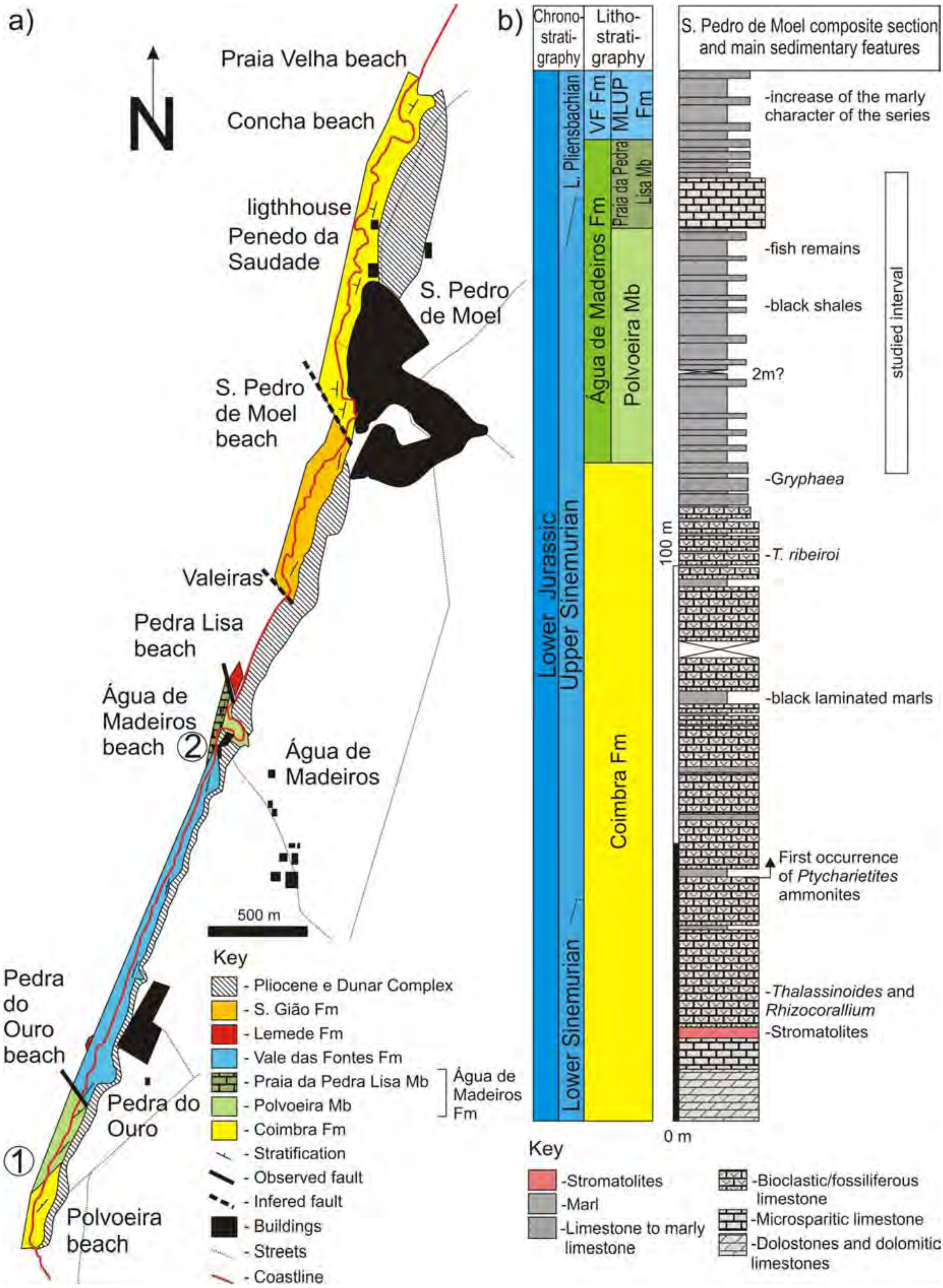


Fig. 3.1.4 (a) Geological map of the Lower Jurassic carbonate units cropping out in the S. Pedro de Moel area (from Duarte et al., 2008) and location of the two studied sections: 1. Polvoeira; 2. Água de Madeiros. (b) Synthetic stratigraphic log of the Sinemurian – Lower Pliensbachian succession in the S. Pedro de Moel area (Duarte et al., 2008; Azerêdo et al., 2010).

The study area for this paper is located south of the village of S. Pedro de Moel (Fig. 3.1.4a) where a complete succession is exposed from the Coimbra to the Vale das Fontes Formations, including both members of the Água de Madeiros Formation (Duarte et al., 2008) (Fig. 3.1.4b). At S. Pedro de Moel, the Água de Madeiros is overlain by the marls and limestones with Uptonia and Pentacrinus (the MLUP Member) of the Vale das Fontes Formation (Fig. 3.1.4b).

3.1.3. Materials and methods

The Água de Madeiros Formation is exposed at Polvoeira and Água de Madeiros (Fig. 3.1.4a). The detailed lithostratigraphy and sedimentology of the formation at these locations was investigated, together with fossil and trace fossil contents and source rock potential. Although there is some structural deformation, an accurate ammonite biostratigraphic scheme is available (Duarte et al., 2011a) and allowed the entire succession to be reconstructed bed-by-bed.

3.1.3.1 Total Organic Carbon (TOC) analyses

The OM present in the Água de Madeiros Formation was analyzed in a total of 95 samples, 64 from the Polvoeira section and 31 from Água de Madeiros (Fig. 3.1.5). After cleaning, the samples were analyzed with a Leco-SC444 analyzer in the Palynofacies and Organic Facies Laboratory of the Federal University of Rio de Janeiro (UFRJ, Brazil), following standard laboratory protocols.

3.1.3.2. Palynofacies

Thirty-one samples were prepared for palynofacies analysis in the same laboratory at UFRJ using standard techniques (see Mendonça Filho et al., 2010b; Mendonça Filho et al., 2011). Organic petrography and palynofacies analyses were performed by optical microscopy using transmitted white light (TWL) and fluorescence mode illumination, (FM) and following the classification scheme proposed by Tyson (1995) modified by Mendonça Filho et al. (2011).

3.1.3.3. Rock-Eval Pyrolysis

Samples with TOC contents above 1 wt % (n = 85) were analyzed by Rock-Eval pyrolysis at Cenpes-Petrobras (Brazil).

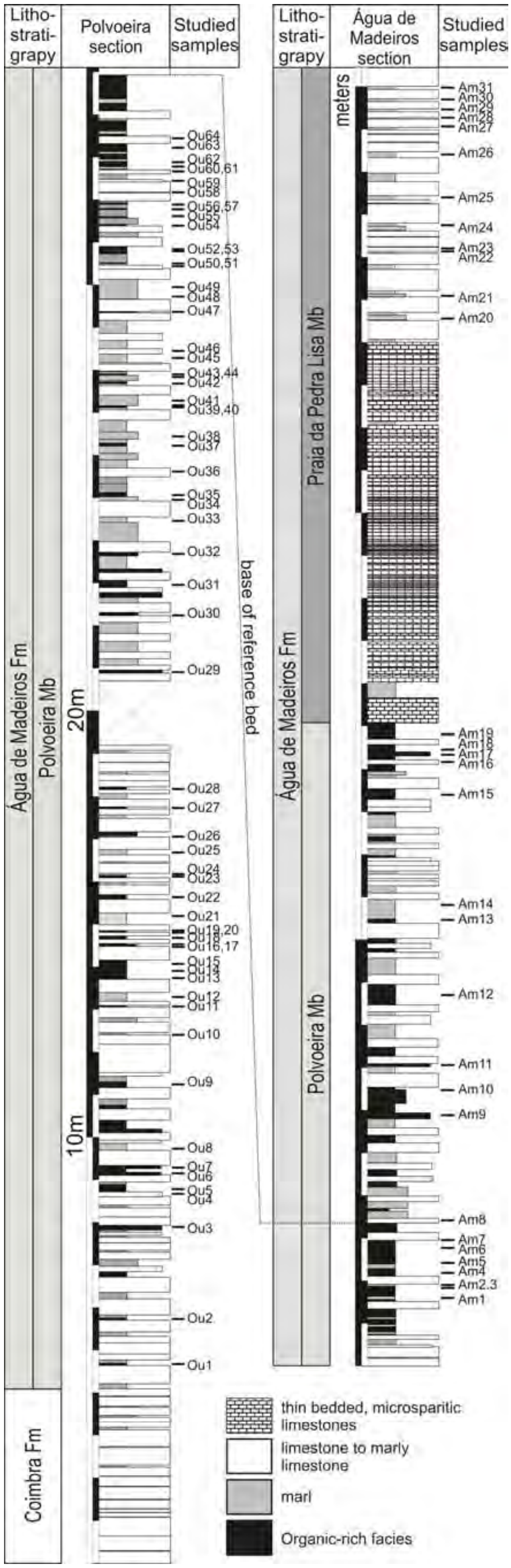


Fig. 3.1.5. High-resolution stratigraphic logs and sampling location of the Água de Madeiros Formation at the Polvoeira (a) and Água de Madeiros (b) locations in the S. Pedro de Moel area. See locations in Fig. 3.1.4a.

About 100 mg of each crushed sample were heated to 600 °C in a helium atmosphere according to analytical procedures outlined by Espitalié et al. (1977, 1985) and Peters (1986). Measurements made include S_1 (mg HC/g rock), S_2 (mg HC/g rock), S_3 (mg CO_2/g rock) and T_{max} (°C) (c.f. Tissot and Welte, 1984). Derived parameters such as Hydrogen Index (HI = S_2/TOCx100), Oxygen Index (OI = S_3/TOCx100) and Production Index [PI = $S_1/(S_1+S_2)$] were also calculated (c.f. Espitalié et al., 1977, 1985; Peters, 1986).

3.1.3.4. Vitrinite Reflectance

Vitrinite reflectance (%R_o) was measured in two whole rock samples from each member of the Água de Madeiros Formation. The analyses were performed with a Carl Zeiss Axioskop 2Plus microscope equipped with a spectrophotometer J&M (MSP 200). Analyses followed the procedures described by the ISO 7404-5 norm (1994), with the exception of the number of readings per sample which was limited by the number of identifiable vitrinite particles in dispersed OM.

3.1.4. High-resolution stratigraphy of the Água de Madeiros Formation

The Água de Madeiros Formation at S. Pedro de Moel has a measured thickness of about 58 m. The Polvoeira and overlying Praia da Pedra Lisa Members have their formal type-sections in the Polvoeira and Água de Madeiros localities (Duarte and Soares, 2002) (Fig. 3.1.4a). High-resolution stratigraphic analysis enabled a good correlation to be made between the two studied sections (Fig. 3.1.5), and a composite section of the Água de Madeiros Formation was compiled (Fig. 3.1.6). Ammonites allow the Água de Madeiros Formation to be dated from the oxynotum chronozone (Late Sinemurian) to the base of the jamesoni chronozone (earliest Pliensbachian) (Duarte et al., 2010, 2011a).

3.1.4.1. Polvoeira Member

The Polvoeira Member occurs at both Polvoeira and Água de Madeiros (Fig. 3.1.5) and overlies the Coimbra Formation. The basal part of the member is dominated by limestones with regular marl–limestone alternations (Fig. 3.1.7a). Carbonates and some marlstones contain a rich benthonic macrofauna including brachiopods, infaunal and epifaunal bivalves, and Rhizocorallium. Organic-rich black shales, generally about 10 cm thick, occur and commonly have a millimetric to submillimetric lamination. The thickest black shale unit is about 50 cm thick (Fig. 3.1.7b).

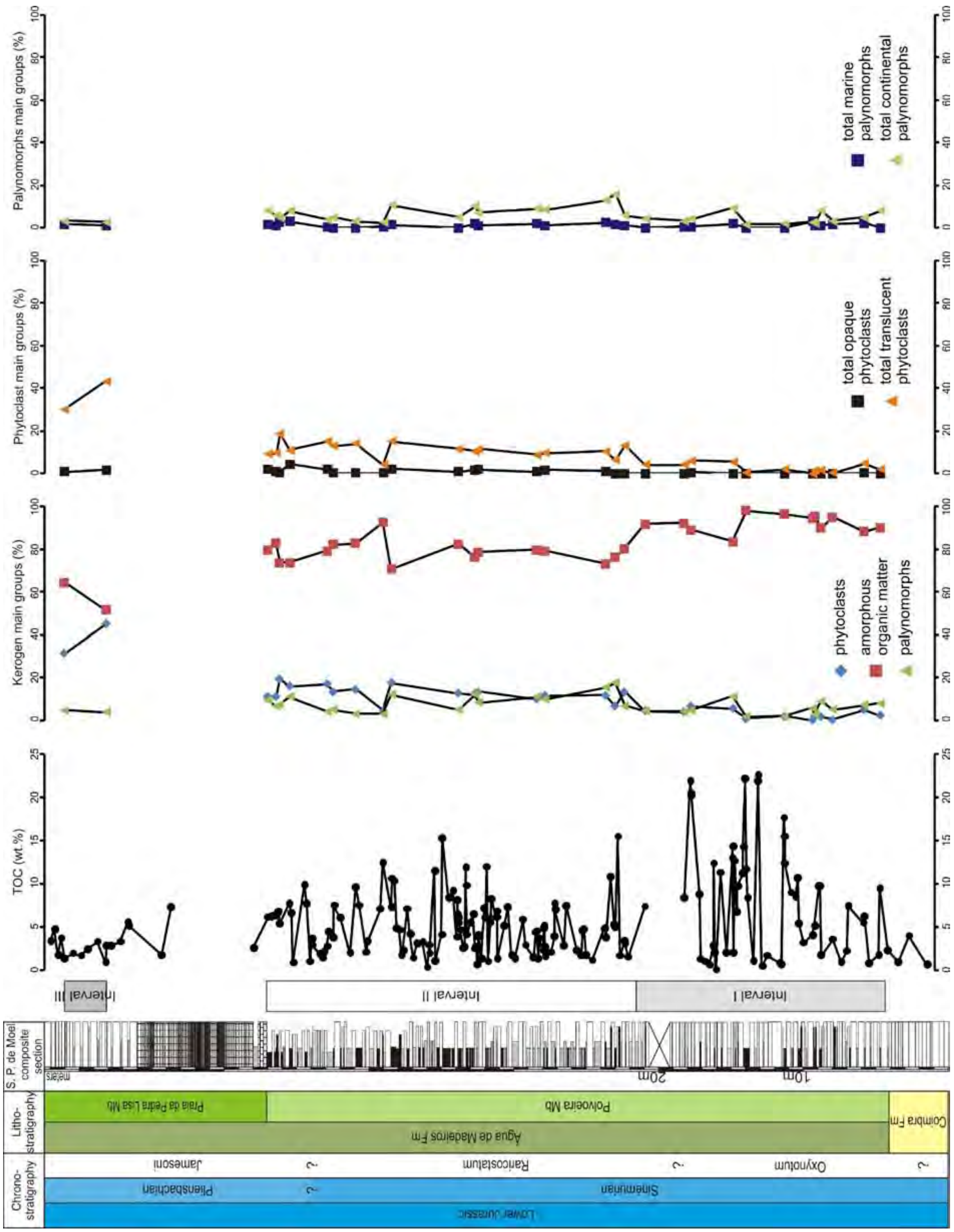


Fig. 3.1.6. Variations in TOC content and palynofacies composition through the Upper Sinemurian - Lower Pliensbachian composite section at S. Pedro de Moel. See text for the meaning of Intervals I, II and III.

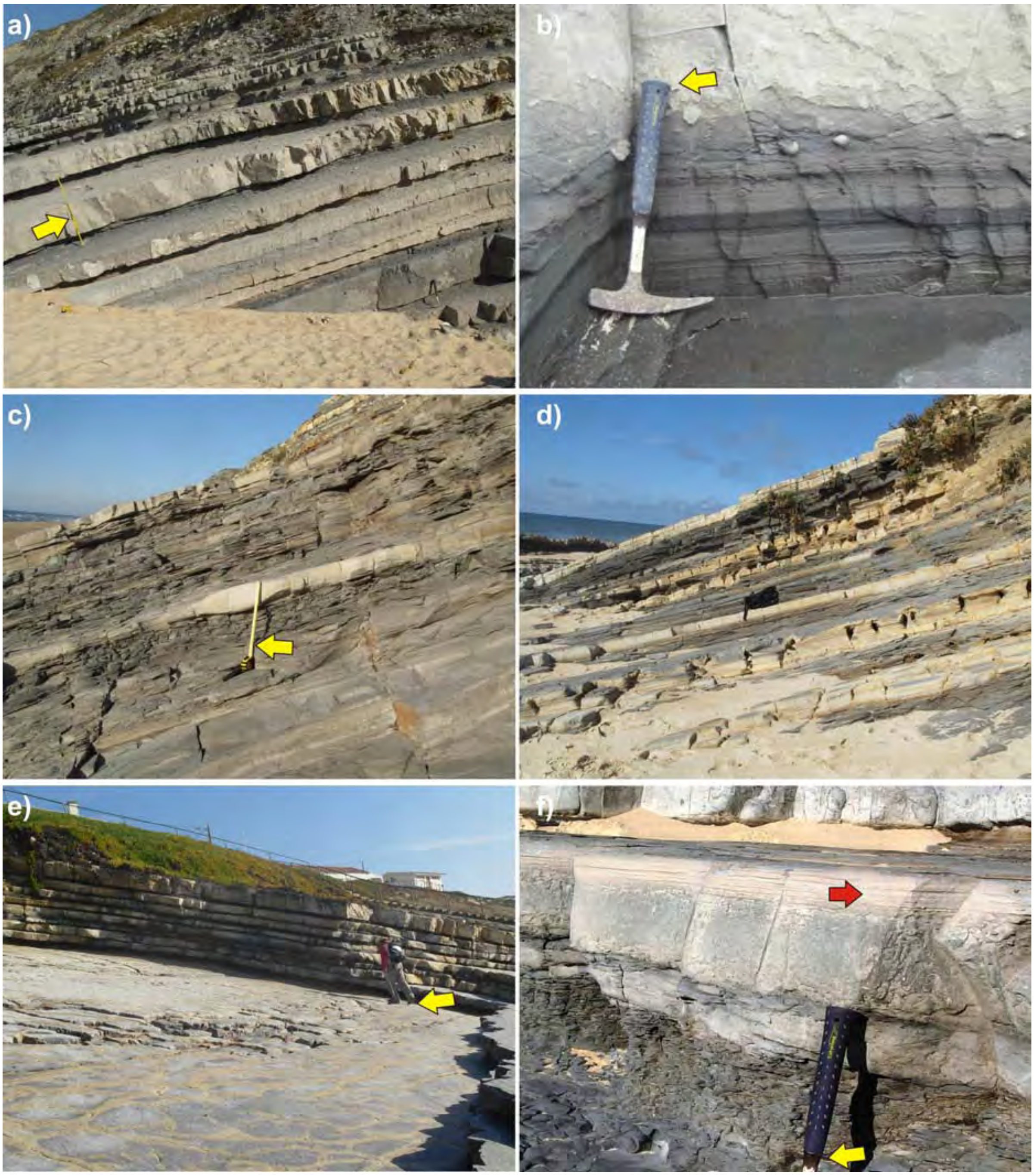


Fig. 3.1.7. Field photographs of the Água de Madeiros Formation in the studied area. (a) General view of bioclastic organic-rich marl–limestones at the base of the Polvoeira Member (Polvoeira section); (b) Close-up of the thickest black shale unit observed in the Água de Madeiros Formation, overlain by Gryphaea-rich limestone facies (Polvoeira section); (c) General view of the grey marly and organic-rich (black shales) dominated facies in the middle part of the Polvoeira Member (top of Polvoeira section); (d) Organic-rich marl–limestone alternations in the upper part of the Polvoeira Member (Água de Madeiros section); (e) General view of the marl – limestone alternations at the top of the Pedra Lisa Member (Água de Madeiros section); (f) Detail of the thin laminated limestone facies (arrow) in the Polvoeira Member with a TOC content of 5.4 wt % (Polvoeira section). Yellow arrows indicate scale markers.

The middle and upper parts of the Polvoeira Member are more argillaceous (Figs. 3.1.7c and 3.1.7d), and there is an increase in nektonic fossils (ammonites and belemnites) and a decrease of benthonics. Limestones in general consist of fossiliferous wackestones which are rich in ostracods and molluscs. Marlstones occur at a decimetric scale and are often grey to dark grey in colour (Figs. 3.1.7c and 3.1.7d). Several beds include intercalations of cm-thick black shales, often containing fossil fish fragments. Large wood fragments also occur in this part of the succession.

3.1.4.2. Praia da Pedra Lisa Member

This carbonate-dominated unit is well exposed in the Água de Madeiros section (Duarte and Soares, 2002) and is approximately 16 m thick (Fig. 3.1.5). The member begins with about 9 m of decimetre- to centimetrethick mudstones to wackestones rich in ostracods and radiolarians, sometimes laminated. Benthic and nektonic macrofauna are scarce; however, ammonites, *Rhizocorallium* and *Thalassinoides* are present in some horizons.

The upper part of the member, approximately 7 m thick, is marked by a gradual increase in interbedded centimetre-scale grey to dark grey marlstones and a thickening of the limestone beds (Fig. 3.1.7e). Some marly intervals are laminated and have high OM contents. The limestones consist of fossiliferous wackestones with molluscs, ostracods, brachiopods, belemnites and ammonites.

3.1.5. Geochemical and Palynofacies results

3.1.5.1. Total Organic Carbon

TOC contents were analysed in the grey to dark grey marlstones and laminated limestone facies of the Água de Madeiros Formation and results are presented in Tables 3.1.1 and 3.1.2 and Fig. 3.1.6. These facies are clearly differentiated by variations in the carbonate content (insoluble residue between 7 and 82 wt %). The TOC data published by Duarte et al. (2010) has been added to Fig. 3.1.6 and a total of 196 TOC determinations were therefore available for this study, covering the entire 58 m of the Água de Madeiros Formation in the S. Pedro de Moel area.

The TOC content reaches a maximum of about 22 wt % in three marlstone (argillaceous) horizons at the base of the middle part of the Polvoeira Member (Fig. 3.1.6). The marlstones had insoluble residues above 50 wt %. The TOC content of the member varies from 9.4 wt % to 6.2 wt %, respectively, from the base to the top of the unit.

Table 3.1.1. Palynofacies and Rock-Eval Pyrolysis data from the Água de Madeiros Formation in the Polvoeira section.

Sample	Lithofacies	Thickness (meters)	IR (wt.%)	TOC (wt.%)	Phytoclats (%)	AOM (%)	Palynomorphs (%)	S_1 (mg HC/ g rock)	S_2 (mg HC/ g rock)	S_3 (mg HC/ g rock)	HI (mg HC/g TOC)	OI (mg HC/g TOC)	T_{max} (°C)	PI
Ou1	BS	469	59	9,6	2	90	8	1,39	53,06	1,43	555	15	418	0,03
Ou2	BS	575	39	6,1	5	88	7	0,92	28,61	1,6	469	26	417	0,03
Ou3	LL	793	13	4	0	95	5	0,75	19,81	1,01	497	25	415	0,04
Ou4	LL	877	7	1,7	2	90	9							
Ou5	BS	885	64	9,7				1,96	61,83	1,2	637	12	422	0,03
Ou6	LL	918	24	5,1	2	96	3							
Ou7	LL	934	29	4,8	0	94	6	0,52	23,26	1,12	486	23	414	0,02
Ou8	DM	998	60	3,1				0,34	12,16	0,78	392	25	424	0,03
Ou9	BS	1125	24	12,3	2	96	2	3,26	62,37	3,86	507	31	425	0,05
Ou10	DM	1246	44	1,7				0,15	3,55	0,71	216	43	421	0,04
Ou11	BS	1308	53	22,5				7	63	8	281	36	426	0,1
Ou12	M	1341	37	1				0,12	1,6	1,93	160	193	424	0,07
Ou13	BS	1391	35	11,6	1	98	2	1,66	70,53	2,6	608	22	424	0,02
Ou14	BS	1401	58	22,1				6,36	45,45	11,81	206	53	426	0,12
Ou15	BS	1416	41	11,1				1,68	50,89	4,55	458	41	423	0,03
Ou16	BS	1451	39	9,7				1,1	45,4	3,7	469	38	421	0,02
Ou17	BS	1456	58	6,7				0,55	30,09	2,87	448	43	421	0,02
Ou18	BS	1474	61	12,6				1,1	34,5	8,2	275	65	426	0,03
Ou19	L	1481	12	1,9				0,23	7,8	0,94	393	47	416	0,03
Ou20	BS	1483	57	14,3	6	83	11	1,78	68,61	4,85	481	34	420	0,03
Ou21	M	1528	42	1,9				0,17	5,4	1,57	276	80	422	0,03
Ou22	BS	1570	57	11,2				1,39	53,7	4,2	479	37	423	0,03
Ou23	BS	1614	59	12,3				1,6	48,2	4,4	392	36	423	0,03
Ou24	DM	1617	50	2,8				0,22	6,79	1,28	244	46	419	0,03
Ou25	M	1674	32	1				0,08	1,08	0,74	114	78	428	0,07
Ou26	M	1705	39	1,2				0,14	3,31	0,5	267	40	420	0,04
Ou27	BS	1773	56	20,1	7	89	5	7	63	14	313	70	426	0,1
Ou28	BS	1820	34	8,3	4	92	4							
Ou29	LL	2092	18	8,8	4	92	4	1,54	50,43	1,53	574	17	415	0,03
Ou30	LL	2231	22	3,3	13	80	7							
Ou31	BS	2296	48	6	6	76	18	1,14	27,23	2,16	453	36	417	0,04
Ou32	BS	2366	36	5,6	12	73	15	0,53	23,17	1,16	416	21	416	0,02
Ou33	M	2454	45	1,1				0,09	1,29	1,25	120	116	431	0,07
Ou34	ML	2499	24	1,7				0,13	4,01	2,02	234	118	429	0,03
Ou35	BS	2514	60	4,7				0,42	19,28	0,68	413	15	428	0,02
Ou36	L	2564	10	2,2				0,12	4,05	0,53	180	24	429	0,03
Ou37	BS	2634	45	7,4				0,36	7,94	1,26	107	17	428	0,04
Ou38	DM	2650	30	2,8				0,25	10,25	0,71	368	26	422	0,02
Ou39	DM	2713	52	3,9				0,4	15,72	0,66	406	17	428	0,02
Ou40	BS	2714	52	7,6				0,43	23,11	2,58	303	34	428	0,02
Ou41	M	2741	34	2,1				0,16	6,18	0,85	301	41	427	0,03
Ou42	M	2776	35	1,6				0,18	5,82	0,57	375	37	425	0,03
Ou43	M	2781	34	2,6	11	79	10							
Ou44	DM	2788	52	4,8				0,43	18,6	1,07	385	22	425	0,02
Ou45	M	2820	52	3,7				0,3	12,74	1,06	348	29	431	0,02

Table 3.1.1. (continuation). Palynofacies and Rock-Eval Pyrolysis data from the Água de Madeiros Formation in the Polvoeira section.

Ou46	LL	2836	23	4,5	10	79	11	0,58	17,76	1,24	398	28	425	0,03
Ou47	DM	2932	38	5,8				0,41	23,28	2,03	401	35	423	0,02
Ou48	M	2986	35	1,3				0,13	3,16	0,72	243	55	427	0,04
Ou49	M	3011	32	1,7				0,11	1,8	0,57	104	33	425	0,06
Ou50	BS	3039	27	7,2				1,16	40,9	1,13	566	16	423	0,03
Ou51	BS	3062	48	5,1				0,52	23,34	0,64	459	13	423	0,02
Ou52	BS	3073	35	6,1				0,16	1,36	1,3	22	21	437	0,11
Ou53	BS	3100	47	6,1				0,2	3,68	0,74	61	12	430	0,05
Ou54	BS	3152	32	8,2				0,3	2,76	1,03	34	13	434	0,1
Ou55	BS	3159	51	5,5				0,38	18,68	3,04	343	56	427	0,02
Ou56	BS	3185	56	11,9				1,46	71,2	3,36	598	28	423	0,02
Ou57	BS	3192	61	6				0,5	23,48	3	389	50	427	0,02
Ou58	ML	3219	22	1,3				0,11	2,46	1,31	187	99	429	0,04
Ou59	LL	3242	24	3,8	13	78	18							
Ou60	L	3265	18	2,4	12	76	12							
Ou61	BS	3275	55	6,4				0,48	22,62	2,48	354	39	428	0,02
Ou62	DM	3295	56	5,5				0,64	25,88	1,14	470	21	425	0,02
Ou63	BS	3324	55	9,7				1,06	49,43	2,62	509	27	424	0,02
Ou64	L	3344	16	2,7				0,25	11,84	1,48	445	56	418	0,02

M – Marlstone; ML – Marly limestone; L – Limestone; DM – Dark grey marlstone; BS – Black shale; LL – Thin laminated limestone.

However, high TOC values occur in the mid-upper part of the Polvoeira Member (Fig. 3.1.6), in parallel with a decrease in the proportion of calcareous facies (compare Figs. 3.1.7a and 3.1.7c). Some high values of TOC, around 12-14 wt %, were recorded in laminated limestones, with lower insoluble residues of 24 wt %.

In the Praia da Pedra Lisa Member, TOC values are relatively high in marls in the upper part of the unit, despite the calcareous nature of the succession. TOC reaches values of 3 to 4 wt %, with a maximum of 7.3 wt % in a mm-thick horizon (Fig. 3.1.6).

3.1.5.2. Organic lithofacies

Frequent organic-rich intervals (with TOC above 2 wt %) are present in the Água de Madeiros Formation in the studied area (Fig. 3.1.6). Based on sedimentological and geochemical criteria (Fig. 3.1.6), the intervals can be divided into three lithofacies: dark grey marlstones (Fig. 3.1.7c), black shales (i.e. fissile marlstones) (Fig. 3.1.7b), and thin laminated limestones (Fig. 3.1.7f). The dark grey marlstone lithofacies is present in both the Polvoeira and Praia da Pedra Lisa Members and TOC values generally do not exceed 6 wt %. Black shales have the highest TOC contents in the entire succession (minimum of 4 wt %). The black shales are laminated (i.e. non-bioturbated) and benthic macrofauna are absent although there are some fish remains. The laminated limestones can be distinguished from the black shales by their higher carbonate content (IR content below 25%; minimum value of 7%), and by their stratigraphic relationship with over- or underlying limestones. These organic-rich facies are particularly evident at the base of the Polvoeira Member.

Table 3.1.2. Palynofacies and Rock-Eval pyrolysis data from the Água de Madeiros Formation at Água de Madeiros section.

Sample	Lithofacies	Thickness (meters)	IR (wt.%)	TOC (wt.%)	Phytoclats (%)	AOM (%)	Palynomorphs (%)	S_1 (mg HC/ g rock)	S_2 (mg HC/ g rock)	S_3 (mg HC/ g rock)	HI (mg HC/g TOC)	OI (mg HC/g TOC)	T_{max} (°C)	PI
AM1	DM	3365	35	4,6				0,53	19,78	1,91	430	42	424	0,03
AM2	BS	3379	52	5,39	13	82	5							
AM3	DM	3388	34	3,8				0,33	15,27	1,91	402	50	425	0,02
AM4	BS	3414	44	9,1				1,1	50,96	2,06	560	23	423	0,02
AM5	BS	3445	50	8,4				0,56	36,1	3,2	432	38	423	0,02
AM6	BS	3489	55	15,2				2,3	72,8	7,5	479	49	419	0,03
AM7	LL	3493	18	4,1				0,41	18,17	1,39	447	34	420	0,02
AM8	L	3538	16	1				0,13	1,97	1,16	189	112	432	0,06
AM9	LL	3782	16	4,3				0,72	19,38	1,2	454	28	422	0,04
AM10	BS	3840	47	7,9	17	71	12	0,61	27,69	3,14	350	40	423	0,02
AM11	BS	3899	26	13,2	5	93	3	1,98	78,14	1,89	590	14	410	0,02
AM12	BS	4089	51	10,4	14	83	3	0,91	47,76	1,44	461	14	416	0,02
AM13	BS	4242	44	4,5	13	82	5	0,36	17,48	1,22	389	27	418	0,02
AM14	DM	4284	51	3,1	17	79	4	0,17	7,79	1,16	252	38	421	0,02
AM15	BS	4545	48	7,3	16	74	11	0,56	22,66	3,72	309	51	420	0,02
AM16	LL	4612	23	5,9	19	74	7	0,69	26,59	1,81	454	31	416	0,02
AM17	LL	4623	19	6,7				1,02	41,28	2,08	612	31	420	0,02
AM18	BS	4637	39	6,9	11	83	7	0,89	35,03	1,85	507	27	416	0,02
AM19	BS	4695	51	6,9	11	80	9	0,69	26,37	1,83	385	27	416	0,03
AM20	DM	5651	87	5,1				0,14	19,35	1,84	354	34	425	0,007
AM21	M	5713	31	2,2				0,06	5,79	2,05	269	95	426	0,01
AM22	M	5805	29	2,8				0,09	11,98	1,62	430	58	425	0,007
AM23	ML	5812	13	0,85	45	51	4							
AM24	DM	5869	61	3,3				0,11	11,18	1,55	344	48	426	0,01
AM25	M	5939	83	2,4				0,05	6,44	1,8	268	75	428	0,008
AM26	M	6039	65	1,9				0,04	5,16	1,97	268	102	431	0,008
AM27	ML	6097	22	1,32	31	64	5							
AM28	DM	6118	39	3,6				0,1	14,09	2,38	387	65	423	0,007
AM29	M	6141	70	1,7				0,04	3,24	2,25	186	129	430	0,01
AM30	DM	6166	44	4,7				0,09	13,79	3,43	297	74	425	0,006
AM31	DM	6192	77	4				0,09	4,25	14,69	108	372	426	0,02

M – Marlstone; ML – Marly limestone; L – Limestone; DM – Dark grey marlstone; BS – Black shale; LL – Thin laminated limestone.

3.1.5.3. Palynofacies

Palynofacies analysis of the Água de Madeiros Formation indicated that three main groups of organic particles are present: amorphous organic matter (AOM), phytoclasts and palynomorphs (Mendonça Filho et al., 2010b; 2011; Menezes et al., 2008; Tyson, 1995).

3.1.5.3.1. AOM

Organic material is dominated by AOM (51.5% to 97.8%) (Fig. 3.1.6), which is most abundant at the base of the Polvoeira Member (always above 83%). The AOM can be divided into three main sub-groups according to the classification scheme proposed by Mendonça Filho et al. (2011). The first sub-group corresponds to particles with a heterogeneous, clotted appearance, made up of an amorphous matrix and with the presence of inclusions. This sub-group is termed AOM s.s. and correspond to the microbiological reworking of phytoplankton or bacterial products (Figs. 3.1.8a, 3.1.8b). The second subgroup, "resins", was rarely observed. The third subgroup correspond to amorphous products resulting from primary microbiological productivity or the degradation of macrophyte tissues. The sub-group comprises a range of AOM from homogeneous sheets with diffuse outlines to cohesive particles with a stratified or laminated appearance (Figs. 3.1.8e, 3.1.8f).

In both cases, fluorescence tends to be greenishyellow to light orange, homogeneous and intense. The amorphous, or as sometimes called "pseudoamorphous", products of macrophyte tissue degradation can be distinguished by a reddish-orange to dark brown colour in TWL and low or nonfluorescent characteristics in FM.

In the Água de Madeiros Formation, amorphous products derived from primary microbiological productivity dominate AOM assemblages, and reach up to 90%. However, in three samples from the Polvoeira Member, AOM *s.s.* represents more than 50% of the total AOM content.

3.1.5.3.2. Phytoclasts

Phytoclasts occur in the majority of the samples, reaching up to 45%, and are dominated by opaque and translucent particles (Fig. 3.1.6). The latter particles have a dark brown colouration in TWL and are the most abundant sub-group, particularly as degraded non-biostructured particles (Mendonça Filho et al., 2011). Opaque phytoclasts are practically absent from the base of the Polvoeira Member, but increase slightly in the mid- to upper parts of this unit, reaching a maximum value of 4.6%. Amorphous phytoclasts, cuticles and membranes are present but are very rare. Phytoclasts are particularly abundant in the Praia da Pedra Lisa Member (Figs. 3.1.8c and 3.1.8d), varying between 31 to 45%, and dominating both the translucent, non-biostructured particles (9.3 to 20.9%) and the biostructured particles. In this part of the succession, opaque constituents are very rare (less than 2%).

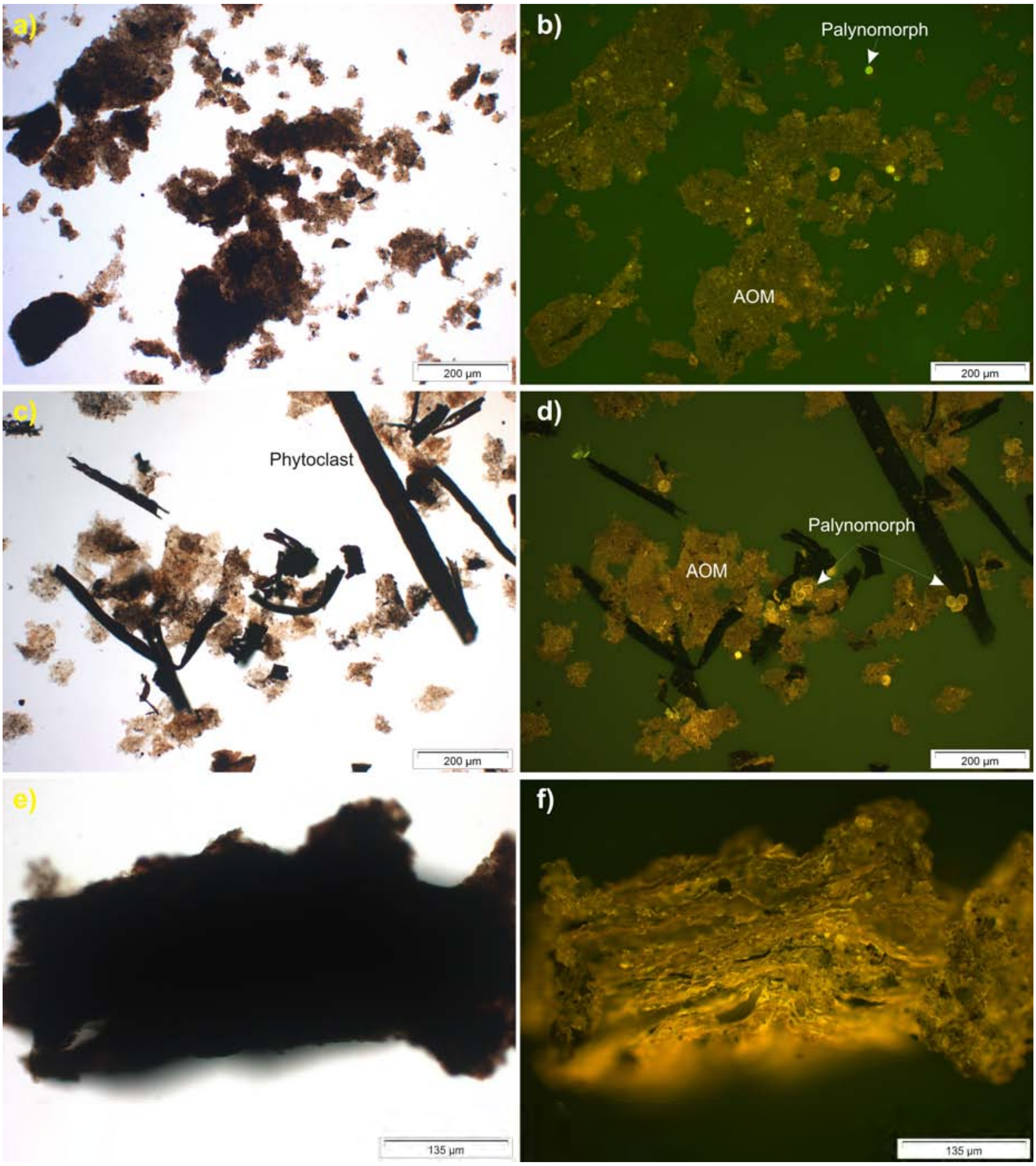


Fig. 3.1.8. Photomicrographs of organic particles in samples from the Água de Madeiros Formation (a, c and e in transmitted white light; b, d and f in fluorescence mode illumination). (a) and (b) Photomicrographs show the dominance of AOM (sample Ou1; Polvoeira Member); (c) and (d). Photomicrographs show the dominance of opaque phytoclasts (sample AMO23; Praia da Pedra Lisa Member); (e) and (f). Amorphous products of primary microbiological productivity, in this case a microbial mat (sample Ou9; Polvoeira Member).

3.1.5.3.3. Palynomorphs

Palynomorphs vary between 2.0% and 17.5% (Fig. 3.1.6) and are represented by sporomorphs (pollen grains and spores), algal spores, acritarchs and prasinophytes. Continental sporomorphs dominate the Polvoeira Member (maximum of 13%), and are mainly represented by pollen grains, especially *Classopollis* in agglomerate and tetrad dispositions. Some samples from the upper part of the Polvoeira and Praia da Pedra Lisa Members show good preservation of freshwater green algal zygospores, reaching maximum abundance values of 5.3% and 3.2% of the kerogen assemblage, respectively. One particle was identified as *Botryococcus* genus. Marine palynomorphs are rare (>3%) and have an irregular stratigraphic distribution. Acritarchs and *Tasmanites* and *Cymatiosphaera* genera of the prasinophyte phycomata are the principal marine palynomorphs in the Água de Madeiros Formation in the studied samples.

3.1.5.4. Rock-Eval pyrolysis

Rock-Eval pyrolysis data are presented in Tables 3.1.1 and 3.1.2 and in Figs. 3.1.9 and 3.1.10. Rock-Eval S_1 and S_2 values vary widely in the Água de Madeiros Formation (0.04 – 6.36 and 1.1 – 78.1 mg HC/g rock, respectively). More than 68% of the studied samples have S_2 above 10 mg HC/g rock. The highest S_2 values were recorded in the Polvoeira Member (average, 26.7; maximum 78.1 mg HC/g rock) (Fig. 3.1.9). S_2 values from the Praia da Pedra Lisa Member were lower (average, 9.5; maximum of 19.35 mg HC/g rock).High values of S_2 are correlated with high HI values (Fig. 3.1.9), up to 637 mg HC/g TOC. Over 80% of the studied samples have HI above 200 mg HC/g TOC. The OI ranges from 12 to 192 mg CO_2/g TOC in the Polvoeira Member, and 33 to 372 mg CO_2/g TOC in the Praia da Pedra Lisa Member, although the last value is anomalous.

T_{max} values vary between 410°C and 437°C, with an average of 424°C, with little variation in the two members of the Água de Madeiros Formation. The PI ranges between 0.006 and 0.12 (Tables 3.1.1 and 3.1.2).

Plotting OI versus HI data (Fig. 3.1.10) shows that most of the analyzed samples fall within the field of Type II kerogen, consistent with the palynofacies observations. A few samples with high HI values (around 600 mg HC/g TOC) from the Polvoeira Member correspond to Type I kerogen (Fig. 3.1.10). Macroscopically these samples correspond to typical black shales and their TOC contents vary between 6.7 and 13.2 wt %.

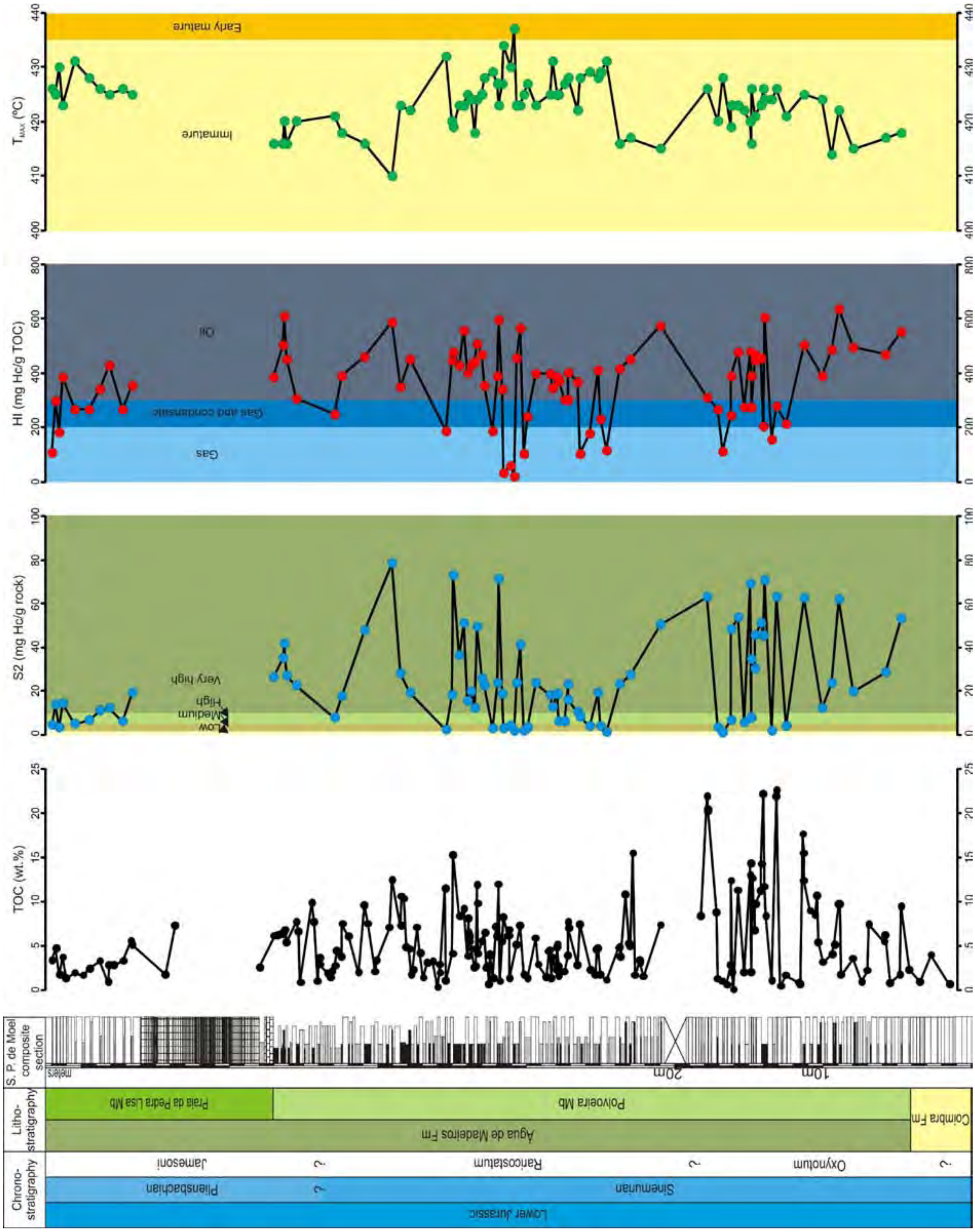


Fig. 3.1.9. Stratigraphic variations of TOC, Rock-Eval S_2 and HI across the Água de Madeiros Formation in the S. Pedro de Moel area. TOC includes data published in Duarte et al. (2010). See text for the meaning of Intervals I, II and III.

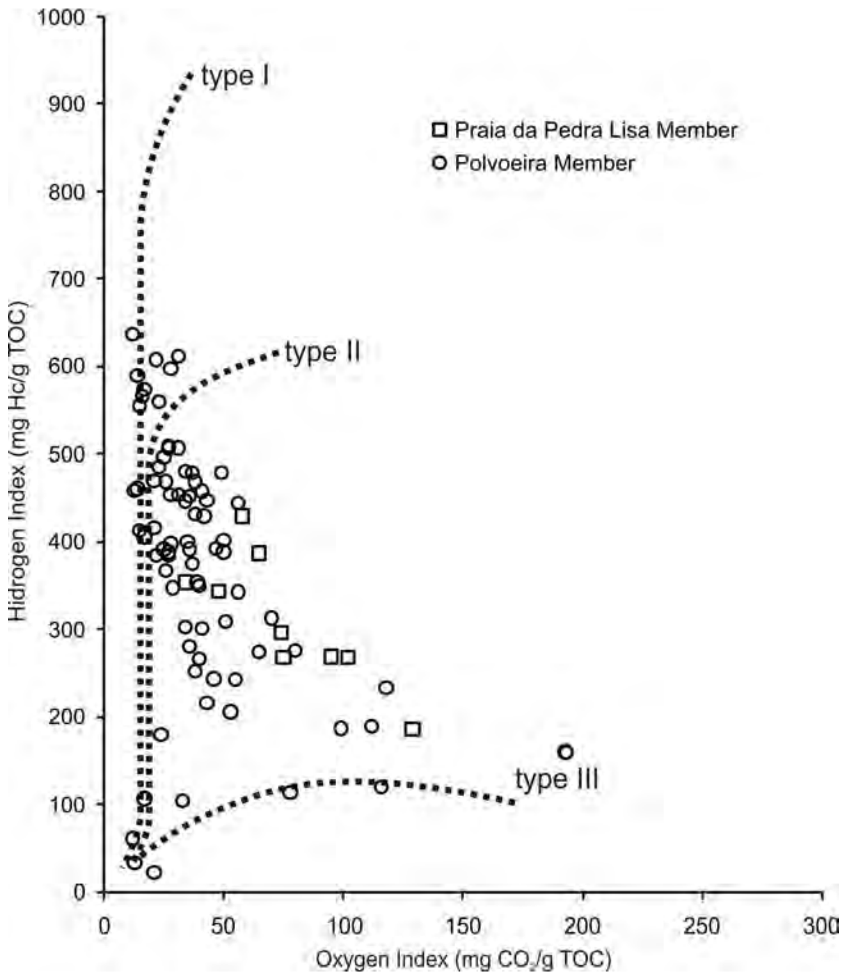


Fig. 3.1.10. Plot of Hydrogen Index versus Oxygen Index for samples from the Polvoeira and Praia da Pedra Lisa Members of the Água de Madeiros Formation at S. Pedro de Moel.

3.1.5.5. Vitrinite Reflectance

Vitrinite reflectance values in the Água de Madeiros Formation vary between 0.42%R_o and 0.45%R_o.

3.1.6. Discussion

3.1.6.1. Organic sedimentary evolution in the Água de Madeiros Formation

Organic-rich facies in the Água de Madeiros Formation are present in a fully-marine marl–limestone succession (Fig. 3.1.7) and are mostly associated with black shales. AOM of marine origin dominates the kerogen assemblage, with a marginal contribution by continental phytoclasts and palynomorphs (Fig. 3.1.11). The presence of the thermophilic genus Classopollis is an important palaeoclimatic indicator (e.g. Vakhrameyev, 1982), suggesting that climatic conditions during the latest Sinemurian – earliest Pliensbachian were most likely warm and dry. Marine palynomorphs are rare (less than 3%) and show an irregular vertical distribution.

Data in Fig. 3.1.6 indicate that there is a stratigraphic control on the distribution of the different kerogen components, and three intervals can be distinguished (I to III):

3.1.6.1.1. Interval I

This interval corresponds to the lower part of the Polvoeira Member (Fig. 3.1.6) which, compared to the underlying Coimbra Formation, is marked by an increase in argillaceous material and OM. The occurrence of bioclastic facies with abundant benthonic macrofauna (mainly brachiopods and bivalves), points to the development of a high-energy shallow-marine carbonate ramp, with some phases of restriction permitting OM preservation. The highest TOC values (>20 wt %) are recorded within this interval, in which thin black shales occur intercalated with bioclastic limestones and marlstones. The kerogen assemblage is dominated by AOM, varying between 83% and 98% (Fig. 3.1.11).

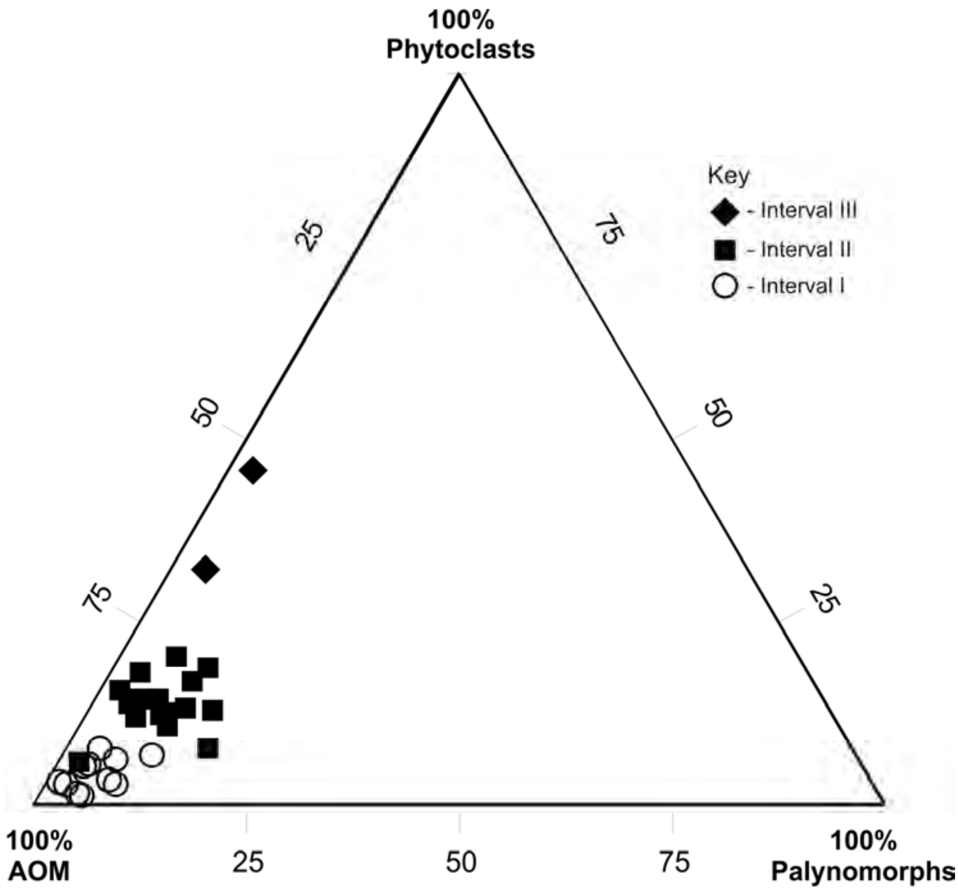


Fig. 3.1.11. Ternary AOM – phytoclast - palynomorph plot of the studied samples from the Água de Madeiros Formation.

Depending on the carbonate content, the AOM has different morphological characteristics; however, it mostly corresponds to amorphous products of primary microbiological productivity (Mendonça Filho et al., 2011). In the marlstone facies, AOM has a typical sheeted aspect. In more carbonate-rich horizons, AOM appears more compact and platy and is stratified or laminated (Fig. 3.1.8), a characteristic that is also observed macroscopically. This differentiated morphology may be linked with bacterial productivity and sedimentation rates, with lower rates favouring the development of a compact, platy aspect (Mendonça Filho et al., 2010a; see also Silva et al., 2011c for a similar example from the Pliensbachian of the Lusitanian Basin). These intervals are interpreted to indicate the establishment of a thriving microbial benthonic assemblage under restricted conditions and variable sedimentation rates.

Proportions of phytoclasts and palynomorphs are similar throughout this stratigraphic interval, reaching no more than 9% (phytoclasts) and 11% (palynomorphs). The phytoclasts are mainly composed of translucent particles, while palynomorphs are enriched in continental sporomorphs with some acritarchs. The "primary" microbiological productivity character of these kerogen assemblages is also confirmed by some high HI values which plot as type I kerogen (Fig. 3.1.10).

In this interval, carbonates include normal-marine benthonic macrofauna (brachiopods and bivalves) (Duarte et al., 2011a), and an increase of marly sedimentation and sporadic ammonite occurrences suggest the development of a shallow-marine environment with low-amplitude relative sea-level changes. The scarcity of opaque phytoclasts (<1%) is consistent with a proximal location (Tyson, 1995).

These depositional conditions are restricted to the S. Pedro de Moel area, suggesting that the area was surrounded by a large, shallow-water carbonate ramp, indicated in the eastern part of the basin by dolomitic limestones and dolostones (vide Duarte et al., 2010) (Fig. 3.1.12). These sedimentary conditions favoured the deposition and preservation of AOM.

3.1.6.1.2. Interval II

Interval II corresponds to the middle and upper part of the Polvoeira Member (Fig. 3.1.6). This interval shows an increase of the marly (argillaceous) facies, alternating with limestones which become more abundant towards the top. Black shales increase in number and in thickness, being associated with more argillaceous facies.

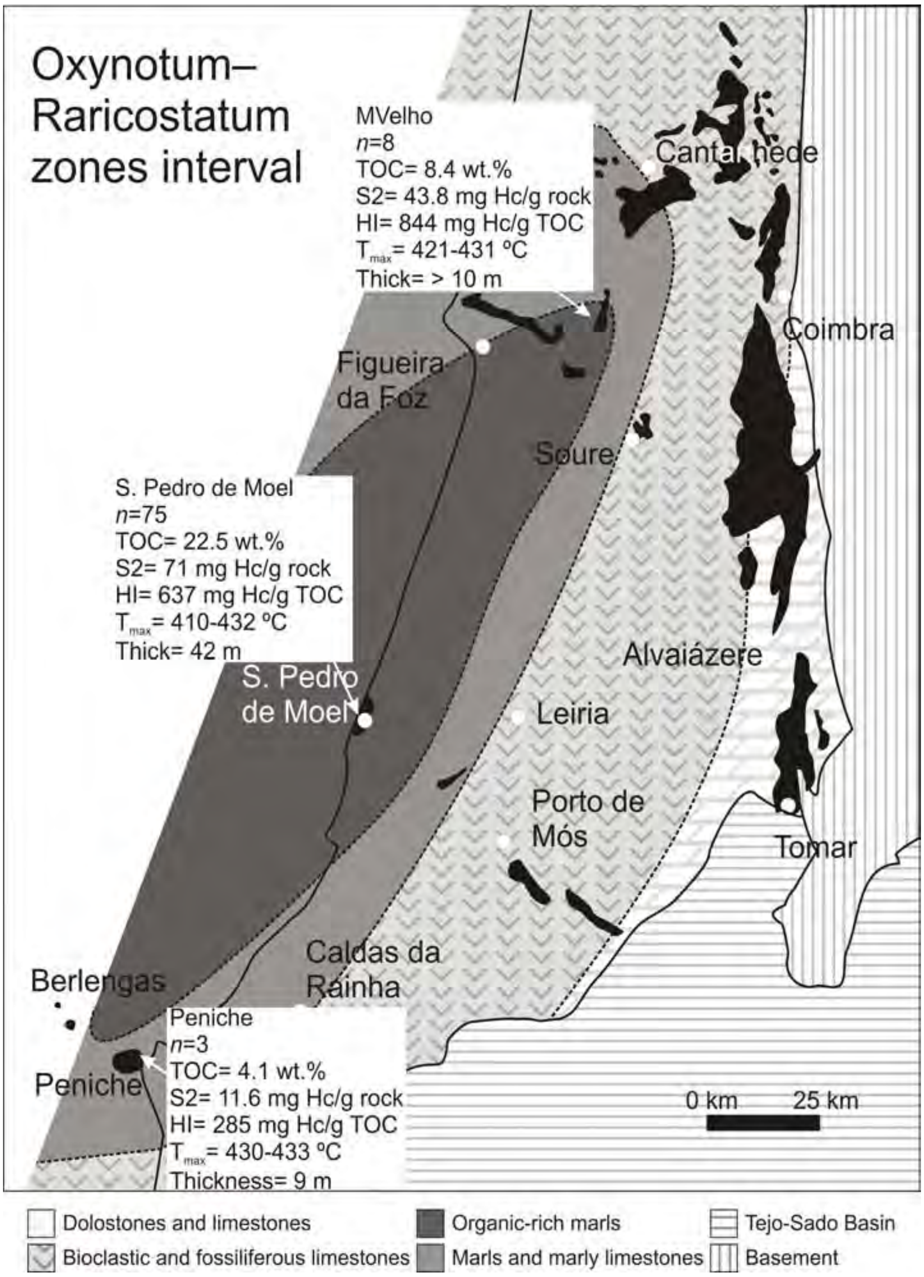


Fig. 3.1.12. Facies (modified from Duarte et al., 2010) and organic geochemical variation across the Lusitanian Basin for the oxynotum-raricostatum Zone interval (time-equivalent to Polvoeira Member deposition). Data from Montemor-o-Velho in F. Silva et al. (2010); data from Peniche are unpublished.

In these intervals, the TOC content reaches about 15 wt %, with background values always exceeding 1 wt %. Although the TOC values are not as high as those observed in the underlying Interval I, organic-rich facies are, in terms of absolute number of occurrences, more abundant.

This interval includes the most complex kerogen assemblage, resulting from an increase in the contents of phytoclasts (5-19%) and palynomorphs (3-18%) (Fig. 3.1.11). This diversity seems to be linked with the analyzed lithofacies. In fact, lowest phytoclasts and palynomorphs and highest AOM contents correspond to organic-rich laminated limestones

(TOC around 13 wt %). In this case, and similar to several examples in Interval I, the AOM corresponds to the amorphous products of primary microbiological activity. In the organic-rich marls, both AOM (between 70 and 83%) and phytoclasts (10-19%) show a more regular distribution. The content of opaque phytoclasts slightly increases in this part of the succession. Palynomorphs are dominated by pollen grains (maximum 11%), with a small contribution by marine particles (mainly acritarchs).

One of the most important features of this interval is the occurrence of fresh-water green algal zygospores in several samples, implying the occurrence nearby of lacustrine or lagoonal environments.

Differences in the kerogen assemblage are the result of a change in the depositional system between the lower and the middle-upper part of the Polvoeira Member. The increasing argillaceous contribution is coupled with the gradual disappearance of benthonic macrofauna (brachiopods and bivalves), an enrichment in nektonics such as ammonites and belemnites, and the occurrence of some pelagic bivalves (Duarte et al., 2011a). These sedimentary characteristics are consistent with the development of a deepening phase, interpreted by Duarte et al. (2010) as a second-order transgressive event. This transgression was responsible for a deepening of the water column, for the increase in the number of OM production sites (probably in mid-ramp locations), and for remobilization/erosion of transitional deposits resulting in a more heterogeneous OM content, which is however dominated by marine (Type II) kerogen.

At a basin scale, the flooding event that characterizes this interval is also recorded in other locations (e.g. Peniche, Figueira da Foz and Montemor-o-Velho), as similar deposits likewise enriched in organic matter (e.g. Duarte et al., 2010; F. Silva et al., 2010). At Peniche, and compared to S. Pedro de Moel, sedimentological and palynofacies data suggest that sediment deposition took place in more proximal conditions on the carbonate ramp (Duarte et al., 2004; 2010), with an increase in continental contribution. Here, in the Polvoeira Member, the phytoclasts content reaches up to 79% and zygospores are abundant (unpublished data).

3.1.6.1.3. Interval III

This interval corresponds to the Praia da Pedra Lisa Member, in which marlstones and OM accumulation are restricted to the upper part. Palynofacies data indicate that it corresponds to the most proximal, but still fully marine, environments recorded in the Água de Madeiros Formation at S. Pedro de Moel. The main feature of this interval is the high content of phytoclasts, reaching 45% of the kerogen (Fig. 3.1.11). Moreover, and compared to the previous interval, the ratio of opaque to translucent phytoclasts decreases significantly, suggesting a shift to a more proximal, shallow-water environment.

This evidence is consistent with other sedimentological and stratigraphic parameters which suggest that deposition occurred during a shallowing phase (Duarte et al., 2010). According to these authors, the lower part of the Praia da Pedra Lisa Member marks a second-order regressive phase which is also observed in other parts of the basin. With the exception of the S. Pedro de Moel area, time equivalent outcrops elsewhere in the basin are composed exclusively of limestones and dolostones, the latter limited to SE of the basin (see Duarte et al., 2010) (Fig. 3.1.12).

3.1.6.2. Source-rock potential of the Agua de Madeiros Formation

Rock-Eval pyrolysis data from samples with TOC values above 1 wt % confirm the high source-rock potential of the Água de Madeiros Formation in the S. Pedro de Moel region (Fig. 3.1.9). The S_2 and HI records, with more than 68% of samples presenting values above 10 mg HC/g rock and 300 mg HC/g TOC, respectively, indicate that there is good potential for oil generation (Espitalié et al. 1985; Peters, 1986). Most of the samples fall within the Type II kerogen field on a graph of OI versus HI (Fig. 3.1.10); some samples from the Polvoeira Member, which exhibit HI values higher than 600 mg HC/g TOC and OI below 31 mg HC/g TOC, plot as Type I kerogen. Despite a limited number of data (n = 9), high HI contents (maximum: 844 mg HC/g TOC) and high S2 (maximum: 44 mg HC/g rock) values were also recorded by F. Silva et al. (2007, 2010) in samples of the Polvoeira Member from the incomplete stratigraphic succession at Montemor-o-Velho (Fig. 3.1.12).

However, T_{max} (410–437°C), PI generally lower than 0.1 and $\%R_o$ lower that 0.45 indicate that the succession is immature or has barely entered the oil generation window. Similar characteristics occur at Montemor-o-Velho where Tmax values between 421 and 431°C for the Polvoeira Member were recorded (F. Silva et al., 2010) (Fig. 3.1.12).

In summary, the data emphasises the high potential for oil generation of the Água de Madeiros Formation although it seems that thermal maturity is below the oil generation window. Organic-rich facies in the formation are in general confined to the study area and the area around Montemor-o-Velho (Duarte et al. 2010) (Fig. 3.1.12). In spite of a poor stratigraphic understanding of many of the wells drilled both off- and onshore (see GPEP, 1986; Rasmussen et al., 1998), the facies maps of Duarte et al. (2010) suggest that the Água de Madeiros Formation (and in particular the organic-rich facies of Polvoeira Member) may in fact be more developed and thicker in the western onshore and the offshore portions of the basin.

Thermal maturity may increase in the subsurface offshore with possible hydrocarbon generation. Indeed, near S. Pedro de Moel, there are some surface seeps (Paredes de Vitória) and oil shows in several wells which have tentatively been linked with a Lower Jurassic source rock (see Beicip-Franlab, 1996; DPEP, 2011).

3.1.6.3. Lower Jurassic source rock potential

3.1.6.3.1. Lusitanian Basin

The "Brenha Formation" (Lower and Middle Jurassic: Fig. 3.1.2) has previously received attention as a potential hydrocarbon source rock in the Lusitanian Basin (e.g. Beicip-Franlab, 1996; DPEP, 2011; GPEP, 1986). In addition to the Água de Madeiros Formation (latest Sinemurian–earliest Pliensbachian), an organic-rich unit also occurs in the Marly Limestone with Organic Facies ("MLOF") Member of Vale das Fontes Formation, dated as early – late Pliensbachian (top ibex – margaritatus ammonite chronozone interval) (e.g. Duarte and Soares, 2002; Duarte et al., 2010; Oliveira et al., 2006; Silva et al., 2011a). The unit has been studied by TOC analysis, Rock-Eval pyrolysis, and palynofacies and biomarker analysis in different locations (e.g. Duarte et al., 2010; Ferreira et al., 2010a; 2010b; F. Silva et al., 2007, 2010; Silva et al., 2010; 2011c).

Although the Polvoeira and MLOF Members are similar in terms of their organic-rich marl–limestone sedimentation, their areal distribution, sedimentological context and kerogen content are quite different. At a basin scale, the sedimentological and lateral facies variations of the MLOF Member are typical of deeper marine conditions (see Duarte et al., 2010). Palynofacies studies (Ferreira et al., 2010a) suggest that the MLOF Member is dominated by AOM although with a more diversified kerogen assemblage as a result of an increase in phytoclasts and palynomorphs (Fig. 3.1.13). A change in character of the kerogen assemblages is also expressed in the pyrolysis data with an increased content of Type III kerogen (Fig. 3.1.14). In the MLOF Member, HI reaches maximum values of 555 mg HC/g TOC at Peniche (Oliveira et al., 2006), 366 mg HC/g TOC at Figueira da Foz, and 550 mg HC/g TOC at Coimbra (F. Silva et al., 2007) (Fig. 3.1.14).

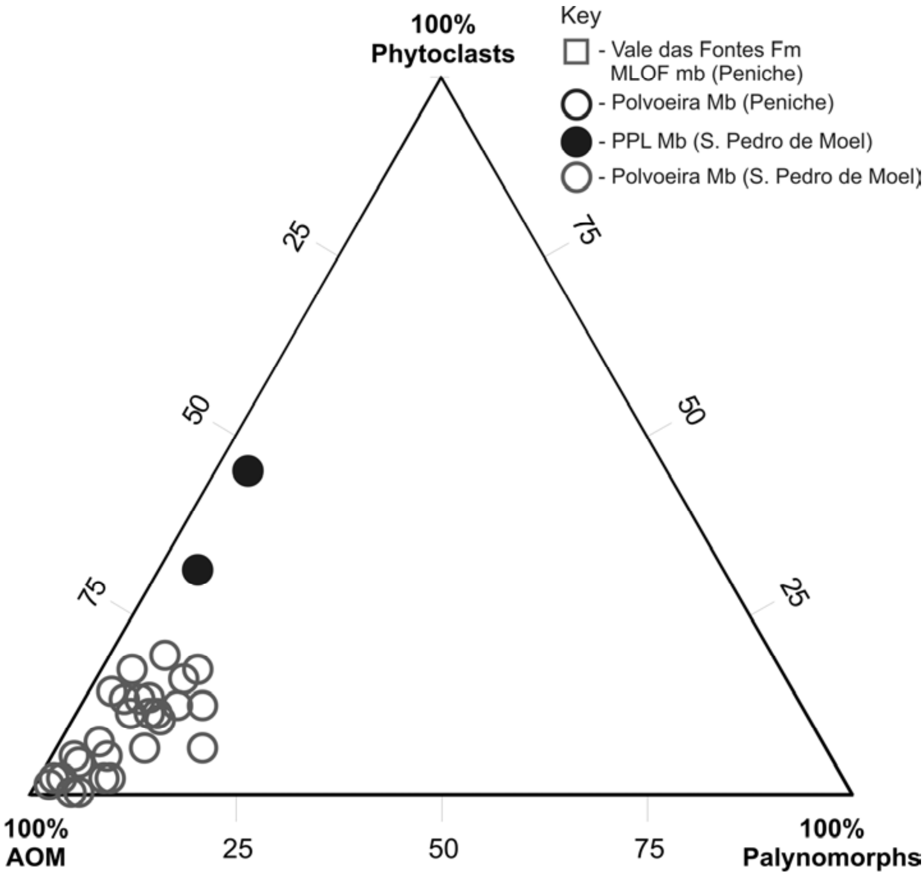


Fig. 3.1.13. AOM – phytoclasts - palynomorphs ternary plot of the Água de Madeiros Formation (this study) and MLOF Member of the Vale das Fontes Formation (data from Ferreira et al., 2010a).

In terms of thermal maturation, T_{max}, and vitrinite reflectance data from the MLOF Member are similar to those obtained for the Água de Madeiros Formation. T_{max} values from Peniche (Oliveira et al., 2006), Figueira da Foz and Coimbra (F. Silva et al., 2010) are generally below 435°C, 438°C and 430°C, respectively. Vitrinite reflectance measured in samples of the MLOF Member from Peniche is below 0.47%R_o (Ferreira et al., 2010b). As with the Água de Madeiros Formation, these indicate the immaturity of the Pliensbachian succession at outcrop. However, the lateral distribution of the organic facies of the MLOF Member at a basin scale (see Duarte et al., 2010) suggests that thermal maturation may have occurred both onshore and offshore in the subsurface of the Lusitanian Basin, in the more deeply buried areas (Stapel et al., 1996). The present study, based on high-resolution stratigraphy and organic geochemistry, will assist with future stratigraphic and facies analysis of the Portuguese offshore Lower Jurassic (Alves et al., 2002; 2006; Pereira and Alves, 2011; Rasmussen et al., 1998), including the stratigraphic reinterpretation of wells available in DPEP (2011).

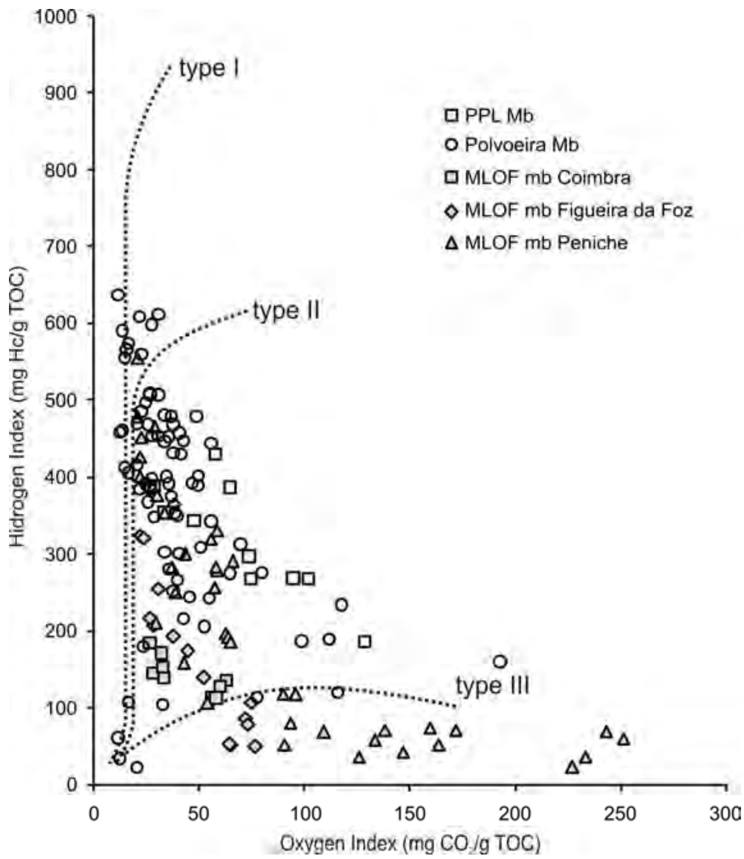


Fig. 3.1.14. Graph of Hydrogen Index versus Oxygen Index for the samples from the Água de Madeiros Formation (this study) and MLOF Member at Peniche (Oliveira et al., 2006), Figueira da Foz (Silva et al., 2007) and Coimbra (Silva et al., 2007).

3.1.6.3.2. Regional source rock potential

At a global scale, especially associated with the early Toarcian Oceanic Anoxic Event (e.g. Jenkyns, 1988), the Lower Jurassic constitutes a time of good OM preservation and formation of potential source rocks (e.g. Bodin et al., 2011; Farrimond et al., 1989; Vandenbroucke and Largeau, 2007), particularly in NW Europe where thick black shale units were developed (e.g. Baudin, 1995; Fleet et al., 1987). In the context of the Sinemurian and Pliensbachian, some peri-Atlantic and western Tethyan basins show similar organic-rich facies to those observed in the Lusitanian Basin (Duarte et al., 2010; Silva et al., 2011b). High oil-generating potential is recorded, for example, in the Atlantic margin basins of Ireland and UK (Scotchman, 2001), the Basque-Cantabrian and Asturias basins of northern Spain (e.g. Borrego et al., 1996; Quesada et al., 1997; Beroiz and Permanyer, 2011), and in the Moroccan Middle Atlas (Sachse et al., 2012). These observations highlight the importance of the NE Atlantic margin in future oil exploration, and in the assessment of the palaeoenvironmental and palaeo-oceanographic conditions that led to the widespread accumulations of organic matter in the Early Jurassic (see Korte and Hesselbo, 2011; Silva et al., 2011b).

3.1.7. Conclusions

The Água de Madeiros Formation (upper Sinemurian – lowermost Pliensbachian) is composed of a fully marine, organic-rich marl–limestone succession which can be divided into the Polvoeira and Praia da Pedra Lisa Members. In this paper, the results of TOC determinations, palynofacies analyses and Rock-Eval pyrolysis are presented, allowing the source rock potential of the succession to be evaluated. The main conclusions are as follows:

1. The Água de Madeiros Formation is composed of three organic-rich lithofacies: dark grey marlstones, black shales and thin laminated limestones which have TOC contents > 1 wt %. The maximum TOC values (22 wt.%) occur in the Polvoeira Member, which also corresponds to the interval with the highest number of black shale intervals.

2. Kerogen assemblages in the Água de Madeiros Formation are dominated by AOM with some contributions by phytoclasts and palynomorphs. Three stratigraphic intervals can be identified on the basis of variations in the palynofacies content which appear to be controlled by changes in the depositional system. Among other features, phytoclasts increase considerably in the upper part of the unit (Praia da Pedra Lisa Member), associated with more proximal and regressive facies.

3. According to the Rock-Eval pyrolysis data, the succession has oil and oil-gas generation potential as suggested by high S_2 and HI values, reaching up to 78.1 mg HC/g rock and 637 mg HC/g TOC, respectively. There are a few horizons with HI values indicating Type I kerogen, but Type II dominates in the greater part of the formation. T_{max} and vitrinite reflectance data indicate that the studied section is immature.

4. Organic geochemical data obtained in this study confirm that the Água de Madeiros Formation at its type-locality is the most organic-rich marine unit present in the basin. Despite its immaturity in the studied area, the data reaffirm the importance of Lower Jurassic deposits as potential hydrocarbon source rocks in both on- and offshore areas.

References

ALVES, T.M., GAWTHORPE, R.L., HUNT, D.W. and MONTEIRO, J.H., 2002. Jurassic tectono-sedimentary evolution of the Northern Lusitanian Basin (offshore Portugal). Marine and Petroleum Geology, 19, 727–754.

ALVES, T.M., MOITA, C., CUNHA, T., ULLNAESS, M., MYKLEBUST, R., MONTEIRO, J.H. and MANUPPELLA, G., 2009. Diachronous evolution of Late Jurassic–Cretaceous continental rifting in the northeast Atlantic (west Iberian margin). Tectonics, 28, TC4003, doi:10.1029/2008TC002337.

ALVES, T.M., MOITA, C., SANDNES, F., CUNHA, T., MONTEIRO, J.H. and PINHEIRO, L.M., 2006. Mesozoic–Cenozoic evolution of North Atlantic continental slope basins: The Peniche basin, western Iberian margin. AAPG Bull., 90, 31–60.

AZERÊDO, A.C., DUARTE, L.V., HENRIQUES, M.H. and MANUPPELLA, G., 2003. Da dinâmica continental no Triásico aos mares do Jurássico Inferior e Médio. Cadernos de Geologia de Portugal. Instituto Geológico e Mineiro, Lisbon, 43pp.

AZERÊDO, A.C., SILVA, R.L., DUARTE, L.V. and CABRAL, M.C., 2010. Subtidal stromatolites from the Sinemurian of the Lusitanian Basin (Portugal). Facies, 56, 211–230.

AZERÊDO, A.C., WRIGHT, V.P. and RAMALHO, M.M., 2002. The Middle–Late Jurassic forced regression and disconformity in central Portugal: eustatic, tectonic and climatic effects on a carbonate ramp system. Sedimentology, 49, 1339–1370.

BAUDIN, F., 1995. Depositional Controls on Mesozoic Source Rocks in the Tethys. In: HUC, A.Y. (Ed.), Paleogeography, Paleoclimate, and Source Rocks. AAPG Studies in Geology, 40, 191–211.

BEICIP-FRANLAB, 1996. Geochemical evaluation of the Lusitanian and Porto basins. Gabinete para a Pesquisa e Exploração de Petróleo (GPEP), Contribution to the MILUPOBAS Project Confidential Report, Lisbon.

BEROIZ, C. and PERMANYER, A., 2011. Hydrocarbon habitat of the Sedano Trough, Basque-Cantabrian Basin, Spain. Journal of Petroleum Geology, 34 (4), 387–410.

BODIN, S., FRÖHLICH, S., BOUTIB, L., LAHSINI, S. and REDFERN, J., 2011. Early Toarcian source rock potential in the Central High Atlas Basin (Central Morocco): Regional distribution and depositional model. Journal of Petroleum Geology, 34 (4), 345–364.

BORREGO, A.G., HAGEMANN, H.W., BLANCO, C.G., VALENZUELA, M. and SUARÉZ DE CENTI, C., 1996. The Pliensbachian (Early Jurassic) “anoxic” event in Asturias, northern Spain: Santa Mera Member, Rodiles Formation. Organic Geochemistry, 25(5-7), 295-309.

DPEP, Divisão para a Pesquisa e Exploração de Petróleo. Ministério da Economia, Governo Português. http://www.dgge.pt/dpep/en/history.htm (retrieved in 9 of November of 2011).

DUARTE, L., 2004. The geological heritage of the Lower Jurassic of Central Portugal: selected sites, inventory and main scientific arguments. Rivista Italiana di Paleontologia Stratigrafia, 110, 381–388.

DUARTE, L.V., 2007. Lithostratigraphy, sequence stratigraphy and depositional setting of the Pliensbachian and Toarcian series in the Lusitanian Basin (Portugal). In: ROCHA, R.B. (Ed): The Peniche section (Portugal). Contributions to the definition of the Toarcian GSSP. International Subcommission on Jurassic Stratigraphy, 17-23.

DUARTE, L.V., COMAS-RENGIFO, M.J., PAREDES, R., CABRAL, M.C., SIIVA, R.L. and AZERÊDO, A.C., 2011a. High-resolution stratigraphy and faunal associations in the Upper Sinemurian organic-rich deposits of the western Iberian margin (Lusitanian Basin, Portugal). Geophysical Research Abstracts, 13, EGU2011-8527-1.

DUARTE, L.V., MENDONÇA FILHO, J.G., SILVA, R.L. and OLIVEIRA, L.C., 2011b. Rock-Eval pyrolysis of the Água de Madeiros Formation (Lower Jurassic) from the Lusitanian Basin, Portugal. Mineralogical Magazine, 75, 785.

DUARTE, L.V., SILVA, R.L., DUARTE, C.B., AZERÊDO, A.C. and COMAS-RENGIFO, M.J., 2008. Litostratigrafia do Jurássico Inferior da região de S. Pedro de Moel (Bacia Lusitânica). In: CALLAPEZ, P. M., ROCHA, R. B., MARQUES, J. F., CUNHA, L. S. and DINIS. P.M. (Eds): A Terra, Conflitos e Ordem. Homenagem ao Professor Ferreira Soares. Museu e Laboratório de Mineralogia e Geologia da Universidade de Coimbra, Coimbra, 175-185.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F., 2010. Organic-rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total Organic Carbon distribution and relation to transgressive-regressive facies cycles. Geologica Acta, 8, 325–340.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das séries margo-calcárias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicações do Instituto Geológico e Mineiro, 89, 135–154.

DUARTE, L.V., WRIGHT, V.P., LÓPEZ, S.F., ELMI, S., KRAUTTER, M., AZERÊDO, A.C., HENRIQUES, M.H., RODRIGUES, R. and PERILLI, N., 2004. Early Jurassic carbonate evolution in the Lusitanian Basin (Portugal): facies, sequence stratigraphy and cyclicity, in: DUARTE, L.V. and HENRIQUES, M.H. (Eds.): Carboniferous and Jurassic Carbonate Platforms of Iberia. 23rd IAS Meeting of Sedimentology Field Trip Guide Book, Coimbra. volume 1, 45–71.

ESPITALIÉ, J., DEROO, G. and MARQUIS, F., 1985. La pyrolyse Rock-Eval et ses applications: première partie. Revue de l'Institut Français du Pétrole, 40, 563–579.

ESPITALIÉ, J., LAPORTE, J.L., MADEC, M., MARQUIS, F., LEPLAT, P., PAULET, J. and BOUTEFEU, F., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. Revue de l'Institut Français du Pétrole, 32, 23–43.

FARRIMOND, P., EGLINTON, G., BRASSEL, S.C. and JENKYNS, H.C., 1989, Toarcian anoxic event in Europe: An organic geochemical study. Marine and Petroleum Geology, 6, 136–147.

FERREIRA, R., MENDONÇA FILHO, J.G., DUARTE, L.V., SILVA, R.L. and MENDONÇA, J.O., 2010a. Variação organofaciológica na sucessão rica em matéria orgânica do Pliensbaquiano de Peniche (Bacia Lusitânica, Portugal). In: FLORES, D. and MARQUES, M., (Eds): Actas X Congresso de Geoquímica dos Países de Língua Portuguesa/XVI Semana de Geoquímica, Porto. Memórias, 14, 301–308.

FERREIRA, R., MENDONÇA FILHO, J.G., DUARTE, L.V., SILVA, R.L. and MENDONÇA, J.O., 2010b. Hydrocarbon generation potential of the Pliensbachian organic-rich series of Peniche (Lusitanian Basin, Portugal): An organopetrographic and thermal maturation assessment integrated analysis. In: PENA DOS REIS, R. and PIMENTEL, N. (Eds.): II Central & North Atlantic Conjugate Margins Conference. Extended Abstracts, Volume III, Lisbon, 116–120.

FLEET, A.J., CLAYTON, C.J., JENKYNS, H.C. and PARKINSON, D.N., 1987, Liassic source rock deposition in western Europe. In: BROOKS, J. and GLENNIE, K. (Eds.): Petroleum Geology of North West Europe, Graham & Trotman, 59–70.

GPEP, 1986. The petroleum potential of Portugal. Gabinete para a Pesquisa e Exploração de Petróleo, Lisbon, Unpublished report DGGE/DPEP, 62pp.

HESSELBO, S.P., JENKYNS, H.C., DUARTE, L.V. and OLIVEIRA, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth and Planetary Science Letters, 253, 455–470.

HISCOTT, R.N., WILSON, R.C.L., GRADSTEIN, F.M., PUJALTE, V., GARCÍA-MONDÉJAR, J., BOUDREAU, R.R. and WISHART, H.A., 1990. Comparative stratigraphy and subsidence history of Mesozoic rift basins of North Atlantic. AAPG Bull., 74, 60–76.

ISO 7404-5, 1994. Methods for the Petrographic Analysis of Bituminous Coal and Anthracite: Part 5. Method of Determining Microscopically the Reflectance of Vitrinite. International Organization for Standardization, Geneva. 11 pp.

JENKYNS, H.C., 1988. The Early Toarcian (Jurassic) Anoxic Event: stratigraphy, sedimentary, and geochemical evidence. American Journal of Science, 288, 101-151.

KORTE, C. and HESSELBO, S.P., 2011. Shallow marine carbon and oxygen isotope and elemental records indicate icehouse-greenhouse cycles during the Early Jurassic. Paleoceanography, 26, PA4219.

LEINFELDER, R.R. and WILSON, R.C.L., 1998. Third-order sequences in an Upper Jurassic rift-related second-order sequence, central Lusitanian Basin, Portugal. In: DE GRACIANSKY, P.-C., HARDENBOL, J., JACQUIN, T. and VAIL, P.R. (Eds.): Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60, 507–525.

MENDONÇA FILHO, J.G., CHAGAS, R.B.A., MENEZES, T.R., MENDONÇA, J.O., DA SILVA, F.S. and SABADINI-SANTOS, E. 2010a. Organic facies of the Oligocene lacustrine system in the Cenozoic Taubaté basin, Southern Brazil. Int. Journ. Coal Geol., 84, 166–178.

MENDONÇA FILHO, J.G., MENEZES, T.R., MENDONÇA, J.O., OLIVEIRA, A.D., CARVALHO, M.A., SANT'ANNA, A.J. and SOUZA, J.T., 2010b. Palinofácies. In: DE SOUZA CARVALHO, I. (Ed.): Paleontologia. Interciência, Rio de Janeiro, 379–413.

MENDONÇA FILHO, J.G., MENEZES, T.R. and MENDONÇA, J.O., 2011. Chapter 5: Organic composition (Palynofacies Analysis). In: FLORES, D. and MARQUES, M. (Eds.): ICCP Training Course on Dispersed Organic Matter. International Committee for Coal and Organic Petrology, Porto, 33–81.

MENEZES, T.R., MENDONÇA FILHO, J.G., ARAÚJO, C.V., SOUZA, I.V.A.F. and MENDONÇA, J.O., 2008. Fácies Orgânica: conceitos, métodos e estudos de casos na indústria do petróleo. Revista Brasileira de Geociências, 38, 80–96.

OLIVEIRA, L.C.V., RODRIGUES, R., DUARTE, L.V. and LEMOS, V., 2006. Avaliação do potencial gerador de petróleo e interpretação paleoambiental com base em biomarcadores e isótopos estáveis do carbono da seção Pliensbaquiano-Toarciano inferior (Jurássico inferior) da região de Peniche (Bacia Lusitânica, Portugal). Boletim de Geociências da Petrobras, 14, 207–234.

PALAIN, C., 1976. Une série détritique terrigène les Grés de Silves: Trias et Lias inférieur du Portugal. Memória dos Serviços Geológicos de Portugal, 25, 377p.

PENA DOS REIS, R., CUNHA, P.M.R., DINIS, J.L. and TRINCÃO, P., 1999. Geologic evolution of Lusitanian Basin during Late Jurassic (Portugal). In: HALL, R.L., SMITH, P.L. (Eds.): Advances in Jurassic Research 2000. GeoResearch Forum, 6, 345–356.

PEREIRA, R. and ALVES, T.M., 2011. Margin segmentation prior to continental break-up: A seismic-stratigraphic record of multiphased rifting in the North Atlantic (Southwest Iberia). Tectonophysics, 505, 17-34.

PETERS, K.E., 1986. Guidelines for evaluating petroleum source rocks using programmed pyrolysis. AAPG Bull., 70, 318–329.

PINHEIRO, L.M., WILSON, R.C.L., PENA DOS REIS, R., WHITMARSH, R.B. and RIBEIRO, A., 1996. The western Iberia margin: a geophysical and geological overview. In: WHITMARSH, R.B., SAWYER, D.S., KLAUS, A. and MASSON, D.G. (Eds.): Proceedings of the Ocean drilling Program. Scientific Results, 149, 3-23.

QUESADA, S., DORRONSORO, C., ROBLES, S., CHALER, R. and GRIMALT, J.O., 1997. Geochemical correlation of oil from the Ayoluengo field to Liassic black shale units in the southwestern Basque-Cantabrian Basin (northern Spain). Organic Geochemistry, 27, 25–40.

RASMUSSEN, E.S., LOMHOLT, S., ANDERSEN, C. and VEJBÆK, O.V., 1998. Aspects of the structural evolution of the Lusitanian Basin in Portugal and the shelf and slope area offshore Portugal. Tectonophysics, 300, 199–225.

SACHSE, V.F., LEYTHAEUSER, D., GROBE, A., RACHIDI, M. and LITTKE, R., 2012. Orgamic geochemistry and petrology of a Lower Jurassic (Pliensbachian) petroleum source rock from Aït Moussa, Middle Atlas, Morocco. Journal Petroleum Geology, 35(1), 5-24.

SCOTCHMAN, I.C., 2001. Petroleum geochemistry of the Lower and Middle Jurassic in Atlantic margin basins of Ireland and the UK. Geological Society, London, Special Publications,188, 31–60.

SILVA, F., DUARTE, L.V., OLIVEIRA, L.C., RODRIGUES, R. and COMAS-RENGIFO, M.J., 2007. Caracterização do Carbono Orgânico Total e pirólise Rock-Eval no intervalo Sinemuriano superior-Pliensbaquiano do sector norte da Bacia Lusitânica (Portugal). In: GOMES, E.P. and ALENCOÃO, A.M. (Eds.): Proceedings of VI Congresso Ibérico de Geoquímica, Vila Real, 564–567.

SILVA, F., DUARTE, L.V., OLIVEIRA, L.C., RODRIGUES, R. and COMAS-RENGIFO, M.J., 2010. Contribution to the knowledge of petroleum generative potential of Late Sinemurian – Pliensbachian of the Lusitanian basin - northern sector (Portugal). In: PENA DOS REIS, R. and Pimentel, N. (Eds.); II Central & North Atlantic Conjugate Margins Conference. Extended Abstracts, Volume III, Lisbon, 256–260.

SILVA, R.L., DUARTE, L.V., AZERÊDO, A.C. and MENDONÇA FILHO, J.G., 2011a. Contributos sedimentológicos e geoquímicos para a modelação dos sistemas petrolíferos portugueses: as séries jurássicas ricas em matéria orgânica da Bacia Lusitânica (Portugal). Modelação de Sistemas Geológicos, Laboratório de Radioactividade Natural da Universidade de Coimbra, Coimbra, 383–391.

SILVA, R.L., DUARTE, L.V., COMAS-RENGIFO, M.J., MENDONÇA FILHO, J.G. and AZERÊDO, A.C., 2011b. Update of the carbon and oxygen isotopic records of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma): Insights from the organic-rich hemipelagic series of the Lusitanian Basin (Portugal). Chemical Geology, 283, 177-184.

SILVA, R.L., DUARTE. L.V., MENDONÇA FILHO, J.G., DA SILVA, F.S., SILVA, T.F. and COMAS-RENGIFO, M.J., 2011c. Recognition of mucilage and microbial events on the Early–Late Pliensbachian (Lusitanian Basin, Portugal). Mineralogical Magazine, 75, 1875.

SILVA, R.L., MENDONÇA FILHO, J.G., DUARTE, L.V., COMAS-RENGIFO, M.J., AZERÊDO, A.C. and FERREIRA, R., 2010. Organic-rich facies of the top Ibex–Margaritatus zones (Pliensbachian) of the

Lusitanian Basin (Portugal): TOC and biomarkers variation. Geochim. et Cosmochim. Acta, 74 (12-S1), A962.

SOARES, A.F. and DUARTE, L.V., 1997. Tectonic and eustatic signatures in the Lower and Middle Jurassic of the Lusitanian Basin. Comunicaciones IV Congreso de Jurasico de España, Alcañiz, 111-114.

SOARES, A.F., ROCHA, R.B., ELMI, S., HENRIQUES, M.H., MOUTERDE, R., ALMERAS, Y., RUGET, C., MARQUES, J., DUARTE, L.V., CARAPITO, C. and KULLBERG, J.C., 1993. Le sous-bassin nord-lusitanien (Portugal) du Trias au Jurassique moyen: histoire d'un "rift avorté". Comptes rendus de l'Académie des sciences de Paris, 317, 1659–1666.

SPIGOLON, A.L.D., BUENO, G.V., PENA DOS REIS, R., PIMENTEL, N. & MATOS, V.G.A.E., 2010. The Upper Jurassic Petroleum System: evidence of secondary migration in carbonate fractures of Cabaços Formation, Lusitanian Basin. In: PENA DOS REIS, R. and Pimentel, N. (Eds.); II Central & North Atlantic Conjugate Margins Conference. Extended Abstracts, Volume III, Lisbon, 274–278.

STAPEL, G., CLOETINGH, S. and PRONK, B., 1996. Quantitative subsidence analysis of the Mesozoic evolution of the Lusitanian basin (western Iberian margin). Tectonophysics, 266, 493-507.

SUAN, G., MATTIOLI, E., PITTET, B., LÉCUYER, C., SUCHÉRAS-MARX, B., DUARTE, L.V., PHILIPPE, M., REGGIANI, L. and MARTINEAU, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. Earth and Planetary Science Letters. 290, 448–458.

THIERRY, J. et al. (40 co-authors), 2000. Late Sinemurian (193-191 Ma). In: DERCOURT, J., GAETANI, M., VRIELYNCK, B., BARRIER, E., BIJU-DUVAL, B., BRUNER, M.F., CADET, J.P., CRASQUIN, S. and SANDULESCU, M., (Eds.): Atlas Peri-Tethys. Palaeogeographical Maps, CCGM/CGMW, Paris, map 7.

TISSOT, B.P. and WELTE, D.H., 1984. Petroleum Formation and Occurrence. Second Edition. Springer-Verlag, Berlin, 699pp.

TYSON, R.V., 1995. Sedimentary Organic Matter. Organic facies and palynofacies. Chapman & Hall, London, 615pp.

UPHOFF, T.L., 2005. Subsalt (pre-Jurassic) exploration play in the northern Lusitanian basin of Portugal. AAPG Bull., 89, 699–714.

VAKHRAMEYEV, V.A., 1982. Classopollis pollen indicator of Jurassic and Cretaceous climate. International Geological Review, 24, 1190–1196.

VANDENBROUCKE, M. and LARGEAU, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry, 38 (5), 719–833.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. and GRADSTEIN, F.M., 1989. The Lusitanian Basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphic and subsidence history. In: TANKARD, A.J. and BALKWILL, H.R. (Eds.): Extensional Tectonics and Stratigraphy of the North Atlantic Margins. AAPG Memoir, 46, 341–361.

WITT, W.G., 1977. Stratigraphy of the Lusitanian Basin. Shell Prospex Portuguesa, Unpublished report, 61pp.

Acknowledgements

The authors wish to thank Luiz Veiga de Oliveira (Petrobras) and Cenpes Petrobras for the Rock-Eval pyrolysis data. Joalice Mendonça from the Palynofacies and Organic Facies Laboratory (UFRJ) is thanked for help with petrographic analyses. Tiago Alves (Cardiff University) and Stéphane Bodin (Bochum University) are thanked for their review comments which much improved the final version of the manuscript. This work has been financially supported by project PTDC/CTE-GIX/098968/2008 "High resolution stratigraphy of the Lower Jurassic organic-rich marine series in the Lusitanian Basin" (FCT-Portugal and COMPETE-FEDER).

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

Ricardo L. Silva, Luís V. Duarte, João G. Mendonça Filho. In review, Geochemical Journal

Abstract

The Sinemurian–lowermost Pliensbachian Água de Madeiros Formation at S. Pedro de Moel (Lusitanian Basin, Portugal) corresponds to organic marl–limestone alternations rich in benthonic and nektonic marine fauna and large fossil wood fragments are occasionally observed in this area (up to 1 meter in length). It was hypothesized, based on some assumptions, that the carbon and nitrogen isotopic composition of these fossil wood fragments can provide useful information about the conditions prior, during and after deposition. Eleven fossil wood samples were collected from marly hemipelagic deposits across the uppermost Sinemurian (Lower Jurassic) at S. Pedro de Moel (Lusitanian Basin, Portugal) and analysed by optical (Transmitted White Light and Fluorescent Mode) and geochemical (total carbon and nitrogen contents and $\delta^{13}C$ and $\delta^{15}N$) methods.

The organic petrography observations show that fossil wood samples include a wide variety of particles, although 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 $\delta^{13}C$ (defined by 8 out of 11 samples) is observed and most samples present high $\delta^{15}N$. All these data suggest that the isotopic composition of the studied samples were affected by sedimentary and diagenetic processes (either biological or related with coalification). Also, the diagenetic processes were, most likely, different through the section, or if similar, they acted with different magnitudes. Future stable isotopic studies on fossil wood have to take into account more detailed screening, as presented in this study, and should be used to ensure that the results are not biased by diagenetic or biological processes.

Keywords: Fossil wood, Carbon and Nitrogen Stable Isotopes, Sinemurian, Lusitanian Basin, Portugal

3.2.1. Introduction

It is often assumed that the C and N isotopic composition of fossil wood can provide important information for discriminating several environmental parameters, such as pCO_2, water availability or even to distinguish between C_3 and C_4 precursors in post-Cretaceous sediments. Over the past years, numerous studies have dealt with the $\delta^{13}C$ of fossil wood and its significance in palaeoenvironmental studies (e.g. van Bergen and Poole, 2002; Gröcke, 2002; Robinson and Hesselbo, 2004; Bechtel et al., 2007, 2008; Diefendorf et al., 2010). A growing use of this kind of data is related to the differentiation of discrete short lived geological intervals where the carbon cycle was globally perturbed, affecting 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 $\delta^{13}C$ of both marine carbonate and fossil wood show coupled trends, reflecting the oceanic and atmospheric carbon reservoirs, the carbon cycle perturbation is of global nature. The main issues in the use of fossil wood isotopic data are related with two main assumptions: 1) $\delta^{13}C$ of fossil wood reflects, to some extent, the $\delta^{13}C$ of atmosphere at the moment of tree growth; 2) although diagenesis have altered the original $\delta^{13}C$ values, it is likely that through a given section all samples have undergone similar diagenetic changes. Whether the first may seem fairly reasonable, the second assumption raises more concern as it tends to ignore lithological constraints (e.g. Gröcke, 1998), degradation associated to the residence time in the continental and marine environments prior to deposition (e.g. Tyson, 1995), early diagenetic/coalification processes (e.g. Suárez-Ruiz and Crelling, 2008), shift in composition due to severe oxidation (including burning) (e.g. Czimczik et al., 2002) and the impact of these processes in the isotopic composition of fossil wood (e.g. Rimmer et al., 2006). On the other hand, $\delta^{15}N$ 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 discrimination of diagenetic and coalification processes.

The uppermost Sinemurian record of the Lusitanian Basin (Portugal) is characterized by organic marl–limestone alternations, rich in benthonic and nektonic macro- and microfauna (Duarte and Soares, 2002; Duarte et al., 2010; 2012) (Fig. 3.2.1). In addition, the series occasionally includes large (up to 1 meter long) fossil wood remains (Fig. 3.2.2). The aim of this work is to determine if fossil wood samples from the Sinemurian–lowermost Pliensbachian Água de Madeiros Formation at S. Pedro de Moel can be confidently used in palaeoenvironmental studies.

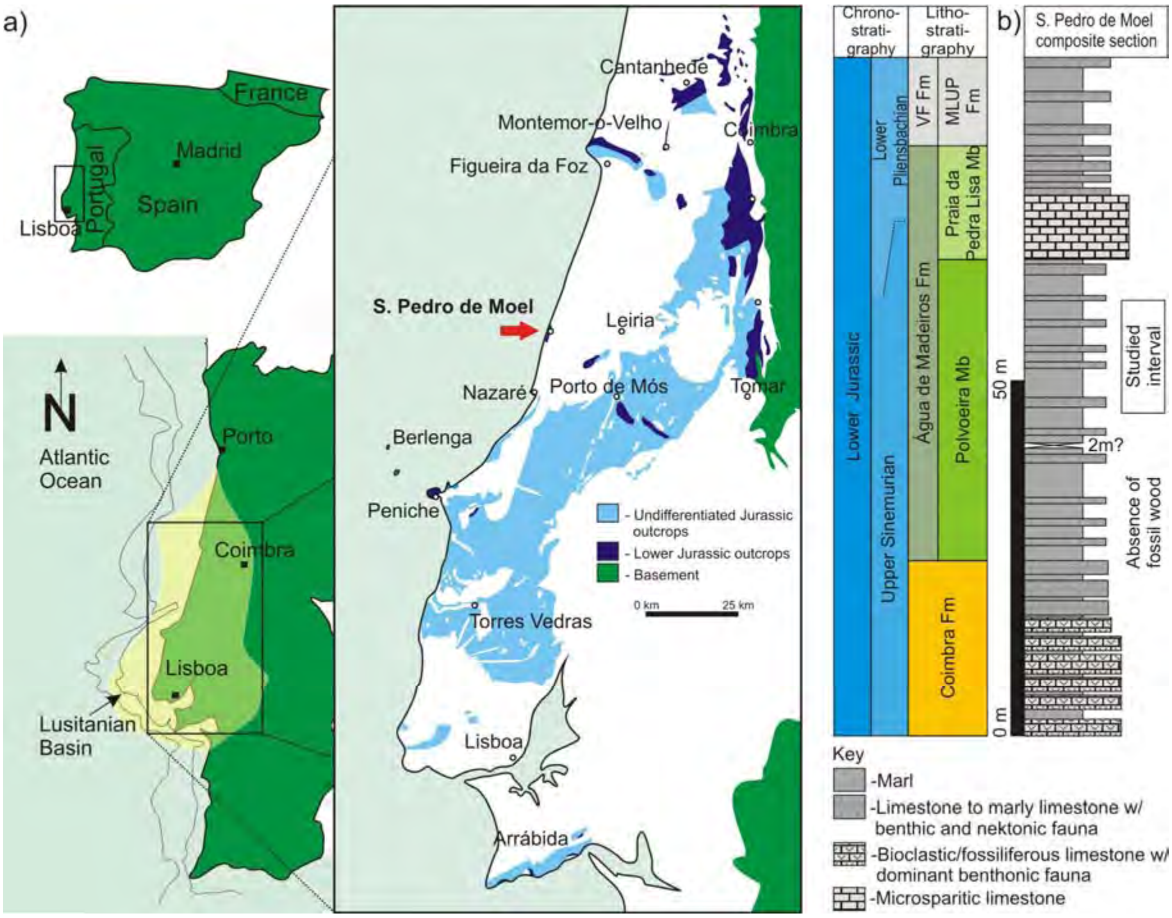


Fig. 3.2.1. a) Geological map of Jurassic in the Lusitanian Basin (modified from Duarte et al., 2010); b) synthetic composite log of the Polvoeira and Água de Madeiros reference sections of Sinemurian age at S. Pedro de Moel, Lusitanian Basin, Portugal (modified from Duarte et al., 2008; Azerêdo et al., 2010).

Fig. 3.2.2. Field aspect 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).

The methods used were visual observation under Transmitted White Light (TWL) and Fluorescence Mode (FM) and elemental (Carbon and Nitrogen), isotopic [$\delta^{13}C_{(PDB)}$ and $\delta^{15}N_{(Air)}$].

3.2.2. Geological Background

S. Pedro de Moel is located along the Portuguese coast, about 110 kilometres 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; Duarte et al., 2012). The focus of this work is the Polvoeira Member of the Água de Madeiros Formation, which crop out in two main locations south of S. Pedro de Moel, the Polvoeira and Água de Madeiros sections (Fig. 3.2. 1). Here, the Polvoeira Member corresponds to a marl dominated unit, composed of marl–limestone alternations and includes several black shale horizons (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). According to these authors, 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. (2011), 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).

3.2.3. Materials and Methods

Based on detailed field work, 11 fossil wood samples (Figs. 1b and 2) were collected and prepared for organic petrography and element and isotopic analysis. Every effort was performed to avoid contamination from the sedimentary matrix. During sampling, lustrous and black material resembling jet was discarded.

After initial crushing, the samples were reacted with HCl (37%) to remove the carbonate fraction and then with HF (40%) to remove the siliceous fraction. At this stage, the sample was divided into two subsets, one to be prepared according to 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 $\delta^{15}N_{(Air)}$ (‰).

The organic petrographic observations were performed by optical microscopy using Transmitted White Light (TWL) and Fluorescence Mode (FM) in the Palynofacies and Organic Facies Laboratory (LAFO) located at Federal University of Rio de Janeiro (Rio de Janeiro, Brazil).

TC and TN contents and $\delta^{13}C_{(PDB)}$ and $\delta^{15}N_{(Air)}$ were determined at the IMAR-CMA (Coimbra University) using dynamic flash combustion (modified Dumas method). Around 0.5mg 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 $\delta^{13}C$ and 0.3‰ for $\delta^{15}N$ (Acetanilide Standard from Thermo Electron Corporation). The fossil wood sample preparation for determination of TC and TN data was not performed according ASTM or ISO standards for sample preparation for ultimate coal analysis; hence, comparison with previously published data is difficult. However, out data is probably comparable with coal ultimate analyses reported as air dry-ash free, since the samples were air dried and inorganic matter (minerals) were remove prior to analysis.

3.2.4. Results

The stratigraphic position, lithological matrix and geochemical data of the studied samples are presented in the Table 3.2.I. In hand-specimen, all samples are black in colour, dull and tend to break in blocks. Lamination and striates are poorly marked, but are sometimes observed. In terms of general macroscopic aspect, the most different sample is V-GP38, which tends to be more lustrous and break into a more brittle way.

Observations in TWL and FM allow detecting a great variation in terms of composition and preservation of fossil wood (Fig. 3.2.3). In TWL, fossil wood varies from opaque to translucent, although with different degrees of opacity. The optical data show that these 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), derive from the lignified parts of terrestrial plants. In samples V-OU224+0.3 (Fig. 3.2.2) and V-GP2T, although particles of fossil wood are visible, the particle assemblages include high amounts of AOM, interpreted as having a probable wood origin (Figs. 3.2.3c; 3.2.3d; 3.2.3e and 3.2.3f). In a few samples, palynomorphs or AOM of marine origin are observed (e.g. Figs. 3.2.3a; 3.2.3b; 3.2.3c; 3.2.3d; 3.2.3e; 3.2.3f; 3.2.3m; 3.2.3n). In FM is possible to observe that in all samples (e.g. Figs. 3.2.3g; 3.2.3h) the wood particles present both fluorescent and non-flourescent particles.

Fluorescence intensity varies between orange-brown (Fig. 3.2.3k) to dark brown (Fig. 3.2.3o). The sample V-GP23T presents high amounts of resins (Figs. 3.2.3k; 3.2.3l). Most of these features are also seen in kerogen from rock samples of the same stratigraphic interval (Poças Ribeiro et al., 2011).

The TC and TN contents vary from 66.7 to 87.6 and 0.3 to 1.4 wt. %, respectively (Table 3.2.1). The C/N (determined using wt.%) ratio varies from 50 to 280, with an average of 87. The $\delta^{13}C$ 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 3.2.1). The $\delta^{15}N$ varies from 0.9 to 5.2 ‰ (Table 3.2.1). The only noteworthy relation observed is between TC contents and $\delta^{13}C$ (Fig. 3.2.4). Although the entire dataset presents a large scatter (r^2=0.20, linear correlation), if we exclude 3 apparent outliers (red circles), r^2 increases to 0.89. Therefore, 8 of the 11 samples present a significant positive correlation between TOC content and $\delta^{13}C$.

Table 3.2.1. 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.

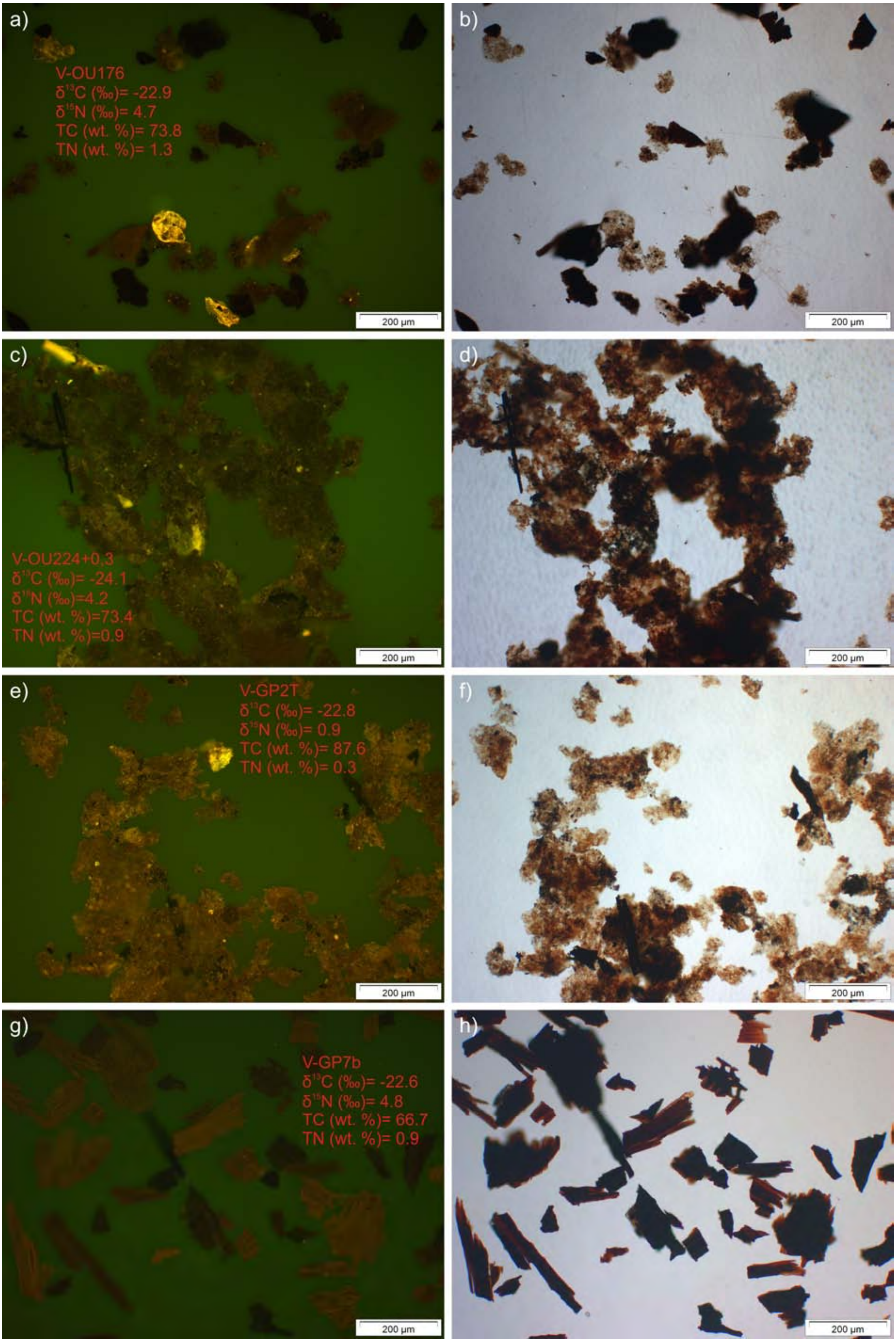
Sample	Stratigraphic Position (cm)	Lithological matrix	TN (wt.%)	TC (wt.%)	$\delta^{15}N_{(Air)}$ ‰	$\delta^{13}C_{(PDB)}$ ‰	C/N
V-GP38	1949	Marl	1.4	67.7	4.5	-25.4	50
V-GP 26B	1670	Black shale	1.0	68.9	4.6	-23.9	68
V-GP23T	1565	Limestone	1.1	71.3	3.3	-24.7	66
V-GP18T	1446	Black shale	1.0	71.5	3.5	-24.5	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

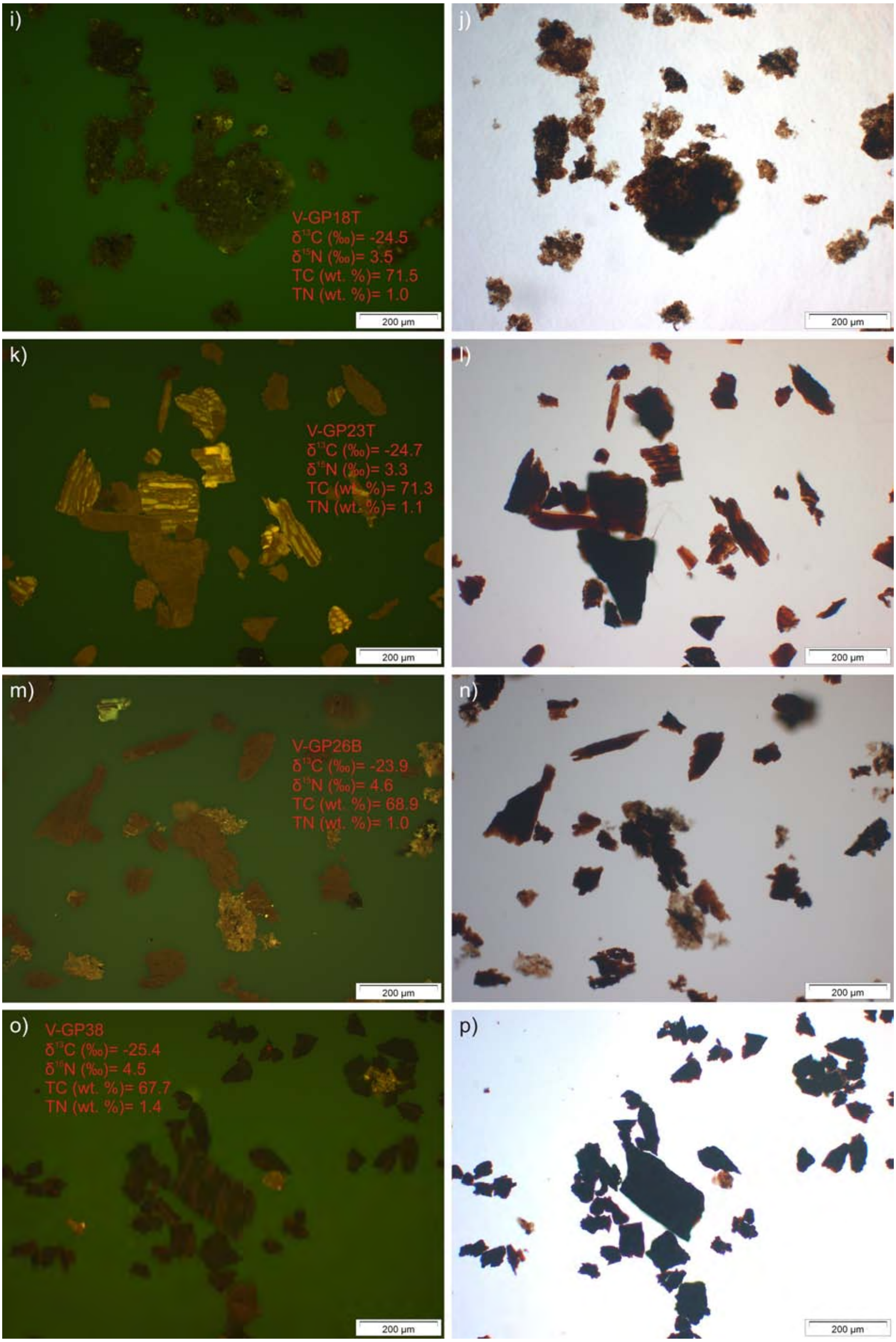
Note: TN = total nitrogen; TC = total carbon; C/N = total carbon/total nitrogen

3.2.5. Discussion

3.2.5.1. Optical observation of fossil wood composition and preservation bias

The original composition of the fossil wood samples was dominated by lignin, cellulose, tannins, colloidal humic gels, proteins and lipid substances (Sýkorová et al., 2005). During the coalification process, the wood remains are chemically and physically modified by biological activity, compaction and thermal alteration (e.g. Suárez-Ruiz and Crelling, 2008).


a)
V-OU176
δ13C (‰)= -22.9
δ15N (‰)= 4.7
TC (wt. %)= 73.8
TN (wt. %)= 1.3
200 µm
b)
200 µm
c)
V-OU224+0,3
δ13C (‰)= -24.1
δ15N (‰)=4.2
TC (wt. %)=73.4
TN (wt. %)=0.9
200 µm
d)
200 µm
e)
V-GP2T
δ13C (‰)= -22.8
δ15N (‰)= 0.9
TC (wt. %)= 87.6
TN (wt. %)= 0.3
200 µm
f)
200 µm
g)
V-GP7b
δ13C (‰)= -22.6
δ15N (‰)= 4.8
TC (wt. %)= 66.7
TN (wt. %)= 0.9
200 µm
h)
200 µm


i)
V-GP18T
δ13C (‰)= -24.5
δ15N (‰)= 3.5
TC (wt. %)= 71.5
TN (wt. %)= 1.0
200 µm
j)
200 µm
k)
V-GP23T
δ13C (‰)= -24.7
δ15N (‰)= 3.3
TC (wt. %)= 71.3
TN (wt. %)= 1.1
200 µm
l)
200 µm
m)
V-GP26B
δ13C (‰)= -23.9
δ15N (‰)= 4.6
TC (wt. %)= 68.9
TN (wt. %)= 1.0
200 µm
n)
200 µm
o)
V-GP38
δ13C (‰)= -25.4
δ15N (‰)= 4.5
TC (wt. %)= 67.7
TN (wt. %)= 1.4
200 µm
p)
200 µm

During the initial phase of coalification (peat stage), the changes are mainly derived from the biological activity and compaction. The cellulosic components are degraded, first by aerobic bacteria and fungi and then by anaerobic bacteria. Afterwards, if compaction continues, the peat is transformed into lignite and the residual cellulosic compounds are transformed into humic compounds. From this point on, thermal reactions dominate the following chemical changes, especially devolatization. It is at this stage (subbituminous rank) that the humic substances become increasingly gelified and vitreous as huminite begins changing to vitrinite (e.g. ICCP, 1998; Sýkorová et al., 2005; Suárez-Ruiz and Crelling, 2008). Following Sýkorová et al. (2005), this stage corresponds to a % of R_o of ≈ 0.5.

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. This is well expressed in the wide range of components that were observed in each sample (see also, for example, Tyson, 1995; Mendonça Filho et al., 2011). One of the main differences from the optical observations of fossil wood is related to the occurrence of apparently well preserved fossil wood (related with humification and gelification), opaque Phytoclasts (oxidised and/or charcoalified) and AOM of probable flora origin (related to microbiological remineralization).

Therefore, it seems clear that the assumption of similar diagenetic (and even syngenetic) conditions for the studied stratigraphic interval do not hold for this case study. In the authors point of view, one of the main difficulties is to know where these processes have taken place, i.e., if in a terrestrial or marine environment. One of the key features of the Palynofacies analyses from Poças Ribeiro et al. (2011), Duarte et al. (2012) and our observations (Figs. 3.2.3c, 3.2.3d) is the occurrence of zygospores, which are interpreted as being derived from fresh-water green algae (e.g. Grenfell, 1995; Mendonça Filho et al., 2011). This suggest that at least a part of the diagenetic evolution of some of the studied fossil woods may have occurred in fluvial/swap/lacustrine/lagoonal environments and then remobilized to be incorporated in the nearby hemipelagic depositional setting.

3.2.5.2. Elemental and isotopic data

Usually, the carbon and nitrogen elemental data is expressed as the C/N ratio and is regarded as an indicator of source, nutritional value or OM alteration (e.g. Tyson, 1995). It

Previous pages: Fig. 3. Fossil wood characteristics in transmitted white light (a, c, e, g, i, k, m, o) and fluorescent mode (b, d, f, h, j, l, n, p) and isotopic and elemental data from the Polvoeira Member (Late Sinemurian) of S. Pedro de Moel.

has been observed that buried plant material has lower C/N ratios than fresh material or, on the other hand, that aerobic or anaerobic conditions causes an increase or decrease of this ratio, respectively (Gröcke, 2002 and references therein). Comparing with modern fresh wood (C/N ratios from 250 to 1340), our data have lower C/N ratios. Besides the many caveats in the use of C/N data (including the methodological bias referred above), the obtained ratios 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 $\delta^{13}C$ of 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; Pool et al., 2006; Preston et al., 2006; Harlow et al., 2006; Bechtel et al., 2007; Galle et al., 2010). Undoubtedly they pose a great deal of problems when interpreting the 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 $\delta^{13}C$ with C.

On the other hand, and more rarely observed, 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). In addition, during microbial activity, thermal degradation and coalification $\delta^{13}C$ is expected to increase (Bechtel et al., 2001; Teichmüller and Teichmüller, 1979).

Since the fossil wood fragments are of Jurassic age, they are derived from C_3 plants. $\delta^{13}C$ of C_3 plants range between -23 and -34 ‰ with an average of approximately -27 ‰. Konh (2010), based on an extensive literature survey, has shown that this variation can be actually much larger and the assumed average can be overestimated by as much as 2 ‰. This natural variation poses a great deal of concern, mainly because it includes much of the scatter observed in our dataset; it is clear that the prediction about the direction of change (i.e. increasing or decreasing) relatively to the original wood carbon isotopic composition is virtually impossible. The organic petrographic observations and the positive correlation between TC and $\delta^{13}C$ (Figs. 3.2.3 and 3.2.4) suggest that the main processes affecting $\delta^{13}C$ are those linked with diagenesis (either biological or related with coalification).

The $\delta^{15}N$ isotopic signal of fossil wood, although seldom used, can also provide important information. It is generally assumed that assimilation and uptake of nitrogen by plants do not exert a major fractioning effect, thus they reflect the isotopic signal of the atmosphere (Ostrom and Macko, 1992).

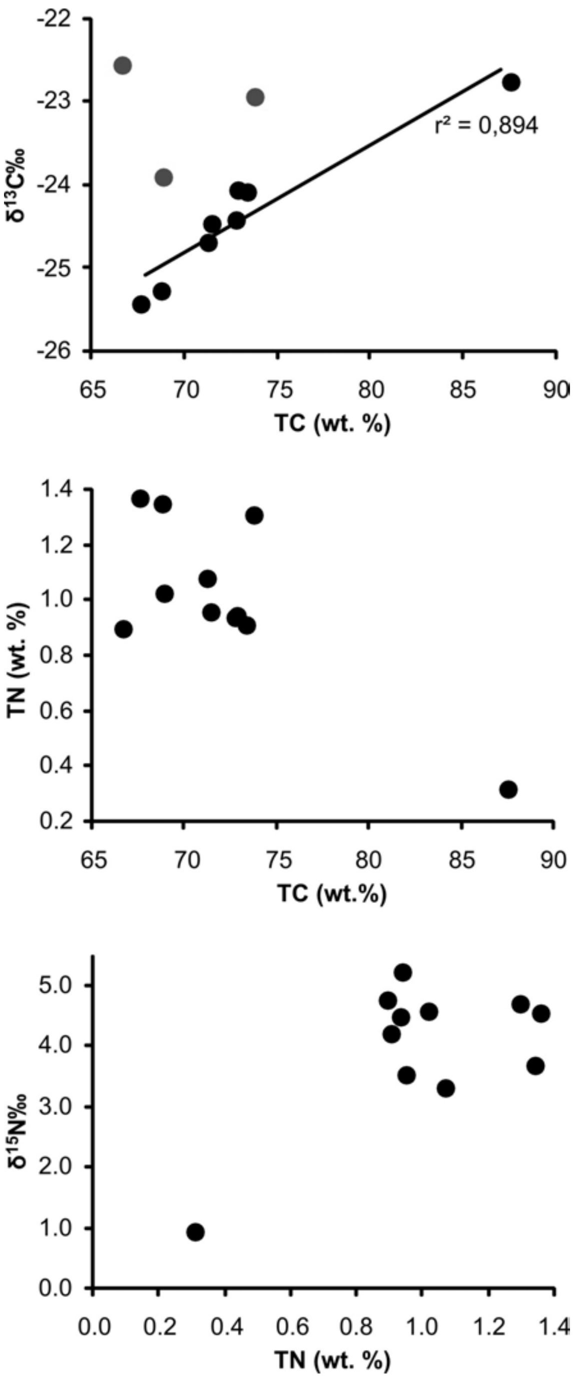


Fig. 3.2.4. Cross plots for $\delta^{13}C$ vs TC, TN vs TC and $\delta^{15}N$ vs TN for the fossil wood samples from the Polvoeira Member (Late Sinemurian) at S. Pedro de Moel (Lusitanian Basin, Portugal). The samples represented in grey were not included in the regression line calculation.

Per contra, studies (e.g. Evans, 2001; Hietz et al., 2010 and references therein) on modern flora show that $\delta^{15}N$ 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 in wood $\delta^{15}N$ values has been associated to N fertilization and/or change in drainage patterns, which are known to increase soil N dynamics and thereby increase soil, leaf and wood $\delta^{15}N$. Diagenesis and coalification also have the capability to change the original $\delta^{15}N$ of fossil wood. During the initial stages of wood decomposition, anaerobic bacteria decomposition, following fungi aerobic activity, is expected to occur (Bechtel et al., 2001; 2003) leaving the residual OM enriched in ^{15}N (Rimmer et al., 2006). Afterwards, the isotopic composition is expected to remain stable until the onset of the bituminous stage (Boudou et al., 1984). The $\delta^{15}N$ dataset do not present much variation. Although the original $\delta^{15}N$ is unknown, it seems likely (see section 5.1) that they were affected by microbial processes. It has been suggested that gelification and humification may be microbiologically mediated (Bechtel et al., 2001; 2003; Rimmer et al., 2006). If the $\delta^{15}N$ of the atmosphere during the Jurassic do not depart significantly from modern day values ($\delta^{15}N$ approximately 0‰) and assuming that plants do not present a major fractionating effect, the fossil wood samples seem to be enriched in ^{15}N due to microbial activity during the peat stage (Rimmer et al., 2006).

In summary, several samples present clear evidence of being affected by several processes, such as microbial degradation or atmospheric oxidation or to include “exotic” compounds (e.g. resin) known to affect the isotopic signal of fossil wood. The comparison of the (limited) isotopic dataset with organic petrography, apparently, does not show any predictable trend (Fig. 3.2.3).

5.2.6. Concluding remarks

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

-The optical observation of the fossil wood samples, the positive correlation between TOC and $\delta^{13}C$ and the high $\delta^{15}N$ suggest that the main processes affecting $\delta^{13}C$ are most likely linked with diagenesis (either biological or related with coalification);

-The data also suggest that the processes controlling diagenesis are not similar for all the studied samples, invalidating one of the main assumptions when using wood isotope data for palaeoenvironmental interpretations.

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

References

AZERÊDO, A.C., SILVA, R.L., DUARTE, L.V. and CABRAL, M.C., 2010. Subtidal stromatolites from the Sinemurian of the Lusitanian Basin (Portugal). Facies, 56, 211–230.

BECHTEL, A., GRATZER, R., SACHSENHOFER, R.F., GUSTERHUBER, J., LÜCKE, A. and PÜTTMANN, W., 2008. Biomarker and carbon isotope variation in coal and fossil wood of Central Europe through the Cenozoic. Palaeogeography, Palaeoclimatology, Palaeoecology, 262, 166–175.

BECHTEL, A., GRUBER, W., SACHSENHOFER, R.F., GRATZER, R. and PÜTTMANN W., 2001. Organic geochemical and stable carbon isotopic investigation of coals formed in low-lying and raised mires within the Eastern Alps (Austria). Organic Geochemistry, 32, 1289–1310.

BECHTEL, A., SACHSENHOFER, S.F., MARKIC, M., GRATZER, R., LÜCKE, A. and PÜTTMANN, W., 2003. Paleoenvironmental implications from biomarker and stable isotope investigations on the Pliocene Velenje lignite seam (Slovenia). Organic Geochemistry, 34, 1277–1298.

BECHTEL, A., WIDERA, M., SACHSENHOFER, R.F., GRATZER, R., LÜCKE, A. and WOSZCZYK, M., 2007. Biomarker and stable carbon isotope systematics of fossil wood from the second Lusatian lignite seam of the Lubstów deposit (Poland). Organic Geochemistry, 38, 1850–1864.

BOSTICK, N.H., 1971. Thermal Alteration of clastic organic matter as an indicator of contact and burial metamorphism in sedimentary rocks. Geoscience and Man, 3, 83–92.

BOUDOU, J.-P., MARIOTTI, A. and OUDIN J.-L., 1984. Unexpected enrichment of nitrogen during the diagenetic evolution of sedimentary organic matter. Fuel, 63, 1508–1510.

CZIMCZIK, C.I., PRESTON, C.M., SCHMIDT, M.W.I., WERNER, R.A. and SCHULZE, E-D., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. Organic Geochemistry, 33, 1207–1223.

DIEFENDORF, A.F., MUELLER, K.E., WING, S.L., KOCH, P.L. and FREEMAN, H.K., 2010. Global patterns in leaf ^{13}C discrimination and implications for studies of past and future climate. PNAS 107, 5738–5743.

DUARTE, L.V., SILVA, R.L., DUARTE, C.B., AZERÊDO, A.C. and COMAS-RENGIFO, M.J., 2008. Litostratigrafia do Jurássico Inferior da região de S. Pedro de Moel (Bacia Lusitânica). In: Callapez, P.M., ROCHA, R.B., MARQUES, J.F., CUNHA, L.S. and DINIS. P.M., (eds). A Terra, Conflitos e Ordem. Homenagem ao Professor Ferreira Soares. Museu e Laboratório Mineralógico e Geológico da Universidade de Coimbra, pp. 175–185.

DUARTE, L.V., SILVA, R.L., MENDONÇA FILHO, J.G., POÇAS RIBEIRO, N. and CHAGAS, R.B.A (2012) High-resolution stratigraphy, Palynofacies and source rock potential of the Água de Madeiros Formation (Upper Sinemurian) of the Lusitanian Basin, Portugal. Journal of Petroleum Geology, 35, 105–126.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F. (2010) Organic-Rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total organic carbon distribution and relation to transgressive-regressive facies cycles. Geologica Acta 8, 325–340.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das séries margo-calcárias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicações do Instituto Geológico e Mineiro, 89, 135–154.

EVANS, R.D., 2001. Physiological mechanisms influencing plant nitrogen isotope composition. Trends in Plant Science, 3, 121–126.

FENG, X. and EPSTEIN, S., 1995. Carbon isotopes of trees from arid environments and implications for reconstructing atmospheric CO_2 concentration. Geochimica et Cosmochimica Acta, 59, 2599–2608.

GALLE, A., ESPER, J., FELLER, U., RIBAS-CARBO, M. and FONTI, P., 2010. Responses of wood anatomy and carbon isotope composition of *Quercus pubescens* saplings subjected to two consecutive years of summer drought. Annals of Forest Science, 67, 809–817.

GRENFELL, H.R., 1995. Probable fossil zygnematacean algal spore genera. *Rev. Palaeobot. Palyno*. 84, 201–220.

GRÖCKE, D. R., 1998. Carbon-isotope analyses of fossil plants as a chemostratigraphic and palaeoenvironmental tool. Lethaia, 31, 1–13.

GRÖCKE, D. R., 2002. The carbon isotope composition of ancient CO_2 based on higher-plant organic matter. Philosophical Transactions of the Royal Society A, 360, 633–658.

GRÖCKE, D.R., HESSELBO, S.P. and JENKYNS, H.C., 1999a. Carbon-isotope composition of Lower Cretaceous fossil wood: Ocean-atmosphere chemistry and relation to sea-level change. Geology, 27, 155–158.

GRÖCKE, D.R., HESSELBO, S.P., JENKYNS, H.C., TAYLOR, G., ROBINSON, S.A. and SCHÖFFEL, H.-J., 1999b. Stable isotope and C/N Ratios of Fossil Wood from the Mesozoic: Insights into Ocean-Atmosphere Links. Ninth Annual V. M. Goldschmidt Conference, Cambridge, USA, pp.1.

HARLOW, B.A., MARSHALL, J.D. and ROBINSON, A.P., 2006. A multi-species comparison of ^{13}C from whole wood, extractive-free wood and holocellulose. Tree Physiology, 26, 767–774.

HASEGAWA, T., 1997. Cenomanian-Turonian carbon isotope events recorded in terrestrial organic matter from northern Japan. Palaeogeography, Palaeoclimatology, Palaeoecology, 130, 251–273.

HESSELBO, S.P., JENKYNS, H.C., DUARTE, L.V. and OLIVEIRA, L.C.V., 2007, Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth Planetary Science Letters, 253, 455–470.

HESSELBO, S.P. and PIEŃKOWSKI, G., 2011. Stepwise atmospheric carbon-isotope excursion during the Toarcian Oceanic Anoxic Event (Early Jurassic, Polish Basin). Earth Planetary Science Letters, 301, 365–372

HIETZ, P., DÜNISCH, O. and WANEK, W., 2010. Long-term trends in nitrogen isotope composition and nitrogen concentration in Brazilian rainforest trees suggest changes in nitrogen cycle. Environmental Science & Technology, 44, 1191–1196.

ICCP., 1998. The new vitrinite classification (ICCP System 1994). Fuel, 77, 349–358.

KANDUČ, T., MARKIČ, M. and PEZDIČ, J., 2005. Stable isotope geochemistry of different lithotypes of the Velenje lignite (Slovenia). Geologija, 48, 83–95.

KONH, M.J., 2010. Carbon isotope compositions of terrestrial C_3 plants as indicators of (paleo)ecology and (paleo)climate. PNAS, 107, 19691–19695.

LOADER, N.J., ROBERTSON, I. and MCCARROLL, D.. 2003. Comparison of stable carbon isotope ratios in the whole wood, cellulose and lignin of oak tree-rings. Palaeogeography, Palaeoclimatology, Palaeoecology, 196, 395–407.

MENDONÇA FILHO, J.G., MENEZES, T.R. and MENDONÇA, J.O., 2011. Chapter 5: Organic composition (Palynofacies Analysis). In: FLORES, D. and MARQUES, M., (eds). ICCP Training Course on Dispersed Organic Matter. International Committee for Coal and Organic Petrology, pp. 33–81.

OSTROM, N.E. and MACKO, S.A., 1992. Sources, cycling, and distribution of water column particulate and sedimentary organic matter in northern Newfoundland fjords and bays: a stable isotope study. In: WHELAN, J. and FARRINGTON, J.W., (eds.) Organic Matter: Productivity, Accumulation, and Preservation in Recent and Ancient Sediments. Columbia University Press, pp. 55–81.

POÇAS RIBEIRO, N., MENDONÇA FILHO, J.G., DUARTE, L.V., SILVA, R.L., MENDONÇA, J.O. and SILVA, T.F., 2011. Palynofacies and organic geochemistry of the Sinemurian marine deposits in the western Lusitanian Basin (Portugal). Memórias 18, 77–78.

POOLE, I., DOLEZYCH, M., KOOL, J., VAN DER BURGH, J. and VAN BERGEN, P.F., 2006. Do stable carbon isotopes of brown coal woods record changes in Lower Miocene palaeoecology?. Palaeogeography, Palaeoclimatology, Palaeoecology, 236, 345– 354.

PRESTON, C. M., TROFYMOW, J. A. and FLANAGAN, L. B., 2006. Decomposition, $\delta^{13}C$, and the "lignin paradox". Canadian Journal of Soil Science, 86, 235–245.

RIMMER, S.M., ROWE, H.D., TAULBEE, D.N. and HOWER, J.C., 2006. Influence of maceral content on $\delta^{13}C$ and $\delta^{15}N$ in a Middle Pennsylvanian coal. Chemical Geology, 225, 77-90.

ROBINSON, S.A. and HESSELBO, S.P., 2004. Fossil-wood carbon-isotope stratigraphy of the non-marine Wealden Group (Lower Cretaceous, southern England). Journal of the Geological Society, 161, 133–145.

SCHLESER, G.H., FRIELINGSDORF, J. and BLAIR, A., 1999. Carbon isotope behaviour in wood and cellulose during artificial aging. Chemical Geology, 158, 121–130.

SUÁREZ-RUIZ, I. and CRELLING, J.C. (eds), 2008. Applied Coal Petrology. The Role of Petrology in Coal Utilization. Elsevier Ltd, Academic Press, 398 pp..

SÝKOROVÁ, I., PICKEL, W., CHRISTANIS, K., WOLF, M., TAYLOR, G.H. and FLORES, D., 2005. Classification of huminite—ICCP System 1994. International Journal of Coal Geology, 62, 85–106.

TEICHMÜLLER, M. and TEICHMÜLLER, R.. 1979. Diagenesis of Coal (Coalification). In: LARSEN G. and CHILINGAR, G.V., (eds). Diagenesis in Sediments and Sedimentary Rocks. Elsevier, pp. 207-246.

TYSON, R.V. (1995) *Sedimentary organic ma*tter. Organic Facies and Palinofacies. Chapman & Hall, 615 pp.

VAN BERGEN, P.F. AND POOLE, I. (2002) Stable carbon isotopes of wood: a clue to palaeoclimate? Palaeogeography, Palaeoclimatology, Palaeoecology,182, 31–45.

YANS, J., GERARDS, T., GERRIENNE, P., SPAGNA, P., DEJAX, J., SCHNYDER, J., STORME, J.-Y. and KEPPENS, E., 2010. Carbon-isotope analysis of fossil wood and dispersed organic matter from the terrestrial Wealden facies of Hautrage (Mons Basin, Belgium). Palaeogeography, Palaeoclimatology, Palaeoecology, 291, 85–105.

Acknowledgements

This work has been financially supported by project PTDC/CTE-GIX/098968/2008 - "High resolution stratigraphy of the Lower Jurassic organic-rich marine series in the Lusitanian Basin" (FCT-Portugal and COMPETE-FEDER). Ricardo L. Silva thanks the FCT-MCE for funding trough a PhD fellowship (ref: SFRH/BD/47362/2008). We wish to thank the LAFO-UFRJ team for all the technical support with sample preparation and organic petrography and Elsa Teresa Rodrigues from the IMAR-CMA (Coimbra University) for the technical support in the elemental and isotopic analyses.

Capítulo 4 | Pliensbaquiano: Formação de Vale das Fontes

4.1. Depositional environment, high-resolution correlation and sequence stratigraphy of the Pliensbachian organic-rich series of the Lusitanian Basin (Portugal)

4.1.1 Introduction

Sequence stratigraphy has been extensively used by academia and industry as a valuable tool in Basin Analysis and numeric modelling of several parameters that govern sedimentation and resource´s availability, ultimately resulting in the de-risking of a given area of prospect (e.g. Howell and Aitken, 1996; Coe, 2003; Brookfield, 2004; Alan and Alan, 2005; Catuneanu, 2006; Miall, 2008; 2010; Hantschel and Kauerauf, 2009; Embry, 2009).

Carbonates share common proprieties with clastics systems, but several key differences should be kept in mind when dealing with the application of the sequence stratigraphic method. Even though both systems respond to changes in base level and are divided by similar surfaces, carbonate accumulation is regarded as "in situ production" whereas clastics are transported to their depositional resting place. In carbonate environments, the main parameter controlling the response to sea-level changes are the organisms (e.g. Schlager, 2005). The carbonate factory depends on the type of carbonate producers which, in turn, depend mainly on physiography and environment. These parameters control, for instance, photosynthesis rates, depth and proximity to the sea surface. The resulting carbonate facies and fabrics are indicative of sea level position, chemistry of the water, etc (e.g. Folk, 1959; Dunham, 1962; Embry and Klovan, 1971; Wright, 1992; Flügel, 2010). More importantly, the carbonate producers react dynamically to changes to their environment having, under favourable conditions, the ability to outpace the creation of accommodation space or, in turn, to respond actively to lowering of the base level (Schlager, 2005). Constructing a refined sequence stratigraphy model for these systems has to take into account all the processes conditioning carbonate sedimentation; its success depends upon the information provided by several disciplines related to Sedimentary Geology (e.g. Catuneanu, 2006; Miall, 2008; 2010).

The works developed over the past and beginning of this century, concerning the Lower Jurassic carbonate series of the Lusitanian Basin, are largely related to sedimentology and paleogeography (e.g. Wilson, 1988; Soares et al. 1993; Duarte, 1997, 2007; Azerêdo et al., 2003; Duarte et al., 2004), biostratigraphy (e.g. Mouterde, 1955, 1967a; Phelps, 1985; Dommergues, 1987; Boomer et al., 1998; N'zaba-Makaya et al., 2003; Dommergues et al., 2004a, 2004b, among others) and lithostratigraphy (Duarte and Soares, 2002; Azerêdo, 2007). In recent years, supported by the preceding studies, the research tend to present a greater diversity of themes, including the refinement of the ammonite and calcareous nannofossils biostratigraphy (e.g. Mouterde et al., 2007; Oliveira et al., 2007; Reggiani et al., 2010a, 2010b, Comas-Rengifo et al., 2013), sequential analysis (Duarte et al., 2004, 2007; Duarte, 2007; Duarte et al., 2010), palaeoenvironmental interpretation based on several fossil groups (e.g. Azerêdo et al., 2010; Reggiani et al., 2010a, 2010b; Silva et al., 2012) and sedimentary characterization based on Total Organic Carbon (TOC) and Rock-Eval pyrolysis (Duarte et al., 2010, 2012), elemental (Silva et al., 2009) or isotope geochemistry [whole rock (Oliveira et al., 2006, Hesselbo et al., 2007; Silva et al., 2011b), kerogen and fossil wood (Silva et al., 2011b) or biogenic calcite (Oliveira et al., 2009; Suan et al., 2008; 2010)], palynofacies (e.g. Ferreira et al., 2010; Silva et al., 2011a; Duarte et al., 2012, Silva et al., 2012; Poças Ribeiro et al., 2013) and biogeochemistry (Silva et al., 2012).

One of the main characteristics of the Pliensbachian series of the Lusitanian Basin is the occurrence of several organic-rich intervals, which include true black shales. These are especially expressive in the time interval comprised between the Early–Late Pliensbachian (Duarte and Soares, 2002; Duarte et al., 2010; Silva et al., 2011b; Silva et al., 2012). The first main step in the characterization of the organic-rich facies of this time interval was the work of Oliveira et al. (2006), where the authors present the geochemical characterization of this time interval in the reference section of Peniche, based on TOC, Rock-Eval pyrolysis and biomarkers. Meanwhile, F. Silva et al. (2006, 2007) extend the characterization (TOC and Rock-Eval pyrolysis) of this kind of facies to the northern part of the basin. Then, Duarte et al. in 2010, based in a detailed biostratigraphic framework, sedimentological data and TOC variation, present a consolidated 2nd-order transgressive–regressive facies cycles scheme for the Lower Jurassic carbonate series of the Lusitanian Basin and compared them with those observed in the Basque-Cantabrian neighbouring basin. Nowadays, these organic-rich levels are intensively studied using several innovative techniques, including isotope geochemistry in kerogen (Silva et al., 2011b), biogeochemistry (Silva et al., 2012), outcrop gamma-ray spectrometry (Correia et al., 2012), biomarkers (Silva et al., 2010; Mendonça Filho et al., 2013) and palynofacies (Ferreira et al., 2010; Silva et al., 2011a; Silva et al., 2012).

Based on the study of four classical and "rediscovered" sections at Tomar, Rabaçal, Peniche and S. Pedro de Moel (Fig. 4.1.1), the aims of this work are to:

-construct, for the first time, a high-resolution basinwide stratigraphic correlation of the main Pliensbachian organic-rich interval and individual black shales;

-establish a 3rd-order sequence stratigraphic scheme for the main Pliensbachian organic-rich interval.

4.1.2. Brief geological setting

The Lusitanian Basin is a small, narrow North–South elongated basin, located on the occidental side of the Iberian Massif and bounded to the west by several basement horsts. This basin is one of the several rift-related peri-tethyan Mesozoic basins whose origin is related with the opening of the Atlantic Ocean (Fig. 4.1.2) (e.g. Wilson et al., 1989; Alves et al., 2002). The studied hemipelagic series of Early–Late Pliensbachian age [top of Ibex (Luridum Subzone)–Margaritatus (base of Gibbosus Subzone) zones] correspond 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 (T–R) facies cycle, the first 2nd-order flooding event recognized at a basinal scale (Fig. 4.1.3) (see Duarte et al., 2010; Silva et al., 2011b and references therein) and is regarded as rift (*s.l.*) related sedimentation (Stapel et al., 1996; Rasmussen et al., 1998; Alves et al., 2002, 2003, 2006, 2009) included in the Upper Triassic–Callovian 1st-order cycle (e.g. Wilson et al., 1989; Soares et al., 1993; Duarte, 1997; Azerêdo et al., 2002, 2003; Duarte et al., 2004).

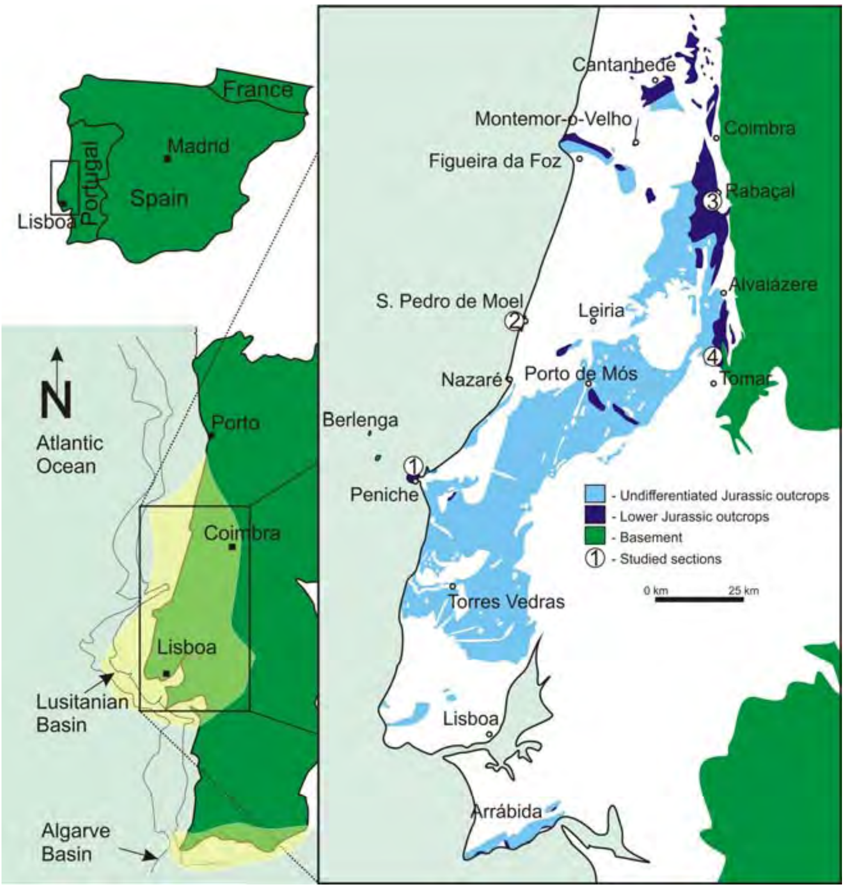


Fig. 4.1.1. Geological map of the Jurassic of the Lusitanian Basin and location of the main studied Pliensbachian outcrops (other sections were locally studied, such as Figueira da Foz or Coimbra). 1) Peniche; 2) S. Pedro de Moel; 3) Rabaçal; 4) Tomar.

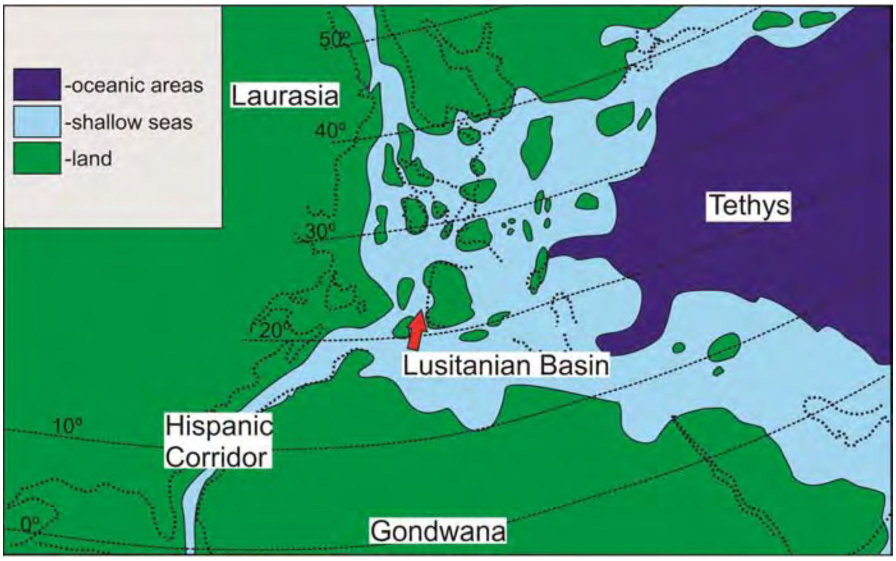


Fig. 4.1.2. Western Tethys palaeogeography and location of the Lusitanian Basin during the late Early Jurassic (modified and simplified from Bassoulet et al., 1993).

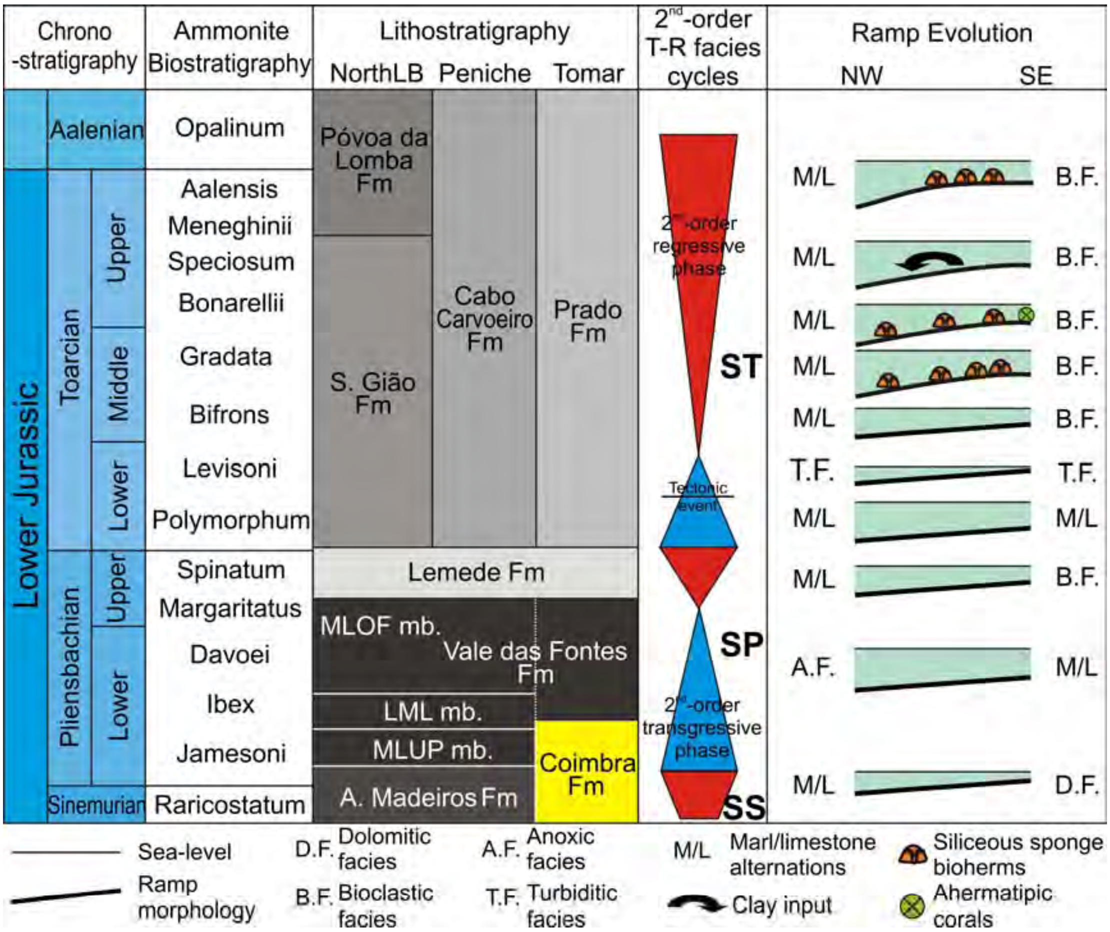


Fig. 4.1.3. Stratigraphic chart for the Late Sinemurian – Early Aalenian succession in most of the Lusitanian Basin (modified from Duarte et al., 2001; Duarte, 2007; Duarte et al., 2011). Fm-Formation; mb-member; MLOF mb-Marly limestones with organic-rich facies member; LML mb- Lumpy marls and limestones member; MLUP mb-Marls and limestones with *Uptonia* and *Pentacrinus* member. SS-Sinemurian sequence; SP-Pliensbachian sequence; ST-Toarcian sequence.

The MLOF mb, when compared with the under- and overlying units (see Fig. 4.1.3 and Duarte and Soares, 2002; Duarte et al., 2010), is characterized by the increasing marly character of the series and by the occurrence of several organic-rich facies, including true black shales, which are particularly well developed in the western, distal hemipelagic sectors of the basin (see Duarte et al., 2010).

4.1.3. Studied sections and biostratigraphic improvements

4.1.3.1. Tomar

The Tomar section is located at the Vale Venteiro locality (UTM coordinates 29 S, 551190m; 4391144m), around 7 kilometres north of Tomar (Fig. 4.1.1). Mouterde et al. (1971) present a review of this area and establish the ammonite biostratigraphic scheme used in more recent works (e.g. Brunel et al., 1998; N'zaba-Makaya et al., 2003; Duarte and Soares, 2002; Duarte, 2007; Duarte et al, 2010; Reggiani et al., 2010a; Suan et al., 2010). Duarte and Soares (2002), contrarily of the overall situation of the northern part of the basin, only recognized the Vale das Fontes Formation without discriminating its members.

In this study, the last 8 metres of the Vale das Fontes Formation and 1 metre of the Lemede Formation were analysed (Fig. 4.1.4). The base of the studied section starts at an extremely fossiliferous and bioturbated yellowish marly limestone interval with abundant bivalves, which is overlain by a thick (~2m) greenish marly package with a few marly-limestone beds, where macrofauna is usually scarce (Fig 4.1.5a). Afterwards, and until the top of the Vale das Fontes Formation, the limestones beds, dominantly mud-wackestone, with rare lenticular bioclastic pack-grainstone levels, dominates over the marls (Fig 4.1.5b). In addition, one bed presents a morphology that resembles the carbonate build-ups locally observed in proximal settings of the basin (i.e. Rabaçal). Within this interval, benthic macrofauna (gastropods, bivalves, brachiopods, echinoderms, etc.) is abundant, as are belemnites. Ammonites are scarce and, usually, poorly preserved. The base of the Lemede Formation is marked by the sharp increase of the bioclastic character of the series, materialized here by a thick fossiliferous pack-grainstone carbonate bed (Fig 4.1.5c and 4.1.5d).

Taking the base of the Lemede Formation as a marker, the thickness of the upper Pliensbachian part of the Vale das Fontes Formation varies between 10 and 20 metres in the Pedreira (Mouterde et al., 1971) and the "Coupe 1500 métres à l'Ouest de l'eglise de Casaes" (Choffat, 1908) sections, respectively (although the latter author recognize that the thickness he mentions is only an approximation). Northwards, Mouterde and Rocha (1980-1981) indicate 11 metres at Ovelheiras, for the same stratigraphic interval. Unfortunately, these sections were not observed because, nowadays, are inaccessible or destroyed.

This section is poorly aged-constrained due to the general scarce ammonite's record. Several *Aegoceras* sp. fragments were recovered at the base of this section; it is not possible to discard that reworking could, locally, result in a younger age for the occurrence of the referred ammonites. For the sake of honesty, it is considered that the studied section encompasses part of the upper Pliensbachian and that the base may include a portion of Davoei Zone. Reggiani et al. (2010a) also establish a calcareous nannofossil biozonation, recognizing the boundary between NJ4a and NJ4b (Last Occurrence of *P. robustus*) close to the base of the studied series.

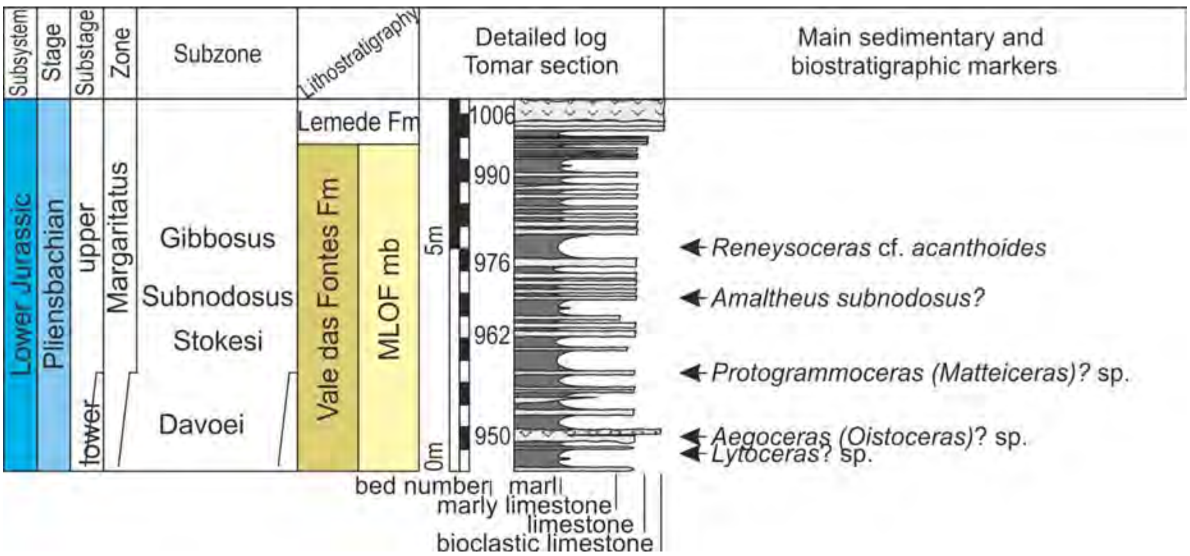


Fig. 4.1.4. Detailed log of the top of Vale das Fontes and Lemede formations in the Tomar (Vale Venteiro) section.

4.1.3.2. Rabaçal

The Rabaçal section (UTM coordinates 29 T, 547477m; 4429283m) is located at 1.8 kilometres southeast of Rabaçal and 4.5 kilometres south of the classical Maria Pares reference section (see, for example, Mouterde et al., 1964-1965; Cubaynes et al, 1988; Duarte, 1997, 2007; Boomer et al., 1998; Dommergues et al., 2002) (Figs. 4.1.1 and 4.1.6). The studied part of this section, ranging about 27 metres in thickness, encompasses almost the entire MLOF mb and the base of the Lemede Formation.

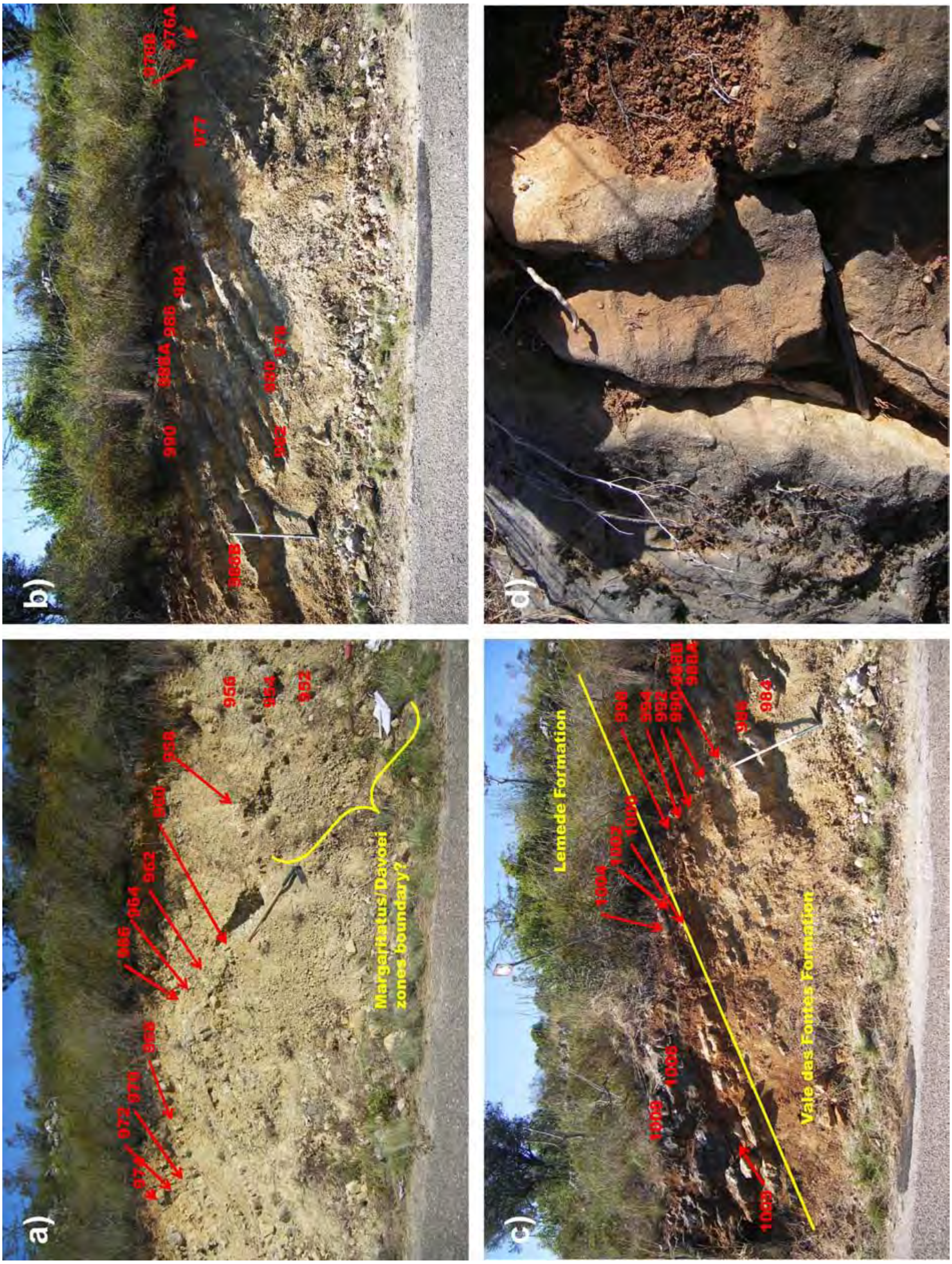


Fig. 4.1.5. Field details of the Vale das Fontes and Lemede formations at Tomar (Vale Venteiro section). a) base of the studied section; b) middle portion of the studied section; c) limit between the Vale das Fontes and Lemede formation; d) grainstone level belonging to the base of the Lemede Formation.

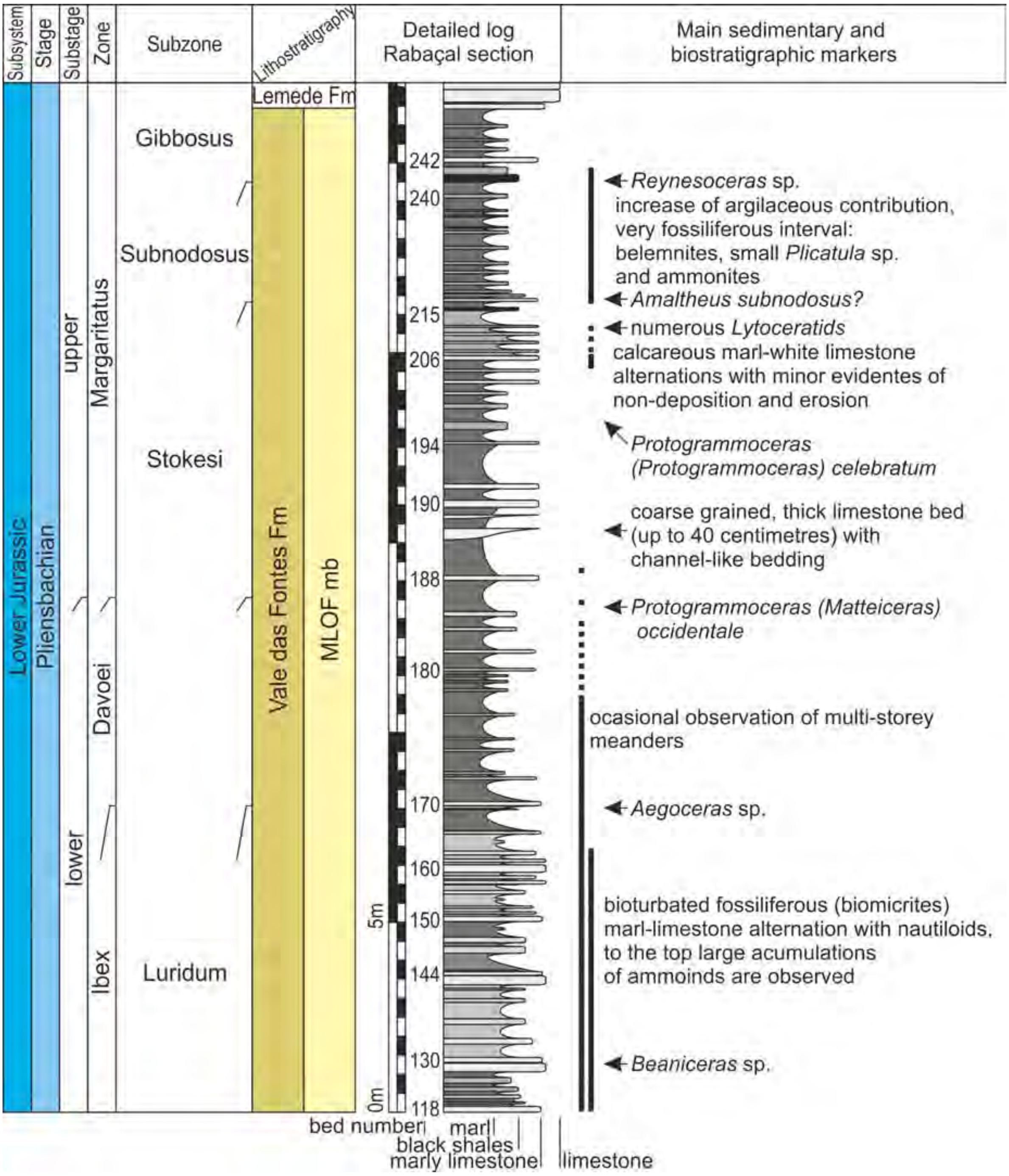


Fig. 4.1.6. Detailed log of the MLOF mb and base of Lemede Formation in the Rabaçal section.

The base of this unit is not securely recognized due to tectonic disturbance. The studied series is very similar to the Maria Pares reference section. The overall tendency is the decrease in the limestone content of the series until the base of the Lemede Formation. This unit starts with a succession of several bioturbated fossiliferous (biomicrites) marl-limestone packages (the so called *calcaires en rangs de pavés*, Cubaynes et al, 1988) with nautiloids (about 6.5 metres) (Figs. 4.1.7a and 4.1.7b), gradually changing into dominant marly lithofacies towards the Lower/Upper Pliensbachian boundary. Benthonic and nektonic macrofauna (e.g. gastropods, bivalves, brachiopods, echinoderms, belemnites, ammonoids) is abundant. Ammonoids are often pyritised. Bioturbation is also significant and occasionally includes multi-storey meanders resembling *Spirorhapne* sp. (a graphoglyptid ichnogenus, see Seilacher, 2007). A coarse grained, thick limestone bed (up to 40 centimetres) with channel-like bedding is observed at this location. Towards the top of the section, a small (approximately 1.5m) pack of dominantly calcareous marl–white limestone alternations (Fig. 4.1.7c), capped by a limestone containing numerous Lytoceratids, is observed. These limestones present evidence of non-deposition periods. Stratigraphic surfaces are sharper and irregular and/or slightly ferruginous. The fauna also presents evidence of resedimentation and taphonomic reworking (see Fernández López, 2000), such as bioerosion and incrustation (especially visible in the large ammonoids) and ferruginous coatings. Afterwards, the series becomes very argillaceous and fossiliferous (whole fossils or bioclasts) (Fig. 4.1.7c), sometimes forming extensive pavements. This interval is remarkable by the ubiquitous presence of belemnites, small *Plicatula* sp. and ammonites, the latter indicating a Subnodosus and base of Gibbosus subzones age for this interval. Sparsely, some very small carbonate build-ups are observed. The organic-rich facies are present throughout the section, but only a few levels are regarded as black shale (*sensu* Duarte et al., 2010; Silva et al., 2012). The transition to the Lemede Formation is rather sharp (Fig. 4.1.7d). At this location, the base of this unit is composed of thick limestones (bioclastic) with minor marly levels.

The ammonite fauna allows a better biostratigraphic control when compared with Tomar (Fig. 4.1.6). Based in new ammonite data, we have recognized the top of Ibex (Luridum Subzone?), Davoei and Margaritatus zones and some of their subzones, with some incertitude on boundaries position. For this interval, comparison with previously published biostratigraphic data (e.g. Mouterde et al., 1964-1965; Dommergues et al., 2002) is difficult because thickness of the MLOF mb at this location seems to be highly variable. The Margaritatus/Spinatum boundary is located within the Lemede Formation, with the first unequivocal *Pleuroceras solare* being observed around 7m above the base of this unit. This observation is in good agreement with the data presented by Mouterde et al. (1964-1965) for the Maria Pares reference section.

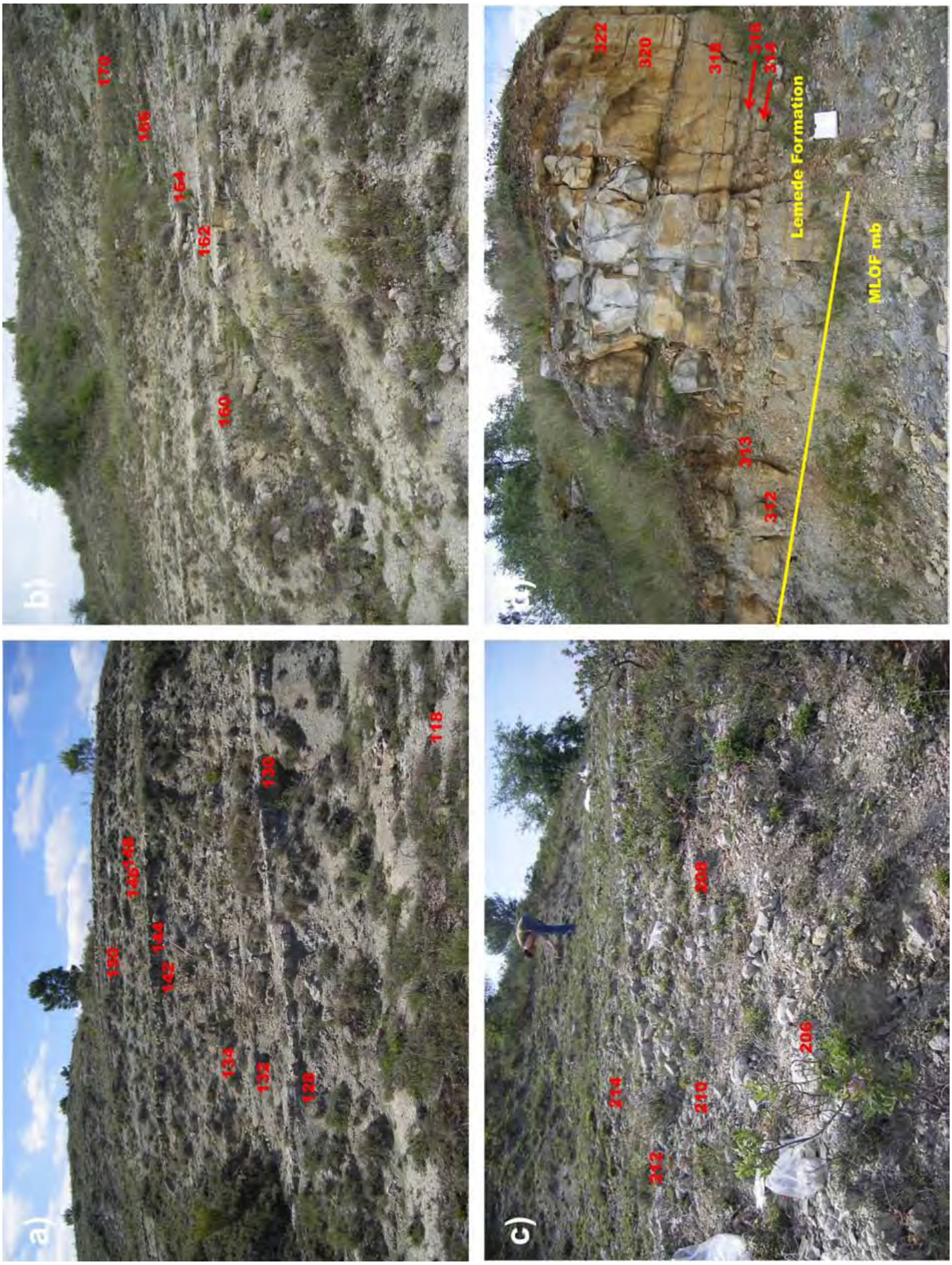


Fig. 4.1.7. Field details of the MLOF mb (Vale das Fontes Formation) and Lemede Formation at Rabaçal. a) base of the studied section; b) middle portion of the studied section; c) upper portion of the studied section d) limit between the Vale das Fontes and the Lemede formations as observed at the Rabaçal village (different bed numbering).

4.1.3.3. Peniche and S. Pedro de Moel

The Peniche and S. Pedro de Moel sections are very similar concerning sedimentary and macropaleontology aspects, despite the higher thickness and more expressive record of the organic-rich facies at S. Pedro de Moel. For simplification, only the Peniche section will be described in detail since it is, nowadays, the reference section for the Vale das Fontes Formation.

At Peniche, the MLOF mb crops out in the Portinho da Areia do Norte beach (UTM coordinates 29 S, 467389m; 4357730m) (Fig. 4.1.1.). Here, it corresponds to approximately 30 metres of marl-limestone alternations, locally with abundant nektonic (belemnites and ammonites) and benthonic (brachiopods, bivalves, crinoids, gastropods, etc) macrofossils (Fig. 4.1.8). This section is characterized by the pervasive occurrence of organic-rich facies, from dark marls and marly limestones, often bioturbated (mainly *Phymatoderma* and *Chondrites* ichogenera) (Fig. 4.1.9a), to true black shales (see Duarte and Soares 2002; Oliveira et al., 2006; Duarte et al., 2010; Silva et al., 2011b, 2012).

The first 4.5 metres of the series, corresponding to the Ibex Zone, are composed of regular marl–limestone alternations grading to a more irregular marl-dominated interval (around 5-6 metres) dated from the Davoei Zone (Fig 4.1.9b). The limit with the Lumpy Marls and Limestones mb is sharp and marked by the disappearance of the lumpy facies, subspherical micritic grumose concretions, showing some cryptalgal oncolite structures (Dromart and Elmi, 1986; Elmi et al., 1988; Duarte and Soares, 2002; Duarte et al., 2010). Organic-rich facies are abundant and usually located at the interface between marls and limestones. Pyrite is very abundant and can be found dispersed, as nodule-like forms or as fossil (including ichnofossils) moulds. At the beginning of the Upper Pliensbachian, the more regular marl-limestone alternations resume, persisting until the limit with the Lemede Formation. Although rarely, it is possible to observe small lenticular coarse bioclastic beds (this feature is observed throughout the section, but it seems clearer in this interval). Despite the regularity of the marl–limestone couplets and black shales occurrences, a minor variation in the lithofacies is observed, approximately at 17 metres thickness mark. This particular variation corresponds to 2 well defined black shale layers, passing upwards to a more calcareous interval, composed of 3 mud-wackestone limestone beds. This interval is dated from the top of the Margaritatus Zone, Stokesi Subzone, Celebratum horizon (Fig. 4.1.9c).

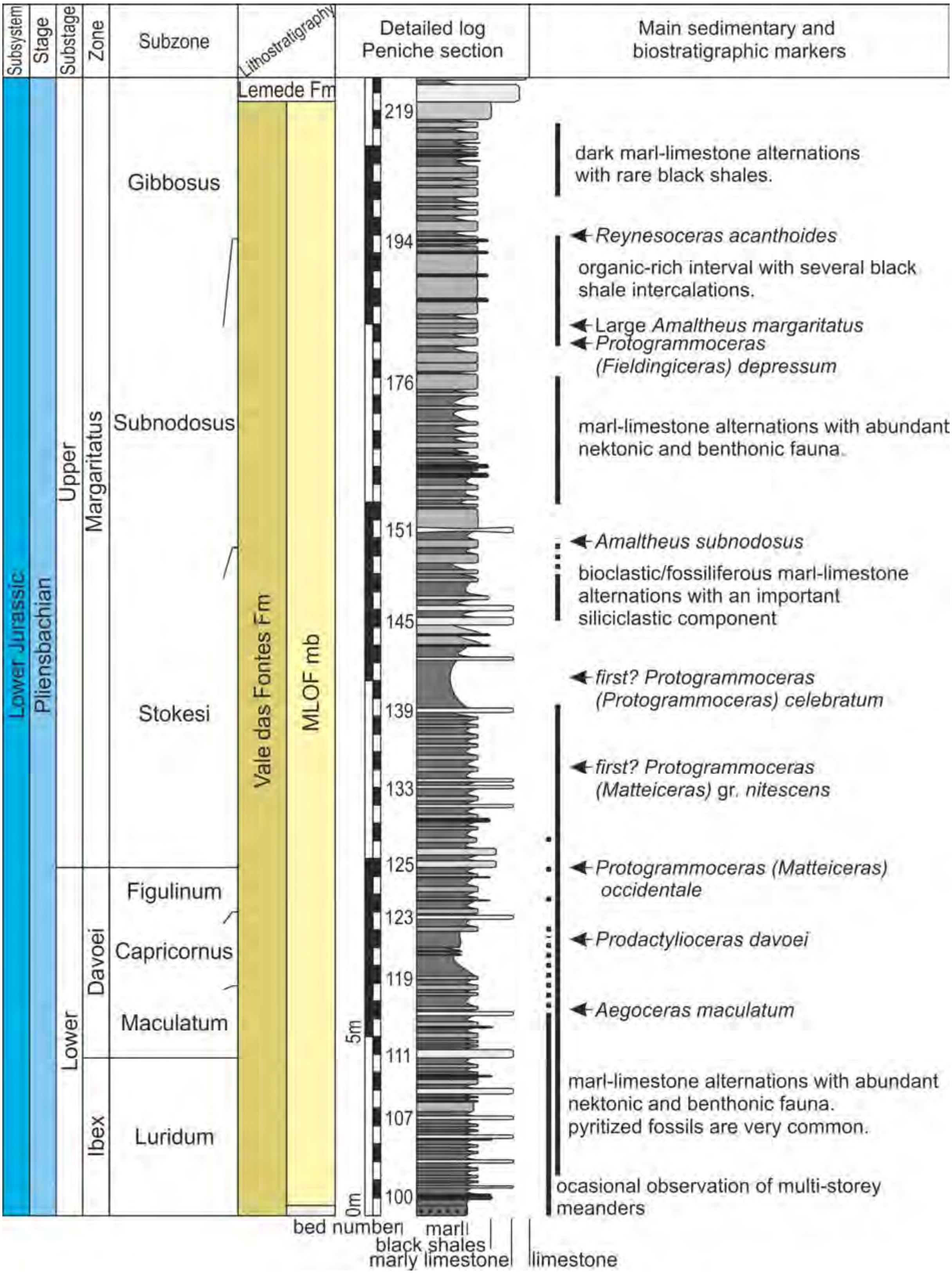


Fig. 4.1.8. Detailed log of the MLOF mb and base of Lemede Formation in the Peniche reference section (modified from Silva et al., 2011b).

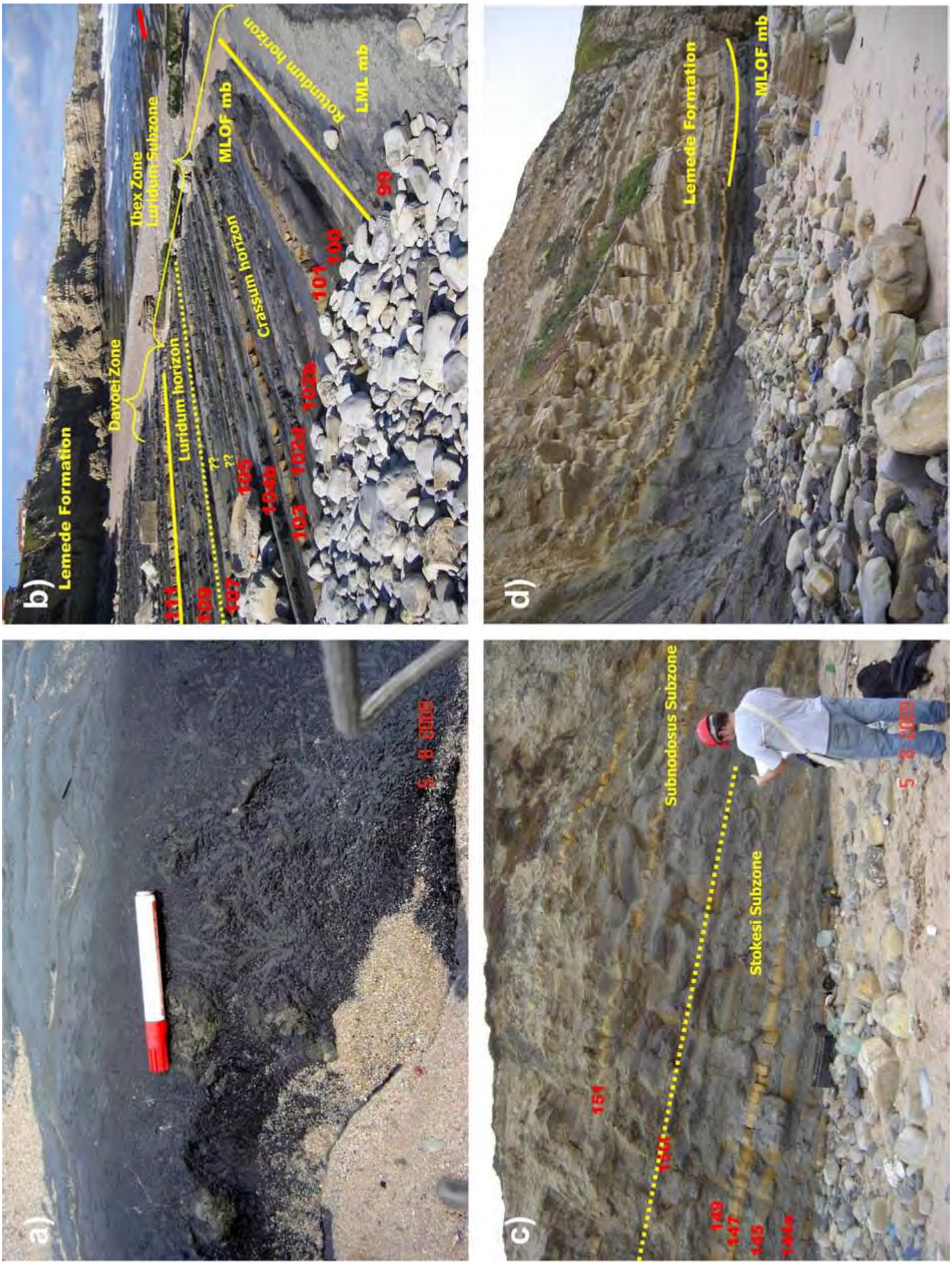


Fig. 4.1.9. Field details of the MLOF mb (Vale das Fontes Formation) and Lemede Formation at Peniche. a) *Chondrites* sp. in a organic-rich interval ; b) base of the studied section; c) middle portion of the studied section; d) limit between the Vale das Fontes and Lemede formations. [a) and c) photos by Rui Ferreira]

The marly interval above is very rich in bioclasts and contains a significant terrigenous fraction, being dated from the Margaritatus Zone, uppermost Stokesi (uppermost Celebratum horizon)–base of Subnodosus (Depressum horizon, first occurrence of the Subzone index fossil, *Amaltheus subnodosus*) subzones. At the 25 metres mark, the development of a thick limestone–marl–black shale package is seen. More information about these black shales is provided below, where they are presented in detail.

This unit is shapely overlain by the Lemede Formation, which is composed of centimetre marl–decimetre limestone bioturbated alternations, very rich in belemnites, ammonoids, bivalves and brachiopods (Fig. 4.1.9d).

The best biostratigraphic control of the studied unit is attained in this section. The entire series is paleontologically very rich, both in nektonic (ammonites and belemnites) and benthonic (brachiopods, bivalves, gastropods, crinoids, echinoids and rare coral debris, etc.) macrofauna. The ammonites occurring throughout the Upper Sinemurian–Middle Toarcian (Gradata Zone) (Mouterde, 1955; Phelps, 1985; Dommergues, 1987), allow a detailed biostratigraphic zonation (e.g. Fig. 4.1.9b), reinforced by additional new data from recent ammonite collection campaigns (see, for example, Silva et al., 2011b) and also by a comprehensive calcareous nannofossil biostratigraphic chart for the Pliensbachian–Toarcian (Perilli and Duarte, 2006; Oliveira et al., 2007; Reggiani et al., 2010a; 2010b). Newly collected bed-by-bed ammonite data are, at a broader scale, in good agreement with the biozonation charts established for the Pliensbachian of the Lusitanian Basin (e.g. Phelps, 1985; Dommergues et al., 1997). Nevertheless, these data allowed improving of some biostratigraphic boundaries. The main one is related with the age of the Lemede Formation, which was previously assigned to the Spinatum Zone (e.g. Mouterde, 1955; Duarte and Soares 2002). The new high-resolution biostratigraphic data reveal that the base of this formation corresponds to the Margaritatus Zone, uppermost Gibbosus Subzone, with a distinct level of *Arieticeras* gr. *algovianum* occurrence found approximately around 3 metres above the base of this unit. This probably corresponds to the same level of *Arieticeras* sp. mentioned in Mouterde et al. (2007) for the Brenha (Figueira da Foz) section, nowadays not assessable. Mouterde and Rocha (1988) had already suggested that the Margaritatus–Spinatum zones boundary was probably located within the Lemede Formation while acknowledging the highly variable nature of this biostratigraphic boundary and its difficult recognition due to the lack of data from the base of the unit.

The S. Pedro de Moel section is briefly described here (see Duarte et al., 2008; 2012 for a detailed account of this section). At S. Pedro de Moel, the main MLOF mb outcrop corresponds to the Praia da Pedra do Ouro (UTM coordinates 29 S, 496014m; 4397388m) (Fig. 4.1.1 and 4.1.10). This section is located in an unfavourable geological setting, forming the axis zone of a major salt-related syncline structure, which fractures it in several blocks (see Duarte et al., 2008; Duarte et al., 2012). Detailed field work and ammonite collection (Fig. 4.1.11) coupled with previously published biostratigraphic data (e.g. Mouterde, 1967b, 1970; Dommergues and Mouterde, 1980; Mouterde and Rocha, 1981, 1988; Mouterde et al., 1983; 2007; Dommergues et al., 2004a) allowed for a confident reconstruction of a major part of this section (see also Silva et al., 2012), especially near the black shale intervals.

4.1.4. High resolution stratigraphy of the studied series: The black shales as a tool of basinal correlation

The organic-rich facies of the MLOF mb vary between massive dark marls to true black shales. The former are often bioturbated and macrofauna is present, although not as diversified as in the non organic-rich facies. The black shales usually have a net laminated base, sometimes non-bioturbated over a few centimetres (Fig. 4.1.12). Generally, they grade upwards to a more bioturbated (mainly *Phymatoderma* and *Chondrites* ichnogenera, Fig. 4.1.9a) calcareous facies (Fig. 4.1.12b and 4.1.12c), where benthonic and nektonic macrofauna is, locally, abundant.

From the analysis of the TOC vertical variation, Duarte et al. (2010 and references therein) defined three main organic-rich intervals, dated from the Davoei, lower and upper Margaritatus zones, which present, at Peniche, maximum TOC values of 12, 15 and 15%, respectively. This section constitutes the reference sector for the study of the Lower–Upper Pliensbachian organic-rich facies, as it is readily accessible and the stratigraphic succession is virtually undisturbed. Since we are aiming to use the black shales as a tool in the basinal correlation of the studied sections (see previous sections), we will focus on the most distinguishable organic-rich laminated marls and black shales. These are aged-constrained to the Ibex/Davoei zones, Davoei/Margaritatus zones limit, upper Stokesi, middle Subnodosus and Subnodosus/Gibbosus subzones of the Margaritatus Zone. Peniche is where the best ammonite control is achieved. For this reason all the black shales occurrences will be tentatively tied to this section using all the available bio- and lithostratigraphic information (Fig 4.1.13).

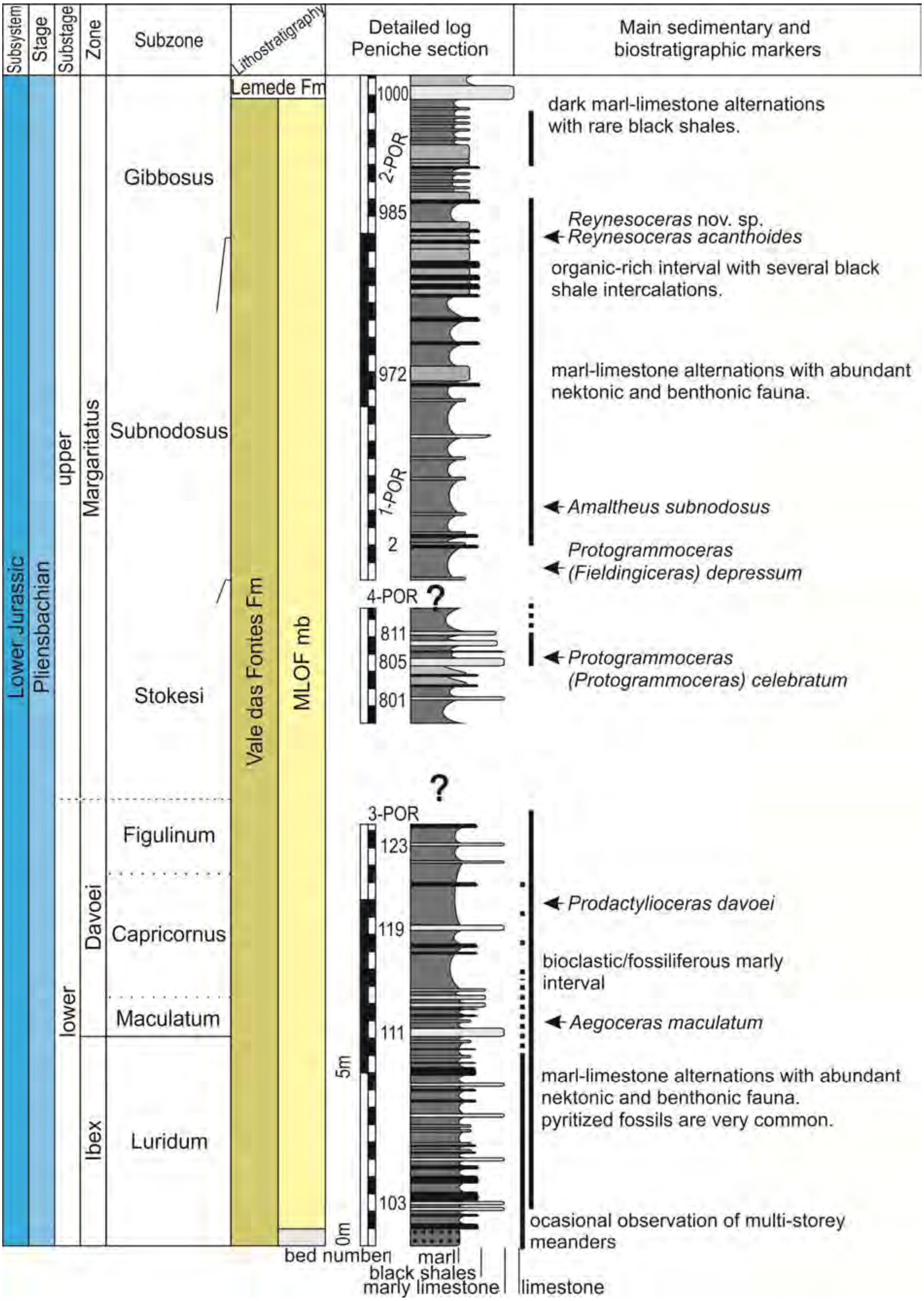


Fig. 4.1.10. Detailed log of the MLOF mb and extreme base of Lemede Formation in the S. Pedro de Moel reference section (modified from Silva et al., 2012).

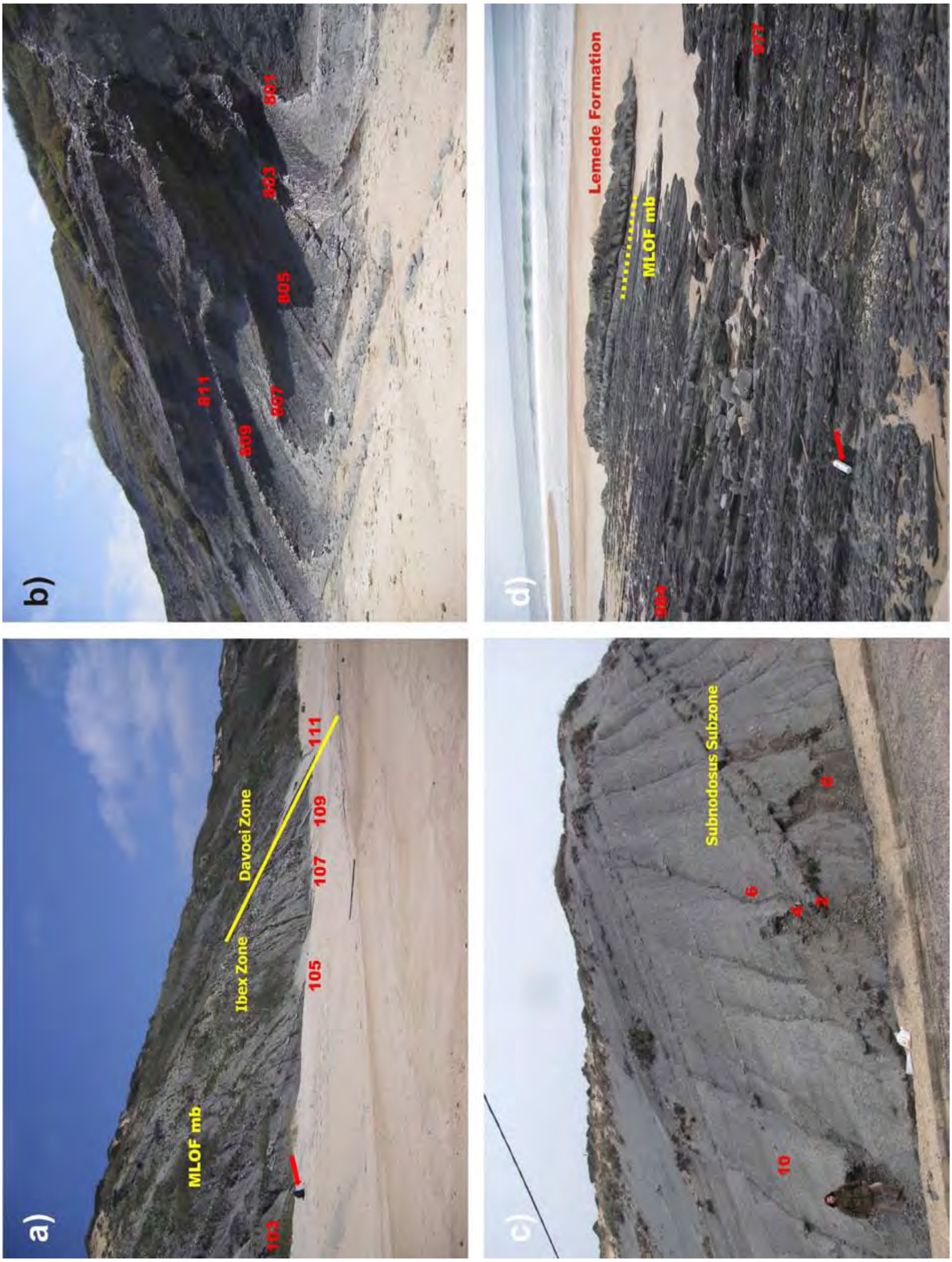


Fig. 4.1.11. Field details of the MLOF mb (Vale das Fontes Formation) and Lemede Formation at S. Pedro de Moel. a) base of the studied section; b) middle portion of the studied section; c) outcrop of the MLOF mb in the road accessing the Pedra do Ouro beach; d) view of the limit between the Vale das Fontes and Lemede formations.

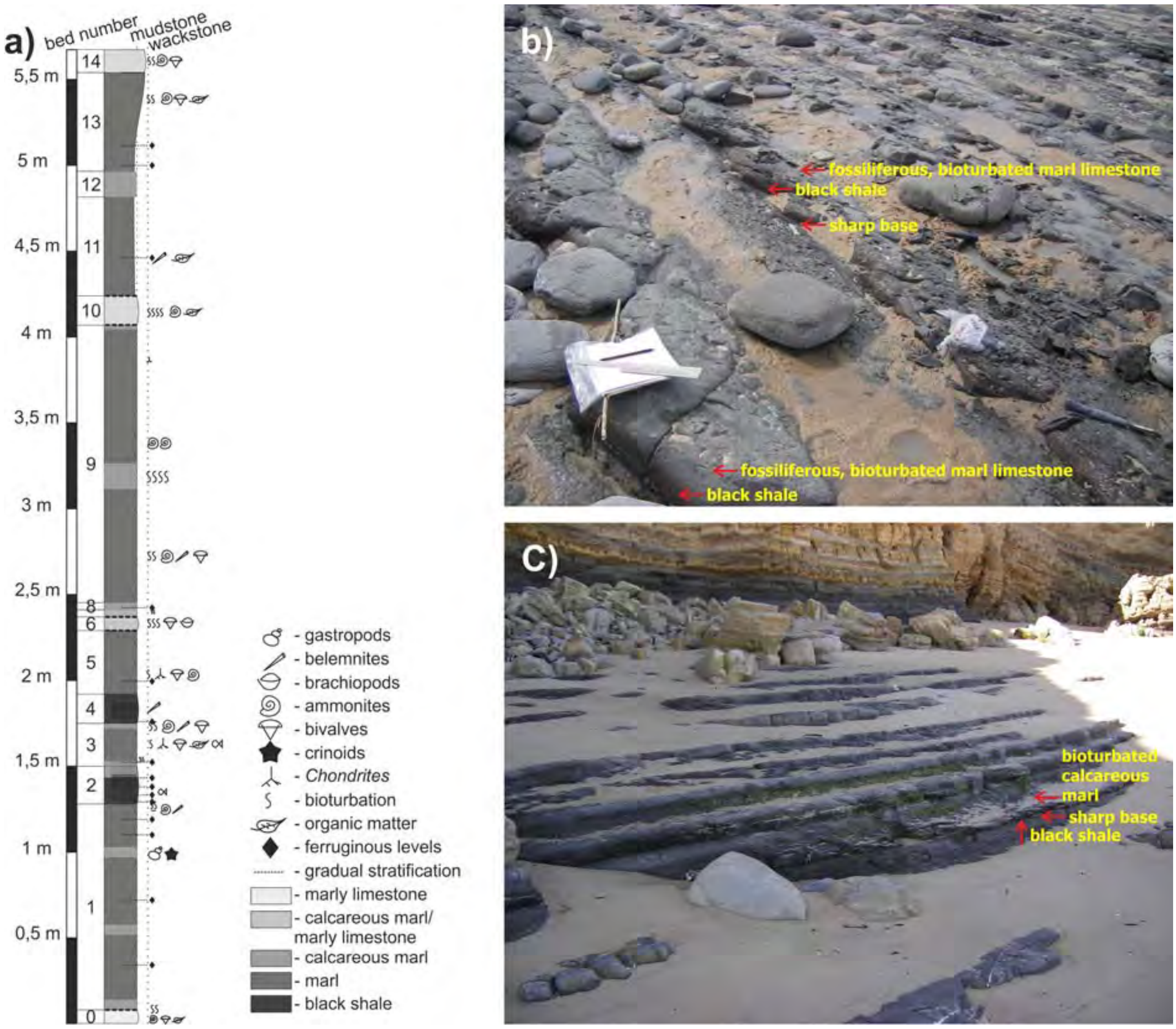


Fig. 4.1.12. Details of the black shale occurrences in the MLOF mb of the Lusitanian Basin: a) high-resolution sedimentological log of the MLOF mb outcrop in the road assessing the Pedra do Ouro beach (see Fig. 4.1.11c); b) black shales occurrences belonging to the Margaritatus Zone, Stokesi Subzone, Celebratum horizon, at S. Pedro de Moel; c) black shales occurrences belonging to the Margaritatus Zone, Subnodosus Subzone, Depressum horizon at Peniche.

4.1.4.1. Ibex/Davoei zones

At Peniche, the highest TOC record is 26.3% in a 2 centimetre black shale (Silva et al., 2011b; 2012). This black shale is located about 80cm above the bed 64 of Phelps et al. (1985), whose base marks the onset of Davoei Zone. This level is probably correlated to a thin black shale with 22.3% of TOC in Rabaçal (Silva et al., 2012). This inference is based on the fact that the limestone bed 170 of Rabaçal section (Fig. 4.1.7), located immediately above this black shale interval, held *Aegoceras* ammonites and both palynofaciological and biogeochemical data suggest that the two levels share many similarities (Silva et al., 2012). In the Figueira da Foz section, F. Silva et al. (2006) reported a TOC value of 22.8% determined in the Davoei Zone, although poorly aged-constrained, which may be also correlate with the previously described levels.

4.1.4.2. Davoei/Margaritatus zones limit

At Peniche, the Davoei/Margaritatus zones limit is bounded by the occurrence of several organic-rich facies (Duarte et al., 2010; Silva et al., 2011b; 2012). The TOC values are lower than in the aforementioned referred black shale interval, but are a good reference for the basinal correlation of this interval. Here, the last black shale of the Davoei Zone has a TOC value of 5.10% and the first of the Margaritatus Zone has TOC around 4% (Oliveira et al., 2006; Duarte et al., 2010; Silva et al., 2011b). At Rabaçal, a similar TOC increase is recorded at this interval, reaching up to about 3%. However, we cannot confidentially assign this level to any particular level of Peniche. It should also be referred that at S. Pedro de Moel, Dommergues and Moutede (1980) placed the Davoei-Margaritatus boundary just above a 1m package of organic-rich facies. These observations suggest that TOC values increase at the boundary between the Davoei/Margaritatus zones.

4.1.4.3. Upper Stokesi Subzone (Celebratum horizon)

In the distal sections of the basin, namely at Peniche and S. Pedro de Moel, this interval is readily identified due to the contrast of the black shales beds with the framing lithofacies. After a dominantly marl interval, two black shales, grading upwards to a more calcareous lithofacies, are capped by a package of three limestone–marl alternations (Fig. 4.1.9c). In turn, this package is overlain by a bioclastic-fossiliferous marly interval. The first black shale presents TOC of 20.70% and 8.65% and the second has TOC values of 11.20% and 4.60% in S. Pedro de Moel and Peniche, respectively (Silva et al., 2012 and unpublished data). New and published ammonite data indicates an upper Stokesi Subzone (Nitescens?/Celebratum horizons) age for this interval. In more proximal settings, i.e. Rabaçal and Tomar, only the limestone package is recognized (see above), although a slight TOC increase is observed at its base at Rabaçal (Duarte et al., 2010). Here, the limestone package, comprising several beds, is overlain by a thick highly fossiliferous marly interval with abundant pyritised macrofauna. The limestone dominance, new ammonite data and data published by Mouterde et al. (1964-65) suggests that these limestones may correlate with those described above for S. Pedro de Moel and Peniche.

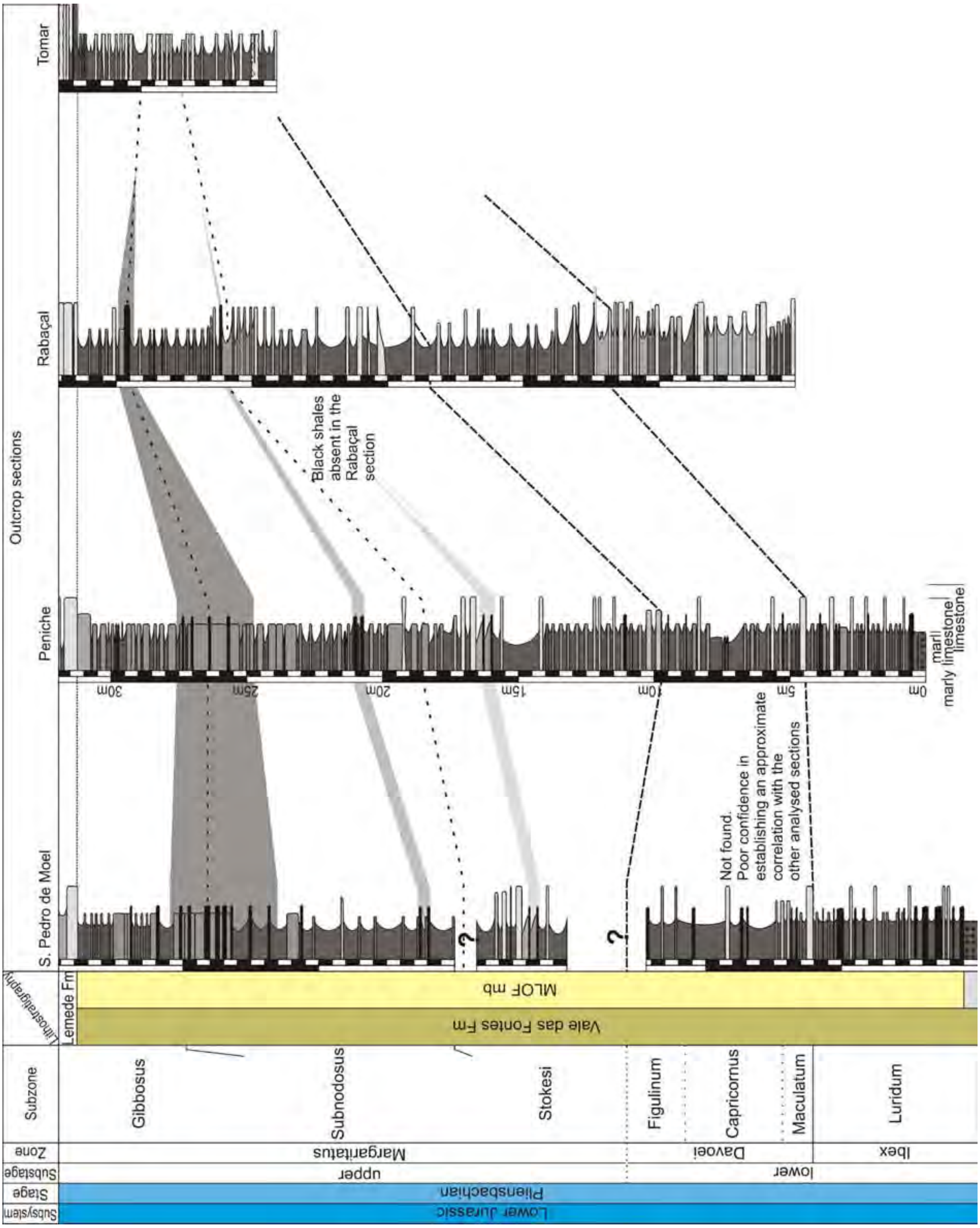


Fig. 4.1.13. High-resolution correlation of the S. Pedro de Moel, Peniche, Rabaçal and Tomar sections.

4.1.4.4. Lower/Middle Subnodosus Subzone

This interval is best observed in the most distal sections of the basin. At S. Pedro de Moel and Peniche, it is characterized by the occurrence of two black shales located in-between a marly succession (Figs. 4.1.12a and 4.1.12c). TOC values of the black shales do not vary much in each section, increasing from about 6% in S. Pedro de Moel to 9% at Peniche (see Silva et al., 2012). Ammonite fauna suggests a middle Subnodosus Subzone age for this interval. The correlation of this period in the studied section at Rabaçal is more difficult, since no lithological evidence, besides the black shale itself, can confidentially be used.

4.1.4.5. Subnodosus–Gibbosus subzones

This interval is readily identified at a basinal scale, from Rabaçal to Figueira da Foz (F. Silva et al., 2006, 2007; Duarte et al., 2010, Silva et al., 2011b; 2012). Although this interval does not correspond to the highest TOC values observed, it is clearly the thickest. In S. Pedro de Moel and Peniche, after a marly dominated interval with a few black shales, the referred package starts with a black shale grading to a thick limestone bed. Then, several black shales are observed, capped by a similar lithofacies (Fig. 4.1.11d). The last black shale occur in-between a more calcareous bed. The TOC values in this interval reach up to 15% in Peniche and 18% in S. Pedro de Moel (Duarte et al., 2010; Silva et al., 2011b; 2012). At Rabaçal, this interval can be correlated with a thick organic-rich laminated marl where TOC reach about 5% (Duarte et al., 2010; Silva et al., 2012).

4.1.5. Depositional environment

Based on sedimentological criteria, it is possible to distinguish three sedimentation domains, relating to the different environmental subdivisions predicted for carbonate ramp systems (see Burchette and Wright, 1992 and references therein), in the Pliensbachian of Lusitanian Basin (Fig. 4.1.14). Westwards, corresponding to Peniche and S. Pedro de Moel sections and Figueira da Foz sector, the main feature of the MLOF mb is its richness in organic-matter (e.g. Duarte and Soares 2002). Ammonites and belemnites are abundant and benthic macrofauna, mainly brachiopods, bivalves and echinoderms occur. This domain corresponds to outer ramp/basin environments. Paleobathimetric estimates based in microfossil data suggest that water column thickness averaged around 100–200 metres (e.g. N'zaba-Makaya et al., 2003; Reggiani et al., 2010a). The central-eastern domain, namely at Rabaçal, is distinguished by the significant occurrence of nautiloids (macro- and, sometimes, micro-shells), the widespread presence of usually small mud-wacke-packstone carbonate build-ups (associated with nautiloids at the base or with large Lytoceratids higher in the section) and occurrence of bones of larger animals (ichthyosaurs?). Locally, organic-rich facies are observed, although these are not expressive when compared with the western domain. This sector corresponds to outer/mid ramp environments. The Tomar sector, in the southeastern domain, represents the shallowest of the studied environments. Ostracods data from N'zaba-Makaya et al. (2003) suggests that here the minimum thickness of the water was more than 50 metres. It contrasts with the other two domains by the lack of organic-rich facies, the increasing limestone and bioclastic character of the series and richness in benthic macrofauna (brachiopods and bivalves). This corresponds mainly to mid-ramp environments. The same type of environment was assigned to the Pliensbachian series exposed in outcrops of the Arrábida mountain range, in the south of the Lusitanian Basin (Manuppella and Azerêdo, 1996; Azerêdo et al., 2003).

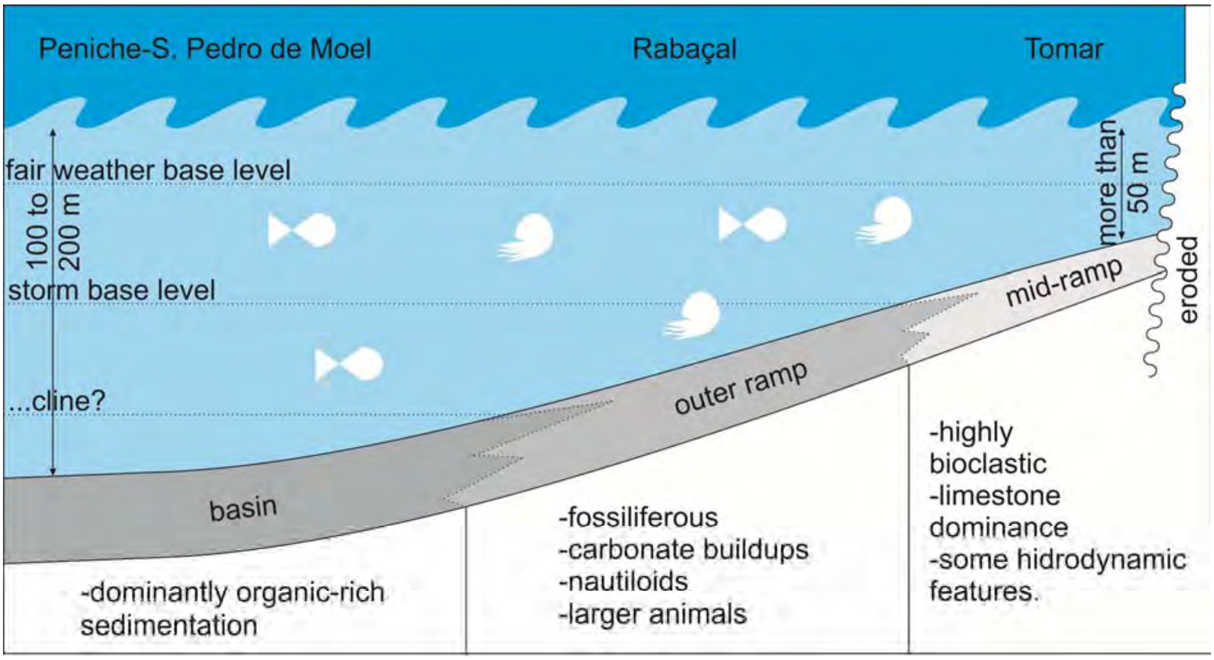


Fig. 4.1.14. Cartoon of the depositional environment of the Lusitanian Basin during the Early-Late Pliensbachian.

From the above, it is clear that the Lower–Upper Pliensbachian series are incomplete, since the most proximal environments are not observable in outcrop anywhere. All the deposits from the proximal environments located eastwards of the nowadays limit of the Lusitanian Basin have been eroded during the evolution of the Iberian Massif and the current eastern limit of the basin corresponds to a complex fault zone (falha Porto-Tomar, e.g. Wilson, 1988; Azerêdo et al., 2003 and references therein). The Lower Jurassic outcrops of the western Iberian Margin (Fig. 4.1.1.), corresponding to the Arrábida mountain range (southernmost outcropping limit of the Lusitanian Basin) and Santiago do Cacém [Santiago do Cacém sub-basin *sensu* Azerêdo et al. (2003 and references therein) or Alentejo Basin *sensu* TGS-NOPEC (see also Pereira and Alves, 2012)], present a marked differentiation in facies development. The former shows a tendency to deepen northwards (e.g. Azerêdo et al., 2003), while the latter records an opposite deepening trend, from North to South (Inverno et al., 1993; Stapel et al., 1996). This evidence suggests the existence of a structural high between the Lusitanian Basin and the Santiago do Cacém subasin or Alentejo Basin (e.g. Stapel et al 1996).

4.1.6. Sequence stratigraphy: 3rd-order depositional cycles and regional correlation

A 2nd-order Transgressive–Regressive (T-R) facies cycles scheme for the Sinemurian–Callovian interval has been already established for the Lusitanian Basin (see Duarte et al., 2004; 2010, Azerêdo et al., 2011) but, although 4th- to 5th-order cycles have also been defined for a part of the Pliensbachian series (Fernández-López et al., 2000), 3rd-order sequences (*sensu* Jacquin and de Graciansky et al., 1998) have remained elusive up to now.

In order to apply the sequence stratigraphy method to the studied series, the conceptual standard workflow of Catuneanu (2006) and Catuneanu et al., (2009, 2010 and 2011) was followed, starting with the definition of a type section, recognition of sequence stratigraphic surfaces and identification of genetic units (systems tracts). These three steps constituted the backbone of the model-dependent analysis, in which a genetic significance is assigned to sequence stratigraphic surfaces, changing them to sequence boundaries, according to a particular sequence stratigraphic model.

4.1.6.1. Sequence stratigraphic surfaces and stratigraphic genetic units

In sequence stratigraphy analysis, seven sequence stratigraphic surfaces are expected to occur in relation to the four events of the base-level cycle, resulting in three major systems tracts, i.e. forced regression, normal regression and transgression (e.g. Catuneanu, 2006; Catuneanu et al., 2009; 2010, 2011). The specificity of the Meso-Cenozoic evolution of the Lusitanian Basin (which resulted in the absence of proximal marine, transitional and continental environments records for the Pliensbachian interval), coupled with the fact that only outcrop data is available (hence no large scale stratal terminations or geometric features can be inferred), makes it difficult to confidently assign the observed sedimentological features to base-level or shoreline trajectory changes and therefore, to a particular shoreline-related system tracts (*sensu* Catuneanu et al., 2011). This is also problematic because offshore depositional trends may uncouple from shoreline environments (e.g. Bruchette and Wright, 1992; Tucker et al., 1993; Einsele, 2000; Coe, 2003). Thus, and following the recommendation of Catuneanu et al. (2009), this work was based on the definition and observation of two unconventional systems tracts [(this nomenclature is preferred over the Shoreline independent systems tracts presented in Catuneanu et al. (2011)] and two sequence stratigraphic surfaces, made up by the arrangement of main discernible architectural element of the studied series: the thickness of limestone and marl beds. The unconventional systems tracts are named Decreasing Limestone Bed Thickness (DLBT) and Increasing Limestone Bed Thickness systems tracts and the bounding sequence stratigraphic surfaces are defined as Trend Inflection Surfaces (TIS) type 1(at the base of ILBT) or type 2 (at the base of DLBT) (Fig 4.1.15). Such definition of sequence stratigraphic surface tallies with the one of Schlager (2005) where "*the original definition of sequence boundary as an unconformity between two units of conformable, genetically related strata does not automatically imply sea-level control. It simply means that at this boundary the pattern of sediment input or sediment dispersal changed abruptly*". Hierarchically, these unconventional sequences correspond to 3rd-order sequences, contained in the 2nd-order Pliensbachian T–R facies cycle (see Duarte et al., 2010).

The definition of these unconventional systems tracts and sequence stratigraphic surfaces (basically outcrop bedding rhythms) was based on the assumption that the weathering profile reflects a variation of carbonate content due to production, dilution and early diagenesis (see Einsele et al., 1991, Einsele, 2000, and references therein for more details), and that the carbonate content threshold that marks the weathering boundary in any section is similar at outcrop scale, although it may vary between locations.

4.1.6.2. Definition of a sequence stratigraphy type section and 3rd-order sequences

The sequence stratigraphy type section corresponds to the Rabaçal section. Three 3rd-order unconventional sequences were recognized in this section and correlated throughout the basin using the available biostratigraphic data and black shales occurrences. The three sequences correspond to the 3rd-order sequence Lower Pliensbachian Ω (LoPΩ), the 3rd-order sequence Lower–Upper Pliensbachian (Lo-UP) and the 3rd-order sequence Upper Pliensbachian A (UPA) (Fig 4.1.15):

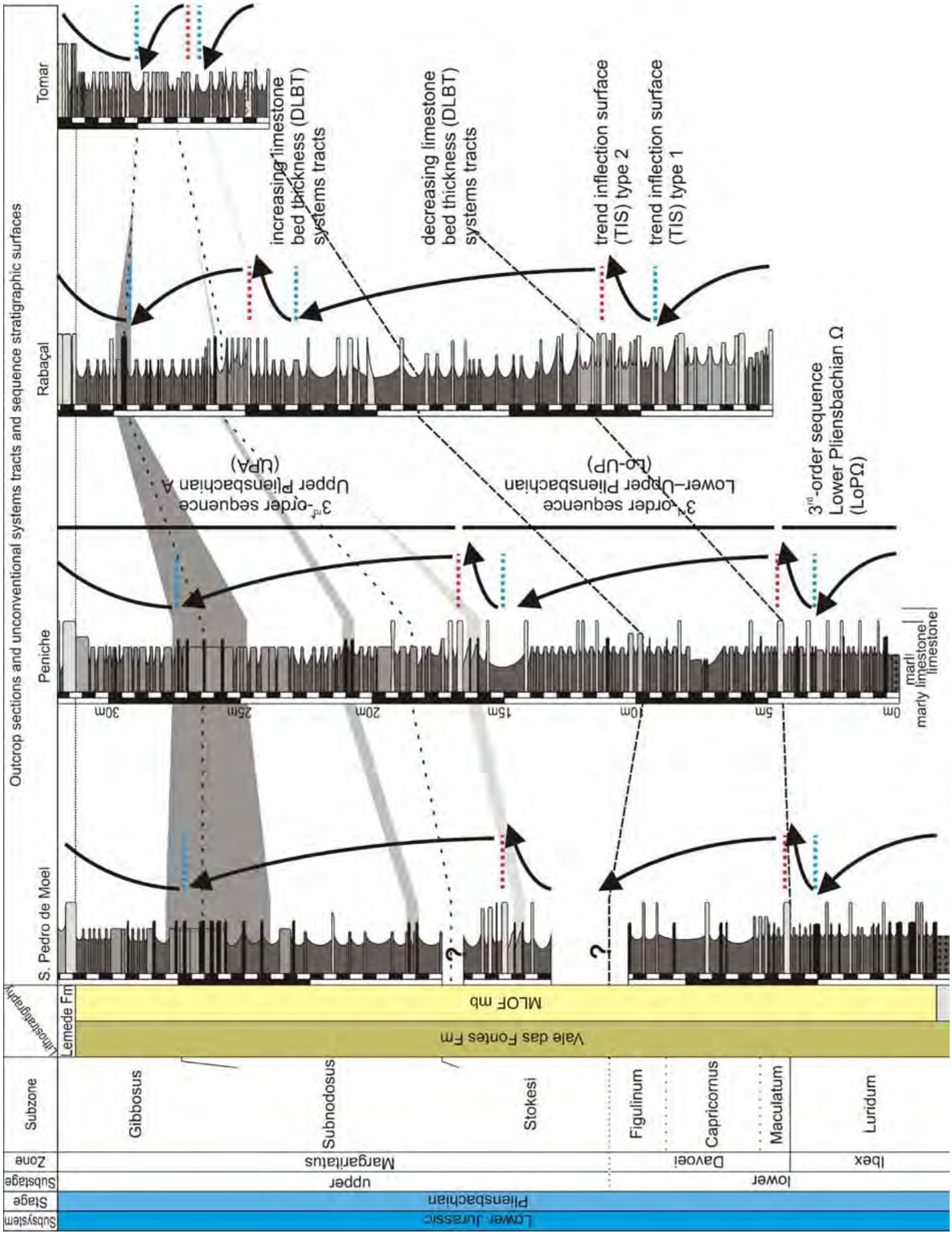


Fig. 4.1.15. High-resolution correlation and inferred unconventional systems tracts and sequence stratigraphic surfaces in S. Pedro de Moel, Peniche, Rabaçal and Tomar sections.

4.1.6.2.1. 3rd-order sequence Lower Pliensbachian Ω (LoPΩ)

The Lower Pliensbachian Ω (LoPΩ) sequence corresponds to the initial part of the MLOF mb. Its base is not defined. In the Rabaçal type section, the recognized part of this sequence is about 6.5 metres thick (Fig. 4.1.7a). The following discussion is a preliminary assessment of this sequence. The DLBT systems tracts (about 4.5 metres) is characterized by an important carbonate (micrite and bioclasts) contribution and sporadic occurrence of black shales. The series has a clear pattern of decreasing limestone contribution, with the marl-limestone couplets usually constituting 5/4:1 bundles. The top of these systems tracts is placed within an organic-rich argillaceous interval, corresponding to the TIS type 1. Laterally, this unit presents some variation, with the black shales being more expressive at S. Pedro de Moel. The ILBT systems tracts is materialized in the Rabaçal type section by a clear increment in the number, thickness and bioclastic character of the limestone beds. The TIS type 2 corresponds roughly to Ibex/Davoei boundary interval and to the top the thickest limestone bed of this interval. At Peniche and S. Pedro de Moel, this boundary is also placed at the top of the thickest limestone bed in this interval (Figs. 4.1.9b and 4.1.11a) whose base corresponds to the base of the Davoei Zone (Phelps, 1985).

The recognized portion of the LoPΩ sequence spans from the Ibex Zone, Luridum Subzone, Crassum (top of Rotundum?) horizon to the extreme base of the Davoei Zone (Phelps, 1985). According to the 2012 Geological Time Scale (Gradstein et al., 2012), the LoPΩ is at least 170k years long.

4.1.6.2.2. 3rd-order sequence Lower–Upper Pliensbachian (Lo-UP)

Of all the sequences defined in this work, the Lower–Upper Pliensbachian (Lo-UP) sequence (with about 14 metres at Rabaçal) is the best constrained one. At Rabaçal, the DLBT systems tracts rests over sequence LoPΩ (diastem?) and its base is very similar throughout the basin. The base of this unit corresponds to a major influx of argillaceous materials and high accumulation of shells (e.g. *Aegoceras* sp.), some evidencing minor transport and exposure features. The good basinal development of this sequence, the black shales and the biostratigraphic data allow correlating this sequence at bed scale. The mid part of the series, apart from some minor variation in siliciclastic and bioclast contents, is very monotonous, hampering the recognition of staking patterns or sequence boundaries and the clear definition of the TIS type 1. At Rabaçal, the top of this sequence, corresponding to the upper part of the ILBT systems tracts, is well expressed in the terrain morphology. The monotonous marly sedimentation gradually gains a more calcareous, fossiliferous and bioclastic character. Here, evidences of prolonged exposure (e.g. ferruginous surfaces), high bioturbation and shell accumulations are observed (see previous section). The TIS type 2 is placed within this calcareous package, bed 206 of the Rabaçal section (Fig. 4.1.7c).

The ammonite data indicates an age ranging from the extreme base of the Davoei Zone to the Margaritatus Zone, Stokesi Subzone, Celebratum horizon. According to the 2012 Geological Time Scale (Gradstein et al., 2012), the Lo-UP is about 1900k years long. Collectively, the faunas indicate a more or less permanent opening towards north boreal domains, although some Tethyan influence is sporadically recognized (Dommergues et al., 2009).

4.1.6.2.3. 3rd-order sequence Upper Pliensbachian A (UPA)

The Upper Pliensbachian A (UPA) sequence corresponds to the top of the MLOF mb and base of the Lemede Formation (Figs 4.1.7c and 4.1.7d). The top of the unit is not defined in this work, but is considered to be located within the Lemede Formation. The assignment of the unconventional systems tracts defined in this part of the series is evident. At Rabaçal, the DLBT systems tracts corresponds to the sediments deposited until the thickest black shale interval (see previous subsections), which represent the Maximum Flooding Interval of the Pliensbachian 2nd-order T–R facies cycle. The TIS type 1 is placed in this interval. The base of these DLBT systems tracts, as in the previous ones, is marked by a major influx of terrigenous materials and a high accumulation of fossils (see previous section). The ILBT correspond to the return of limestone dominated sedimentation over the whole of the basin, which is materialized, in part, by the Lemede Formation. The UPA is more than 1500ky long (Gradstein et al., 2012).

4.1.6.3. Model-dependent analysis

In the definition of the 2nd-order T–R facies cycles for the Lusitanian Basin, Duarte et al. (2010) adopted the model proposed by Jacquin and de Graciansky (1998). According to the latter authors, the T–R facies cycles are composed of four types of 3rd-order depositional sequences: infilling and forestepping during regressive phases and aggrading and backstepping during transgressive phases. These units are defined by the shelfal accommodation changes and bounded by unconformities or correlative conformities induced by 3rd- or 4th-order relative sea-level falls (Mitchum, 1977; Van Wagoner et al., 1987). However, and as in the current case study, such approach is limited by the difficult recognition of correlative conformities based only in outcrop data (see, for example, Embry, 2009). Much debate has been generated around this concept over the recent years (see Catuneanu, 2006; Catuneanu et al., 2009, 2010, 2011), being the current agreement that correlative conformities can only be recognized by the integration of seismic and outcrop data (e.g. Catuneanu et al., 2009). The fact that correlative conformities cannot be confidentially defined inhibits the depositional (Mitchum et al., 1977 and consequent derivations) and genetic (Frazier, 1974; Galloway, 1989) sequence models being used. In a very simplistic way, DLBT and the ILBT can be regarded as corresponding to fining- and coarsening-upward successions, respectively. Using such reasoning, the DLBT represents a transgressive unit and ILBT a regressive unit. The logic is that a coarsening-upward succession (increasing limestone and bioclastic character) reflects a shift of the current location to higher energy settings, thus shallowing and progradation, while fining-upward successions indicate a decline in the environmental energy, similarly to a deepening, retrogradation event, i.e. Walter Law of facies (e.g. Posamentier and Allen, 1999; Einsele, 2000, Coe, 2003, Schlager, 2005). This way, TIS type 1 can be regarded as the maximum flooding surface (MFI) and the TIS type 2 to the maximum regressive surface (MRS)/transgressive surface (TS) (see Catuneanu, 2011). This simple division is in good agreement with observed sedimentological data, where the TIS type 1 is associated with the finest and organic-rich sedimentation and the TIS type 2 is associated with shallow-water exposure features and the earliest signs of transgression (Fig. 4.1.15 and 4.1.16).

In addition, these inferences are in good agreement with the foraminifera (Rey et al., 2000), ostracods (N'zaba-Makaya et al., 2003) and gamma-ray outcrop data in Correia et al., (2012). It seems that, at this stage, the Transgressive-Regressive sequence model (Jonhson and Murphy, 1984; Embry and Johannessen, 1992; Embry, 1993, 2009) is a good fit to the above hypothesis, where the DLBT are equivalent to the Transgressive systems tracts and the ILBT are the Regressive systems tracts (Fig. 4.1.16).

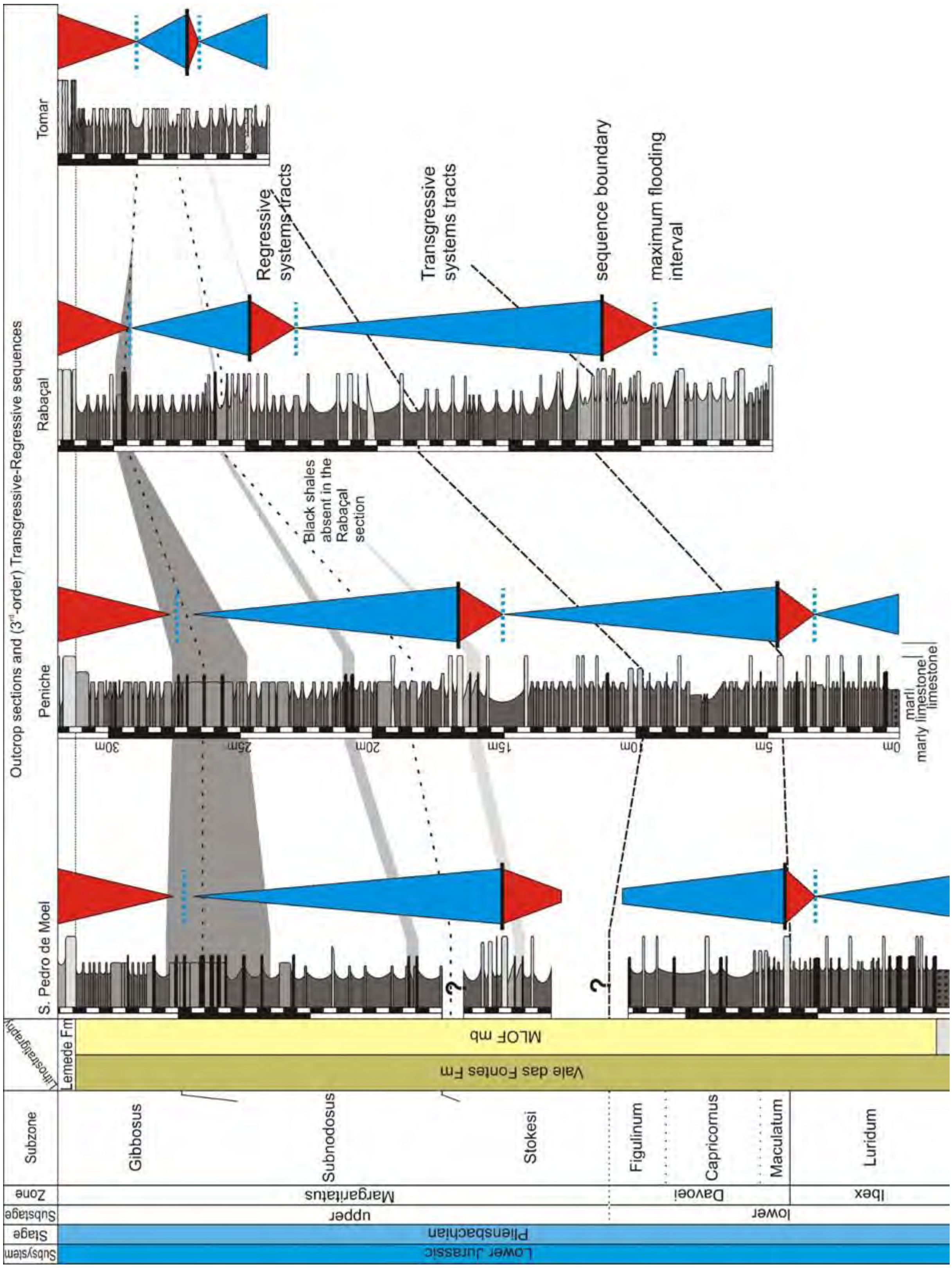


Fig. 4.1.16. High-resolution correlation and Trangressive-Regressive sequences in S. Pedro de Moel, Peniche, Rabaçal and Tomar sections.

4.1.7. Paleogeography and sequence stratigraphic similarities between the European epeiric seas during the Early/Late Pliensbachian

The Lower Jurassic series of the Lusitanian Basin have long been regarded as corresponding to a low-energy carbonate ramp depositional environment, deepening to N–NW (e.g. M. P. Watkinson and Wilson and Exton, 1979, in Wilson, 1988; Duarte, 1997, 2007; Duarte et al., 2004) and probably located on the dominant leeward side of the Iberian Massive at 20-30º N (e.g. Bassoulet et al., 1993; van de Schootbrugge et al., 2005, Arias, 2008). For many years, geologists working in the Lusitanian Basin used the classical paleogeographical reconstructions provided by Decourt and collaborators (1993, 2000) (Fig. 4.1.17a and 4.1.17b). However, improvements in the geological knowledge, namely about paleocontinents position (e.g. Schettino, 2009; Skogseid, 2010; Osete et al., 2011), paleobiogeography provinces (e.g. Arias 2008; Dommergues et al., 2009) and the data available from the Lusitanian Basin (e.g. Wilson and Exton, 1979, in Wilson, 1988; Duarte, 1997, 2007; Duarte et al., 2004; 2010; Silva et al., 2011b) lead us to construct and use an alternative model for the Pliensbachian paleogeography of the Lusitanian Basin (Fig. 4.1.17c), complemented with data from neighbouring basins (e.g. Cubaynes et al., 1984; Fleet et al., 1987; Tankard and Balkwill, 1989; Hiscott et al., 1990; Enachescu, 1992; Michalík, 1993; Baudin, 1995; Pinheiro et al., 1996; Quesada et al., 1997, 2005; Cobianchi and Picotti, 2001; Scotchman, 2001; Aurell et al., 2002, 2003; Perilli and Comas-Rengifo, 2002; Stampfli and Borel, 2002; Simms et al., 2004; Wielens et al., 2006; Alves et al., 2006; Arias, 2006; 2008; Emmanuel et al., 2006; Nikitenko et al., 2008; Lachkar et al., 2009; Bodin et al., 2011; Dommergues et al., 2011; Pereira and Alves, 2012; Sachse et al., 2012). At this stage this is a preliminary best-fit model (Fig. 4.1.17c); hence, we will not be described it in detail. This model calls attention to two main issues regarding the more popular models:

a) a plethora of evidences suggest that the basin was mostly open towards north, sharing many sedimentological and paleontological similarities with Northern Spain (Fig. 4.1.18) (e.g. Borrego et al., 1996; Quesada et al., 1997; Badenas et al., 2009, 2012; Comas-Rengifo and Goy, 2010), which is in sharp contrast with the previous models (Fig. 4.1.17a and 4.1.17b);

b) the incompleteness of the Pliensbachian record of the Lusitanian Basin resulted in an overestimation of the aerial expression of the Iberian Massif (Fig. 4.1.17c). These observations have a profound impact in the establishment of faunal and floral exchange paths and suggest a higher interconnection between the European basins.

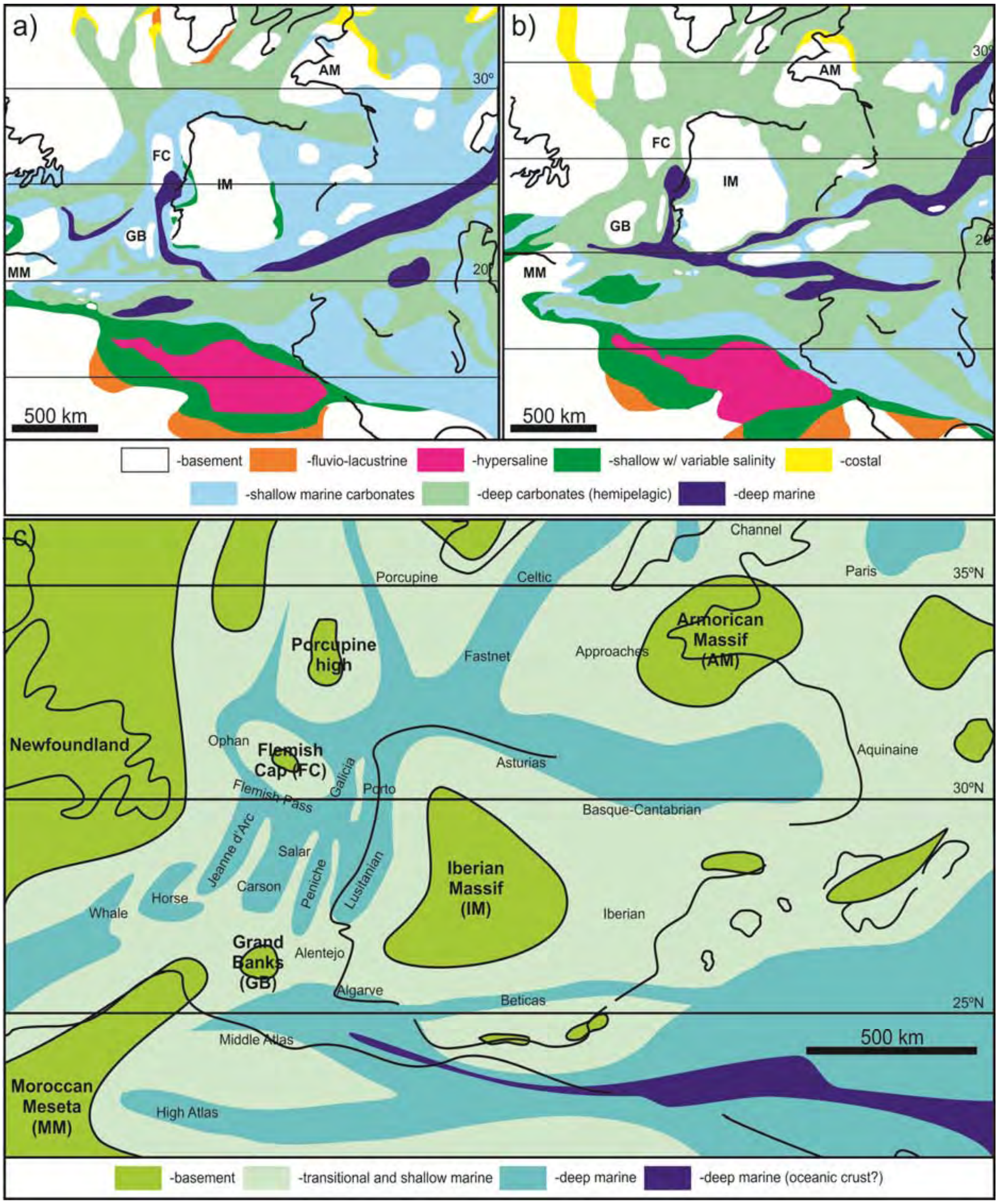


Fig. 4.1.17. Paleogeographic reconstructions for the Early Jurassic. a) Late Sinemurian (Thierry and coll. *in* Decourt et al., 2000); b) Middle Toarcian (Thierry and Barrier and coll. *in* Decourt et al., 2000); c) this work.

De Graciansky et al. (1998) presented a general Mesozoic sequence stratigraphic scheme for the European basins, based on a sequence stratigraphic model presented in the same volume by Jacquin and de Graciansky (1998). Other authors favoured a more "standardised" definition of depositional sequence, as the case of Hesselbo (2008). Hence, and in order to compare them with the sequence stratigraphic scheme proposed for the

Lusitanian Basin, the published sequence stratigraphic data has been transformed to the transgressive-regressive sequence model (see previous section, Fig. 4.1.16). Overall, this procedure results in a downgrade of the available data (from all the systems tracts available to a simple transgressive-regressive systems tracts scheme) and a change of the placement of sequence boundaries. The change of their placement is the result of the amalgamation of the lowstand, forced lowstand and highstand systems tracts into single regressive systems tracts and because the definition of sequence boundary is dependent of the chosen sequence stratigraphic model (e.g. Catuneanu et al., 2009). It is highlighted that this is a tentative approach to compare the data from the Lusitanian Basin with the data available from other locations, within the uncertainties and limitations in the application of the sequence method to the studied series.

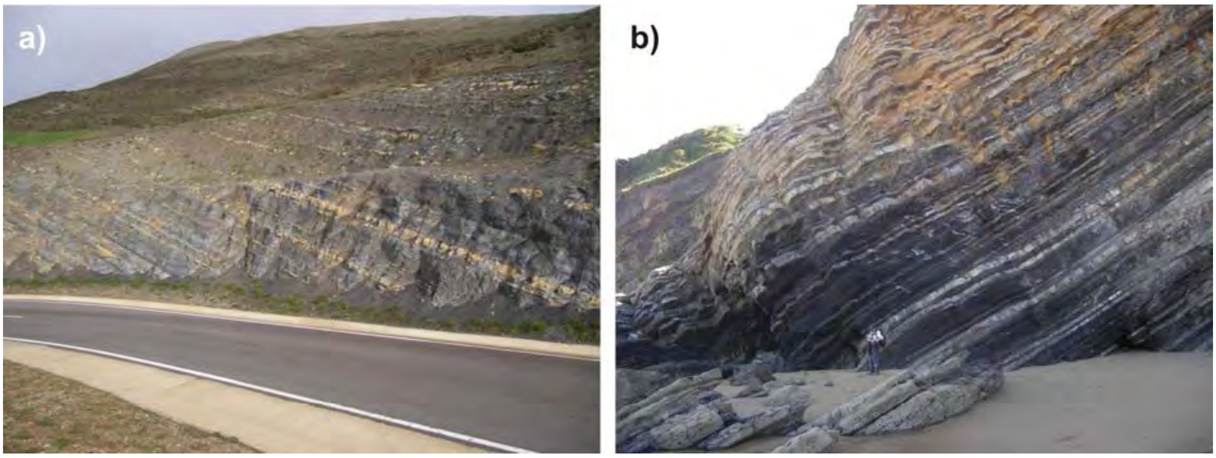


Fig. 4.1.18. Marl–limestone alternations from: a) S. Andrés section, Basque-Cantabrian Basin; Early Pliensbachian; b) Playa de Vega section, Asturias Basin, Late Pliensbachian, Compare with the limit between the MLOF mb. and the Lemede Formation in the Lusitanian Basin (e.g. 4.1.7d; 4.1.9d).

Regardless of the nomenclature, if all the sequence stratigraphic data are "normalized" for the sequence stratigraphic scheme used for the Lusitanian Basin, it is clear that several events can be traced at a European scale (Fig. 4.1.19), as already referred by de Graciansky et al. (1998). At a greater detail it is seen that the Early/Late Pliensbachian boundary marks a major change in the sequence stratigraphic architecture of the several European basins. Following the trends already evidenced by the paleobiogeographical data (see, for example, Dommergues et al., 2009; Dera et al., 2010) the Upper Pliensbachian series of several locations are much more similar, in terms of sequence stratigraphy, than the Lower Pliensbachian ones.

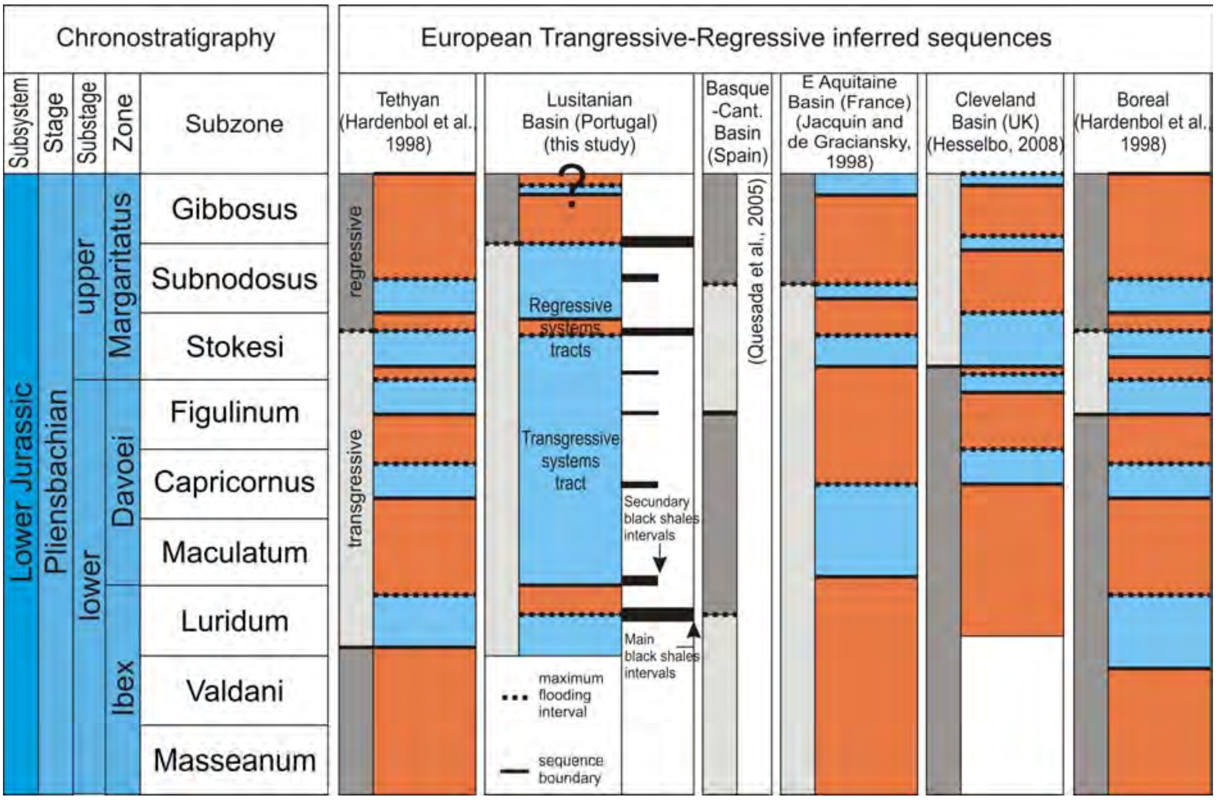


Fig. 4.1.19. Comparison between the different 3rd-order Trangressive-Regressive sequences of several European locations.

During the Late Pliensbachian it is possible to infer multiple flooding events that can be traced at a regional scale (Fig. 4.1.19). The main events recorded in this study for the Lusitanian Basin correspond to the upper Stokesi (Nitescens?/Celebratum horizons) Subzone, Subnodosus Subzone, Subnodosus/Gibbosus (Ragazzoni horizon) Subzones. The upper Stokesi Subzone (Nitescens?/Celebratum horizons) maximum flooding interval can be traced over most of the Tethyan and Boreal domains, marking a phase of extensive interconnection of the European epicontinental seas, well expressed in the northwards expansion of Tethyan faunas, inclusively *Protogrammoceras celebratum*, the first Tethyan/Boreal common horizon index ammonite from the Pliensbachian ammonite biozonation (see Dommergues et al., 1997). The Subnodosus Subzone flooding interval is subtly recorded in the Lusitanian Basin as a 4^{th}- to 5^{th}-order sequence. However, in de Graciansky et al. (1998) this is a major 3^{rd}-order maximum flooding interval. The Subnodosus/Gibbosus (Ragazzoni horizon) Subzones interval, although corresponding to a 2^{nd}-order maximum flooding interval of the Pliensbachian T-R facies cycle in the Lusitanian Basin, is poorly recorded elsewhere. This event marks the rapid switch from a northwards expansion of southern ammonite faunas [notice that *Reynesoceras ragazzoni* is the subzone index ammonite for both Tethyan and Boreal domains (Dommergues et al., 1997)] to a domination of boreal ammonites in the Lusitanian Basin record (see references above). The northwards expansion of southern ammonite faunas is traceable up to SW Germany (Schweigert, 2005). With the exception of the Cleveland Basin (Hesselbo, 2008), it seems that this flooding interval does not have a high-order counterpart. In the Lusitanian, Basque-Cantabrian and Asturian basins, these intervals correspond to the deposition of organic-rich facies (e.g. Borrego et al., 1996; Queseda et al., 1997; Duarte et al., 2010; Silva et al., 2011b; 2012 and references therein) (Fig. 4.1.18).

The regressive phases seems to record a more autocyclical control in the series. The best recorded regressive phase in the Lusitanian Basin corresponds to the regressive phase of the Lo-UP sequence (Fig. 4.1.16). This cycle seems to be correlatable in many basins, although the top sequence boundary seems to be diachronous.

4.1.8. Conclusions

The main results of this paper are summarized below:

-new, detailed sedimentological and biostratigraphic data from the main Lower–Upper Pliensbachian outcrops of the Lusitanian Basin enabled the high resolution correlation of the studied series and the definition of a 3rd-order sequence stratigraphic scheme;

-in the MLOF mb of the Vale das Fontes Formation three unconventional sequences were defined for the Pliensbachian time interval (upper Ibex–Margaritatus zones). The unconventional systems tracts are named Decreasing Limestone Bed Thickness (DLBT) and Increasing Limestone Bed Thickness systems tracts and the bounding sequence stratigraphic surfaces are defined as Trend Inflection Surfaces (TIS) type 1(at the base of ILBT) or type 2 (at the base of DLBT);

-these sequences correspond to the 3rd-order sequence Lower Pliensbachian Ω (LoPΩ), the 3rd-order sequence Lower–Upper Pliensbachian (Lo-UP) and the 3rd-order sequence Upper Pliensbachian A (UPA);

-the newly defined sequences in the Lusitanian Basin for the MLOF mb seem to be linked to, or at least reflected in, several neighbouring basins;

-this paper suggests that the Pliensbachian European epeiric seas share a more similar story than previously admitted.

References

ALLAN, P.A. and ALLAN, J.R., 2005. Basin Analysis. Principles and Applications (2nd ed). Blackwell Publishing.

ALVES, T.M., GAWTHORPE, R.L., HUNT, D.W. and MONTEIRO, J.H., 2002. Jurassic tectono-sedimentary evolution of the Northern Lusitanian Basin (offshore Portugal). Marine and Petroleum Geology, 19, 727–754.

ALVES, T.M., MANUPPELLA, G., GAWTHORPE, R.L., HUNT, D.W. AND MONTEIRO, J.H., 2003. The depositional evolution of diapir- and fault-bounded rift basins: examples from the Lusitanian Basin of West Iberia. Sedimentary Geology 162, 273–303.

ALVES, T.M., MOITA, C., SANDNES, F., CUNHA, T., MONTEIRO, J.H. and PINHEIRO, L.M., 2006. Mesozoic–Cenozoic evolution of North Atlantic continental slope basins: The Peniche basin, western Iberian margin. AAPG Bull., 90, 31–60.

ALVES, T.M., MOITA, C., CUNHA, T., ULLNAESS, M., MYKLEBUST, R., MONTEIRO, J.H. and MANUPPELLA, G., 2009. Diachronous evolution of Late Jurassic–Cretaceous continental rifting in the northeast Atlantic (west Iberian margin). Tectonics, 28, TC4003, doi:10.1029/2008TC002337.

ARIAS, C., 2006. Northern and Southern Hemispheres ostracod palaeobiogeography during the Early Jurassic: Possible migration routes. Palaeogeography, Palaeoclimatology, Palaeoecology 233, 63– 95.

ARIAS, C., 2008. Palaeoceanography and biogeography in the Early Jurassic Panthalassa and Tethys Oceans. Gondwana Research, 14, 306–315.

AURELL, M., MELÉNDEZ, G., OLORIZ, F., BÁDENAS, B., CARACUEL, J., GARCÍA-RAMOS, J.C., GOY, A., LINARES, A., QUESADA, S., ROBLES, S., RODRIGUEZ-TOVAR, F.J., ROSALES, I., SANDOVAL, J., SUÁREZ DE CENTI, C., TAVERA, J.M. and VALENZUELA, M., 2002. 11-Jurassic. In: GIBBONS, W. and MORENO, T. (Eds.), The Geology of Spain. Geological Society, London, pp. 213–254.

AURELL, M., ROBLES, S., BÁDENAS, B., ROSALES, I., QUESADA, S., MELÉNDEZ, G. and GARCÍA-RAMOS, J.C., 2003. Transgressive–regressive cycles and Jurassic palaeogeography of northeast Iberia. Sedimentary Geology, 162, 239-271.

AZERÊDO, A.C., 2007. Formalização da litostratigrafia do Jurássico Inferior e Médio do Maciço Calcário Estremenho (Bacia Lusitânica). Comunicações Geológicas, 94, 29–51.

AZERÊDO, A.C., DUARTE, L.V. and SILVA, R.L., 2011. Facies, architecture and sequence evolution of the Lower and Middle Jurassic carbonate ramp succession from the Lusitanian Basin, Portugal. Abstract book of the 28th IAS meeting of Sedimentology, 1 p.

AZERÊDO, A.C., WRIGHT, V.P. and RAMALHO, M.M., 2002. The Middle–Late Jurassic forced regression and disconformity in central Portugal: eustatic, tectonic and climatic effects on a carbonate ramp system. Sedimentology, 49, 1339–1370.

AZERÊDO, A.C., SILVA, R.L., DUARTE, L.V. and CABRAL, M.C., 2010. Subtidal stromatolites from the Sinemurian of the Lusitanian Basin (Portugal). Facies, 56, 211–230.

AZERÊDO, A.C., DUARTE, L.V., HENRIQUES, M.H. and MANUPPELLA, G., 2003. Da dinâmica continental no Triásico aos mares do Jurássico Inferior e Médio. Cadernos de Geologia de Portugal. Instituto Geológico e Mineiro.

BÁDENAS, B., AURELL, M., GARCÍA-RAMOS, J.C., GONZÁLEZ, B. and PIÑUELA, L., 2009. Sedimentary vs. diagenetic control on rhythmic calcareous successions (Pliensbachian of Asturias, Spain). Terra Nova, 21, 162–170.

BÁDENAS, B., AURELL, M., ARMENDÁRIZ, M., ROSALES, I., GARCÍA-RAMOS, J.C., and PIÑUELA, L., 2012. Sedimentary and chemostratigraphic record of climatic cycles in Lower Pliensbachian marl–limestone platform successions of Asturias (North Spain). Sedimentary Geology, 281, 119–138.

BASSOULET, J.-P., ELMI, S., POISSON, A., CECCA, F., BELLION, Y.,GUIRAUD, R. and BAUDIN, F., 1993. Middle Toarcian (184–182 Ma). In: DERCOURT, J., RICOU, L.E. and VRIELYNCK, B. (Eds.), Atlas Tethys Paleoenvironmental Maps, BEICIP-FRANLAB, Rueil-Malmaison, pp. 63–80.

BAUDIN, F., 1995. Depositional Controls on Mesozoic Source Rocks in the Tethys. In: HUC, A.Y. (Ed.), Paleogeography, Paleoclimate, and Source Rocks. AAPG Studies in Geology, 40, 191–211.

BODIN, S., FRÖHLICH, S., BOUTIB, L., LAHSINI, S. and REDFERN, J., 2011. Early Toarcian source rock potential in the Central High Atlas Basin (Central Morocco): Regional distribution and depositional model. Journal of Petroleum Geology, 34, 345–364.

BOOMER, I., AINSWORTH, N.R. and EXTON, J., 1998. A re-examination of the Pliensbachian and Toarcian Ostracoda of Zambujal, west-central Portugal Journal of Micropalaeontology, 17, 1–14.

BORREGO, A.G., HAGEMANN, H.W., BLANCO, C.G., VALENZUELA, M. and SUÁREZ DE CENTI, C., 1996. The Pliensbachian (Early Jurassic) "anoxic" event in Asturias, northern Spain: Santa Mera Member, Rodiles Formation. Organic Geochemistry, 25 (5–7), 295–309.

BROOKFIELD, M.E., 2004 Principles of Stratigraphy. Blackwell Publishing.

BURCHETTE, T.P. and WRIGHT, V.P., 1992. Carbonate ramp depositional systems. In: Sellwood, B.W. (ed), Ramps and Reefs. Sedimentary Geology, 79, 3–57.

BRUNEL, F., BONNET, L., RUGET, C., REY, J., MOUTERDE, R. and ROCHA, R., 1998. Variations des associations de Foraminifères dans le Domérien du bassin lusitanien en relation avec les flutuations de l'environment. Comunicações do Instituto Geológico e Mineiro, 84, A49–A52.

CATUNEANU, O., 2006. Principles of Sequence Stratigraphy. Elsevier B.V..

CATUNEANU, O., GALLOWAY, W.E., KENDALL, C.G.ST.C., MIALL, A.D., POSAMENTIER, H.W., and STRASSER, A., 2011. Sequence Stratigraphy: Methodology and Nomenclature. Newsletters on Stratigraphy, 44, 173–245.

CATUNEANU, O., ABREU, V., BHATTACHARYA, J.P., BLUM, M.D., DALRYMPLE, R.W., ERIKSSON, P.G., FIELDING, C.R., FISHER, W.L., GALLOWAY, W.E., GIBLING, M.R., GILES, K.A., HOLBROOK, J.M., JORDAN, R., KENDALL, C.G.ST.C., MACURDA, B., MARTINSEN, O.J., MIALL, A.D., NEAL, J.E., NUMMEDAL, D., POMAR, L., POSAMENTIER, H.W., PRATT, B.R., SARG, J.F., SHANLEY, K.W., STEEL, R.J., STRASSER, A., TUCKER, M.E. and WINKER, C., 2009. Towards the standardization of sequence stratigraphy. Earth-Science Reviews, 92, 1–33.

CATUNEANU, O., BHATTACHARYA, J. P., BLUM, M. D., DALRYMPLE, R.W., ERIKSSON, P.G., FIELDING, C.R., FISHER, W.L., GALLOWAY, W.E., GIANOLLA, P., GIBLING, M.R., GILES, K.A., HOLBROOK, J.M., JORDAN, R., KENDALL, C.G.ST.C., MACURDA, B., MARTINSEN, O.J., MIALL, A.D., NUMMEDAL, D., POSAMENTIER, H.W., PRATT, B.R., SHANLEY, K.W., STEEL, R. J., STRASSER, A.

and TUCKER, M.E., 2010. Sequence stratigraphy: common ground after three decades of development. First Break, 28, 21–34.

CHOFFAT, P., 1908. Contribution a la connaissance du Lias et du Dogger dans la région de Thomar. Comunicações dos Serviços Geológicos de Portugal 7, 140–167.

COBIANCHI, M. and PICOTTI, V., 2001, Sedimentary and biological response to sea-level and palaeoceanographic changes of a Lower-Middle Jurassic Tethyan platform margin (Southern Alps, Italy). Palaeogeography, Palaeoclimatology, Palaeoecology, 169, 219–244.

COE, A.L., 2003. The sedimentary record of sea-level change. Cambridge University Press.

COMAS-RENGIFO, M.J. and GOY,A., 2010. Caracterización biocronoestratigráfica del Sinemuriense Superior y el Pliensbachiense entre los afloramientos de la Playa Vega y Lastres (Asturias). In: García-Ramos, J.C. (Coord.), Las sucesionesmargo-calcáreasmarinas del Jurásico Inferior y las series fluviales del Jurásico Superior. Acantilados de la playa de Vega (Ribadesella). Guía de campo (excursión A), V Congreso del Jurásico de España, Servitec, Oviedo, pp. 10–18.

COMAS-RENGIFO, M.J., DUARTE, L.V., GOY, A., PAREDES, R. and SILVA, R.L., 2013. El Sinemuriense Superior (cronozonas Oxynotum y Raricostatum) en la región de S. Pedro de Moel (Cuenca Lusitánica, Portugal). Comunicações Geológicas 100, Volume Especial I (in press).

CORREIA, G.G, DUARTE, L.V., PEREIRA, A. and SILVA, R.L., 2012. Outcrop gamma-ray spectrometry: Applications to the Sinemurian–Pliensbachian organic-rich facies of the Lusitanian Basin (Portugal). Journal of Iberian Geology, 38, 373-388.

CUBAYNES, R, BOUTET, C, DELFAUD, J. and FAURÉ, P., 1984. La mégaséquence d'ouverture du Lias quercynois (Bordure sud-ouest du Massif Central Français). Bulletin des Centres de Recherches Exploration-Production Elf Aquitaine, 8, 333–370.

CUBAYNES, R., MARQUES, J.F. and RUGET C., 1988. L'ecozone à *cladocrinus* dans le Carixien-Domérien de la coupe de Maria Pares (Rabaçal, Condeixa, Portugal). In: Rocha, R.B. and Soares, A.F., 2nd International Symposium on Jurassic Stratigraphy. International Subcommission on Jurassic Stratigraphy, Instituto Nacional de Investigação Científica. Centro de Estratigrafia e Paleobiologia da Universidade Nova de Lisboa : Centro de Geociências da Universidade de Coimbra, vol 2, 677–686.

DE GRACIANSKY, P.C., JACQUIN, T. and HESSELBO, S.P., 1998. The Ligurian Cycle: an overview of Lower Jurassic 2nd-order transgressive/regressive facies cycles in western Europe. In: de GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P.R. (eds.). Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication 60, 467–479.

DERA, G., NEIGE, P., DOMMERGUES, J-L., FARA, E., LAFFONT, R., and PELLENARD P., 2010. High-resolution dynamics of Early Jurassic marine extinctions: the case of Pliensbachian-Toarcian ammonites (Cephalopoda). Journal of the Geological Society 167, 21–33.

DERCOURT, J., RICOU, L.E. and VRIELYNCK, B. (Eds.), 1993. Atlas Tethys Paleoenvironmental Maps, BEICIP-FRANLAB, Rueil-Malmaison.

DERCOURT, J., GAETANI, M., VRIELINCK, B., BARRIER, E., BIJU-DUVAL, B., BRUNER, M.F., CADET, J.P., CRASQUIN, S., SANDULESCU, M. (Eds.), 2000. Atlas Peri-Tethys, Palaeogeographical Maps. CCGM/CGMW, Paris.

DOMMERGUES, J-L., 1987. L'évolution chez les Ammonitina du Lias Moyen (Carixien, Domerien basal) en Europe occidentale. Documents des Laboratoires de Géologie Lyon, 98, 1-297.

DOMMERGUES J-L. and MOUTERDE, R., 1980. Modalités d'installation et d'évolution des Harpoceratines (*Ammonitina*) au Domérien inférieur dans le Sud-Ouest de l'Europe (France, Portugal). Geobios, 13, 289-325.

DOMMERGUES, J.-L., FARA, E. and MEISTER C., 2009. Ammonite diversity and its palaeobiogeographical structure during the early Pliensbachian (Jurassic) in the western Tethys and adjacent areas. Palaeogeography, Palaeoclimatology, Palaeoecology, 280, 64–77.

DOMMERGUES, J.-L., MEISTER C. and MOUTERDE, R., 1997. Pliensbachien. In: CARIOU, E. and HANTZPERGUE P. (eds), Groupe français d'étude du Jurassique: Biostratigraphie du Jurassique ouest-européen et méditerranéen: zonations paralleles et distribution des invertébrés et microfossiles. Bulletin des Centres de Recherche Exploration-Production Elf-Aquitaine, Mémoire 17, 15–23.

DOMMERGUES, J.-L., MEISTER C. and MOUTERDE, R., 2002. *Fuciniceras paradoxus* nov. sp. (Harpoceratinae, Ammonitina) from the Domerian of Portugal. Remark about the taxonomic meaning of a paradoxical set of features. Geobios, 35, 457–468.

DOMMERGUES, J.-L., MEISTER, C. and NEIGE, P. 2004a. *Fuciniceras capilliolusitanicum* nov. sp., une nouvelle espèce d'ammonite du Domérien lusitanien (Pliensbachien, Portugal). Revue de Paléobiologie 23, 373–386.

DOMMERGUES, J-L., MEISTER, C. and ROCHA, R.B., 2011. The Pliensbachian ammonites of the Algarve Basin (Portugal) and their palaeobiogeographical significance for the "Iberia-Newfoundland" conjugate margins. Swiss Journal of Geosciences, 104, 81–96.

DOMMERGUES, J-L., MEISTER, C., NEIGE, P. and ROCHA, R.B., 2004b. Endemic Sinemurian (Early Jurassic) ammonites from the Lusitanian Basin (Portugal). Revue de Paléobiologie, 23, 529-549.

DROMART, G. and ELMI, S., 1986. Développement de structures cryptalgaires en domaine pélagique au cours de l'ouverture des bassins jurassiques (Atlantique central, Téthys occidentale). Comptes rendus de l'Académie des sciences de Paris, Série 2, 303(4), 311–316.

DUARTE, L.V., 1997. Facies analysis and sequential evolution of the Toarcian-Lower Aalenian series in the Lusitanian Basin (Portugal). Comunicações do Instituto Geológico e Mineiro, 83, 65-94.

DUARTE, L.V., 2007. Lithostratigraphy, sequence stratigraphy and depositional setting of the Pliensbachian and Toarcian series in the Lusitanian Basin (Portugal). In R. B. Rocha (ed.). The Peniche section (Portugal). Contributions to the definition of the Toarcian GSSP. International Subcommission on Jurassic Stratigraphy, 17-23.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das series margo-calcárias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicações do Instituto Geológico e Mineiro, 89, 135-154.

DUARTE, L.V., KRAUTTER, M. and SOARES A.F., 2001. Bioconstructions à spongiaires siliceux dans le Lias terminal du Bassin lusitanien (Portugal) : stratigraphie, sédimentologie et signification paléogéographique. Bulletin de la Société Géologique de France, 172, 637–646.

DUARTE, L.V., OLIVEIRA, L.C., and RODRIGUES, R., 2007. Carbon isotopes as a sequence stratigraphic tool: examples from the Lower and Middle Toarcian marly limestones of Portugal. Boletín Geológico y Minero, 118, 3-18.

DUARTE, L.V., SILVA, R.L., and MENDONÇA FILHO, J.G., 2011. The Lower Jurassic of the west coast of Portugal: stratigraphy and organic matter in carbonate sedimentation. In: FLORES, D., MARQUES, M., (eds), 63rd Annual meeting of the International Committee for Coal and Organic Petrology - Field Trip Guide Book, Memórias nº 17, 42 pp..

DUARTE, L.V., SILVA, R.L., DUARTE, C.B., AZERÊDO, A.C. and COMAS-RENGIFO, M.J., 2008. Litostratigrafia do Jurássico Inferior da região de S. Pedro de Moel (Bacia Lusitânica). In: CALLAPEZ, P. M., ROCHA, R. B., MARQUES, J. F., CUNHA, L. S. and DINIS. P.M. (Eds): A Terra, Conflitos e Ordem. Homenagem ao Professor Ferreira Soares. Museu e Laboratório de Mineralogia e Geologia da Universidade de Coimbra, Coimbra, 175-185.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F., 2010. Organic-rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total Organic Carbon distribution and relation to transgressive-regressive facies cycles. Geologica Acta, 8, 325–340.

DUARTE, L.V., SILVA, R.L., MENDONÇA, FILHO., J.G., POÇAS RIBEIRO, N. and CHAGAS, R.B.A., 2012. High-resolution stratigraphy, Palynofacies and source rock potential of the Água de Madeiros Formation (Upper Sinemurian) of the Lusitanian Basin, Portugal. Journal of Petroleum Geology, 35, 105–126.

DUARTE, L.V., WRIGHT, V.P., LÓPEZ, S.F., ELMI, S., KRAUTTER, M., AZERÊDO, A.C., HENRIQUES, M.H., RODRIGUES, R. and PERILLI, N., 2004. Early Jurassic carbonate evolution in the Lusitanian Basin (Portugal): facies, sequence stratigraphy and cyclicity, in: DUARTE, L.V. and HENRIQUES, M.H. (Eds.): Carboniferous and Jurassic Carbonate Platforms of Iberia. 23rd IAS Meeting of Sedimentology Field Trip Guide Book, Coimbra. volume 1, 45–71.

DUNHAM, R.J., 1962, Classification of carbonate rocks according to depositional texture. In: HAM, W. E. (ed.), Classification of carbonate rocks: American Association of Petroleum Geologists Memoir, p. 108-121.

EINSELE, G., 2000. Sedimentary Basins: Evolution, Facies, and Sediment Budget (2nd ed), Springer-Verlag.

EINSELE G., RICKEN W., and SEILACHER A., (eds), 1991. Cycles and events in stratigraphy. Springer-Verlag.

ELMI, S., ROCHA, R.B. and MOUTERDE, R., 1988. Sediméntation pelagique et encroutements crytalgaires: les calcaires grumuleux du Carixien portugais. Ciências da Terra, 9, 69–90.

EMBRY, A.F., 1993, Transgressive-regressive (T-R) sequence analysis of the Jurassic succession of the Sverdrup Basin, Canadian Arctic Archipelago. Canadian Journal of Earth Sciences, 30, 301–320.

EMBRY, A.F., 2009, Practical Sequence Stratigraphy. Canadian Society of Petroleum Geologists, Online at www.cspg.org.

EMBRY, A.F., and JOHANNESSEN, E. P., 1992. T–R sequence stratigraphy, facies analysis and reservoir distribution in the uppermost Triassic-Lower Jurassic succession, western Sverdrup Basin, Arctic Canada. In: VORREN, T.O., BERGSAGER, E., DAHL-STAMNES, O.A., HOLTER, E., JOHANSEN, B., LIE E. and LUND, T.B. (eds) Arctic Geology and Petroleum Potential. Norwegian Petroleum Society (NPF), Special Publication 2, pp. 121–146.

EMBRY, A.F. and KLOVAN, J.E., 1971. A Late Devonian reef tract on Northeastern Banks Island, NWT: Canadian Petroleum Geology Bulletin, 19, 730–781.

EMMANUEL, L., RENARD, M., CUBAYNES, R., DE RAFELIS, M., HERMOSO, M., LECALLONEC, L., LE SOLLEUZ, A. and REY, J., 2006. The “Schistes Carton” of Quercy (Tarn, France): a lithological signature of a methane hydrate dissociation event in the early Toarcian. Implications for correlations between Boreal and Tethyan realms. Bulletin de la Société géologique de France, 177, 237–247.

ENACHESCU, M.E., 1992. Enigmatic basins offshore Newfoundland. Canadian Journal of exploration Geophysics, 28, 44–61.

FERNÁNDEZ-LÓPEZ, S.R., 2000. Temas de Tafonomía. Departamento de Paleontología Universidad Complutense de Madrid.

FERNÁNDEZ-LÓPEZ, S., DUARTE, L.V. and HENRIQUES, M.H., 2000. Ammonites from lumpy limestones in the Lower Pliensbachian of Portugal: taphonomic analysis and palaeoenvironmental implications. Revista de la Sociedad Geológica de España, 13, 3–15.

FERREIRA, R., MENDONÇA FILHO, J.G., DUARTE, L.V., SILVA, R.L. and MENDONÇA, J.O., 2010. Hydrocarbon generation potential of the Pliensbachian organic-rich series of Peniche (Lusitanian Basin, Portugal): An organopetrographic and thermal maturation assessment integrated analysis. In: PENA DOS REIS, R. and PIMENTEL, N. (Eds.): II Central & North Atlantic Conjugate Margins Conference. Extended Abstracts, Volume III, Lisbon, 116–120.

FLEET, A.J., CLAYTON, C.J., JENKYNS, H.C. and PARKINSON, D.N., 1987, Liassic source rock deposition in western Europe. In: BROOKS, J. and GLENNIE, K. (Eds.): Petroleum Geology of North West Europe, Graham & Trotman, pp. 59–70.

FLÜGEL, E., 2010. Microfacies of Carbonate Rocks. Analysis, Interpretation and Application (2nd ed). Springer-Verlag.

FOLK, R.L., 1959, Practical petrographic classification of limestones: American Association of Petroleum Geologists Bulletin, 43, 1–38.

FRAZIER, D.E., 1974. Depositional episodes: their relationship to the Quaternary stratigraphic framework in the northwestern portion of the Gulf Basin. University of Texas at Austin, Bureau of Economic Geology, Geological Circular, 4(1).

GALLOWAY, W.E., 1989. Genetic stratigraphic sequences in basin analysis, I. Architecture and genesis of flooding-surface bounded depositional units. AAPG Bulletin, 73, 125–142.

GRADSTEIN, F.M., OGG J.G., SCHMITZ, M.D. and OGG. G.M., 2012. The Geologic Time Scale 2012, 2 volumes, Elsevier

HANTSCHEL, T. and KAUERAUF, A.I., 2009. Fundamentals of Basin and Petroleum Systems Modeling. Springer-Verlag.

HARDENBOL, J., THIERRY, J., FARLEY, M.B., JACQUIN, T., DE GRACIANSKY, P.C. and VAIL, P., 1998, Mesozoic and Cenozoic sequence chronostratigraphic framework of European basins. In: Graciansky, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P., (eds) Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication 60, 3–13, charts 1-8.

HESSELBO, S.P., 2008. Sequence stratigraphy and inferred relative sea-level change from the onshore British Jurassic. Proceedings of the Geologists' Association, 119, 19–34.

HESSELBO, S.P., JENKYNS, H.C., DUARTE, L.V. and OLIVEIRA, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth and Planetary Science Letters, 253, 455–470.

HISCOTT, R.N., WILSON, R.C.L., GRADSTEIN, F.M., PUJALTE, V., GARCÍA-MONDÉJAR, J., BOUDREAU, R.R. and WISHART, H.A., 1990. Comparative stratigraphy and subsidence history of Mesozoic rift basins of North Atlantic. AAPG Bulletin, 74, 60–76.

HOWELL J.A. and AITKEN, J.F., 1996. High Resolution Sequence Stratigraphy: Innovations and Applications. Geological Society, London, Special Publications 104.

INVERNO, C.M.C., MANUPELLA, G., ZBYSZEWSKI, G., PAIS J. and RIBEIRO, M. L., 1993, Notícia explicativa da folha 42 C, Santiago do Cacém, 1:50.000, Serviços Geologicos de Portugal, Lisbon 75 pp..

JACQUIN, T. and DE GRACIANSKY, P.C., 1998. Transgressive-regressive (second order) facies cycles: the effects of tectonoeustacy. In: de GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P. (eds.), Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Special Publication, 60, 445-466.

JOHNSON, J.G. and MURPHY, M.A., 1984. Time-rock model for Siluro-Devonian continental shelf, western United States. Geological Society of America Bulletin, 95, 1349–1359.

LACHKAR, N., GUIRAUD, M., EL HARFI A., DOMMERGUES, J-L., DERA, G. and DURLET, C., 2009. Early Jurassic normal faulting in a carbonate extensional basin: characterization of tectonically driven platform drowning (High Atlas rift, Morocco). Journal of the Geological Society, 166, 413–430.

MANUPPELLA, G. and AZERÊDO, A. C., 1996. Contribuição para o conhecimento da geologia da região de Sesimbra. Comunicações Instituto Geológico e Mineiro, 82, 37–50.

MENDONÇA FILHO, J.G., SILVA, T.F., SILVA, R.L., DUARTE, L.V., POÇAS RIBEIRO, N., 2013. Distribuição dos biomarcadores e sua relação com a matéria orgânica nas series jurássicas de S. Pedro de Moel, Bacia Lusitânica. Comunicações Geológicas 100, Volume Especial I, (in press).

MIALL, A.D. (ed), 2008. Sedimentary basins of the world. The sedimentary basins of the United States and Canada. Elsevier B.V..

MIALL, A.D. 2010. The Geology of Stratigraphic Sequences. Springer-Verlag.

MICHALÍK, J., 1993, Notes on the Paleogeography and Paleotectonics of the Western Carpathian area during the Mesozoic. Mitteilungen Österreichisches Geologisches Gesellschaft 86, 101–110.

MITCHUM, R. M., JR., 1977. Seismic stratigraphy and global changes of sea level, part 11: glossary of terms used in seismic stratigraphy. In, PAYTON, C. E. (ed.), Seismic Stratigraphy – Applications to Hydrocarbon Exploration. American Association of Petroleum Geologists Memoir, 26, 205–212.

MITCHUM, R.M., JR., VAIL, P.R. and THOMPSON, S., III., 1977. Seismic stratigraphy and global changes of sea-level, part 2: the depositional sequence as a basic unit for stratigraphic analysis. In, PAYTON, C. E. (ed.), Seismic Stratigraphy – Applications to Hydrocarbon Exploration. American Association of Petroleum Geologists Memoir, 26, 53–62.

MOUTERDE, R., 1955. Le Lias de Peniche. Comunicações dos Serviços Geológicos de Portugal, 36, 5-33.

MOUTERDE, R., 1967a. Le Lias du Portugal. Vue d'ensemble et division en Zones. Comunicações dos Serviços Geológicos de Portugal, 52, 209-226.

MOUTERDE, R., 1967b. Le Lias Moyen de São Pedro de Muel (Portugal). (Premiere partie). Comunicaçoes dos Serviços Geológicos de Portugal *52*, 185–208.

MOUTERDE, R., 1970. Lias Moyen de Sao Pedro de Muel (Portugal). Deuxième partie: Paléontologie. 1. Céphalopodes. Comunicaçoes dos Serviços Geológicos de Portugal, 54, 39–74.

MOUTERDE, R. and ROCHA, R.B., 1980-1981. Le Lias de la région de Rio de Couros (Nord de Tomar). Boletin Sociedade Geologica de Portugal, 22, 209–220.

MOUTERDE, R. and ROCHA, R.B., 1981. Atlas des fossiles caractéristiques du Lias portugais. I. - Lias inférieur. Ciências da Terra, 6: 49-76

MOUTERDE, R. and ROCHA, R.B., 1988. Essai de biozonation du Domérien portugais. Ciências da Terra, 3, 66–68.

MOUTERDE, R., DOMMERGUES, J-L., and ROCHA, R.B., 1983. Atlas des fossiles caractéristiques du Lias portugais. II-Carixien. Ciências da Terra, 7, 187–254.

MOUTERDE, R., ROCHA, R.B. and RUGET, C., 1971. Le Lias moyen et supérieur de la région de Tomar. Comunicações dos Serviços Geológicos de Portugal, 55, 55–86.

MOUTERDE, R., RUGET, C. and MOITINHO DE ALMEIDA, F., 1964-65. Coupe du Lias au Sud de Condeixa. Comunicações dos Serviços Geológicos de Portugal, 48, 61–91.

MOUTERDE, R., DOMMERGUES, J-L., MEISTER, C. and ROCHA, R.B., 2007. Atlas des fossiles caractéristiques du Lias portugais. III a) Domérien (Ammonites). Ciências da Terra, 16, 67-111.

NIKITENKO, B., SHURYGIN, B. and MICKEY, M.B., 2008. High resolution stratigraphy of the Lower Jurassic and Aalenian of Arctic regions as the basis for detailed palaeobiogeographic reconstructions. Norwegian Journal of Geology, 88, 267–278.

N'ZABA-MAKAYA, O., ANDREU, B., BRUNEL, F., MOUTERDE, R., REY, J. and ROCHA, R., 2003. Biostratigraphie et paléoécologie des puplements d'ostracodes dans le Domérien du Bassin Lusitanien, Portugal. Ciências da Terra, 15, 21-44.

OLIVEIRA, L.C.V., RODRIGUES, R., DUARTE, L.V. and LEMOS, V., 2006. Avaliação do potencial gerador de petróleo e interpretação paleoambiental com base em biomarcadores e isótopos estáveis do carbono da seção Pliensbaquiano-Toarciano inferior (Jurássico inferior) da região de Peniche (Bacia Lusitânica, Portugal). Boletim de Geociências da Petrobras, 14(2), 207-234.

OLIVEIRA, L.C., DUARTE L.V., SILVA R.L. and RODRIGUES R., 2009. Belemnite $\delta^{18}O$ and $\delta^{13}C$ record of the Lusitanian Basin Pliensbachian carbonate series (Portugal). Geochimica and Cosmochimica Acta, 73 (13S), A969.

OLIVEIRA, L.C.V., DUARTE, L.V., LEMOS, V.B., COMAS-RENGIFO, M.J. and PERILLI, N., 2007. Bioestratigrafia de nanofósseis calcários e correlação com as zonas de amonites do Pliensbaquiano-Toarciano basal (Jurássico inferior) de Peniche (Bacia Lusitânica, Portugal). In: CARVALHO, I.S., CASSAB, R.C.T., SCHWANKE, C., CARVALHO, M.A., FERNANDES, A.C.S., RODRIGUES, M.A.C., CARVALHO, M.S.S., ARAI, M. and OLIVEIRA, M.E.Q. (eds.). Paleontologia: Cenários de Vida, Proceedings of XIX Congresso Brasileiro de Paleontologia, Búzios (Brazil), Editora Interciência, 411-420.

OSETE, M-L., GÓMEZ, J.J., PAVÓN-CARRASCO, F.J., VILLALAÍN, J.J., PALENCIA-ORTAS, A., RUIZ-MARTÍNEZ, V.C. and HELLER, F., 2011. The evolution of Iberia during the Jurassic from palaeomagnetic data. Tectonophysics 502, 105–120.

PEREIRA, R. and ALVES, T.M., 2012. Tectono-stratigraphic signature of multiphased rifting on divergent margins (deep-offshore southwest Iberia, North Atlantic). Tectonics, 31, TC4001.

PHELPS, M., 1985. A refined ammonite biostratigraphy for the Middle and Upper Carixian (Ibex and Davoei zones, Lower Jurassic) in North-West Europe and stratigraphical details of the Carixian-Domerian boundary. Geobios, 18, 321-362.

PERILLI, N. And COMAS-RENGIFO, M.J., 2002. Calibration of Pliensbachian calcareous nannofossils events in two ammonite-controlled sections from Northern Spain. Rivista Italiana di Paleontologia e Stratigrigrafia, 108 (1), 133–152.

PERILLI, N. and DUARTE, L.V., 2006. Toarcian nannobiohorizons from the Lusitanian Basin (Portugal) and their calibration against ammonite zones. Rivista Italiana di Paleontologia e Stratigrafia, 112, 417–434.

PINHEIRO, L.M., WILSON, R.C.L., PENA DOS REIS, R., WHITMARSH, R.B. and RIBEIRO, A., 1996. The western Iberia margin: a geophysical and geological overview. In: WHITMARSH, R.B., SAWYER, D.S., KLAUS, A. and MASSON, D.G. (Eds.): Proceedings of the Ocean drilling Program. Scientific Results, 149, 3-23.

POÇAS RIBEIRO, N., MENDONÇA FILHO, J.G., DUARTE, L.V., SILVA, R.L., MENDONÇA, J.O., SILVA, T.F., 2013. Palynofacies and Organic Geochemistry of the Sinemurian carbonate deposits in the western Lusitanian Basin (Portugal): Coimbra and Água de Madeiros Formations. International Journal of Coal Geology. International Journal of Coal Geology, 111, 37–52.

POSAMENTIER, H.W. and ALLEN, G. P., 1999, Siliciclastic sequence stratigraphy: concepts and applications. SEPM Concepts in Sedimentology and Paleontology no. 7, p. 210.

QUESADA, S., ROBLES, S. and ROSALES, I., 2005. Depositional architecture and transgressive–regressive cycles within Liassic backstepping carbonate ramps in the Basque–Cantabrian Basin, northern Spain. Journal of the Geological Society, 162, 531–548.

QUESADA, S., DORRONSORO, C., ROBLES, S., CHALER, R. and GRIMALT, J.O., 1997. Geochemical correlation of oil from the Ayoluengo field to Liassic black shale units in the southwestern Basque–Cantabrian Basin (northern Spain). Organic Geochemistry, 27, 25–40.

REY, J., BONNET, L., BRUNEL, F., RUGET, C., CUBAYNES, R, MOUTERDE, R and BORDALO DA ROCHA, R., 2000. Comparaison des associations de foraminifères dans le Domérien des bassins aquitain (France) et lusitanien (Portugal). Geobios, 33, 135–144.

RASMUSSEN, E.S., LOMHOLT, S., ANDERSEN, C. and VEJBÆK, O.V., 1998. Aspects of the structural evolution of the Lusitanian Basin in Portugal and the shelf and slope area offshore Portugal. Tectonophysics, 300, 199–225.

REGGIANI, L., MATTIOLI, E. and PITTET, B., 2010a. Spatial distribution of Late Pliensbachian (Early Jurassic) calcareous nannofossils within the Lusitanian basin (Portugal). Geobios, 43, 87–97.

REGGIANI, L., MATTIOLI, E., PITTET, B., DUARTE, L.V., VEIGA DE OLIVEIRA, L.C. and COMAS-RENGIFO, M.J., 2010b. Pliensbachian (Early Jurassic) calcareous nannofossils from the Peniche section (Lusitanian Basin, Portugal): A clue for palaeoenvironmental reconstructions. Marine Micropaleontology, 75(1-4), 1–16.

SACHSE, V.F., LEYTHAEUSER, D., GROBE, A., RACHIDI, M. and LITTKE, R., 2012. Organic geochemistry and petrology of a Lower Jurassic (Pliensbachian) petroleum source rock from Aït Moussa, Middle Atlas, Morocco. Journal Petroleum Geology, 35, 5–24.

SCHETTINO, A. AND TURCO, E., 2009. Breakup of Pangaea and plate kinematics of the central Atlantiand Atlas regions. Geophysical Journal Internacional, 178, 1078–1097.

SCHLAGER, W., 2005. Carbonate Sedimentology and Sequence Stratigraphy, SEPM Concepts in Sedimentology and Paleontology 08, SEPM Foundation Inc..

SCHWEIGERT, G. 2005. The occurrence of the Tethyan ammonite genus *Meneghiniceras* (Phylloceratina: Juraphyllitidae) in the Upper Pliensbachian of SW Germany. Stuttgarter Beiträge zur Naturkunde Serie B (Geologie und Paläontologie), 356, 15 S.

SCOTCHMAN, I.C., 2001. Petroleum geochemistry of the Lower and Middle Jurassic in Atlantic margin basins of Ireland and the UK. Geological Society, London, Special Publications,188, 31-60.

SEILACHER, A., 2007. Trace Fossil Analysis. Springer-Verlag.

SIMMS, M.J., CHIDLAW, N., MORTON, N. and PAGE, K.N., 2004. British Lower Jurassic Stratigraphy. Geological Conservation Review Series, 30, Joint Nature Conservation Committee.

SILVA, F., DUARTE, L.V., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and RODRIGUES, R., 2006. A Formação de Vale das Fontes no sector norte da Bacia Lusitânica (Portugal): caracterização e avaliação preliminar da distribuição do Carbono Orgânico Total. In: MIRÃO, J. and BALBINO, A., (Eds.), Actas do VII Congresso Nacional de Geologia vol. II, Évora, pp. 669–672.

SILVA, F., DUARTE, L.V., OLIVEIRA, L.C.V., RODRIGUES, R. and COMAS-RENGIFO, M.J., 2007. Caracterização do Carbono Orgânico Total e pirólise *Rock-Eval* no intervalo Sinemuriano superior-Pliensbaquiano do sector norte da Bacia Lusitânica (Portugal). In: GOMES, E.P. and ALENCOÃO, A.M. (Coords.), Actas do VI Congresso Ibérico de Geoquímica, Vila Real, pp. 564–567.

SILVA, R.L., DUARTE, L.V., OLIVEIRA, L.C.V., 2009. Compositional classification of sedimentary rocks based in geochemical indicators: the case of the Upper Pliensbachian–Lower Toarcian of Peniche (Portugal) (translated from Portuguese). Extended abstracts of the VII Congreso Ibérico-X Congreso Nacional de Geoquímica. Biblioteca Electrónica de la Excma. Diputación Provincial de Soria, vol. 17, 118–127.

SILVA, R.L., DUARTE, L.V., AZERÊDO, A.C., and MENDONÇA FILHO, J.G., 2011a. Contributos sedimentológicos e geoquímicos para a modelação dos sistemas petrolíferos portugueses: as séries jurássicas ricas em matéria orgânica da Bacia Lusitânica (Portugal). Modelação de Sistemas Geológicos, Laboratório de Radioactividade Natural da Universidade de Coimbra, pp. 383–391.

SILVA, R.L., DUARTE, L.V., COMAS-RENGIFO, M.J., MENDONÇA FILHO, J.G. and AZERÊDO, A.C., 2011b. Update of the carbon and oxygen isotopic records of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma): Insights from the organic-rich hemipelagic series of the Lusitanian Basin (Portugal). Chemical Geology, 283, 177–184.

SILVA, R.L., MENDONÇA FILHO, J.G., DUARTE, L.V., COMAS-RENGIFO, M.J., AZERÊDO, A.C. and FERREIRA, R., 2010. Organic-rich facies of the top Ibex–Margaritatus zones (Pliensbachian) of the Lusitanian Basin (Portugal): TOC and biomarkers variation. Geochimica et Cosmochimica Acta, 74 (12-S1), A962

SILVA, R.L., MENDONÇA FILHO, J.G., DA SILVA, F.S., DUARTE, L.V., SILVA, T.F., FERREIRA, R. and AZERÊDO, A.C. 2012. Can biogeochemistry aid in the palaeoenvironmental/early diagenesis reconstruction of the ~187 Ma (Pliensbachian) organic-rich hemipelagic series of the Lusitanian Basin (Portugal)?. Bulletin of Geosciences, 87, 373–382.

SKOGSEID, J., 2010. The Orfhan Basin - a key to understanding the kinematic linkage between North and NE Atlantic Mesozoic rifting. II Central & North Atlantic Conjugate Margins Conference, Lisbon, 13–23.

SOARES, A.F., ROCHA, R.B., ELMI, S., HENRIQUES, M.H., MOUTERDE, R., ALMERAS, Y., RUGET, C., MARQUES, J., DUARTE, L.V., CARAPITO, C. and KULLBERG, J.C., 1993. Le sous-bassin nord-lusitanien (Portugal) du Trias au Jurassique moyen: histoire d'un "rift avorté". Comptes rendus de l'Académie des sciences de Paris, 317, 1659–1666.

STAMPFLI, G.M. and BOREL, G.D. 2002. A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. Earth and Planetary Science Letters, 196, 17-33.

STAPEL, G., CLOETINGH, S., and PRONK, B., 1996, Quantitative subsidence analysis of the Mesozoic evolution of the Lusitanian Basin (western Iberian margin), Tectonophysics, 266, 493–507.

SUAN, G., MATTIOLI, E., PITTET, B., MAILLIOT, B. and LECUYER, C., 2008. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal. Paleoceanography, 23, PA1201

SUAN, G., MATTIOLI, E., PITTET, B., LECUYER, C., SUCHERAS-MARX, B., DUARTE, L.V., PHILIPPE, M., REGGIANI, L. and MARTINEAU, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. Earth and Planetary Science Letters, 290, 448–458.

TANKARD, A.J. and BALKWILL, H.R. (eds), 1989. Extensional Tectonics and Stratigraphy of the North Atlantic Margins. AAPG Memoir 46, American Association of Petroleum Geologists.

TUCKER, M. E., CALVET, F., and HUNT, D., 1993. Sequence stratigraphy of carbonate ramps: systems tracts, models and application to the Muschelkalk carbonate platforms of eastern Spain. In: POSAMENTIER H.W., SUMMERHAYES, C.P., HAQ B.U. and ALLEN, G.P. (eds), Sequence Stratigraphy and Facies Associations. International Association of Sedimentologists, Special Publication, 18, 397–415.

VAN DE SCHOOTBRUGGE B., BAILEY, T., ROSENTHAL, Y., KATZ, M.E., WRIGHT, J.D., FEIST BURKHARDT, S., MILLER, K.G. and FALKOWSKI, P.G., 2005. Early Jurassic climate change and the radiation of organic-walled phytoplankton in the Tethys Ocean. Paleobiology 31, 73–97.

VAN WAGONER, J. C., MITCHUM, R. M., POSAMENTIER, H.W. and VAIL, P. R., 1987. An overview of sequence stratigraphy and key definitions. In, BALLY, A.W. (Ed.), Atlas of Seismic Stratigraphy, volume 1. AAPG Studies in Geology, 27, 11–14.

WIELENS, J.B.W. JAUER, C.D. and WILLIAMS, G.L., 2006. Is there a viable petroleum system in the carson and salar basins, offshore newfoundland? Journal of Petroleum Geology, 29, 303–326.

WILSON, R.C.L., 1988. Mesozoic Development of the Lusitanian Basin, Portugal. Revista de la Sociedad Geológica de España, 1, 393–407.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. and GRADSTEIN, F.M., 1989. The Lusitanian Basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphic and subsidence history. In: TANKARD, A.J. and BALKWILL, H.R. (Eds.): Extensional Tectonics and Stratigraphy of the North Atlantic Margins. AAPG Memoir, 46, 341–361.

WRIGHT, V.P., 1992. A revised classification of limestones. Sedimentary Geology, 76, 177–185.

4.2. Update of the carbon and oxygen isotopic records of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma): insights from the organic-rich hemipelagic series of the Lusitanian Basin (Portugal)

Ricardo L. Silva, Luís V. Duarte, María J. Comas-Rengifo, João G. Mendonça Filho, Ana C. Azerêdo, 2011,

Chemical Geology, 283, 177–184

Abstract

A high-resolution carbon and oxygen isotopic bulk carbonate record from organic-rich hemipelagic series of Early–Late Pliensbachian age (~187 Ma) is presented for the Lusitanian Basin (Portugal) and compared to the record of other sedimentary basins. This dataset provides an excellent basis for discussing newly raised questions concerning the hypothesis of major carbon cycle perturbations prior to the Toarcian Oceanic Anoxic Event. In addition to the recognition in the studied series of two positive carbon isotope excursions previously defined elsewhere, corresponding to the Ibex and Margaritatus (uppermost Stokesi–Gibbosus subzones) zones, a third positive excursion is identified here for the first time, at the Davoei Zone. In the Lusitanian Basin these excursions are associated with organic-rich facies intervals. The younger excursion may be related to worldwide enhanced preservation of organic matter in the Margaritatus Zone. We suggest that until these organic-rich facies are well age constrained at a wider scale and high-resolution carbon data are provided from other locations, and that worldwide anoxia is proven, this interval should be referred to as an Organic Matter Preservation Interval (Late Pliensbachian OMPI). This period is probably linked with the complex chain of events that eventually led to the Toarcian Oceanic Anoxic Event.

Keywords: Carbon and oxygen stable isotopes, Organic-rich hemipelagic series; Pliensbachian (Early Jurassic, ~187 Ma); Lusitanian Basin; Portugal

4.2.1. Introduction

Recently, much of the research dealing with the Early–Late Pliensbachian interval (c.a. 187 Ma) has been focused on palaeontological or palaeo-biogeographical problems, such as ammonoid and brachiopod migrations/extinctions or changes in nannofossil assemblages, and on palaeoceanographic or palaeoclimatic variations, such as carbon cycle perturbations, icehouse climatic conditions, ocean current patterns, Oceanic Anoxic Events, and their link to the Toarcian Oceanic Anoxic Event (T-OAE) (e.g. Dera et al., 2009, 2010; Dommergues et al., 2009; Reggiani et al., 2010a,b; Ruban, 2009; Suan et al., 2010; van de Schootbrugge et al., 2010). In spite of the increasing work on these issues, it is still unclear which mechanisms are behind the palaeoceanographic changes that occurred at a global scale and, conversely, which factors controlled local palaeoenvironmental conditions.

Here, we present for the first time a high-resolution carbon and oxygen isotopic bulk carbonate record from organic-rich hemipelagic carbonates, coupled with kerogen data, obtained from the reference section of Peniche (Lusitanian Basin, hereafter called LB), which is age-constrained to the top Ibex–Margaritatus zones (Pliensbachian) by an precise ammonite and nannofossil biostratigraphy. These data from the LB are compared to geochemical data from other Tethyan and non-Tethyan areas, in order to discriminate the local vs. global patterns in the carbon and oxygen isotope records. Taking into account the privileged palaeogeographic position of the LB, between the Tethyan and the Boreal realms and near the Hispanic Corridor, this study has important implications for the discussion of the palaeoenvironmental conditions that existed at that time and sheds light on the events predating the T-OAE.

4.2.2. Geological setting

The LB is a small North–South elongated basin located on the western side of the Iberian Massif, whose origin is linked to the opening of the Atlantic Ocean (e.g. Wilson et al., 1989). The Lower Jurassic record of this basin is dominated by marl–limestone alternations, with organic-rich facies particularly represented in its western margin (Figs. 4.2.1 and 4.2.2). These series, with abundant nektonic and benthonic macrofossils, are included in the Upper Triassic–Callovian 1st-order cycle (Azerêdo et al., 2003; Soares et al., 1993; Wilson et al., 1989).

The studied series of Pliensbachian age (~187Ma), corresponding to the top Ibex (Luridum Subzone)–Margaritatus (Gibbosus Subzone) zones, includes the Marly-limestones with organic-rich facies member (MLOF mb) of the Vale das Fontes Formation (Fm) and the base of the Lemede Fm (Dommergues, 1987; Duarte and Soares, 2002; Duarte et al., 2004, 2010; Mouterde et al., 2007; Oliveira et al., 2007; Phelps, 1985). In previous studies, the base of the Lemede Fm was assigned to the Spinatum Zone, but new ammonite data show that it corresponds to the uppermost Gibbosus Subzone, Margaritatus Zone. At Peniche (Fig. 4.2.1), the MLOF mb (the main focus of this work) crops out in the Portinho da Areia do Norte beach. Here, it corresponds to approximately 30 m of marl–limestone alternations, locally with abundant nektonic (belemnites and ammonites) and benthonic (brachiopods, bivalves, crinoids and gastropods) macrofossils (Fig. 4.2.3). This series, which displays little lateral variation in facies, represents deposition in a north-western dipping low energy carbonate ramp environment (Duarte, 2007; Duarte et al., 2004). The organic-rich facies in this section ranges from dark marls and marly limestones, massive to laminated and often bioturbated (mainly *Chondrites* ichogenus), to true black-shales.

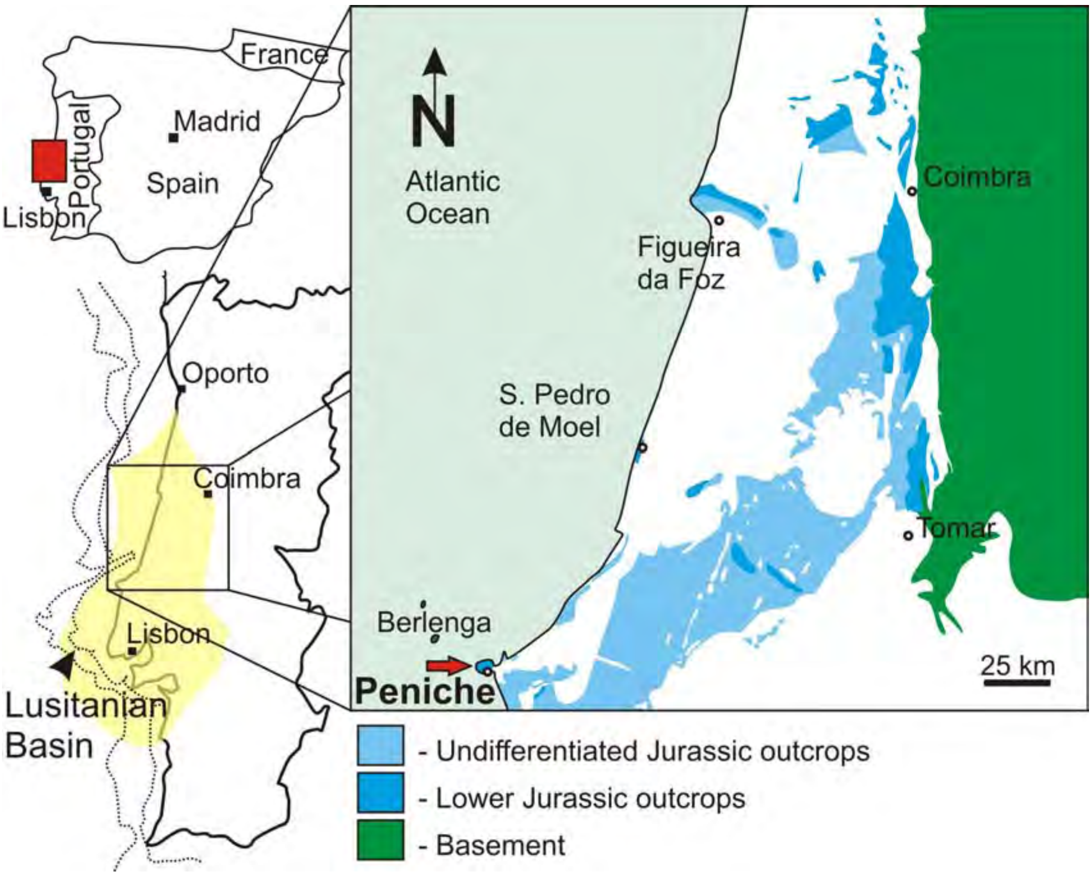


Fig. 4.2.1. Simplified geological map of the central-northern part of the Lusitanian Basin (Portugal) and distribution of the carbonate units of Lower Jurassic age. The organic-rich hemipelagic series of the Late Pliensbachian are particularly well-represented in the coastal sections of Peniche, S. Pedro de Moel and Figueira da Foz.

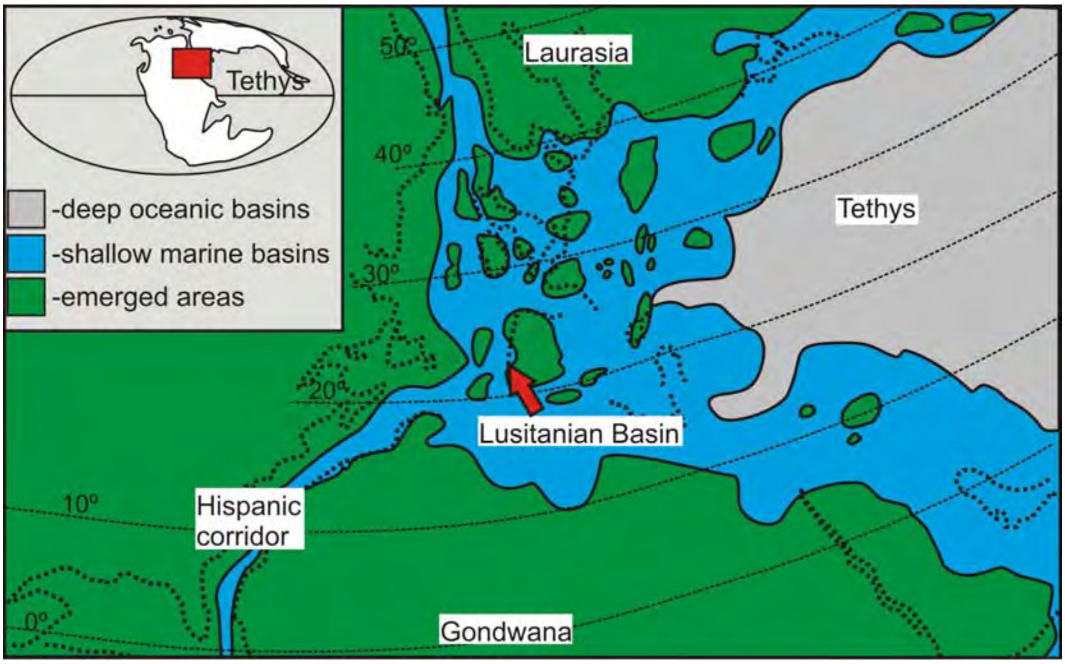


Fig. 4.2.2. Western Tethys palaeogeography and location of the Lusitanian Basin during the late Early Jurassic (modified and simplified from Bassoulet et al., 1993). During this time interval, several shallow basins developed across the margins of the Tethys Ocean, most of them dominated by carbonate environments.

The total organic carbon (TOC) content of the MLOF mb is generally high (>3 wt.%), reaching a maximum of 26.3 wt.% at the Ibex–Davoei transition (Duarte et al., 2010; Silva et al., 2010). The younger organic-rich interval (top of Subnodosus/base of Gibbosus subzones) is recorded at a basin scale and corresponds to the maximum flooding interval of the Pliensbachian transgressive–regressive (T–R) facies cycle (Duarte et al., 2010) (Figs. 4.2.3 and 4.2.4).

4.2.3. Materials and methods

For this study, $\delta^{13}C$ and $\delta^{18}O$ have been measured in 147 carbonate samples collected in the field with a battery-powered hand-drill. All the analyses were performed using a Thermo Electron Delta V Advantage mass spectrometer with an automated carbonate preparation device (GasBench III) at the Cardiff University stable isotope laboratory. Stable isotope results were calibrated to the PDB scale by international standard NBS19. The analytical precision is better than ±0.1‰ for both isotopic ratios. Nine additional samples were analysed for $\delta^{13}C$ in kerogen. These were prepared according to standard methodology (Mendonça Filho et al., 2002; Tyson, 1995), and $\delta^{13}C$, calibrated to the PDB scale, was determined in the IMAR-CMA (Coimbra University), using Flash EA for Thermo Electron Delta V Advantage mass spectrometer.

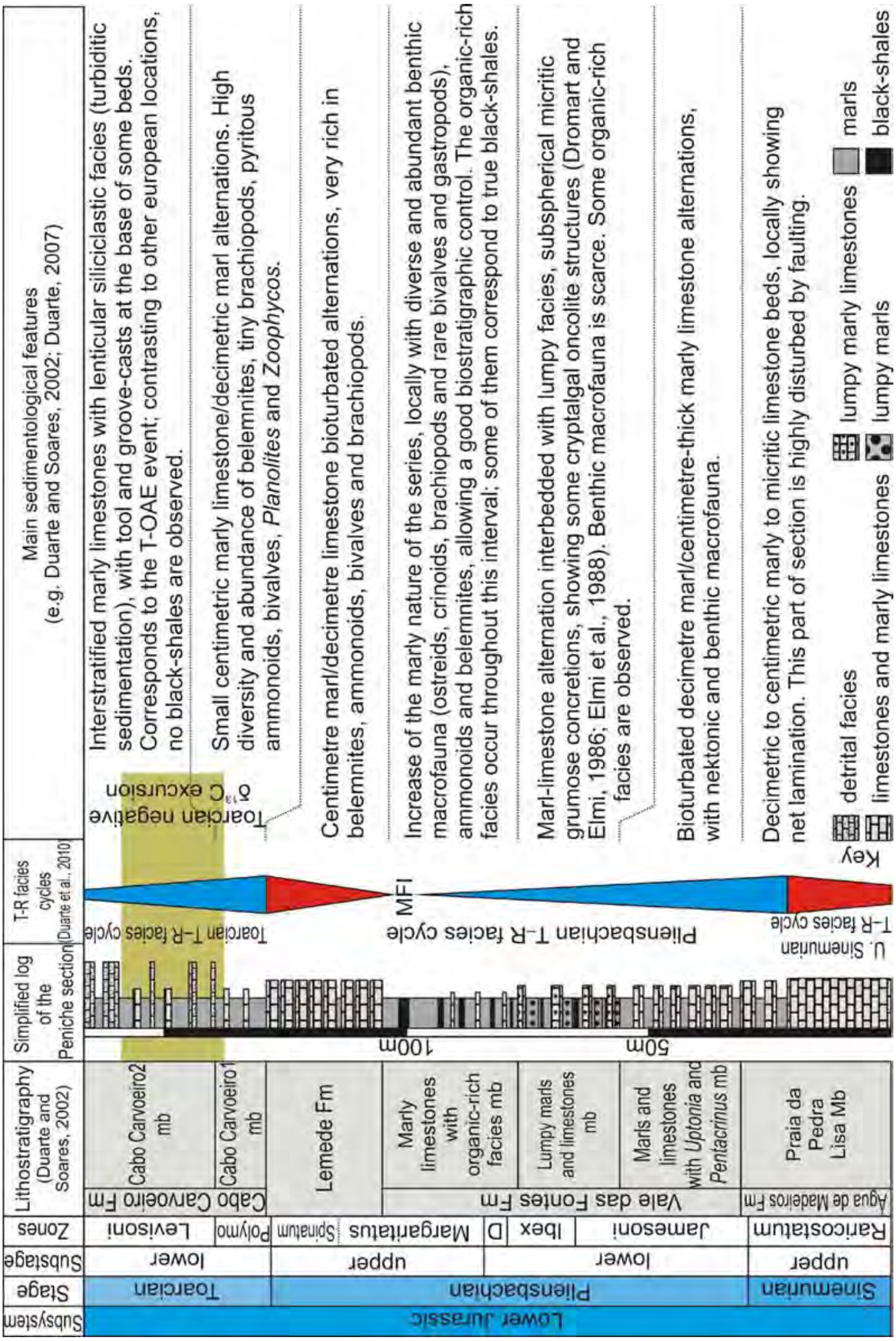


Fig. 4.2.3. Biostratigraphy, lithostratigraphic units and main sedimentological features of the uppermost Sinemurian lower Toarcian series of the reference section of Peniche (UTM coordinates of the base of the presented section: 29S MD 467,525 mE, 4,358,050 mN). The organic-rich facies are particularly represented, at a basinal scale, in the Marly limestones with organic-rich facies mb (except at Tomar), although localized occurrences are observed in other units, for example, in the Lumpy marls and limestones mb (see Dromart and Elmi, 1986; Elmi et al., 1988, in addition to the references in the text). Abbreviations: D - Davoei; Polymo-Polymorphum.

Internal precision is better than ±0.1‰ for $\delta^{13}C$ (Acetanilide Standard from Thermo Electron Corporation). TOC content was determined with a SC-144DR LECO analyzer in the LAFO Laboratory (Federal University of Rio de Janeiro), with an analytical precision of ±0.1%.

4.2.4. $\delta^{13}C$ and $\delta^{18}O$ record of the Early–Late Pliensbachian at Peniche

The $\delta^{13}C$ in the carbonates of the studied Peniche section varies between −1.29‰ and 1.76‰ (Fig. 4.2.4). The $\delta^{13}C$ evolves to more positive values of about 1‰ from the base of the section and then decreases again towards the Ibex/Davoei Zone boundary, reaching −0.86‰. Moving upwards, $\delta^{13}C$ values increase until reaching a maximum of 1.44‰ in the middle part of the Davoei Zone (Capricornus–lowermost Figulinum? subzones). The upper Davoei–lowermost Margaritatus (Stokesi Subzone) is characterized by a slight decrease of about 0.6‰ in $\delta^{13}C$. Starting at the uppermost Stokesi Subzone, an increasing trend is recorded upwards where $\delta^{13}C$ values reach a maximum of 1.66‰ at the beginning of the Subnodosus Subzone.

This trend is interrupted by a drop of around 1‰ just prior to the Subnodosus/Gibbosus organic-rich interval. The MLOF mb and Lemede Fm limit is marked by a sharp decrease of about 1.6‰ in $\delta^{13}C$ and then by the return to more positive values, of about 1.3‰.

$\delta^{13}C$ of kerogen varies between −28.92‰ and −26.35‰. Even though this parameter depends on the composition of the individual components of kerogen and some caution must be taken when considering these values, it is significant that this parameter follows the trends of the bulk carbonate data.

The $\delta^{18}O$ values in the studied Peniche section vary between −4.91‰ and −1.30‰ (Fig. 4.2.4). The $\delta^{18}O$ tends to decrease from the base of the studied section to the base of the Davoei Zone, followed by a rapid positive excursion of approximately 1.2‰, then, the decreasing trend is resumed at the middle Davoei Zone and continues until the middle Margaritatus Zone. Subsequently, the values show a slight increasing trend in the top Subnodosus and Gibbosus subzones.

4.2.5. Diagenetic alteration

The $\delta^{13}C$ variation interval is representative of normal marine values, whereas the low $\delta^{18}O$ values (average−3.86‰) indicate some degree of diagenetic overprinting, probably resulting from burial diagenesis.

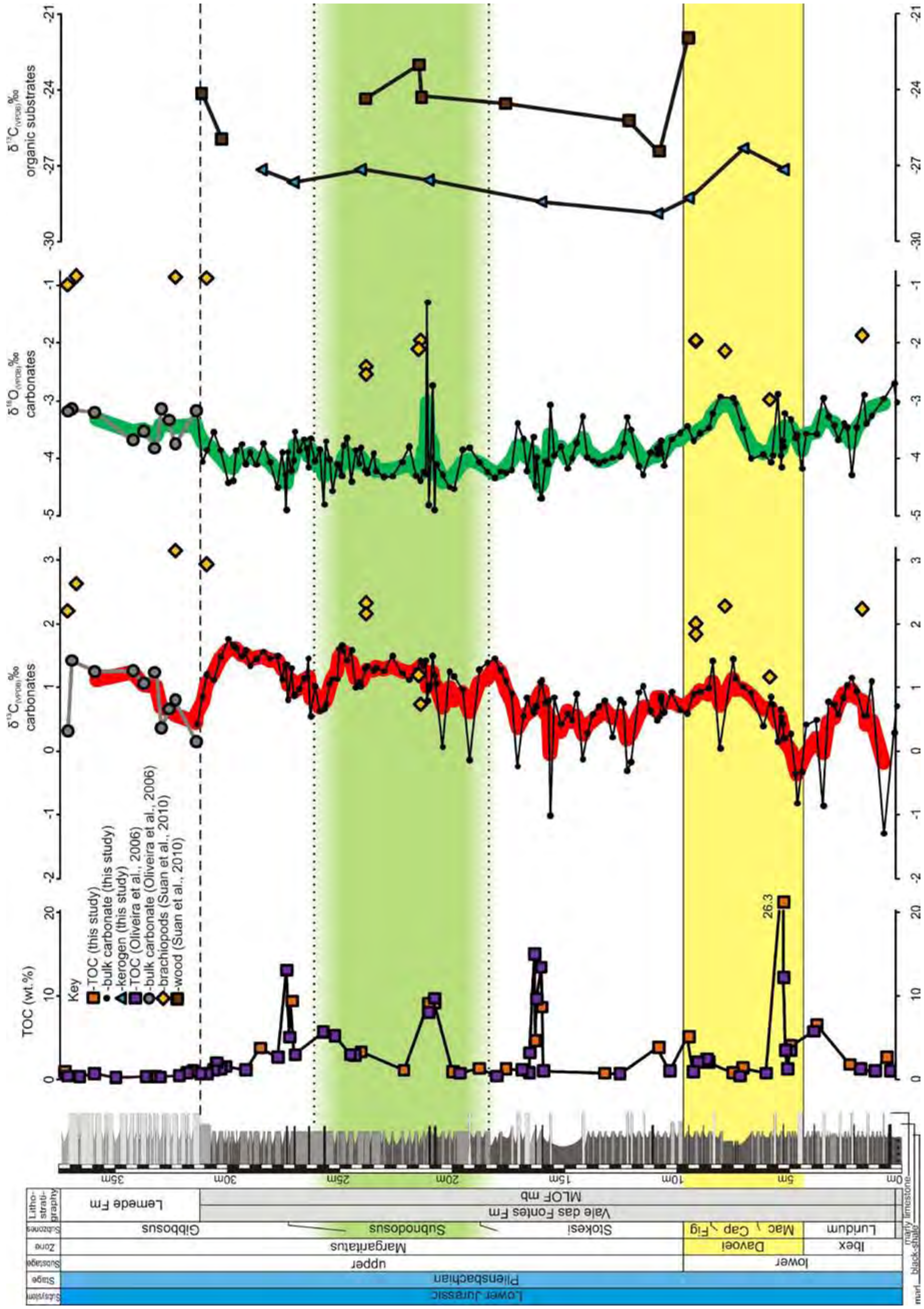


Fig. 4.2.4. TOC, $\delta^{13}C$ and $\delta^{18}O$ records in bulk carbonate, kerogen, brachiopods and wood of the reference section of Peniche. The thick red and green lines correspond to a five point running average. Three $\delta^{13}C$ positive excursions are defined corresponding to the Ibex Zone (Luridum Subzone), Davoei Zone and uppermost Stokesi–Gibbosus subzones. Abbreviations: Mac - Maculatum; Cap - Capricornus; Fig - Figulinum.

However, although within the range of normal marine values, $\delta^{13}C$ values present some scatter (Fig. 4.2.4). Even though carbon isotopic fractionation has a very low thermal dependence, it reflects the source of the dissolved bicarbonate and can be affected if carbon from other components (e.g. organic matter) is introduced in the system (Marshall, 1992). Regarding our dataset, the more calcareous lithotypes tend to present the most negative $\delta^{13}C$ values (see, for example, the marly limestone bed just below the upper Stokesi Subzone black-shale doublet, Fig. 4.2.4). These lithotypes often display evidence of having been more resilient to compaction (e.g. less deformed bioturbation structures), thus indicating early cementation. It is possible that very early cementation, related to bacterial processes linked with organic matter decay and/or marine cements, may have been the cause for the observed scatter of $\delta^{13}C$ data (e.g. Coimbra et al., 2009; Dickson et al., 2008; Marshall, 1992).

Several studies based on carbon and oxygen isotopes from different materials, namely bulk carbonate data (Oliveira et al., 2006), belemnites (data in Jenkyns et al., 2002; Oliveira et al., 2009), brachiopods and wood (Suan et al., 2010), have been published for the Peniche section (Fig. 4.2.4). Due to the small number of samples in these studies, comparison with our high-resolution dataset is limited but there is good overall agreement among the different isotopic records.

Based on the data presented above, we suggest that bulk carbonate (and with some caution kerogen) main trends reflect carbon isotopic palaeoenvironmental variations. Regarding oxygen isotopes, although the absolute values are diagenetically overprinted, the similarity among the different records from the different analysed materials may suggest that the long term variation of this isotopic record is also mainly related to palaeoenvironmental conditions.

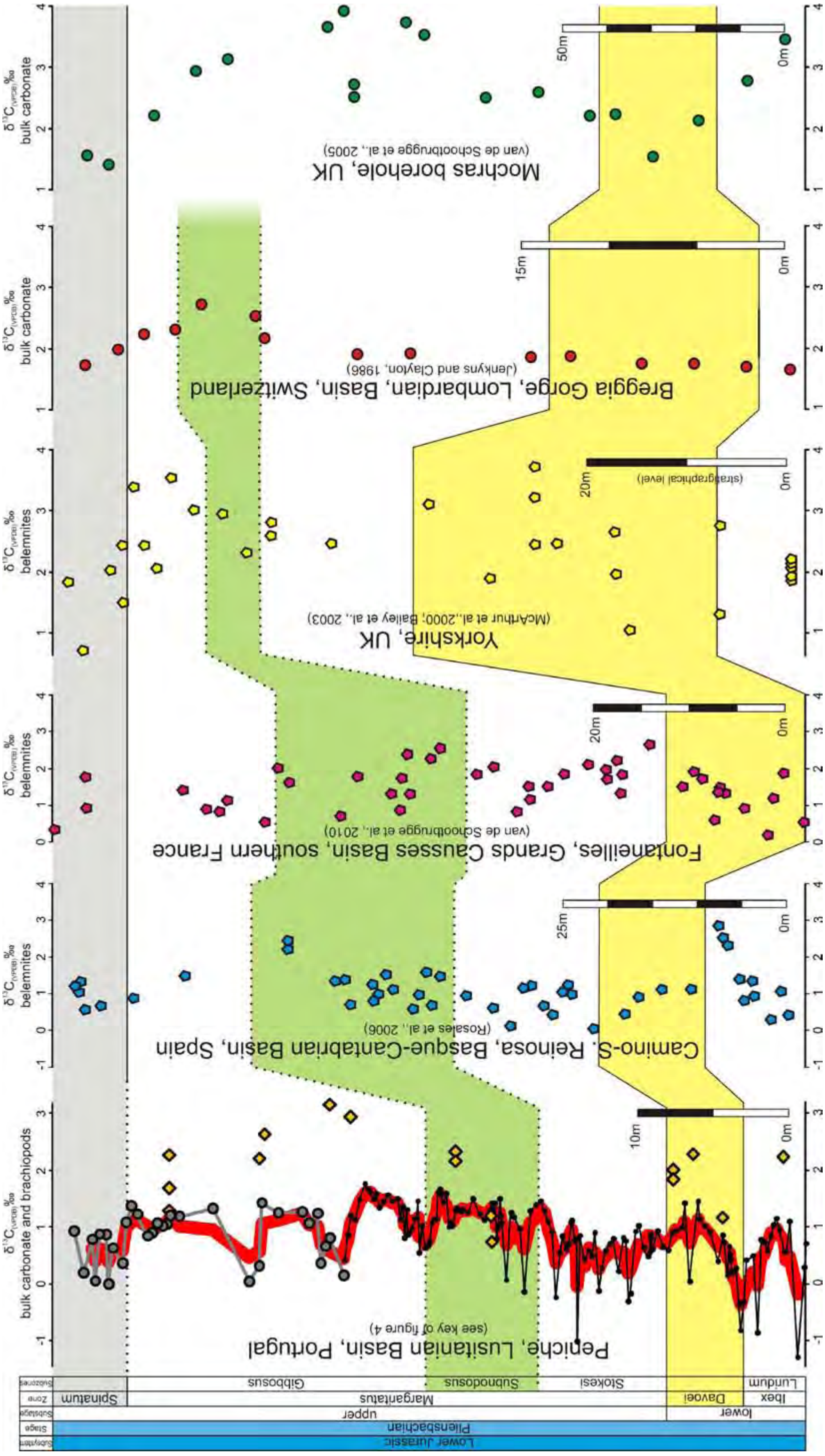
4.2.6. Comparison of the Early–Late Pliensbachian $\delta^{13}C$ record from several basins: global vs. local trends

Stable carbon isotopes are one of the most important tools for studying a variety of sedimentary series, as they can be used to characterize and/or to trace changes in the various carbon reservoirs, from continental environments and atmosphere to oceans and organisms. The main factors and processes that affect the $^{13}C/^{12}C$ ratio are the equilibrium between oceanic dissolved inorganic carbon and atmospheric CO_2, photosynthesis and respiration/remineralisation/preservation of organic matter (e.g. Newton and Bottrell, 2007;

Emerson and Hedges, 2008). In marine environments, and particularly in epeiric sea settings, these processes are governed by the complex interplay between several local (e.g. different carbonate producers, transgressive–regressive cycles) to global (e.g. worldwide preservation of organic matter, variation of continental weathering, input of volcanogenic light CO2) mechanisms (e.g. Hesselbo et al., 2000; Holmden et al., 1998; Immenhauser et al., 2003; Kump and Arthur, 1999; Marshall, 1992; Panchuk et al., 2006; Patterson and Walter, 1994; Swart and Eberli, 2005; Wefer and Berger, 1991; Weissert et al., 1998).

Comparing the major trends of the $\delta^{13}C$ and $\delta^{18}O$ records in the Peniche section (LB, Fig. 4.2.5) with those in time-equivalent series from other locations around the world, namely from southern Switzerland and Italy (Jenkyns and Clayton, 1986; Marino and Santantonio, 2010; Morettini et al., 2002), United Kingdom (Bailey et al., 2003; Katz et al., 2005; McArthur et al., 2000; van de Schootbrugge et al., 2005), Spain (Rosales et al., 2001, 2004a,b, 2006), Germany (Bailey et al., 2003), France (Dera et al., 2009; van de Schootbrugge et al., 2010) and Argentina (Valencio et al., 2005), it is possible to identify a global pattern and to conclude that the Peniche data are consistent with it. Based on an overview of the published data, Jenkyns et al. (2002) discriminated two major positive $\delta^{13}C$ excursions for the Pliensbachian interval, one in the Ibex Zone and another probably corresponding to the Subnodosus Subzone of the Margaritatus Zone. In the LB, three positive excursions are identified, in the Luridum (Ibex Zone), upper Maculatum?–Capricornus–lowermost Figulinum? (Davoei Zone) and uppermost Stokesi–Gibbosus subzones (Margaritatus Zone) (Figs. 4.2.4 and 4.2.5). Concerning the $\delta^{18}O$ record, a discussion of the possible global trend is hampered by the nature of our samples, but it is worth noting that the tendency towards increasing $\delta^{18}O$ values in bulk carbonate samples, as well as in belemnites and brachiopods from the Peniche section, starting at the upper Subnodosus–extreme base of the Gibbosus subzone (Margaritatus Zone) is apparently coeval with the same trend observed in other basins (Bailey et al., 2003; Rosales et al., 2001, 2004a,b, 2006).

The interval comprised between the top of the Ibex and the Davoei zones in the LB corresponds to two positive $\delta^{13}C$ excursions, with a decrease of carbon isotope values at the Ibex–Davoei boundary. The first positive excursion seems to be coeval with the one recorded in the Basque–Cantabrian Basin (Spain), dated from the Luridum Subzone (Quesada et al., 2005).


Peniche, Lusitanian Basin, Portugal
(see key of figure 4)
Camino-S. Reinosa, Basque-Cantabrian Basin, Spain
(Rosales et al., 2006)
Fontaneilles, Grands Causses Basin, southern France
(van de Schootbrugge et al., 2010)
Yorkshire, UK
(McArthur et al.,2000; Bailey et al., 2003)
(stratigraphical level)
Breggia Gorge, Lombardian, Basin, Switzerland
(Jenkyns and Clayton, 1986)
Mochras borehole, UK
(van de Schootbrugge et al., 2005)
bulk carbonate and brachiopods
belemnites
bulk carbonate
Lower Jurassic
Pliensbachian
lower
upper
Ibex
Davoei
Margaritatus
Spinatum
Luridum
Stokesi
Subnodosus
Gibbosus
Subsystem
Stage
Substage
Zone
Subzones
10m
25m
20m
15m
50m
0m

Although limited by the absence of high resolution, well age constrained data, the Ibex Zone $\delta^{13}C$ positive excursion recorded in the Iberian Peninsula is probably correlated with those recorded in central Italy (Morettini et al., 2002), United Kingdom (Katz et al., 2005; van de Schootbrugge et al., 2005) and Argentina (Valencio et al., 2005). The Davoei Zone excursion is only recorded in the LB, in bulk carbonate, belemnites, brachiopods, kerogen and wood. Because of the lack of high resolution, well age constrained data, this excursion cannot be clearly related to the positive $\delta^{13}C$ values recorded in Yorkshire (Bailey et al., 2003), southern France (van de Schootbrugge et al., 2010) and in Italy (Campo al Bello section, Morettini et al., 2002) (Fig. 4.2.5).

In the LB, these two positive excursions are related with organic-rich facies, which are best observed in S. Pedro de Moel (to the north of Peniche, Fig. 4.2.1), the basin depocenter (where TOC reaches up to 10.9 wt.%, unpublished data). The burial of isotopically light organic carbon, a consequence of the photosynthesis fractionation effect, generates a relative enrichment in ^{13}C of the inorganic carbon dissolved in seawater and therefore an increase in the $\delta^{13}C$ of marine carbonates. Rosales et al. (2006) interpreted their Luridum Subzone (Ibex Zone) positive excursion as being related to the inferred T–R cycles and variable rates of organic matter preservation. The associated organic rich facies seem also to be correlative with other northern Spanish locations (Bádenas et al., 2009; Borrego et al., 1996; Herrero, 1998; Perilli and Comas-Rengifo, 2002; Quesada et al., 1997, 2005; Rosales et al., 2006). The Davoei organic-rich interval observed in the Lusitanian Basin correlates with the one in the Inner Hebrides, Scotland (Phelps, 1985). This suggests, at least, a regional control on the occurrence of these organic-rich facies and on the associated positive carbon excursions.

The uppermost Stokesi–Gibbosus subzones positive $\delta^{13}C$ trend is also related to an organic matter preservation interval. In fact, the youngest black-shale interval recorded at the top of the Subnodosus/base of the Gibbosus subzones is representative at a basinal scale and corresponds to the maximum flooding interval of the Pliensbachian T–R facies cycle (Duarte et al., 2010). This black-shale interval is preceded by a negative $\delta^{13}C$ excursion of around 1‰. The onset of this excursion occurs after a small increase of $\delta^{13}C$ coupled with a short lived increase in the nannofossils *Schizosphaerella* spp. and *Crepidolithus crassus*, the

Previous page: Fig. 4.2.5. Comparison of the $\delta^{13}C$ record from several basins across the western Tethys. Although the first two positive excursions in carbon isotope values are not recorded in all data sets, the Margaritatus Zone positive excursion is a global feature of the carbon isotope record.

latter being interpreted as a deep-dweller species linked to stratified water-masses and a deep nutricline (Reggiani et al., 2010a,b and references therein). We suggest that the drop in $\delta^{13}C$ results from the release into the marine reservoir of the ^{12}C previously accumulated in the sea-floor sediments during a period of enhanced preservation of organic matter, probably due to water column stratification. Immediately afterwards, when $\delta^{13}C$ increases (although punctuated by small negative shifts) and between the black-shale levels there occurs one of the most prominent placolith records (several species of this group have been interpreted as meso- to eutrophic shallow-dwellers, Reggiani et al., 2010a,b and references therein). It is possible that during this period, overturn of nutrient enriched bottom waters may have become periodic (alternating with intervals of enhanced organic matter preservation), resulting in a greater nutrient availability in the upper part of the water column, as indicated by the high abundance of placoliths, and controlling the deposition of the well defined black-shales.

4.2.7. Is the Margaritatus Zone organic-rich facies the result of an OAE?

Virtually all existing datasets that encompass the Margaritatus Zone record a positive trend of $\delta^{13}C$. The only exception is observed in southern France, where Late Pliensbachian bulk carbonate samples show a decrease in $\delta^{13}C$ in the Margaritatus Zone (reaching −3‰ in the uppermost Spinatum Zone), probably as the result of diagenesis (van de Schootbrugge et al., 2010). It has been proposed that the Margaritatus Zone positive $\delta^{13}C$ excursion is the result of the worldwide deposition of isotopically-light organic matter in a transgressive context (Hallam, 1981), probably triggered by worldwide oceanic anoxia (OAE sensu Schlanger and Jenkyns, 1976) in the Subnodosus or Gibbosus subzones (Jenkyns, 1988; Suan et al., 2010). These organic-rich intervals are known from the western part of Europe namely Portugal (Duarte et al., 2010), Northern Spain (e.g. Borrego et al., 1996; Comas-Rengifo and Goy, 2010; Quesada et al., 1997, 2005; Rosales et al., 2006), France (Bessereau et al., 1995; Léonide et al., 2007; van de Schootbrugge et al., 2010) and Austria (Kodina et al., 1988), and also from Siberia, Canadian Arctic and Arctic platform of Alaska (see Nikitenko and Mickey, 2004). Other (upper?) Pliensbachian organic-rich deposits, although poorly age constrained, are also known from several North European locations (Fleet et al., 1987) and western Canada (Asgar-Deen et al., 2003; Riediger, 2002). The burial of the isotopically-light organic matter, which ultimately is reflected in carbon storage, may have had important consequences. For instance, CO_2 depleted atmospheric levels, resulting from the carbon storage, have been invoked as a possible mechanism triggering the onset of transient icehouse climatic conditions that operated during the uppermost Margaritatus (Gibbosus Subzone)–Spinatum zones (Suan et al., 2010).

Despite the research efforts made in the last years to unravel the mechanisms behind the events that predate the T-OAE (e.g. Hesselbo et al., 2007), many questions remain. Concerning the organic-rich facies: are the worldwide organic-rich deposits synchronous or is their deposition staggered in time? If they are synchronous, what is the duration of this event? Tackling these and the remaining issues will take a great deal of effort in the forthcoming years. For now, it is suggested that, until these organic-rich facies are well age constrained and high resolution carbon and oxygen data are provided from the worldwide reference sections or other new areas, and worldwide anoxia is proven, this interval should be referred to as an Organic Matter Preservation Interval (Late Pliensbachian OMPI), avoiding, for now, the use of the term OAE. This distinction is made in order to recognize that although the observed worldwide burial of organic matter in the Late Pliensbachian may have had an important impact on the global carbon cycle, its synchronism, causes and consequences are yet to be determined.

4.2.8. Conclusions

This study presents a high-resolution stable carbon and oxygen isotope record from bulk carbonate and kerogen from organic-rich hemipelagic deposits observed in the Peniche section (Lusitanian Basin, Portugal), age constrained to the Early–Late Pliensbachian, Early Jurassic (~187 Ma).

In addition to the recognition in Portugal of two previously defined positive carbon isotope excursions, located at the Ibex and Margaritatus zones (Jenkyns et al., 2002), a third positive excursion is identified here for the first time, corresponding to the Davoei Zone. Moreover, our knowledge of the stratigraphical onset and duration of the younger excursion is improved as, according to these new data, it is shown to range from the upper Stokesi through the Gibbosus subzones (Margaritatus Zone).

In the Lusitanian Basin, these excursions are related to intervals of enhanced preservation of organic matter, which can also be traced to other basins suggesting, at least, a regional control. In fact, the Margaritatus excursion, which predates the Toarcian Oceanic Anoxic Event, seems to correlate with a global period of occurrence of organic-rich facies. Due to the current lack of knowledge about the causes and consequences of this event, we propose that this interval should be referred to as an Organic Matter Preservation Interval (Late Pliensbachian OMPI), avoiding, for now, the use of the term OAE.

References

ASGAR-DEEN, M., HALL, R., CRAIG, J. and RIEDIGER, C., 2003. New biostratigraphic data from the Lower Jurassic Fernie Formation in the subsurface of west-central Alberta and their stratigraphic implications. Canadian Journal of Earth Sciences, 40, 45–63.

AZERÊDO, A.C., DUARTE, L.V., HENRIQUES, M.H. and MANUPPELLA, G., 2003. Da dinâmica continental no Triásico aos mares do Jurássico Inferior e Médio. Cadernos de Geologia de Portugal. Instituto Geológico e Mineiro, Lisboa.

BÁDENAS, B., AURELL, M., GARCÍA-RAMOS, J.C., GONZÁLEZ, B. and PIÑUELA, L., 2009. Sedimentary vs. diagenetic control on rhythmic calcareous successions (Pliensbachian of Asturias, Spain). Terra Nova, 21, 162–170.

BAILEY, T.R., ROSENTHAL, Y., MCARTHUR, J.M., VAN DE SCHOOTBRUGGE, B. and THIRLWALL, M.F., 2003. Paleoceanographic changes of the Late Pliensbachian–Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. Earth and Planetary Science Letters, 212, 307–320.

BASSOULET, J.-P., ELMI, S., POISSON, A., CECCA, F., BELLION, Y.,GUIRAUD, R., BAUDIN, F., 1993. Middle Toarcian (184–182 Ma). In: DERCOURT, J., RICOU, L.E. and VRIELYNCK, B. (Eds.), Atlas Tethys Paleoenvironmental Maps, BEICIP-FRANLAB, Rueil-Malmaison, pp. 63–80.

BESSEREAU, G., GUILLOCHEAU, F. and HUC, A.-Y., 1995. Source Rock Occurrence in a Sequence Stratigraphic Framework: the Example of the Lias of the Paris Basin. In: HUC, A.-Y. (Ed.), Paleogeography, Paleoclimate, and Source Rocks, AAPG Studies in Geology No. 40, AAPG, Tulsa, pp. 273–301.

BORREGO, A.G., HAGEMANN, H.W., BLANCO, C.G., VALENZUELA, M. and SUÁREZ DE CENTI, C., 1996. The Pliensbachian (Early Jurassic) "anoxic" event in Asturias, northern Spain: Santa Mera Member, Rodiles Formation. Organic Geochemistry, 25 (5–7), 295–309.

COIMBRA, R., IMMENHAUSER, A. and OLÓRIZ, F., 2009. Matrix micrite $\delta^{13}C$ and $\delta^{18}O$ reveals synsedimentary marine lithification in Upper Jurassic Ammonitico Rosso limestones (Betic Cordillera, SE Spain). Sedimentary Geology, 219, 332–348.

COMAS-RENGIFO, M.J., and GOY, A., 2010. Caracterización biocronoestratigráfica del Sinemuriense Superior y el Pliensbachiense entre los afloramientos de la Playa Vega y Lastres (Asturias). In: GARCÍA-RAMOS, J.C. (Coord.), Las sucesionesmargo-calcáreasmarinas del Jurásico Inferior y las series fluviales del Jurásico Superior. Acantilados de la playa de Vega (Ribadesella). Guía de campo (excursión A), V Congreso del Jurásico de España, Servitec, Oviedo, pp. 10–18.

DERA, G., PUCÉAT, E., PELLENARD, P., NEIGE, P., DELSATE, D., JOACHIMSKI, M.M., REISBERG, L. and MARTINEZ, M., 2009. Water mass exchange and variations in seawater temperature in the NW Tethys during the Early Jurassic: evidence from neodymium and oxygen isotopes of fish teeth and belemnites. Earth and Planetary Science Letters, 286, 198–207.

DERA, G., NEIGE, P., DOMMERGUES, J.-L., FARA, E., LAFFONT, R. and PELLENARD, P., 2010. High resolution dynamics of Early Jurassic marine extinctions: the case of Pliensbachian–Toarcian ammonites (Cephalopoda). Journal of the Geological Society, 167, 21–33.

DICKSON, J.A.D., WOOD, R.A., BU AL ROUGHA, H. and SHEBL, H., 2008. Sulphate reduction associated with hardgrounds: Lithification afterburn! Sedimentary Geolology, 205, 34–39.

DOMMERGUES, J.-L., 1987. L'évolution chez les Ammonitina du Lias Moyen (Carixien, Domerien basal) en Europe occidentale. Documents des Laboratoires de Geologie, Lyon, 98, 1–297.

DOMMERGUES, J.-L., FARA, E. and MEISTER, C., 2009. Ammonite diversity and its palaeobiogeographical structure during the early Pliensbachian (Jurassic) in the western Tethys and adjacent areas. Palaeogeography, Palaeoclimatology, Palaeoecology, 280, 64–77.

DROMART, G. and ELMI, S., 1986. Développement de structures cryptalgaires en domaine pélagique au cours de l'ouverture des bassins jurassiques (Atlantique central, Téthys occidentale). Comptes rendus de l'Académie des sciences de Paris 2, 303 (4), 311–316.

DUARTE, L.V., 2007. Lithostratigraphy, sequence stratigraphy and depositional setting of the Pliensbachian and Toarcian series in the Lusitanian Basin (Portugal). In: ROCHA, R.B. (ed.), The Peniche Section (Portugal), Contributions to the Definition of the Toarcian GSSP. International Subcommission on Jurassic Stratigraphy, pp. 17–23.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das séries margo-calcárias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicações Instituto Geológico e Mineiro, 89, 135–154.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F., 2010. Organic-Rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total organic carbon distribution and relation to transgressive–regressive facies cycles. Geologica Acta, 8 (3), 325–340.

DUARTE, L.V., WRIGHT, V.P., FERNÁNDEZ-LÓPEZ, S.F., ELMI, S., KRAUTTER, M., AZERÊDO, A.C., HENRIQUES, M.H., RODRIGUES, R. and PERILLI, N., 2004. Early Jurassic carbonate evolution in the Lusitanian Basin (Portugal): facies, sequence stratigraphy and cyclicity. In: DUARTE, L.V. and HENRIQUES, M.H. (Eds.), Carboniferous and Jurassic Carbonate Platforms of Iberia. Field Trip Guide Book of the 23 rd IAS Meeting of Sedimentology Volume 1, pp. 45–71.

ELMI, S., ROCHA, R.B. and MOUTERDE, R., 1988. Sediméntation pelagique et encroûtements crytalgaires: les calcaires grumeleux du Carixien portugais. Ciências da Terra, 9, 69–90.

EMERSON, S.R., HEDGES, J.I., 2008. Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press, New York.

FLEET, A.J., CLAYTON, C.J., JENKYNS, H.C., PARKINSON, D.N., 1987. Liassic source rock deposition in western Europe. In: BROOKS, J., GLENNIE, K. (eds.), Petroleum Geology of North West Europe. Graham & Trotman, London, pp. 59–70.

HALLAM, A., 1981. A revised sea-level curve for the early Jurassic. Journal of the Geological Society, 138, 735–743.

HERRERO, C., 1998. Foraminíferos del Pliensbachiense en la sección de Camino (Cuenca Vasco-Cantábrica, España). Cuad. Geol. Ibér. 24, 121–139.

HESSELBO, S.P., GRÖCKE, D.R., JENKYNS, H.C., BJERRUM, C.J., FARRIMOND, P., MORGANS BELL, H.S. and GREEN, O.R., 2000. Massive dissociation of gas hydrates during a Jurassic oceanic anoxic event. Nature, 406, 392–395.

HESSELBO, S.P., JENKYNS, H.C., DUARTE, L.V. and OLIVEIRA, L.C.V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). Earth and Planetary Science Letters, 253, 455–470.

HOLMDEN, C., CREASER, R.A., MUEHLENBACHS, K., LESLIE, S.A. and BERGSTRÖM, S.M., 1998. Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: Implications for secular curves. Geology, 26 (6), 567–570.

IMMENHAUSER, A., DELLA PORTA, G., KENTER, J.A.M. and BAHAMONDE, J.R., 2003. An alternative model for positive shifts in shallow-marine carbonate $\delta^{13}C$ and $\delta^{18}O$. Sedimentology, 50, 953–959.

JENKYNS, H.C., 1988. The Early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary and geochemical evidence. American Journal of Science, 288, 101–151.

JENKYNS, H.C. and CLAYTON, C.J., 1986. Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. Sedimentology 33, 87–106.

JENKYNS, H.C., JONES, C.E., GRÖCKE, D.R., HESSELBO, S.P. and PARKINSON, D.N., 2002. Chemostratigraphy of the Jurassic system: applications, limitations and implications for palaeoceanography. Journal of the Geological Society, 159, 351–378.

KATZ, M.E., WRIGHT, J.D., MILLER, K.D., CRAMER, B.S., FENNEL, K. and FALKOWSKI, P.G., 2005. Biological overprint of the geological carbon cycle. Marine Geology, 217, 323–338.

KODINA, L.A., BOGATCHEVA, M.P. and LOBITZER, H., 1988. An organic geochemical study of Austrian bituminous rocks. Jb. Geol. B-A, Band 131. Heft 2, 291–300.

KUMP, L.R. and ARTHUR, M.A., 1999. Interpreting carbon-isotope excursions: carbonates and organic matter. Chemical Geology, 161, 181–198.

LÉONIDE, P., FLOQUET, M. and VILLIER, L., 2007. Interaction of tectonics, eustasy, climate and carbonate production on the sedimentary evolution of an early/middle Jurassic extensional basin (Southern Provence Sub-basin, SE France). Basin Research, 19, 125–152.

MARINO, M. and SANTANTONIO, M., 2010. Understanding the geological record of carbonate platform drowning across rifted Tethyan margins: Examples from the Lower Jurassic of the Apennines and Sicily (Italy). Sedimentary Geology, 225, 116–137.

MARSHALL, J.D., 1992. Climatic and oceanographic isotopic signals from the carbonate rock record and their preservation. Geological Magazine, 129 (2), 143–160.

MCARTHUR, J.M., DONOVAN, D.T., THIRLWALL, M.F., FOUKE, B.W. and MATTEY, D., 2000. Strontium isotope profile of the early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belemnite palaeotemperatures. Earth and Planetary Science Letters 179, 269–285.

MENDONÇA FILHO, J.G., CARVALHO, M.A. and MENEZES, T.R., 2002. Palinofácies. In: DUTRA, T.L. (Ed.), (Coord.), Técnicas e Procedimentos de Trabalho com Fósseis e Formas Modernas Comparativas. Unisinos eds., São Leopoldo, pp. 20–24.

MORETTINI, E., SANTANTONIO, M., BARTOLINI, A., CECCA, F., BAUMGARTNER, P.O. and HUNZIKER, J.C., 2002. Carbon isotope stratigraphy and carbonate production during the Early–Middle Jurassic:

examples from the Umbria–Marche–Sabina Apennines (central Italy). Palaeogeography, Palaeoclimatology, Palaeoecology, 184, 251–273.

MOUTERDE, R., DOMMERGUES, J.-L., MEISTER, C. and ROCHA, R.B., 2007. Atlas des fossiles caractéristiques du Lias portugais. III a) Domérien (Ammonites). Ciências da Terra, 16, 67–111.

NEWTON, B. and BOTTRELL, S., 2007. Stable isotopes of carbon and sulphur as indicators of environmental change: past and present. Journal of the Geological Society, 164, 691–708.

NIKITENKO, B.L. and MICKEY, M.B., 2004. Foraminifera and ostracodes across the Pliensbachian– Toarcian boundary in the Arctic Realm (stratigraphy, palaeobiogeography and biofacies). In: BEAUDOIN, A.B. and HEAD, M.J. (Eds.), The Palynology and Micropalaeontology of Boundaries. Geological Society Special Publication nº 230. The Geological Society, London, pp. 137–174.

OLIVEIRA, L.C.V., RODRIGUES, R., DUARTE, L.V. and LEMOS, V., 2006. Avaliação do potencial gerador de petróleo e interpretação paleoambiental com base em biomarcadores e isótopos estáveis do carbono da seção Pliensbaquiano–Toarciano inferior (Jurássico inferior) da região de Peniche (Bacia Lusitânica, Portugal). Boletin de Geociências Petrobras, 14 (2), 207–234.

OLIVEIRA, L.C.V., DUARTE, L.V., LEMOS, V.B., COMAS-RENGIFO, M.J. and PERILLI, N., 2007. Bioestratigrafia de nanofósseis calcários e correlação com as zonas de amonites do Pliensbaquiano–Toarciano basal (Jurássico inferior) de Peniche (Bacia Lusitânica, Portugal). In: CARVALHO, I.S., CASSAB, R.C.T., SCHWANKE, C., CARVALHO, M.A., FERNANDES, A.C.S., RODRIGUES, M.A.C., CARVALHO, M.S.S., ARAI, M. and OLIVEIRA, M.E.Q. (Eds.), Paleontologia: Cenários de Vida. Proceedings of XIX Congresso Brasileiro de Paleontologia, Búzios (Brazil), Editora Interciência, pp. 411–420.

OLIVEIRA, L.C., DUARTE, L.V., SILVA, R.L. and RODRIGUES, R., 2009. Belemnite $\delta^{18}O$ and $\delta^{13}C$ record of the Lusitanian Basin Pliensbachian carbonate series (Portugal). Geochimica et Cosmochimica Acta, 73 (13 S), A969.

PANCHUK, K.M., HOLMDEN, C.E. and LESLIE, S.A., 2006. Local controls on carbon cycling in the Ordovician midcontinent region of North America, with implication for carbon isotope secular curves. Journal of Sedimentary Research, 76, 200–211.

PATTERSON, W.P. and WALTER, L.M., 1994. Depletion of ^{13}C in seawater ΣCO_2 on modern carbonate platforms: Significance for the carbon isotopic record of carbonates. Geology, 22, 885–888.

PERILLI, N. and COMAS-RENGIFO, M.J., 2002. Calibration of Pliensbachian calcareous nannofossils events in two ammonite-controlled sections from Northern Spain. Rivista Italiana di Paleontologia Stratigrafia, 108 (1), 133–152.

PHELPS, M., 1985. A refined ammonite biostratigraphy for the Middle and Upper Carixian (Ibex and Davoei zones, Lower Jurassic) in North-West Europe and stratigraphical details of the Carixian–Domerian boundary. Geobios, 18, 321–362.

QUESADA, S., DORRONSORO, C., ROBLES, S., CHALER, R. and GRIMALT, J.O., 1997. Geochemical correlation of oil from the Ayoluengo field to Liassic black shale units in the southwestern Basque–Cantabrian Basin (northern Spain). Organic Geochemistry, 27, 25–40.

QUESADA, S., ROBLES, S. and ROSALES, I., 2005. Depositional architecture and transgressive–regressive cycles within Liassic backstepping carbonate ramps in the Basque–Cantabrian Basin, northern Spain. Journal of the Geological Society, 162, 531–548.

REGGIANI, L., MATTIOLI, E. and PITTET, B., 2010a. Spatial distribution of Late Pliensbachian (Early Jurassic) calcareous nannofossils within the Lusitanian Basin (Portugal). Geobios, 43, 87–97.

REGGIANI, L., MATTIOLI, E., PITTET, B., DUARTE, L.V., VEIGA DE OLIVEIRA, L.C. and COMAS-RENGIFO, M.J., 2010b. Pliensbachian (Early Jurassic) calcareous nannofossils from the Peniche section (Lusitanian Basin, Portugal): a clue for palaeoenvironmental reconstructions. Marine Micropaleontology, 75 (1–4), 1–16.

RIEDIGER, C.L., 2002. Hydrocarbon source rock potential and comments on correlation of the Lower Jurassic Poker Chip Shale, west-central Alberta. Bulletin of Canadian Petroleum Geology, 50 (2), 263–276.

ROSALES, I., QUESADA, S. and ROBLES, S., 2001. Primary and diagenetic isotopic signal in fossils and hemipelagic carbonates: the Lower Jurassic of northern Spain. Sedimentology, 48, 1149–1169.

ROSALES, I., QUESADA, S. and ROBLES, S., 2004a. Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque–Cantabrian Basin, northern Spain. Palaeogeography, Palaeoclimatology, Palaeoecology, 203, 253–275.

ROSALES, I., ROBLES, S. and QUESADA, S., 2004b. Elemental and oxygen isotope composition of Early Jurassic belemnites: salinity vs. temperature signals. Journal of Sedimentary Research, 74, 342–354.

ROSALES, I., QUESADA, S. and ROBLES, S., 2006. Geochemical arguments for identifying second-order sea-level changes in hemipelagic carbonate ramp deposits. Terra Nova, 18, 233–240.

RUBAN, D.A., 2009. Brachiopod decline preceded the Early Toarcian mass extinction in the Northern Caucasus (northern Neo-Tethys Ocean): A palaeogeographical context. Revue de Paléobiologie, 28 (1), 85–92.

SCHLANGER, S.O. and JENKYNS, H.C., 1976. Cretaceous oceanic anoxic events: causes and consequences. Geol. Mijnbouw 55 (3–4), 179–184.

SILVA, R.L., MENDONÇA FILHO, J.G., DUARTE, L.V., COMAS-RENGIFO, M.J., AZERÊDO, A.C. and FERREIRA, R., 2010. Organic-rich facies of the top Ibex–Margaritatus zones (Pliensbachian) of the Lusitanian Basin (Portugal): TOC and biomarkers variation. Geochimica et Cosmochimica Acta, 74 (12-S1), A962.

SOARES, A.F., ROCHA, R.B., ELMI, S., HENRIQUES, M.H., MOUTERDE, R., ALMÉRAS, Y., RUGET, C., MARQUES, J., DUARTE, L.V., CARAPITO, C. and KULLBERG, J.C., 1993. Le sous-bassin nordlusitanien (Portugal) du Trias au Jurassique moyen: histoire d'un “rift avorté”. Comptes rendus de l'Académie des sciences de Paris 317, 1659–1666.

SUAN, G., MATTIOLI, E., PITTET, B., LÉCUYER, C., SUCHÉRAS-MARX, B., DUARTE, L.V., PHILIPPE, M., REGGIANI, L. and MARTINEAU, F., 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. Earth and Planetary Science Letters, 290, 448–458.

SWART, P.K. and EBERLI, G., 2005. The nature of the $\delta^{13}C$ of periplatform sediments: Implications for stratigraphy and the global carbon cycle. Sedimentary Geology, 175, 115–129.

TYSON, R.V., 1995. Sedimentary organic matter. Organic Facies and Palynofacies. Chapman & Hall, London.

VALENCIO, S.A., CAGNONI, M.C., RAMOS, A.M., RICCARDI, A.C. and PANARELLO, H.O., 2005. Chemostratigraphy of the Pliensbachian, Puesto Araya Formation (Neuquén Basin, Argentina). Geologica Acta 3 (2), 147–154.

VAN DE SCHOOTBRUGGE, B., BAILEY, T.R., ROSENTHAL, Y., KATZ,M.E.,WRIGHT, J.D., MILLER, K.G., FEIST- BURKHARDT, S. and FALKOWSKI, P.G., 2005. Early Jurassic climate change and the radiation of organic walled phytoplankton in the Tethys Ocean. Paleobiology, 31 (1), 73–97.

VAN DE SCHOOTBRUGGE, B., HARAZIM, D., SORICHTER, OSCHMANN, W., FIEBIG, J., PÜTTMANN, W. PEINL, M., ZANELLA, F., TEICHERT, B., HOFFMANN, J., STADNITSKAIA, A. and ROSENTHAL, Y., 2010. The enigmatic ichnofossil Tisoa siphonalis and widespread authigenic seep carbonate formation during the Late Pliensbachian in southern France. Biogeosciences Discussions, 7, 4181–4222.

WEFER, G. and BERGER, W.H., 1991. Isotope paleontology: growth and composition of extant calcareous species. Marine Geology, 100, 207–248.

WEISSERT, H., LINI, A., FÖLLMI, K. and KUHN, O., 1998. Correlation of Early Cretaceous carbon isotope stratigraphy and platform drowning events: a possible link? Palaeogeography, Palaeoclimatology, Palaeoecology, 137, 189–203.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. and GRADSTEIN, F.M., 1989. The Lusitanian basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphy, and subsidence history. AAPG Memoire, 46, 341–361.

Acknowledgments

We wish to thank Julia Becker from the School of Earth & Ocean Sciences (Cardiff University) and Elsa Teresa Rodrigues form the IMAR-CMA (Coimbra University) for technical support in the carbon and oxygen isotopes analysis. We thank the Chemical Geology Editor in-Chief Laurie Reisberg for her helpful suggestions and Emanuela Mattioli and an anonymous reviewer for their significant contributions in improving the original manuscript. V. Paul Wright is thanked for having kindly revised the English. This paper is a contribution to the Projects PTDC/CTE-GIX/098968/2008 (Foundation for Science and Technology, Portuguese Government) and CGL2008-03112/BTE (Ministry of Science and Technology, Spanish Government).

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

Ricardo L. Silva, João G. Mendonça Filho, Frederico S. da Silva, Luís V. Duarte, Taís F. Silva, Rui Ferreira and Ana C. Azerêdo, 2012, Bulletin of Geosciences 87(2), 373–382

Abstract

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 [O2] 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 sulphide-rich depleted environments. The good overall match between the determined lipid contents and specific depositional/early diagenetical conditions seem to favour 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.

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

4.3.1. Introduction

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 and Hedges, 1993; Parrish, 1995; Tyson, 1995; Peters et al., 2005; Vandenbroucke and 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 addition, 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 and 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, 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 (Mendonca 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. 4.3.1 and 4.3.2), 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. 4.3.2), 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 and 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 had 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.

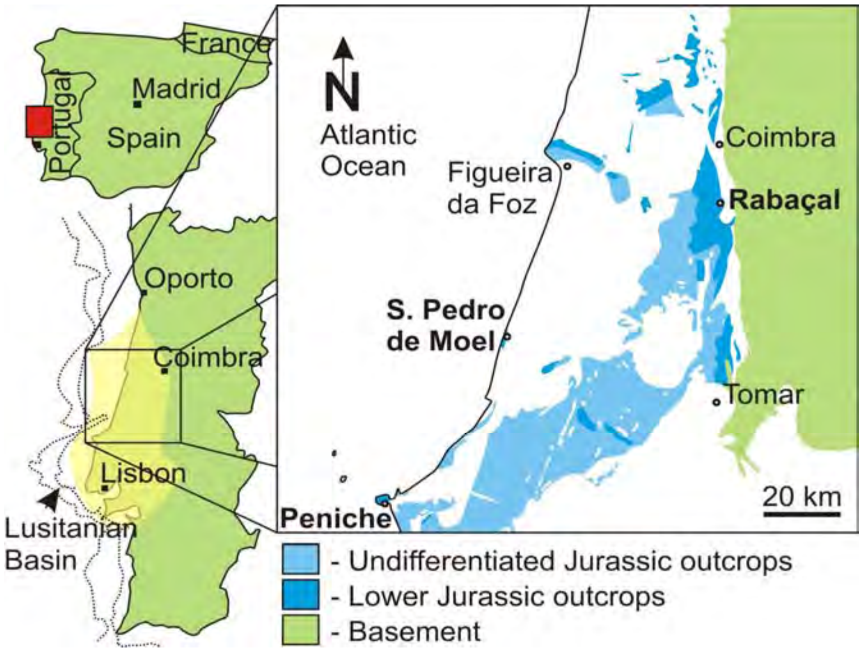


Fig. 4.3.1. Simplified geological map of the Lusitanian Basin and location of the studied sections.

4.3.2. 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 2nd-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 200m (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. 4.3.1 and 4.3.2). 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.

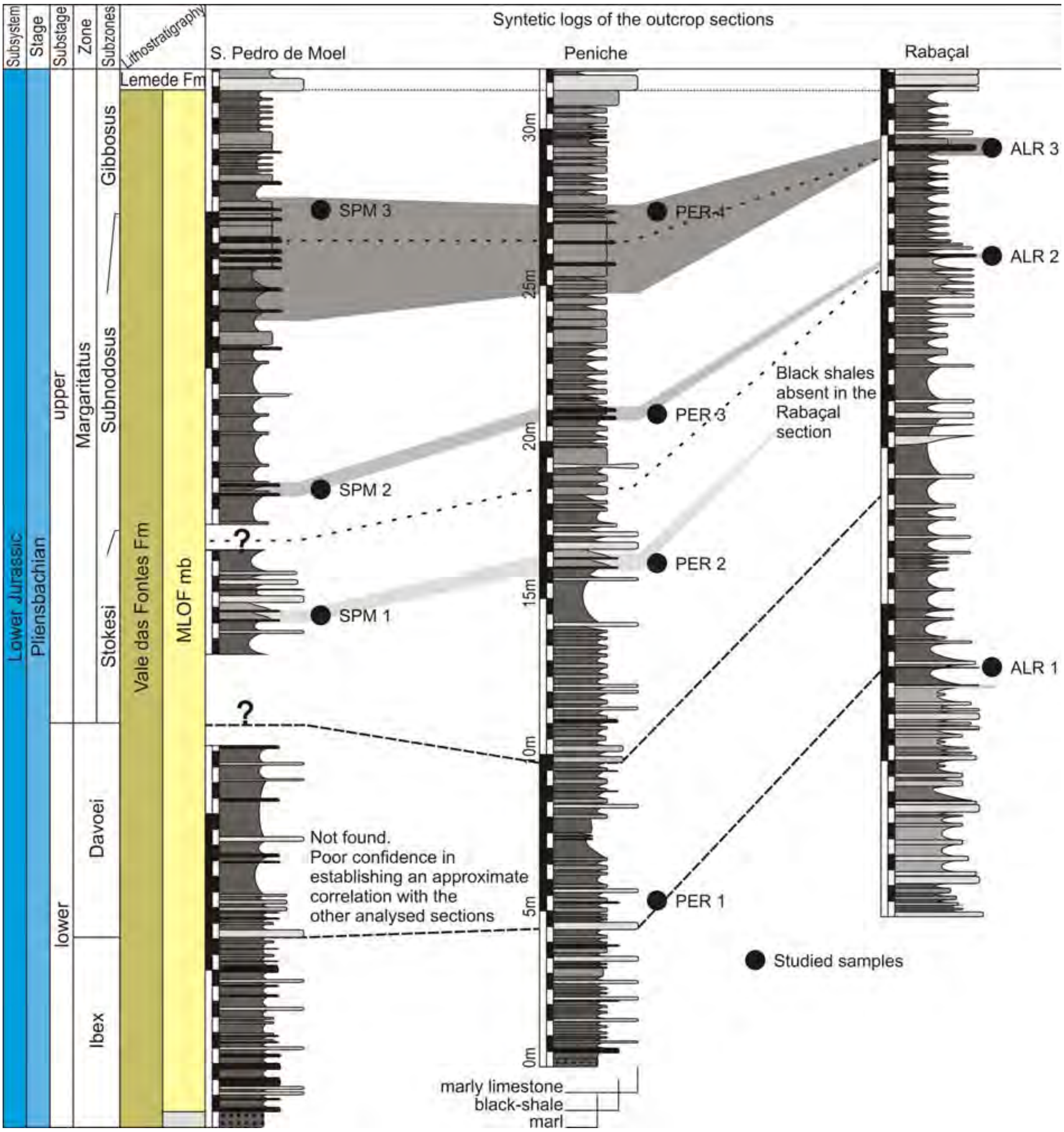


Fig. 4.3.2. Stratigraphic logs of the Rabaçal, Peniche and S. Pedro de Moel outcrop sections, where are highlighted the main organic-rich intervals with black shales (*s.l.*) and its lateral extension. The S. Pedro de Moel section is incomplete due to intense tectonic disturbance, but ammonite data allow a confident correlation with the remaining sections.

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; Silva et al., 2011a, 2011b; Fig. 4.3.1). 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).

4.3.3. Material 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 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 4.3.1 and Fig. 4.3.2). 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 ± 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 Mendonca Filho (1999), Menezes et al., (2008) and Mendonca 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 (Niteroi, 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 and Danovaro, 1994; Dell'Anno et al., 2002; S. Silva et al., 2010) and older sediments (Oligocene, Mendonca 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 and Hatcher (1972). Concentrations are expressed as glucose equivalents.

– Lipid analysis: extraction by direct elution with chloroform and methanol and analyzed according to Marsh and 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 and Danovaro (1994). Analytical precision is better than 6% for protein and carbohydrate determinations and 8% for the lipid determination.

4.3.4. Results and discussion

4.3.4.1. 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 4.3.1). The highest TOC and S values from the Rabaçal and Peniche sections are observed in the Ibex/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).

Table 4.3.1. 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)

Samples	Time interval	TOC[a] (wt.%)	S[b] (wt.%)	Biogeochemistry (μg/g rock)				Pr/Ph[f]
				LIP[c]	CHO[d]	PTN[e]	Total	
Rabaçal								
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
Peniche								
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
S. Pedro de Moel								
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

(a) Total organic carbon; (b) Sulphur; (c) Lipids; (d) Carbohydrates; (e) Proteins; (f) Pristane/Phytane.

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 Mendonca Filho et al., 2011) presents a variable fluorescence and a highly heterogeneous "clotted" fabric (Fig. 4.3.3A, 4.3.3B, 4.3.3D). This AOM corresponds to mucilaginous aggregates (Decho and 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.

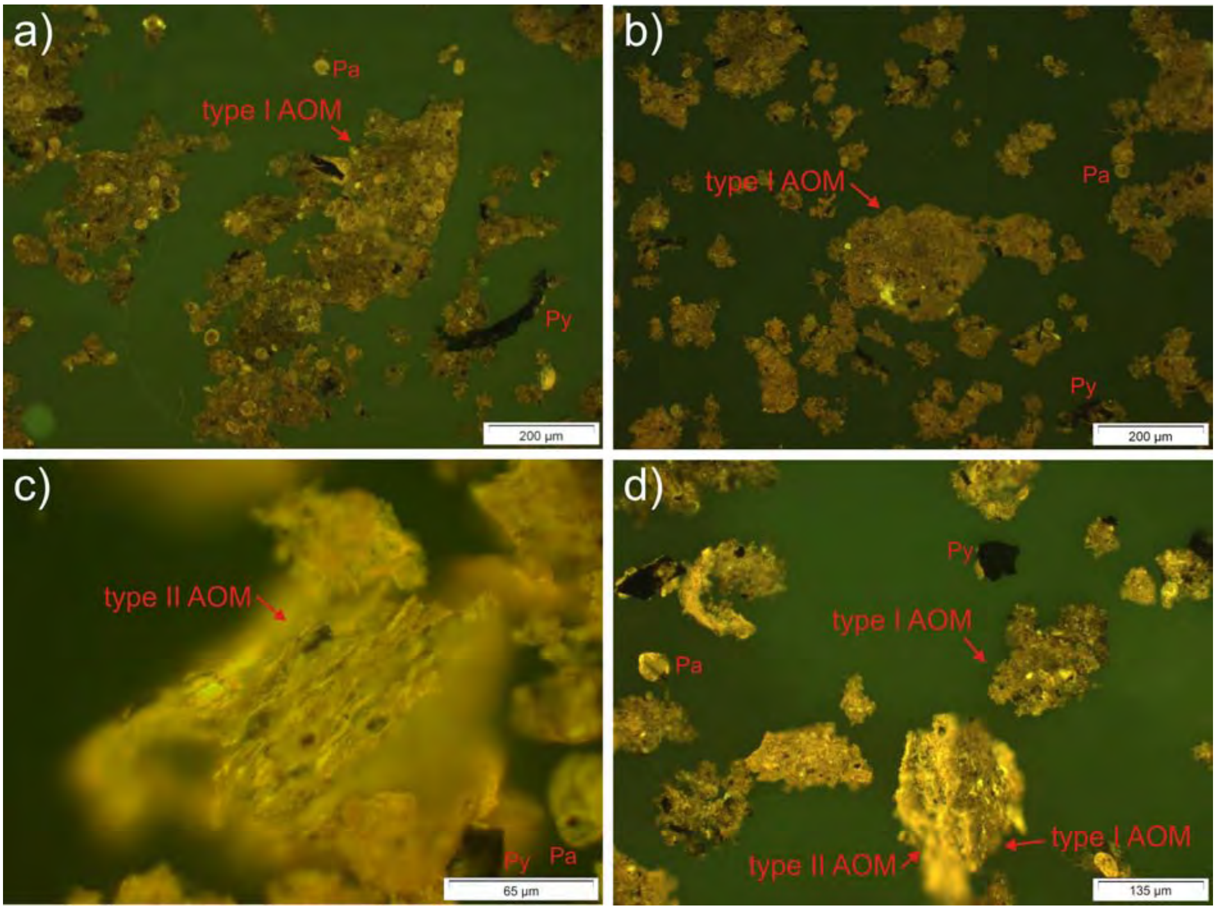


Fig. 4.3.3. Organic petrography aspects of the kerogen assemblages from the studied sections. A-PER 3; B POR-2; C-ALR 1; D-PER 4. All photos were taken in fluorescence mode. Abbreviations: Py-phytoclasts; Pa-palynomorphs.

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 organoelemental 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 and Welte, 1978; Mendonca Filho et al., 2010a, 2010c). The type II AOM (amorphous products of bacteria and microbial mats subgroups of Mendonca Filho et al., 2011) occurs as a highly fluorescent homogenous AOM (pelicular AOM *sensu* Combaz, 1980, Fig. 4.3.3C, 4.3.3D) 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 Mendonca Filho et al., 2010a, 2010c, 2011).

4.3.5. 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 4.3.1). 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 ± 9, 19 ± 4 and 16 ± 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 and 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 and 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 and 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 Damste et al., 1995; Sun et al., 2002; Farrimond et al., 2003; Lee et al., 2004; Farrimond et al., 2003; Bowden *et al.* 2006; Lu et al., 2010) but it has been shown that it mainly depends on O_2 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_2 contents (Kohnen et al., 1990, 1992; Harvey et al., 1995; Sun et al., 2002; Ding and 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_2 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 4.3.1 and Figs. 4.3.2 and 4.3.4), 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 4.3.1). 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 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 4.3.1 and Fig. 4.3.4).

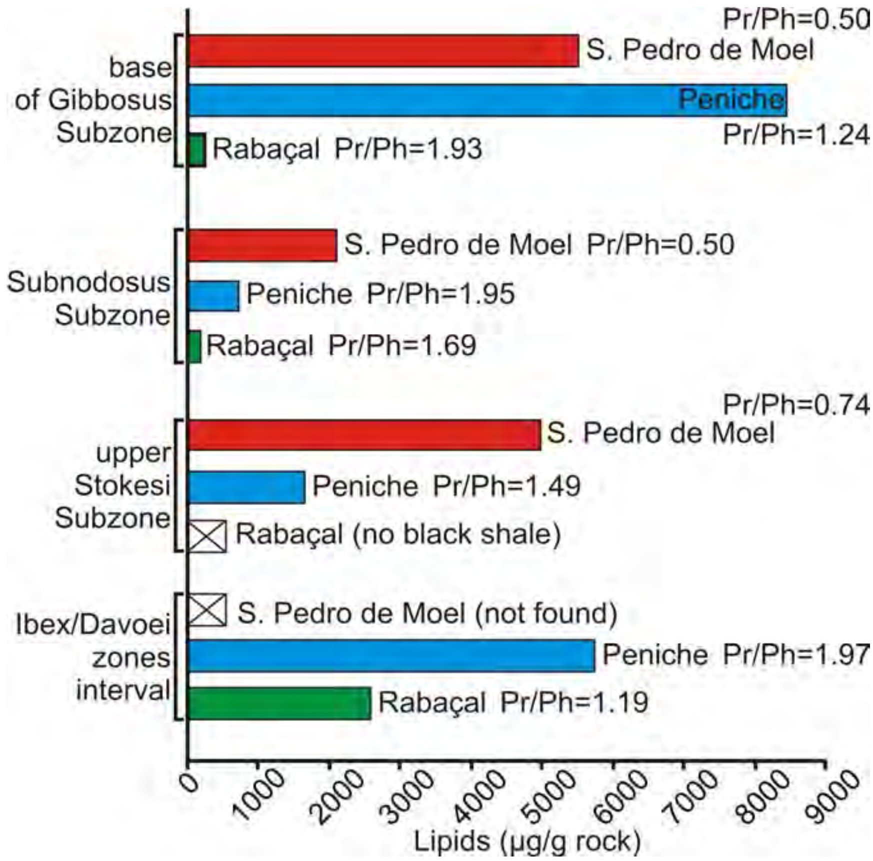


Fig. 4.3.4. Lateral and temporal variation of the lipids content and the pr/ph ratio in the Rabaçal, Peniche and S. Pedro de Moel outcrop sections.

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. 4.3.2), the samples from the Gibbosus Subzone present the highest lipid contents, whereas those from the Subnodosus Subzone present the lowest ones (Fig. 4.3.4). 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 2nd-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 4.3.1) and AOM contents (80% and 84%, respectively) but are markedly different with respect to AOM typology (Table 4.3.1). While AOM from sample PER 3 mostly corresponds to the type I (mucilaginous aggregates, Fig. 4.3.3A), in sample PER 4 it is composed of both types (mucilaginous aggregates and microbial biofilms, Fig. 4.3.3D). The presence of microbial biofilms suggests low sedimentation rates and/or environmental restriction linked to the maximum flooding interval of the 2nd-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), 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_2 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 4.3.1) 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 idea that the lipid content of the studied material can be used as a proxy to bottom water/early diagenesis O_2 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.

4.3.6. 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-bounds during early diagenesis (Sinninghe Damste et al., 1995 and references therein) and can be released during late diagenesis/early catagenesis due to cleavage of carbon-sulphur bounds (Sinninghe Damste 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 hydropyrolysis 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_o = 0.47 and T_{max} (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.

4.3.7. 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_2 concentrations are low. It has been demonstrated that $[O_2]$ 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.

References

ALLDREDGE, A.L., PASSOW, U. and LOGAN, B.E., 1993. The abundance and significance of a class of large, transparent organic particles in the ocean. Deep-Sea Research Part I: Oceanographic Research Papers, 40(6), 1131–1140.

AZERÊDO, A.C., WRIGHT, V.P. and RAMALHO, M.M., 2002. The Middle- Late Jurassic forced regression and disconformity in central Portugal: eustatic, tectonic and climatic effects on a carbonate ramp system. Sedimentology, 49(6), 1339–1370.

BALZANO, S., PANCOST, R.D., LLOYD, J.R. and STATHAM, P.J., 2011. Changes in fatty acid composition in degrading algal aggregates. Marine Chemistry, 124(1–4), 2–13.

BOWDEN, S.A., FARRIMOD, P., SNAPE, C.E. and GORDON, D.L., 2006. Compositional differences in biomarker constituents of the hydrocarbon, resin, asphaltene and kerogen fractions: An example from the Jet Rock (Yorkshire, UK). Organic Geochemistry, 37(3), 369–383.

BREGER, I.A. 1966. Geochemistry of lipids. Journal of the American Oil Chemists' Society, 43(4), 197–202.

BRUNEL, F., BONNET, L., RUGET, C., REY, J., MOUTERDE, R. and ROCHA, R., 1998. Variations des associations de Foraminifères dans Le Domerien du Bassin Lusitanien, en relation avec les fluctuations de l'environnement. Instituto Geológico e Mineiro, 84(1), A49–A52.

CAPONE, D.G., BRONK, D.A., MULHOLLAND, M.R. and CARPENTER, E.J., 2008. Nitrogen in the Marine Environment (2nd edition). Academic Press Publications (Elsevier).

COMBAZ, A. 1980. Les kerogènes vus au microscope,. In: DURAND, B. (ed.) Kerogen. Insoluble organic matter from sedimentary rocks. Editions Technip, Paris, pp. 55–111.

DECHO, A.W. and HERNDL, G.J., 1995. Microbial activities and the transformation of organic matter within mucilaginous material. Science of the Total Environment, 165(1–3), 33–42.

DELL'ANNO, A., MEI, M.L., PUSCEDDU, A. and DANOVARO, R., 2002. Assessing the trophic state and eutrophication of coastal marine systems: a new approach based on the biochemical composition of sediment organic matter. Marine Pollution Bulletin, 44(7), 611–622.

DING, H. and SUN, M.-Y. 2005. Biochemical degradation of algal fatty acids in oxic and anoxic sediment-seawater interface systems: effects of structural association and relative roles of aerobic and anaerobic bacteria. Marine Chemistry, 93(1), 1–19.

DUARTE, L.V., 2007. Lithostratigraphy, sequence stratigraphy and depositional setting of the Pliensbachian and Toarcian series in the Lusitanian Basin (Portugal), In: ROCHA, R.B., (ed.), The Peniche section (Portugal), Contributions to the definition of the Toarcian GSSP. International Subcommission Jurassic Stratigraphy, pp. 17–23.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F., 2010. Organic-Rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total organic carbon distribution and relation to transgressive-regressive facies cycles. Geologica Acta 8(3), 325–340.

DUARTE, L.V. and SOARES, A.F., 2002. Litostratigrafia das series margo-calcarias do Jurássico Inferior da Bacia Lusitânica (Portugal). Comunicações Instituto Geológico Mineiro, 89, 135–154.

EMERSON, S.R. and HEDGES, J.I., 2008. Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press.

FABIANO, M. and DANOVARO, R., 1994. Composition of organic matter in sediments facing a river estuarine (Tyrrhenian Sea): relationships with bacteria and microphytobenthic biomass. Hydrobiologia, 277(2), 71–84.

FARRIMOND, P., LOVE, G.D., BISHOP, A.N., INNES, H.E., WATSON, D.F. and SNAPE, C.E. 2003. Evidence for the rapid incorporation of hopanoids into kerogen. Geochimica et Cosmochimica Acta, 67(7), 1383–1394.

FERREIRA, R., MENDONCA FILHO, J.G., DUARTE, L.V., SILVA, R.L. and MENDONCA, J.O. 2010. Hydrocarbon generation potential of the Pliensbachian organic-rich series of Peniche (Lusitanian Basin, Portugal): An organopetrographic and thermal maturation assessment integrated analysis. In: PENA DOS REIS, R. and PIMENTEL, N. (eds), Rediscovering the Atlantic: New ideas for an old sea. Extended Abstracts. II Central & North Atlantic Conjugate Margins Conference, Lisbon, pp. 116–120.

GERCHAKOV, S.M. and HATCHER, P.G., 1972. Improved technique for analysis of carbohydrates in sediment. Limnology and Oceanography, 17, 938–943.

HEDGES, J.I., BALDOCK, J.A., GELINAS, Y., LEE, C., PETERSON, M.L. and WAKEHAM, S.G., 2002. The biochemical and elemental compositions of marine plankton: A NMR perspective. Marine Chemistry 78(1), 47–63.

HARTREE, E.F., 1972. Determination of protein: A modification of the Lowry method that gives a linear photometric response. Analytical Biochemistry, 48(2), 422–427.

HARVEY, H.R., TUTTLE, J.H. and BELL, J.T., 1995. Kinetics of phytoplankton decay during simulated sedimentation: Changes in biochemical composition and microbial activity under oxic and anoxic conditions. Geochimica et Cosmochimica Acta, 59(16), 3367–3377.

JENSEN, M.M., HOLMER, M. and THAMDRUP, B., 2005. Composition and diagenesis of neutral carbohydrates in sediments of the Baltic-North Sea transition. Geochimica et Cosmochimica Acta, 69(16), 4085–4099.

KEIL, R.G. and HEDGES, J.I., 1993. Sorption of organic matter to mineral surfaces and the preservation of organic matter in costal marine sediments. Chemical Geology, 107, 385–388.

KOHNEN, M.E.L., SINNIGHE DAMSTE, J.S., KOCK-VAN DALEN, A.C., TEN HAVEN, H.L., ROLLKOTTER, J. and DE LEEUW, J.W., 1990. Origin and diagenetic transformations of C25 and C30 highly branched isoprenoid sulphur componds: further evidence for the formations of organically bound sulphur during early diagenesis. Geochimica et Cosmochimica Acta, 54(11), 3053–3063.

KOHNEN, M.E.L., SCHOUTEN, S., SINNINGHE DAMSTE, J.S., DE LEEUW, J.W., MERRIT, D. and HAYES, J.M., 1992. Improved recognition of palaeobiochemicals by a combined molecular sulphur and isotope geochemical approach. Science 256, 358–362.

KOVAC, N., BAJT, O., FAGANELI, J., SKET, B. and OREL, B., 2002. Study of macroaggregate composition using FT-IR and 1H-NMR spectroscopy. Marine Chemistry, 78(4), 205–215.

LARGEAU, C. and DERENNE, S., 1993. Relative efficiency of the Selective Preservation and Degradation Recondensation pathways in kerogen formation. Source and environment influence on their contributions to type I and II kerogens. Organic Geochemistry, 20(5), 611–615.

LEE, C., WAKEHAM, S.G. and ARNOSTI, C., 2004. Particulate organic matter in the sea: the composition conundrum. AMBIO, 33(8), 565–575.

LU, D., SONG, Q. and WANG, X., 2010. Decomposition of algal lipids in clay-enriched marine sediment under oxic and anoxic conditions. Chinese Journal of Oceanology and Limnology, 28(1), 131–143.

MARSH, J.B. and WEINSTEIN, D.B., 1966. A simple charring method for determination of lipids. Journal of Lipid Research, 7, 574–576.

MENDONCA FILHO, J.G., 1999. *Aplicação de estudos de Palinofácies e fácies Orgânica em rochas do Paleozóico da Bacia do Paraná, Sul do Brasil*. Ph.D. thesis, Universidade Federal do Rio Grande do Sul, Rio Grande do Sul, Brazil.

MENDONCA FILHO, J.G., CARVALHO, M.A. and MENEZES, T.R. 2002. Palinofacies. In: Dutra, T.L. (ed.) Técnicas e Procedimentos para o Trabalho com Fósseis e Formas Modernas Comparativas. Unisinos, São Leopoldo, pp. 20–24.

MENDONCA FILHO, J.G., CHAGAS, R.B.A., MENEZES, T.R., MENDONCA, J.O., DA SILVA, F.S. and SABADINI-SANTOS, E., 2010a. Organic facies of the Oligocene lacustrine system in the Cenozoic Taubate basin, Southern Brazil. International Journal of Coal Geology, 84(3–4), 166–178.

MENDONCA FILHO, J.G., ARAUJO, C.V., BORREGO, A.G., COOK, A., FLORES, D., HACKLEY, P., HOWER, J.C., KERN, M.L., KOMMEREN, K., KUS, J., MASTALERZ, M., MENDONCA, J.O., MENEZES, T.R., NEWMAN, J., RANASINGHE, P., SOUZA, I.V.A.F., SUAREZ-RUIZ, I. and UJIIE, Y. 2010b., Effect of concentration of dispersed organic matter on optical maturity parameters: Interlaboratory results of the organic matter concentration working group of the ICCP. International Journal of Coal Geology, 84(3–4), 154–165.

MENDONCA FILHO, J.G., MENEZES, T.R. and MENDONCA, J.O., 2011. Chapter 5: Organic composition (Palynofacies Analysis). In: FLORES, D. & MARQUES, M. (eds), ICCP Training Course on Dispersed Organic Matter. International Committee for Coal and Organic Petrology, Porto, pp. 33–81.

MENDONCA FILHO, J.G., MENEZES, T.R., MENDONCA, J.O., OLIVEIRA, A.D., CARVALHO, M.A., SANT'ANNA, A. J. and SOUZA, J. T., 2010c. Palinofácies. In: SOUZA CARVALHO, I. (ed.) Paleontologia. Interciência, Rio de Janeiro, pp. 379–413.

MENEZES, T.R., MENDONCA FILHO, J.G., ARAUJO, C., SOUZA, I.V.A.F. and MENDONCA, J.O., 2008. Facies Orgânica: conceitos, métodos e estudos de casos na indústria do petróleo. Revista Brasileira de Geociências, 38, 80–96.

MOODLEY, L., NIGAM, R., INGOLE, B., PRAKASH BABU, C., PANCHANG, R., NANAJKAR, M., SIVADAS, S., VAN BREUGEL, P., VAN IJZERLOO, L., RUTGERS, R., HEIP, C.H.R., SOETAERT, K. and MIDDELBURG, J.J., 2011. Oxygen minimum seafloor ecological (mal) functioning. Journal of Experimental Marine Biology and Ecology, 398(1–2), 91–100.

MOUTERDE, R., DOMMERGUES, J.-L., MEISTER, C. and ROCHA, R.B., 2007. Atlas des fossiles caracteristiques du Lias portugais. III a) Domerien (Ammonites). Ciências da Terra, 16, 67–111.

MURRAY, I.P., LOVE, G.D., SNAPE, C.E. and BAILEY, N.J.L., 1998. Comparison of covalently-bound aliphatic biomarkers released via hydropyrolysis with their solvent-extractable counterpart for a suite of Kimmeridge clays. Organic Geochemistry, 29(5–7), 1487–1505.

N'ZABA-MAKAYA, O., ANDREU, B., BRUNEL, F., MOUTERDE, R., REY, J. and ROCHA, R.B., 2003. Biostratigraphie et paléoécologie des peuplements d'ostracodes dans le Domérien du Bassin Lusitanien, Portugal. Ciências da Terra, 15, 21–44.

NGUYEN, R.T. and HARVEY, H.R., 2001. Preservation of protein in marine systems: Hydrophobic and other noncovalent associations as major stabilizing forces. Geochimica et Cosmochimica Acta, 65(9), 1467–1480.

OLIVEIRA, L.C.V., RODRIGUES, R., DUARTE, L.V. and LEMOS, V., 2006. Avaliação do potencial gerador de petróleo e interpretação paleoambiental com base em biomarcadores e isótopos estáveis do carbono da secção Pliensbaquiano-Toarciano inferior (Jurássico inferior) da região de Peniche (Bacia Lusitânica, Portugal). Boletim Geociências Petrobras, 14(2), 207–234.

OZAKI, K., TAJIMA, S. and TAJIKA, E., 2011. Conditions required for oceanic anoxia/euxinia: Constraints from a one-dimensional ocean biogeochemical cycle model. Earth and Planetary Science Letters, 304(1–2), 270–279.

PACTON, M., FIET, N. and GORIN, G.E., 2007. Bacterial activity and preservation of sedimentary organic matter: The role of exopolymeric substances. Geomicrobiology Journal, 24 (7–8), 571–581.

PAN, C., PENG, D., ZHANG, M., YU, L. SHENG, G. and FU, J., 2008. Distribution and isomerization of C31–C35 homohopanes and C29 steranes in oligocene saline lacustrine sediments from Qaidam Basin, Northwest China. Organic Geochemistry, 39(6), 646–657.

PANTOJA, S., GUTIERREZ, M.H., AMPUERO, P. and TEJOS, E., 2011. Degradation capability of the coastal environment adjacent to the Itata River in central Chile (36.5° S). Biogeoscience Discussions, 8, 1335–1367.

PARRISH, J.T., 1995. Paleogeography of C_{org}-rich rocks and the preservation versus production controversy,. *In* HUC, A.-Y. (ed.), Paleogeography, paleoclimate, and source rocks. AAPG Studies in Geology 40, AAPG, Tulsa, pp. 1–20.

PETERS, K.E., WALTERS, C.C. and MOLDOWAN, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in Petroleum Exploration and Earth History (2nd edition). Cambridge University Press, Cambridge.

PUSCEDDU, A., BIANCHELLI, S., CANALS, M., SANCHEZ-VIDAL, A., DE MADRON, X.D., HEUSSNER, S., LYKOUSIS, V., DE STIGTER, H., TRINCARDI, F. and DANOVARO, R., 2010. Organic matter in sediments of canyons and open slopes of the Portuguese, Catalan, Southern Adriatic and Cretan Sea margins. Deep Sea Research Part I: Oceanographic Research Papers, 57(3), 441–457.

RICE, D.L. 1982. The detritus nitrogen problem: new observations and perspectives from organic geochemistry. Marine Ecology – Progress Series, 9, 153–162.

SINNINGHE DAMSTE, J.S., VAN DUIN, A.C.T., HOLLANDER, D., KOHNEN, M.E.L. and DE LEEUW, J.W., 1995. Early diagenesis of bacteriohopanepolyol derivatives: Formation of fossil homohopanoids. Geochimica et Cosmochimica Acta, 59(24), 5141–5147.

SCHOUTEN, S., DE GRAAF, W., SINNINGHE DAMSTE, J.S., VAN DRIEL, G.B. and DE LEEUW, J.W., 1994. Laboratory simulation of natural sulphurisation: II. Reaction of multi-functionalized lipids with inorganic polysulphides. Organic Geochemistry, 22(3–5), 825–834.

SIMON, M., GROSSART, H.-P., SCHWEITZER, B. and PLOUG, H., 2002. Microbial ecology of organic aggregates in aquatic ecosystems. Aquatic Microbial Ecology, 28, 175–211.

SILVA, F.S., SABADINI SANTOS, E., LAUT, L.L.M., SANCHEZ-NUÑES, L., DA FONSECA, E.M., BAPTISTA-NETO, J.A.,MENDONCA FILHO, J.G. and CRAPEZ, M.A.C., 2010. Geomicrobiology and biochemical composition of two sediment cores from Jurujuba Sound-Guanabara Bay – SE Brazil. Anuário do Instituto de Geociências-UFRJ, 33(2), 24–35.

SILVA, R.L., DUARTE, L.V., AZERÊDO, A.C. and MENDONCA FILHO, J.G., 2011a. Contributos sedimentologicos e geoquimicos para a modelacão dos sistemas petroliferos portugueses: as series jurassicas ricas em materia organica da Bacia Lusitanica (Portugal). In: *Modelação de Sistemas Geológicos*. Laboratorio de Radioactividade Natural da Universidade de Coimbra, Coimbra, 383–391.

SILVA, R.L., DUARTE, L.V., COMAS-RENGIFO, M.J. and AZERÊDO, A.C. 2010a. Top Ibex-Margaritatus (Pliensbachian) series of the Lusitanian Basin (Portugal): sedimentology, events and high-resolution correlation. Abstract book of the Special meeting of the Société Géologique de France in honor of Serge Elmi, 95–96

SILVA, R.L., DUARTE, L.V., COMAS-RENGIFO, M.J., MENDONCA FILHO, J.G. and AZERÊDO, A. C., 2011b. Update of the carbon and oxygen isotopic records of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma): Insights from the organic-rich hemipelagic series of the Lusitanian Basin (Portugal). Chemical Geology, 283, 177–184.

SILVA, R.L., MENDONCA FILHO, J.G., DUARTE, L.V., COMAS-RENGIFO, M.J.,AZERÊDO, A.C. and FERREIRA, R. 2010b. Organic-rich facies of the top Ibex–Margaritatus zones (Pliensbachian) of the Lusitanian Basin (Portugal): TOC and biomarkers variation. Geochimica et Cosmochimica Acta, 74(12-S1), A962.

SUN, M.-Y.,ALLER, R.C., LEE, C. and WAKEHAM, S.G., 2002. Effects of oxygen and redox oscillation on degradation of cell-associated lipids in superficial marine sediments. Geochimica et Cosmochimica Acta, 66(11), 2003–2012.

TEGELAAR, E.W., DE LEEUW, J.W., DERENNE, S. and LARGEAU, C., 1989. A reappraisal of kerogen formation. Geochimica et Cosmochimica Acta, 53(11), 3103–3106.

TISSOT, B.P. and WELTE, D.H., 1978. Petroleum formation and occurrence. A new approach to oil and gas exploration. Springer Verlag.

TYSON, R.V. 1995. Sedimentary organic matter. Organic Facies and Palynofacies. Chapman & Hall.

VANDENBROUCKE, M. and LARGEAU, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry 38(5), 719–833.

VERDUGO, P., ALLDREDGE, A.L., AZAM, F., KIRCHMAN, D.L., PASSOW, U. and SANTSCHI, P.H., 2004. The oceanic gel phase: a bridge in the DOM–POM continuum. Marine Chemistry, 92, 67–85.

VERSTEEGH, G.J.M., ZONNEVELD, K.A.F. and DE LANGE, G.J., 2010. Selective aerobic and anaerobic degradation of lipids and palynomorphs in the Eastern Mediterranean since the onset of sapropel S1 deposition. Marine Geology, 278(1–4), 177–192.

ZONNEVELD, K.A.F., VERSTEEGH, G.J.M., KASTEN, S., EGLINTON, T.I., EMEIS, K.-C., HUGUET, C., KOCH, B.P., DE LANGE, G.J., DE LEEUW, J.W., MIDDELBURG, J.J., MOLLENHAUER, G., PRAHL, F.G., RETHEMEYER, J. and WAKEHAM, S.G., 2010. Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record. Biogeosciences, 7, 483–511.

Acknowledgements

This work is a contribution to project PTDC/CTE-GIX/098968/2008 "High resolution stratigraphy of the Lower Jurassic organic-rich marine series in the Lusitanian Basin", supported by the FCT-MCTES and COMPETE-FEDER (Portugal). We thank Maria Jose Comas-Rengifo for the help with the biostratigraphic data and the reviewers Achim Bechtel and Bohdan Křibek for their significant contributions to improve the original manuscript. R.L. Silva wishes to acknowledge the FCT-MCTES for his Ph.D. fellowship (SFRH/BD/47362/2008), L.V. Duarte the project PEst-C/MAR/UI0284/2011 and A.C. Azerêdo the project PEst-OE/CTE/UI0263/2011.

Capítulo 5 | Oxfordiano: Formação de Cabaços

5.1. Palynofacies and TOC analysis of marine and non-marine sediments across the Middle-Upper Jurassic boundary in the Central-Northern Lusitanian Basin (Portugal)

Ricardo L. Silva, João G. Mendonça Filho, Ana C. Azerêdo, Luís V. Duarte. *In press, Facies.*
DOI: 10.1007/s10347-013-0369-x

Abstract

The Middle–Upper Jurassic transition is a geodynamic benchmark in the evolutionary story of several peri-Atlantic basins. Contrary to the vast Tethyan and peri-Tethyan areas, in the Lusitanian Basin (Portugal), this interval corresponds to a major basinwide disconformity preceded by a complex forced regression which induced sharp facies variations across the depositional systems. The Middle Jurassic units below are fully marine, whereas the Upper Jurassic sediments (lower?-middle Oxfordian), correspond to freshwater/brackish lacustrine, grading into punctuated brackish-restricted lagoonal and shallow-marine palaeoenvironments.

This study presents Total Organic Carbon and palynofacies data of 34 samples (total analysed thickness of about 85 metres) collected from three key sections encompassing the Middle-Upper Jurassic transition in the central-northern sectors of the Lusitanian Basin. The palynofacies of the analysed part of Middle Jurassic units (Cabo Mondego Formation) are characteristic of marine environments at their base, evidencing upwards a regressive trend of the depositional systems. Total Organic Carbon content is generally low, reaching up to 1.94 wt%. The Upper Jurassic Cabaços Formation presents kerogen assemblages mostly of continental origin, although punctuated by minor intervals of marine influence. Total Organic Carbon content is more variable, reaching up to 30.56 wt.%. Intraclasts of redeposited fragments of microbial mats were found incorporated in the kerogen assemblages, which point to highly dynamic erosional and depositional processes. Diversity of *Botryococcus* sp. occurrences was confirmed as an indicator of degree of palaeoenvironmental stability.

The vertical distribution and comparison of the kerogen assemblages of the different sections put in evidence major changes of these parameters among relatively close settings and along narrow vertical intervals, attesting the high sedimentary dynamics observed in the Lusitanian Basin.

Keywords: Total Organic Carbon; Palynofacies; Microbial mat intraclasts; Middle–Upper Jurassic; Lusitanian Basin, Portugal

5.1.1. Introduction

The prospect for hydrocarbons is based on a wide range of methodologies, one being the development of a geodynamic basin model aiming at deduction of several properties of the rock bodies in a particular area of exploration. Palynofacies analysis is one of the tools that are currently included in the full spectrum of basin analysis and in production of geological models as it allows the direct quantification and qualification of the organic matter present in a specific rock. Studies of palynofacies may be helpful in designing geological models for carbonate sedimentary systems is difficult, mainly because they require an extensive knowledge about the various physical, chemical, geological and biological parameters that govern deposition in these environments. Palynofacies analysis gives information about organic matter provenance and palaeobiological and sedimentary dynamics, besides providing an idea about oil and gas generation potential (e.g. Muller, 1959; Batten, 1973, 1991, 1996; Tyson, 1984, 1993, 1995; Bustin, 1988; Traverse, 1988, 2007; Williams, 1992; Batten and Stead, 2005; Martín-Closas et al., 2005; Zavattieri et al., 2008; Pieńkowski and Waksmundzka, 2009; Mendonça Filho et al., 2011, 2012). Tyson (1995) introduced the modern concept of palynofacies, in which it corresponds to *a body of sediment containing a distinctive assemblage of palynological organic matter thought to reflect a specific set of environmental conditions or to be associated with a characteristic range of hydrocarbon-generating potential*. Kerogen, for the purpose of this study, consists in the particulate organic matter residue isolated from a sedimentary rock after complete dissolution of the rock matrix with HCl and HF (non-oxidative acids) (e.g. Tyson, 1995; Zavattieri et al., 2008; Mendonça Filho et al., 2012).

The aim of this work is to present, for the first time, a Total Organic Carbon (TOC) and palynofacies survey of the Middle–Upper Jurassic boundary units (Cabo Mondego and Cabaços Formation) in the Central-Northern sectors of the Lusitanian Basin, based on three key sections of this basin: Cabo Mondego (Figueira da Foz), Pedrógão and Vale de Ventos (Maciço Calcário Estremenho). The former two sections are located in the West of the basin (coastline) and the latter in the East (Fig. 5.1.1). Perceiving the palaeoenvironmental parameters that allowed the preservation of OM in these units, in particular in the Cabaços Formation, is of importance for the current works related to hydrocarbon exploration in the Lusitanian Basin and neighboring basins.

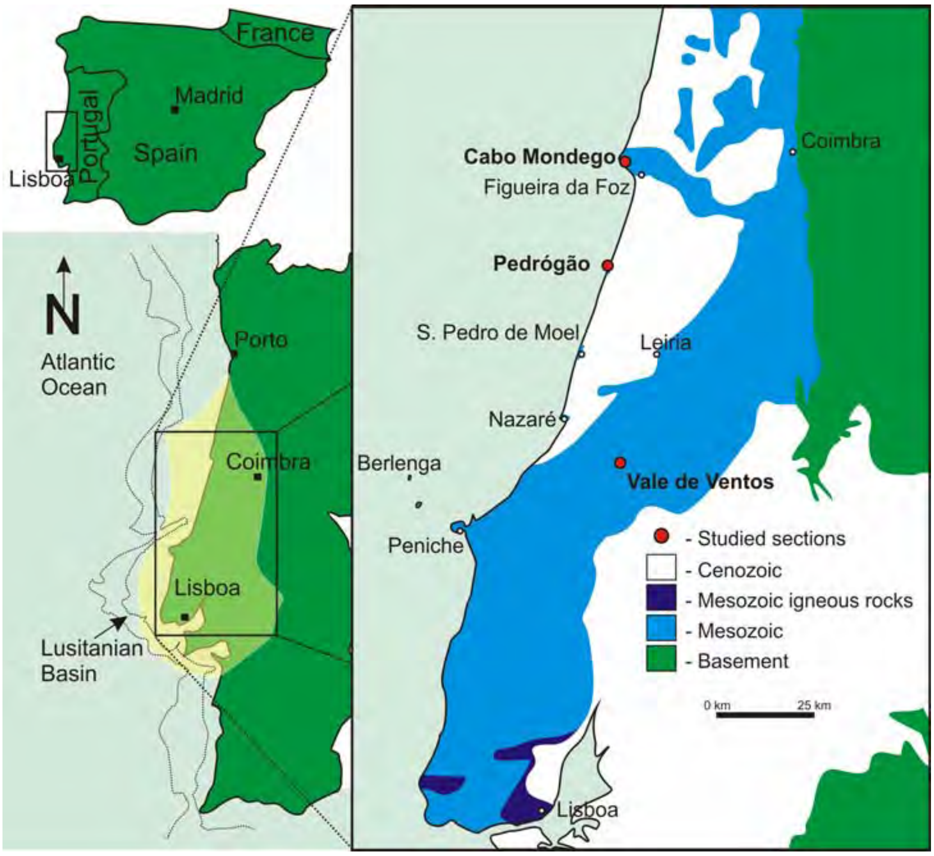


Fig. 5.1.1. Simplified geological map of the Lusitanian Basin, highlighting the distribution of sediments of Jurassic age, and location of the studied sections.

5.1.2. Geological background

The Lusitanian Basin is a small, narrow North-South elongated basin, located at the western side of the Iberian Massif and, as several other Mesozoic peri-Tethyan basins, its origin is linked to the opening of the Atlantic Ocean (e.g. Wilson et al., 1989). The sedimentary infill of this basin is exclusively of Mesozoic age (ranging from the Triassic to the Cretaceous), covered by Cenozoic deposits (e.g. Wilson et al., 1989; Pinheiro et al., 1996; Rasmussen et al., 1998; Alves et al., 2002). Most of these sediments are of Jurassic age and carbonates compose much of the stratigraphic series (e.g. Azerêdo et al., 2003; Duarte et al., 2010).

During the Jurassic, two main extension and rifting episodes have conditioned the development of the Lusitanian Basin (e.g. Wilson et al., 1989; Pinheiro et al., 1996). The first, of Triassic age, marks the onset of the development of this basin, creating an irregular topography of fault-bounded blocks (e.g. Wilson et al., 1989) in-filled by the red siliciclastic and evaporitic facies belonging to the Silves and Dagorda Formations of Triassic–Hettangian age (Fig. 5.1.2). The Sinemurian–Callovian deposits are mostly represented by carbonates nature and represent deposition during a major phase of quiescence, although punctuated by minor episodes of tectonic activity (e.g. Soares et al., 1993; Azerêdo et al., 2003). The sedimentary series of this age are informally divided in the Coimbra (dolostones, dolomitic limestones and limestones), Candeeiros (inner ramp limestones) and Brenha (mid-outer ramp marls and limestones) groups (e.g. Witt, 1977; GPEP, 1986; Wilson et al., 1989; Rasmussen et al., 1998) (Fig. 5.1.2). The second major episode of rifting and extension occurred during the Late Jurassic and Cretaceous and led to the separation between Iberia and Newfoundland areas (e.g. Pinheiro et al., 1996). The first deposits are still carbonates (e.g. Cabaços and Montejunto formations) but rapidly the sedimentation gains a siliciclastic character which predominates until the closure of the basin during the late Cretaceous (e.g. Leinfelder and Wilson, 1989, 1998; Rey et al., 2006).

Within the evolutionary context of the Lusitanian Basin, the Middle–Upper Jurassic transition is one of its most important geodynamic phases (Fig. 5.1.2), corresponding to a major basinwide disconformity and stratigraphic gap, spanning from the latest Callovian to the early Oxfordian in the west whereas, to the east, it locally develops on upper Bathonian limestones (e.g. Ruget-Perrot, 1961; Ramalho, 1971; Mouterde et al., 1979; Azerêdo et al., 1998, 2002a, b). The development of the disconformity was preceded by a complex forced regression, inducing sharp facies variations across the depositional system (Azerêdo et al., 2003). To the east (as observed at Vale de Ventos) inner ramp upper Bathonian carbonates (Serra de Aire Formation; Azerêdo, 2007) are capped by a major erosional and exposure surface whereas, to the west, as at Cabo Mondego (Figueira da Foz) and Pedrógão, upper Callovian mid-outer ramp deposits (Cabo Mondego Formation, sensu Azerêdo et al., 2003) evolve to littoral facies through more subtle discontinuities. The oldest Upper Jurassic sediments resting on the disconformity (lower-middle Oxfordian; Cabaços Formation) correspond to freshwater/brackish lacustrine, restricted lagoonal and shallow-marine palaeoenvironments (Azerêdo et al., 2002a; Azerêdo and Cabral, 2004; Azerêdo and Wright, 2004). The lack of good biostratigraphic biomarkers hampers a precise age assignment of this unit, though available data suggest an Oxfordian age. In the west and south of the basin (namely at Cabo Mondego, Pedrógão, Serra d'El-Rei and Serra de Montejunto), the Middle Jurassic immediately below the disconformity is dated according to ammonite biostratigraphy (Ruget-Perrot, 1961; Mouterde et al., 1979; Alméras et al., 1991) as Upper Callovian, reaching up to the Athleta Zone only at Pedrógão (the uppermost Callovian Lamberti Zone is not recognized).

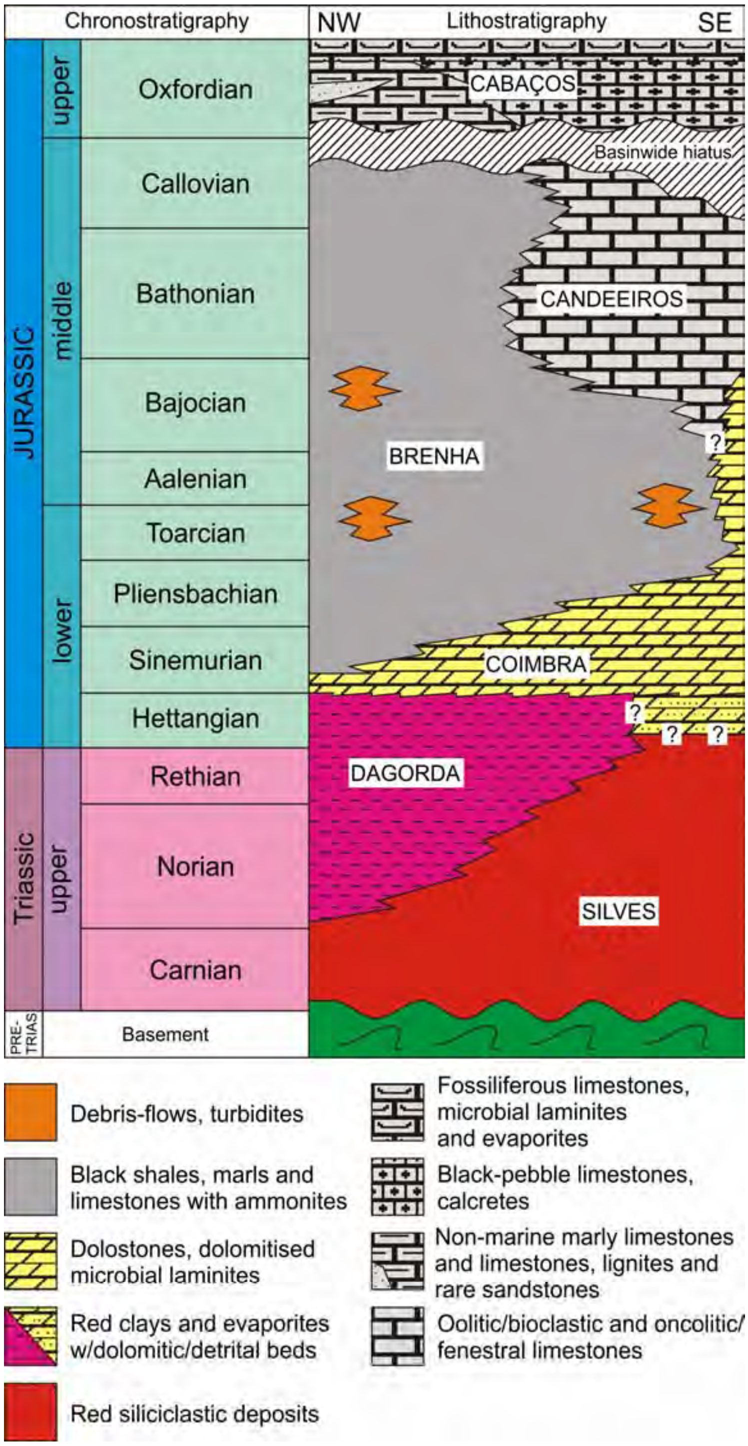


Fig. 5.1.2. Generic lithostratigraphic scheme of the Triassic–lowermost Upper Jurassic sedimentary series of the Lusitanian Basin (modified from Azerêdo et al., 2002a and references therein).

The lowermost deposits of the Cabaços Formation have no age-diagnostic fossils and it is possible that they could encompass the Lower Oxfordian or even the uppermost Callovian, as clearly stated by Azerêdo et al. (2002a). Towards the intermediate part of the unit there is a consistent occurrence of the dasycladacean *Heteroporella lusitanica* (Ramalho,

1970) across the basin, suggesting the Oxfordian age. This is also true for the classical type region of Torres Vedras (south of the basin) in levels that are apparently equivalent to, or immediately underlying, marine intercalations where a few ammonite findings were documented by Choffat (1893), belonging to the middle Oxfordian Transversarium Biozone (cf. Ruget-Perrot, 1961; Ramalho, 1971, 1981). In addition, the overlying marine Montejunto Formation yielded ammonites of middle and late Oxfordian age high above those with *H. lusitanica* (cf. Ruget-Perrot, 1961; Mouterde et al., 1979). Over the whole of the basin (including Cabo Mondego, Pedrogão and Vale de Ventos sections), towards the middle-upper part of the Cabaços Formation, which becomes gradually more shallow-marine influenced, the lituolid foraminifera *Alveosepta jaccardi* (Schrodt, 1894) (middle Oxfordian-Kimmeridgian) and *Pseudocyclammina parvula* Hottinger, 1967 (Middle Oxfordian-Tithonian) appear (e.g. Ramalho, 1971, 1981; Leinfelder et al., 1988; Azerêdo et al., 1998, 2002a, b). Using the *H. lusitanica* beds as an approximate correlation interval, the best age fit for the Cabaços Formation is early?-middle Oxfordian, less possibly spanning until initial late Oxfordian. Moreover, recent age results obtained by Schneider et al. (2009) using an independent methodology (Sr isotopes determined in oysters from the Cabaços Formation and other Upper Jurassic units from the basin), are in agreement with the assumed dating. Until new data justifies differently, the stratigraphic constraint of the Cabaços Formation is kept as stated.

The sea-level fall observed in the Lusitanian Basin during the Middle–Late Jurassic transition is also recorded elsewhere within the peri-Atlantic (e.g. Ramajo and Aurell, 2008) and Tethyan (e.g. Dromart et al., 2003a) regions, though there are differences in timing of sea-level pulses and a few singularities in the Lusitanian Basin (e.g. Azerêdo et al., 2002a and references therein). In the latter, the expression of this event is somewhat distinct from similar basins, namely the forced regression preceding the onset of combined fluctuations eventually leading to reflooding, the signature of prolonged exposure and the subtle changes in climatic conditions. For the Lusitanian Basin, in particular, Wilson et al. (1989) suggested that the Callovian–Oxfordian disconformity could be related to a Middle Callovian jump in the location of the ocean ridge of the newly opened southern North Atlantic, while Leinfelder (1993) considered that it resulted from regional European tectonics related to North Atlantic and West Tethys rifting.

Nevertheless, Middle-Late Jurassic geotectonic development and sea-level changes in the Lusitanian and other peri-Atlantic basins differs dramatically from geodynamics and sedimentary development of the whole Tethyan and peri- Tethyan Europe, showing quite opposite tectonic and sedimentary trends. Based in paleomagnetic and biostratigraphical data (see Lewandowski et al. 2005), it was suggested that during the Middle Callovian–Early Oxfordian time span, a relatively fast opening of oceanic domain took place in the Tethys, which was associated with sudden deepening of sea, upwelling of cold oceanic waters into the epi-platform areas, chemical corrosion of earlier accumulated carbonates and appearance of condensed deposits. This major geotectonic sea-floor spreading phase was named "Metis Geotectonic Event" (Matyja and Wierzbowski 2006). It is clear that the Middle–Late Jurassic transition corresponds to an important change in the tectonic and palaeoceanographic conditions over a large region of the globe resulting, for example, in intense mid-ocean ridge hydrothermal activity (Jones et al. 1994), change in ocean chemistry (e.g. Rais et al. 2007), and drastic cooling of sea water at lower and middle latitudes (Dromart et al. 2003b).

In the Jurassic geological record of the Lusitanian Basin (Portugal), various intervals rich in organic matter are recognized. Of these, only two are of basin-wide extent: the MLOF mb (marly limestones with organic-rich facies member) of Vale das Fontes Formation, representing Pliensbachian age (Duarte et al. 2010; Silva et al. 2011a) and the Cabaços Formation (early?/middle Oxfordian) (e.g. Azerêdo et al. 2002a, Silva et al. 2011a).

5.1.3. Description of the studied sections

The Cabo Mondego (Figueira da Foz), Pedrógão and Vale de Ventos (Maciço Calcário Estremenho) sections represent the best records of the Middle–Upper Jurassic transition in the Lusitanian Basin and, consequently, have been the focus of detailed sedimentological, paleontological and palynological studies (e.g. Ruget-Perrot, 1961; Azerêdo et al., 1998, 2002a, b; Colin et al., 2000; Cabral and Colin, 2002; Barrón and Azerêdo, 2003; Pereira et al., 2003; Azerêdo and Cabral, 2004; Azerêdo and Wright, 2004). The main features of the analysed intervals from each section are summarized below; a more detailed account may be found in Wright (1985), Azerêdo et al. (1998, 2002a) and Barrón and Azerêdo (2003).

5.1.3.1. Cabo Mondego section

The Cabo Mondego section is located at Cabo Mondego, Figueira da Foz (Fig. 5.1.1). Due to accessibility issues the samples have been taken from two different locations, but the series can be confidently reconstructed (Figs 5.1.3 and 5.1.4). The Cabo Mondego Formation was sampled in an outcrop located about 200 meters south of the Cabo Mondego lighthouse and the Cabaços Formation was sampled in the outcrop located inside the CIMPOR cement factory. The Cabo Mondego Formation at the studied site is mainly composed of marl–limestone alternations with a marine macrofossil assemblage including, among others, brachiopods, bivalves and ammonites.

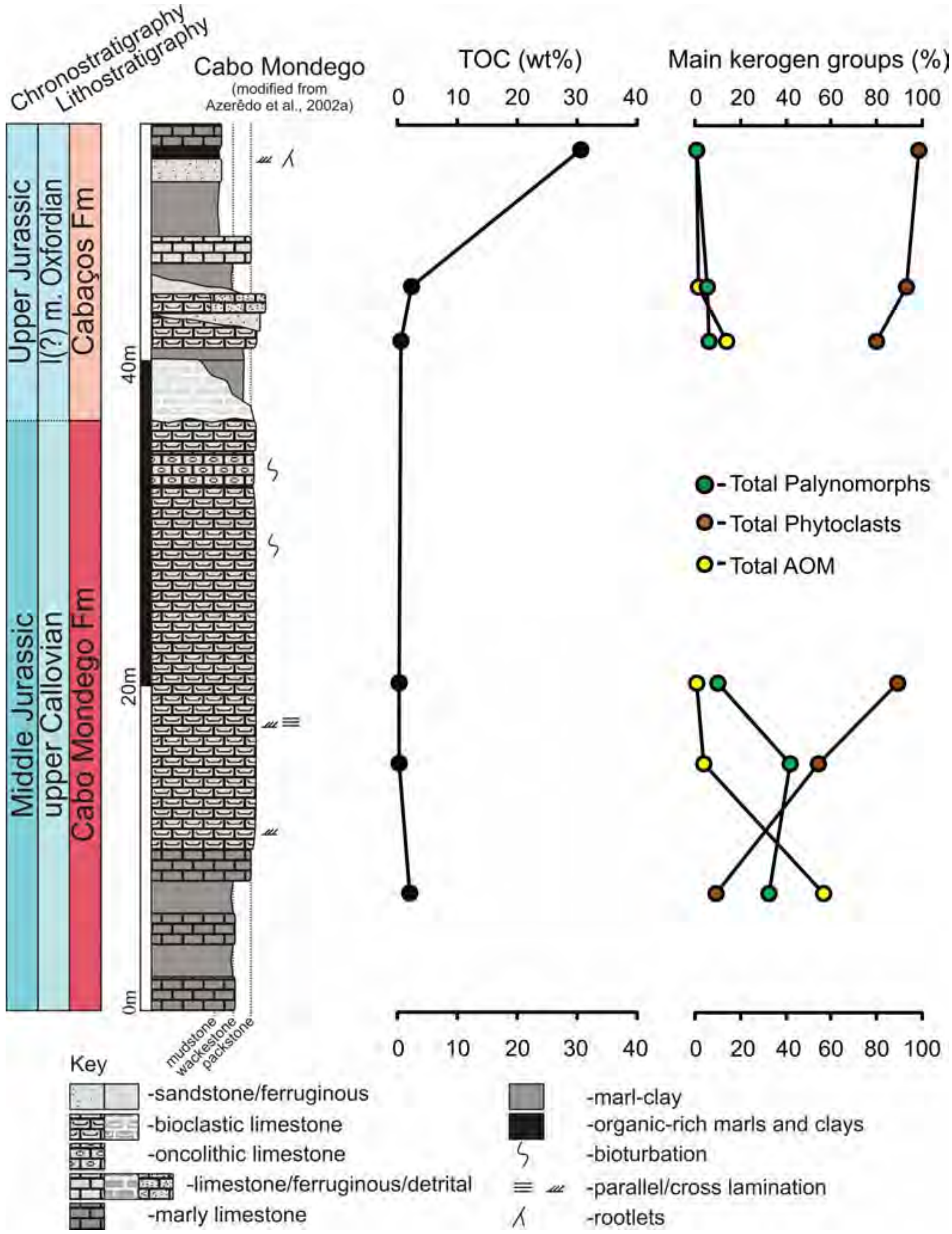


Fig. 5.1.3. Main stratigraphic features, TOC and phytoclasts, AOM and palynomorphs data from the Cabo Mondego section, Figueira da Foz (Lusitanian Basin, Portugal). Please notice that only the studied interval is represented in the stratigraphical column; for complete section the reader may refer to Azerêdo et al. (2002a).

Fig. 5.1.4. Field aspects of the Cabo Mondego section at Cabo Mondego, Figueira da Foz (Lusitanian Basin, Portugal); a) upper part of the Cabo Mondego Formation (upper Callovian) (sample CM2); b) general view of the base of the Cabaços Formation; c) uppermost part of the studied interval, sample CM6; d) dinosaur footprint observed higher in the section (the foot print is about 30cm wide).

The uppermost part of this unit is represented by a 30 metres-thick carbonate sandbody, sharply overlaying the marl–limestone alternations (Wright, 1985; Azerêdo and Wright, 2004). The top is marked by an irregular, scalloped and bored surface which, according to Azerêdo et al., (2002a), represents the Middle–Upper Jurassic disconformity (see Carapito Krausshar, 2008 for a contrasting point of view). The last metres of the marl–limestone alternations (Fig. 5.1.4a) and a few marly intervals at the base of the carbonate sandbody were sampled.

Only the first 15 metres of the Cabaços Formation were studied and the samples were chosen from exemplary lithofacies, representing the common marly lithotypes of this section. The series starts (about 6.5 metres) with an association of sandstones with oysters, *in situ* oyster-coral bioherms, coral rudstones, oyster-rich mudstones and bioclastic limestones with corals (Fig. 5.1.4b). The uppermost part of the studied interval consists of limestones, mudstones, shales and sandstones, where the organic-rich facies are particularly visible (Fig. 5.1.4c). The entire series records large scale fluctuations in marine versus freshwater influence, clearly depicted in the fossil assemblages (see Azerêdo et al., 2002a, b). Overall, the marine influence decreases upwards, where dinosaur footprints can be observed (Fig. 5.1.4d). These series are interpreted as representing evidence of the development of a costal sedimentation, represented by partly vegetated brackish to freshwater embayments and lagoons and relatively small deltas (Wright, 1985; Azerêdo et al., 2002a; Azerêdo and Wright, 2004).

The previous authors support their interpretation in the lack of evidence of significant tidal cyclicity or other tidal features, the thinness and often lenticular nature of the sandstone units, with mixed in-situ oyster-coral bioherms and coral debris but laterally passing to low-energy depositional processes, which altogether they considered to be reminiscent of small deltaic influxes within mixed marine-brackish, low-energy shallow lagoons.

5.1.3.2. Pedrógão section

The Pedrógão section is located about 30 kilometres south of Figueira da Foz (Figs. 5.1.1, 5.1.5 and 5.1.6). At its base, the studied interval (~9 metres) of the Cabo Mondego Formation is essentially marly with some limestone intercalations and includes a diversified assemblage of marine benthonic and nektonic fauna, for example, brachiopods, bivalves, echinoderms, foraminifers, ostracods, and ammonites (e.g. Azerêdo et al., 2002a; Azerêdo and Cabral, 2004). The latter allows dating this part of the section from the Upper Callovian, Athleta Biozone (Ruget-Perrot, 1961; Alméras et al., 1991). Towards the top, the series becomes more calcareous, presents minor erosion surfaces and the faunal assemblages change into shallow marine ones with reworked non-marine (e.g. charophytes) fossils (Fig. 5.1.6a).

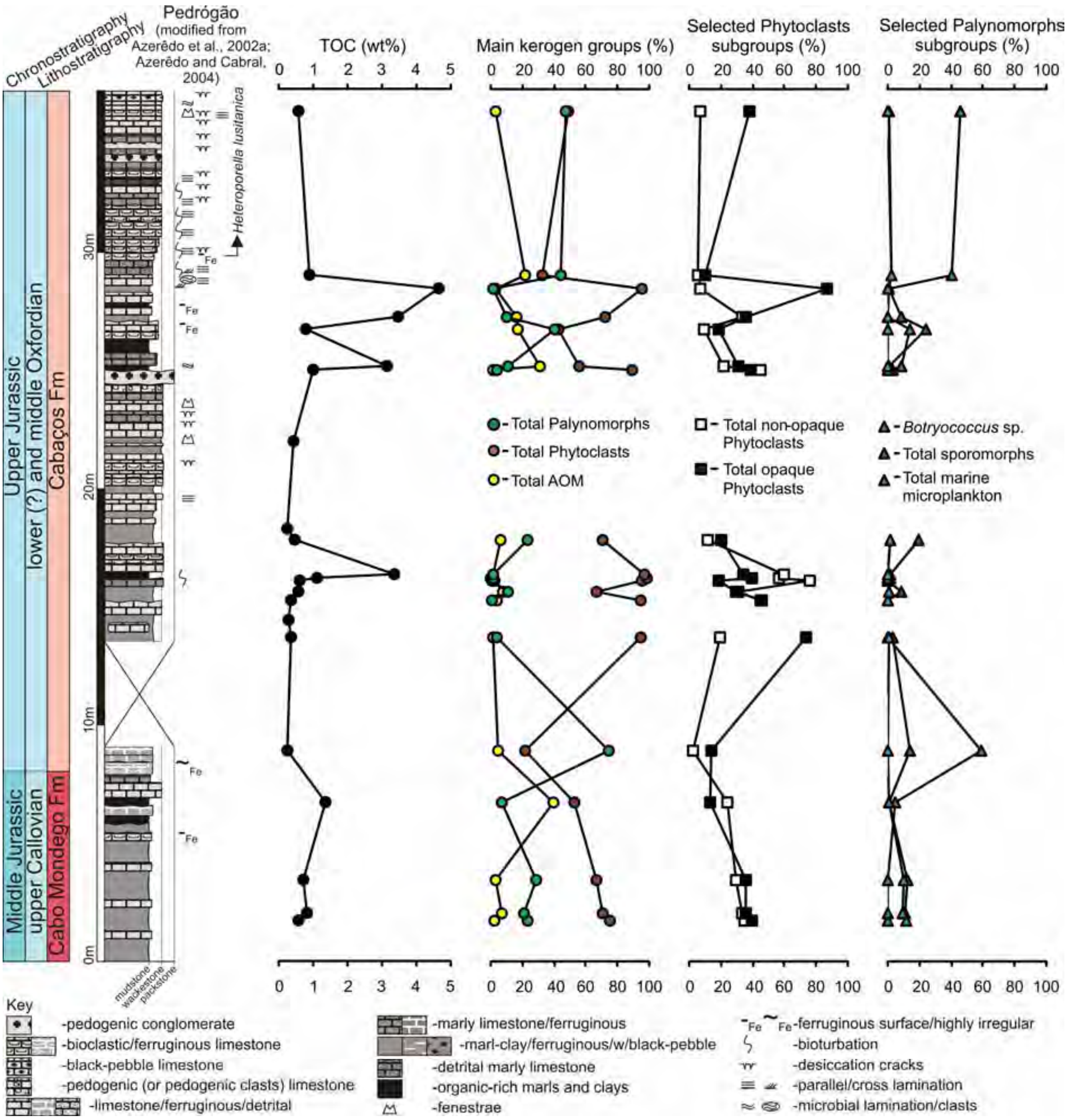


Fig. 5.1.5. Main stratigraphic features, TOC, phytoclasts, AOM and palynomorphs and selected subgroups data from the Pedrógão section (Lusitanian Basin, Portugal). Please notice that only the studied interval is represented in the stratigraphical column; for complete section the reader may refer to Azerêdo et al. (2002a).

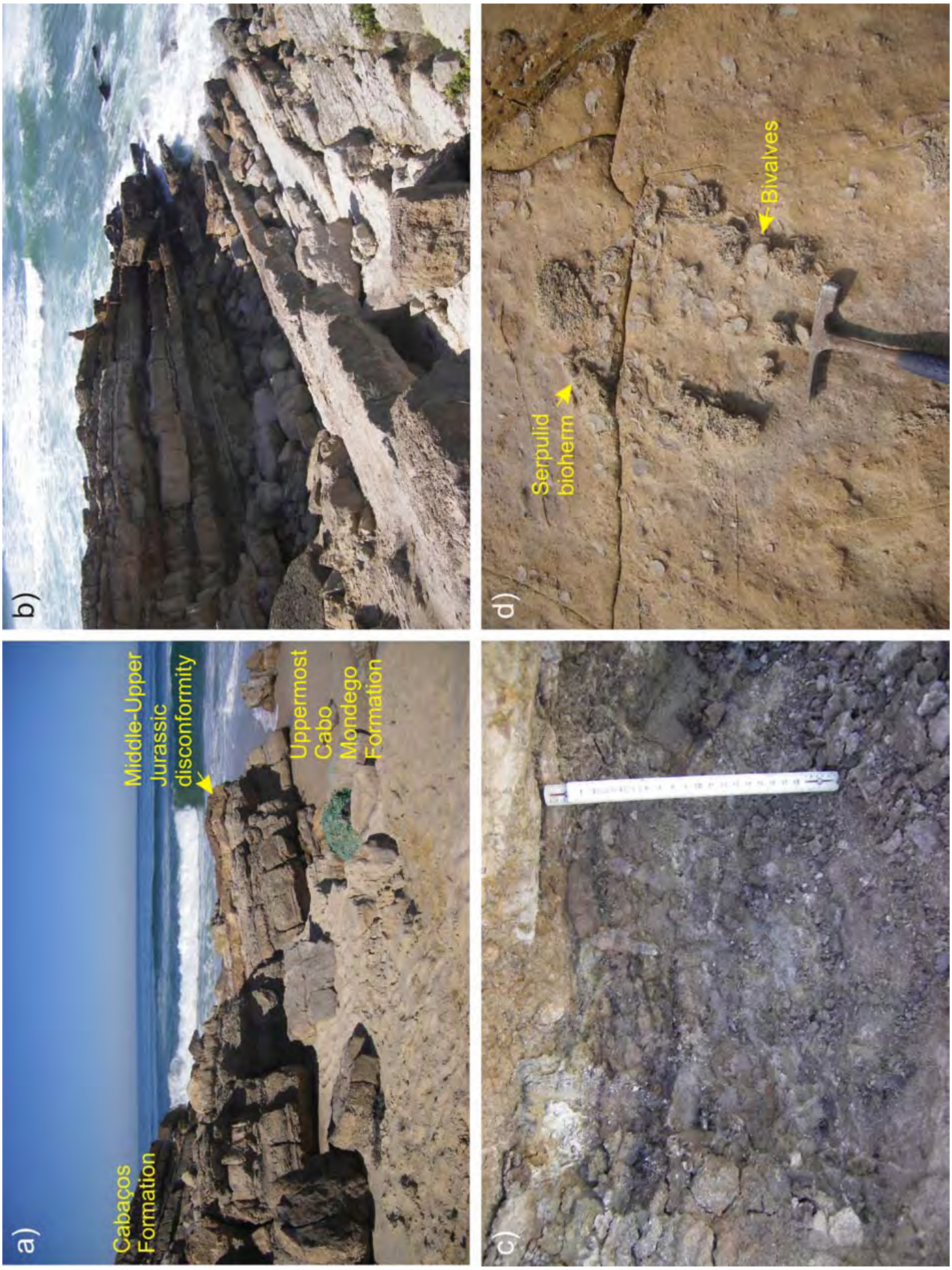


Fig. 5.1.6. Field aspects of the Pedrógão section (Lusitanian Basin, Portugal); a) general view of the limit between the Cabo Mondego and Cabaços formations; b) mid-upper part of the studied section. Along the bedding planes of the limestones in the lower right of the photography it is possible to observe desiccation cracks; c) detail of the marly lithofacies (ruler is in centimetres); d) thick-shelled bivalve concentration and serpulid bioherms.

Some dark grey argillaceous levels are present and include reptile teeth and fossil wood fragments (e.g. Azerêdo et al., 2002a). The top of this formation is defined at the top of a ferruginous limestone bed. This surface is strongly irregular and, according to Azerêdo et al. (2002a), it corresponds to a disconformity surface. It is overlain by a ferruginous charophyte coquina that marks the onset of the deposition related to the Cabaços Formation.

At Pedrógão, the studied part of the Cabaços Formation (~25 metres) is characterized by the intercalation of marls, marly limestones and ferruginous limestones (Fig. 5.1.6b and 5.6c). Less frequently, lignite, pedogenic and microbial facies are observed. At specific places, desiccation features (e.g. desiccation cracks) and minor erosion surfaces are present. This interval is characterized by the absence of marine fossils and the presence of non-marine bivalves, gastropods, abundant charophytes and a moderately diversified assemblage of ostracods (e.g. Cabral et al., 1998; Azerêdo and Cabral, 2004). At the top of the studied interval, the series becomes more calcareous, fossiliferous and bioclastic and desiccation and pedogenic features become more marked. The fossil assemblages include abundant dasyclads, charophytes and ostracods, thick-shelled bivalves, gastropods and serpulids (Fig. 5.1.6d) and rare echinoid fragments, the later denoting a increased and intermittent marine influence in the depositional environment (e.g. Azerêdo et al., 2002a; Azerêdo and Cabral, 2004). These authors assigned this succession to a complex association of shallow fresh-brackish (with short-lived marine influence) water paralic to marginal-marine restricted environments with frequent subaerial exposure.

5.1.3.3. Vale de Ventos section

The Vale de Ventos section is located at the heart of the Maciço Calcário Estremenho, about 35 kilometres south of Leiria (Figs. 5.1.1, 5.1.7 and 5.1.8). Here, the Cabaços Formation rests on top of Upper Bathonian limestones belonging to the Serra de Aire Formation (Azerêdo, 2007). Only the Cabaços Formation was sampled. At this location, the Serra de Aire Formation levels consist of compact oncolitic limestones (Fig. 5.1.8a) capped by a ferruginous palaeokarstic surface, coupled with an angular unconformity relative to the overlying levels of the Oxfordian Cabaços Formation (Azerêdo et al., 1998) (Fig 5.8b). Here, the studied interval (~9 metres) of the Cabaços Formation is made of pedogenic limestones, black-pebble conglomerates, lignitic clays and marls and marly limestones (Figs 5.1.8c and 5.1.8d). Petrographic features suggest a high degree of exposure (Azerêdo et al., 1998). Similarly to Pedrógão, the base of the section does not contain marine fossils but freshwater ostracods, charophytes, porostromates and gastropods are abundant. This section corresponds to a very shallow protected inland system (ponds, marshes and peats) without any marine influence and subjected to intense subaerial exposure, gradually changing into a restricted lagoon (freshwater-oligohaline) with a minor marine component where dasyclad and lituolid foraminifers occur (e.g. Azerêdo et al. 1998, 2002a, b; Cabral et al. 1999; Cabral and Colin 2002; Azerêdo and Cabral 2004).

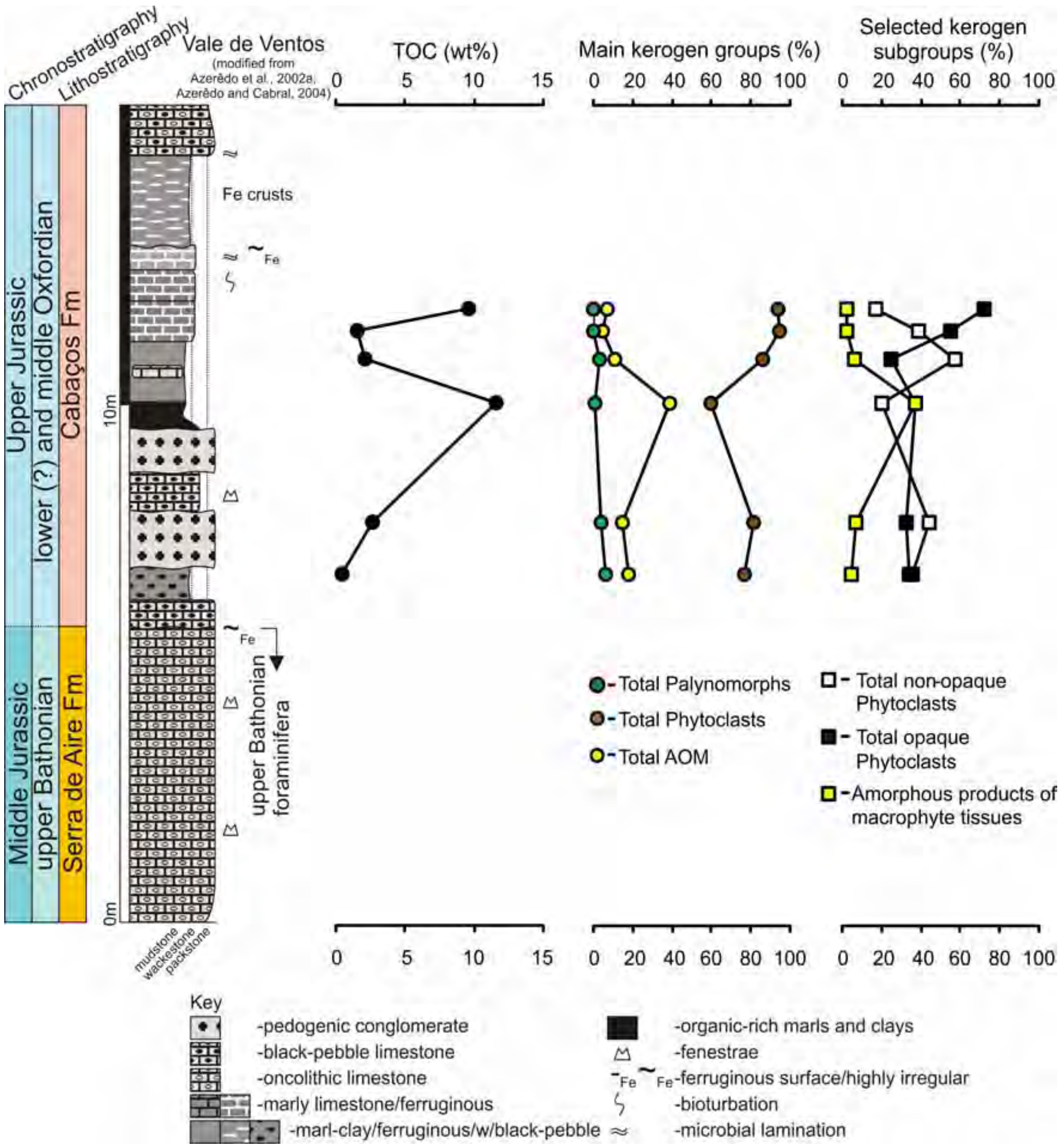


Fig. 5.1.7. Main stratigraphic features, TOC, phytoclasts, AOM and palynomorphs and selected subgroups data from the Vale de Ventos section, Maciço Calcário Estremenho (Lusitanian Basin, Portugal). Please notice that only the studied interval is represented in the stratigraphical column (the first occurrence of *H. lusitanica* at this location is ~6 m above); for complete section the reader may refer to Azerêdo et al. (2002a).

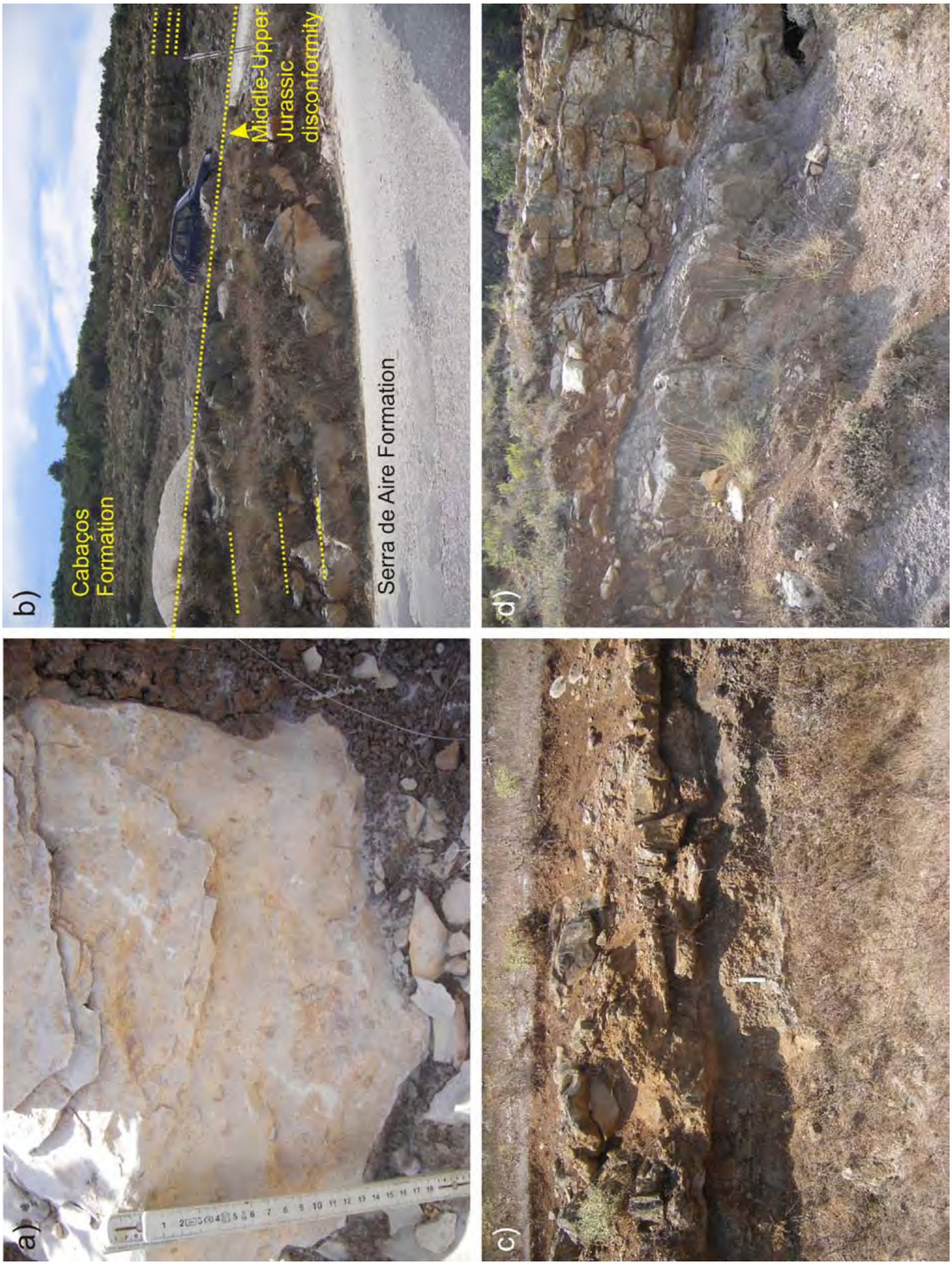


Fig. 5.1.8. Field aspects of the Vale de Ventos section, Maciço Calcário Estremenho (Lusitanian Basin, Portugal); a) compact oncolitic limestone of late Bathonian age belonging to the Serra de Aire Formation (ruler is in centimetres); b) general view of the limit (angular unconformity) between the Serra de Aire and Cabaços formations; c) base of the Cabaços Formation showing pedogenic limestones and black-pebble conglomerates; d) detail of the organic-rich facies in the Vale de Ventos section.

5.1.4. Materials and Methods

From the intervals described in the previous section, 34 samples were collected (6 from Cabo Mondego (Figueira da Foz), notation CM; 22 from Pedrógão, notation P and 6 from Vale de Ventos, notation VV, for Total Organic Carbon (TOC), Total Sulphur (TS), Insoluble Residue (IR) and palynofacies analysis. Broadly, the samples correspond to marly lithotypes and are grey to dark grey in colour. Some present millimetric to submillimetric lamination.

The TOC, TS, IR and palynofacies analyses were conducted in the Palynofacies and Organic Facies Laboratory (LAFO) of the Rio de Janeiro Federal University (Rio de Janeiro, Brazil) (Table 5.1.1). The TOC, TS and IR contents were determined using a SC-144DR LECO analyzer, with an analytical precision of ± 0.1 wt.% (based in duplicate and triplicate sample analysis and analysis of international standards, see also Duarte et al. 2010, 2012; Silva et al. 2011a, 2011b, 2012).

The palynofacies analysis was performed by optic microscopy using Transmitted White Light (TWL) and Fluorescence Mode (FM), following the methodology and classification scheme for the organic matter groups and subgroups of Tyson (1995) and later modified and described in detail by Mendonça Filho et al. (2011, 2012). The three main groups of classification used were phytoclasts, palynomorphs and amorphous organic matter, in addition to intraclasts (see explanation below) and undetermined.

Three samples from the Pedrógão section did not yield enough material for palynofacies analysis (Table 5.1.2). Due to the general poor preservation of pollen grains and spores (resulting in high counts of undetermined elements), the low total percentage (most often <5%) of these particles and the less than 5% difference between spores and pollen in most of the studied samples, the spores/pollen ratio cannot be calculated in a consistent manner; hence it will not be presented here. For a detailed account of the palynological aspects of the Pedrógão section, the reader is referred to Barrón and Azerêdo (2003).

5.1.5. Results: TOC, TS and palynofacies analysis

5.1.5.1. Cabo Mondego Formation

At Pedrógão, the TOC contents of the first three samples are low (up to 0.81 wt.%) but the TS corresponds to the highest values determined in the entire section (Table 5.1.1). The kerogen assemblages of the lowermost three samples do not present a major compositional variation (Table 5.1.2), although the increasing poor preservation of the palynomorphs, clearly expressed in destruction of dinoflagellate cysts (Fig. 5.1.9a), indicates a progressively higher energy environment.

Table 5.1.1. Total Organic Carbon (TOC), Total Sulphur (TS) and Insoluble Residue (IR) data of the Cabo Mondego (Figueira da Foz), Pedrógão and Vale de Ventos sections of the Lusitanian Basin (Portugal).

samples	Stratigraphic unit	TOC (wt.%)	TS (wt.%)	IR (wt.%)
Cabo Mondego (Figueira da Foz) section				
CM1	CM F	1.94	0.75	21
CM2	CM F	0.34	0.02	41
CM3	CM F	0.33	0.03	23
CM4	C F	0.54	1.10	44
CM5	C F	2.45	0.59	63
CM6	C F	30.56	2.62	70
Vale de Ventos section				
VV1	C F	0.43	0.13	14
VV2	C F	2.70	0.12	46
VV3	C F	11.64	0.45	90
VV4	C F	2.13	0.07	31
VV5	C F	1.52	0.04	9
VV6	C F	9.60	0.37	90
Pedrogão section				
P1	CM F	0.57	0.56	21
P2	CM F	0.81	0.69	35
P3	CM F	0.71	0.58	25
P4	CM F	1.35	0.04	12
P5	C F	0.26	0.02	8
P6	C F	0.35	0.01	26
P7	C F	0.30	0.01	21
P8	C F	0.36	0.00	31
P9	C F	0.57	0.01	38
P10	C F	0.62	0.01	40
P11	C F	1.10	0.00	68
P12	C F	3.35	0.02	85
P13	C F	0.46	0.00	44
P14	C F	0.25	0.00	31
P15	C F	0.44	0.00	25
P16	C F	1.00	0.02	25
P17	C F	3.16	0.05	82
P18	C F	0.78	0.01	22
P19	C F	3.48	0.07	17
P20	C F	4.67	0.06	58
P21	C F	0.91	0.02	12
P22	C F	0.58	0.02	9

CM F - Cabo Mondego Formation; C F - Cabaços Formation

Table 5.1.2. Palynofacies data of the Cabo Mondego (Figueira da Foz), Pedrógão and Vale de Ventos sections of the Lusitanian Basin (Portugal).

		phytoclasts group (%)					amorphous organic matter (AOM) group (%)					palynomorphs group (%)												
									amor-phous products			sporomorphs				microplankton								
																	marine							
samples	stratigraphic unit	total opaque	total non-opaque	cuticles and cuticle + innermost part of cuticle epidermis	membranes	total phytoclasts	resin	AOM s.s.	products of macrophyte tissues	products from bacteria and microbial mats	Total AOM	spores	pollen	undetermined	total sporomorphs	*Botryococcus* sp.	dinoflagellate cysts	*Prasynophite* phycomata	acritarcs	undetermined	total marine microplankton	total microplankton (includes undifened)	total palynomorphs (includes zoomorphs and indetermined)	intraclasts (%)	undifferentiated (%)
Cabo Mondego (Figueira da Foz) section																									
CM1	CM	9	1	0	0	10	0	55	2	0	57	0	0	3	3	1	3	0	1	1	5	6	32	1	0
CM2	CM	40	12	1	1	54	2	1	1	1	5	7	14	15	36	1	1	0	1	0	2	5	41	0	0
CM3	CM	50	35	1	1	87	1	0	0	1	2	0	2	8	10	0	1	0	0	0	1	1	11	0	0
CM4	C F	28	40	8	2	78	2	1	12	1	16	2	2	1	5	0	1	0	0	0	1	1	6	0	0
CM5	C F	14	43	35	1	93	0	1	1	0	2	2	0	1	3	0	0	0	0	0	0	1	5	0	0
CM6	C F	5	2	89	0	96	1	1	0	0	2	0	1	0	1	1	0	0	0	0	0	1	2	0	0
Vale de Ventos section																									
VV1	C F	34	35	4	3	76	3	0	5	10	18	2	3	1	6	0	0	0	0	0	0	0	6	0	0
VV2	C F	32	44	2	2	80	2	0	7	6	15	1	2	1	4	0	0	0	0	0	0	0	4	0	1
VV3	C F	37	20	2	1	60	1	0	36	1	38	0	0	0	0	0	0	0	0	0	0	1	1	1	0
VV4	C F	25	57	1	2	85	1	0	6	4	11	1	0	1	2	0	0	0	0	0	0	1	3	1	0
VV5	C F	55	37	1	1	94	0	0	2	2	4	0	0	0	0	0	0	0	0	0	0	1	1	1	0
VV6	C F	71	17	1	4	93	1	0	3	3	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pedrogão section																									
P1	CM	40	33	0	0	73	1	0	1	2	4	1	11	0	12	0	11	0	0	0	11	11	23	0	0
P2	CM	35	33	1	1	70	1	1	2	3	7	1	9	0	10	0	8	1	0	0	9	10	21	0	2
P3	CM	36	29	1	1	67	0	1	1	2	4	2	8	2	12	0	9	0	1	0	10	13	27	0	2
P4	CM	13	24	12	3	52	1	0	29	10	40	0	0	1	1	5	0	0	0	0	1	6	7	0	1
P5	C F	14	2	1	4	21	1	0	1	4	6	10	3	0	13	59	0	0	0	0	0	59	73	0	0
P6	C F	73	19	1	1	94	1	0	0	1	2	1	1	1	3	0	0	1	0	0	1	1	4	0	0
P7	C F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P8	C F	45	43	2	2	92	1	1	0	3	5	1	0	0	1	1	0	0	0	0	0	1	3	0	0
P9	C F	29	31	4	2	66	0	2	1	5	8	5	3	1	9	1	1	0	0	0	1	2	11	0	15
P10	C F	19	73	1	1	94	0	1	1	1	3	0	1	0	1	1	0	0	0	0	0	1	2	0	1
P11	C F	39	56	2	1	98	0	0	0	1	1	1	1	0	1	0	0	0	0	0	0	0	1	0	0
P12	C F	34	57	3	1	95	0	1	1	1	3	0	1	0	2	0	0	0	0	0	0	0	2	0	0
P13	C F	20	11	16	23	70	2	0	2	2	6	11	7	2	20	2	0	0	0	2	2	4	24	0	0
P14	C F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P15	C F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P16	C F	37	45	1	5	88	0	1	0	1	2	2	0	1	3	1	0	0	0	0	0	1	4	0	6
P17	C F	30	21	3	1	55	1	0	18	12	31	1	0	0	1	9	0	0	0	0	0	9	11	3	0
P18	C F	19	9	6	9	43	3	1	0	12	16	10	4	10	24	14	0	0	0	0	0	14	41	0	0
P19	C F	36	33	1	2	72	1	0	5	11	17	2	4	3	9	0	0	0	0	0	0	0	10	1	0
P20	C F	85	6	1	1	93	1	0	1	2	4	0	1	0	1	1	0	1	0	0	1	2	3	0	0
P21	C F	10	6	14	3	33	2	0	2	18	22	1	1	0	2	39	2	0	0	0	2	41	43	2	0
P22	C F	37	7	3	1	48	0	2	0	2	4	0	1	0	1	45	1	0	0	0	1	46	47	0	1

CM - Cabo Mondego Formation; C F - Cabaços Formation; - – not determined

The last sample (P4) of this unit marks the first major change in the TOC and TS contents and in the kerogen assemblages. TOC increases to 1.35 wt.% and TS decreases to 0.04 wt.%. The kerogen assemblage, when compared with the previous ones of the same unit (e.g. sample P1), is marked by the decrease of continental and marine palynomorphs, the first occurrence of the *Botryococcus* Kützing 1849 genus (see also Barrón and Azerêdo, 2003) and an increase in Amorphous Organic Matter (AOM), mainly of terrestrial origin (these particles retain some morphological aspects of macrophyte tissues but due to the intense alteration/reworking are included in the AOM group, Fig. 5.1.9b, see also Mendonça Filho et al., 2012). In this sample, the phytoclast group also decreases in abundance and changes in character, mainly due to the sharp decrease of the contribution of opaque particles and increasing content of cuticles and membranes. The presence of cuticles and membranes suggests some degree of proximity to the source area (Tyson, 1995; Mendonça Filho et al., 2011). At Figueira da Foz, a decrease in TOC and TS contents is recorded from 1.94 to 0.33 wt.% and 0.75 to 0.03 wt.%, respectively. The kerogen assemblage changes from AOM *s.s.*/palynomorph (Fig. 5.1.9c) to phytoclast dominated (Fig. 5.1.9d) (Table 5.1.2). The increase of the phytoclast group is related to the increase in both opaque and non-opaque fractions. The palynomorph group decreases in importance to the top of the section. However, these particles are very difficult to analyse because of their poor degree of mechanical preservation and the pervasive occurrence of pyrite framboids or pyrite impressions, rendering their accurate identification very difficult.

5.1.5.2. Cabaços Formation

The TOC and TS data from the studied part of the Cabaços Formation present a large variation within each section and from one to the other (Table 5.1.1 and Figs. 5.1.3, 5.1.5 and 5.1.7). The highest TOC value of 30.6 wt. % was determined in the Cabo Mondego section. In Vale de Ventos and Pedrógão sections, TOC reaches up to 11.64 wt. % and 4.67 wt. %, respectively. The TOC variation is often related with the opaque phytoclast content, where an increase of TOC corresponds to an increase of phytoclasts content. The TS contents are generally low, although reaching up to 2.6 wt. % in the Cabo Mondego section.

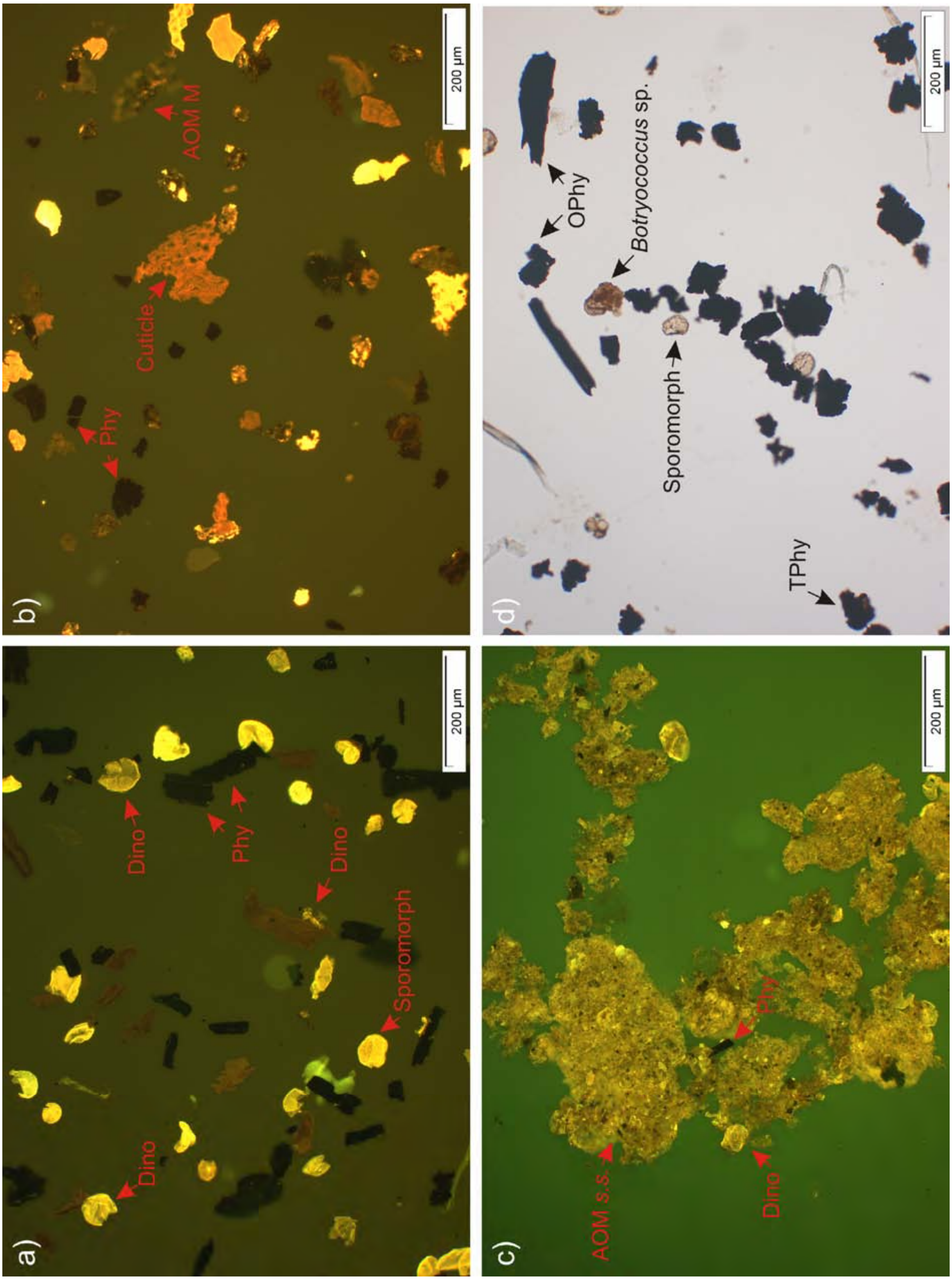
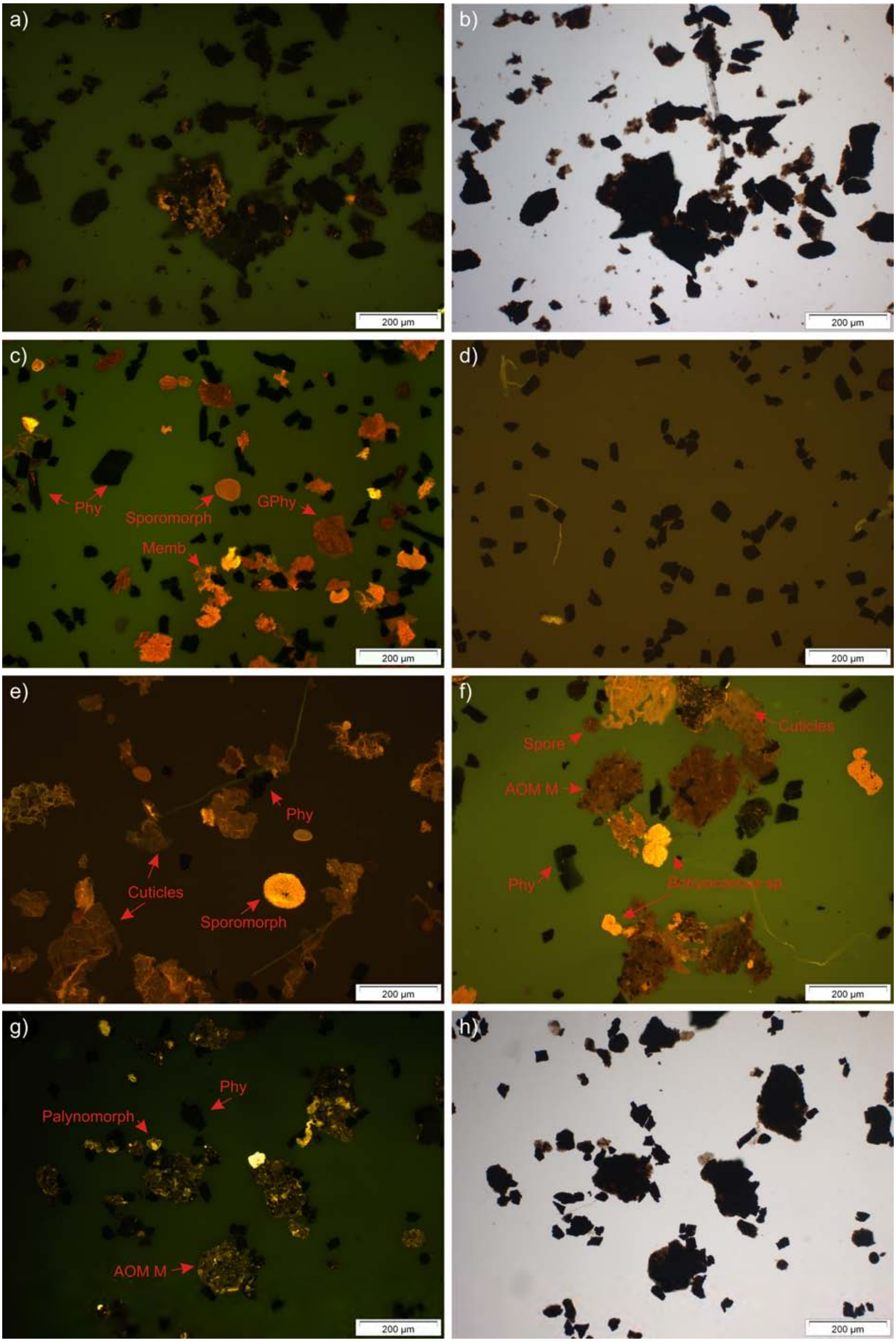


Fig. 5.1.9. Particular aspects of the kerogen assemblage of the Cabo Mondego Formation; a) sample P1 (Pedrógão section); b) sample P4 (Pedrógão section); c) sample CM1(Cabo Mondego section); d) sample CM3 (Cabo Mondego section); Phy – phytoclast; OPhy – opaque phytoclasts; TPhy – non-opaque phytoclasts; AOM M – amorphous organic matter, amorphous products of macrophyte tissues; AOM *s.s.* - amorphous organic matter *s.s.*; Dino – dinoflagellate. a), b) and c) fluorescent mode; d) transmitted white light.

In the Cabo Mondego section (Table 5.1.2; Fig. 5.1.3), the phytoclast group content is always above ~80%, but from CM4 to CM6 AOM and palynomorph contents decrease. The most distinctive feature of this section is the massive presence of particles belonging to the phytoclast group, made up of cuticle layer fragments associated with innermost part of epidermis (Fig. 5.1.10a and 5.10b) (see Mendonça Filho et al., 2011; Spigolon et al., 2011). In optical observation, these particles appear as phytoclasts coated with a thin fluorescent cuticle, sometimes with stomata. This kind of particles comprises about 90% of the kerogen assemblages of the sample CM6. This is the sample with the highest determined TOC content (30.6 wt.%, Table 5.1.1) and is heavily impregnated with hydrocarbons.

The kerogen assemblages at Pedrógão (Table 5.1.2; Fig. 5.1.5) are mostly composed of phytoclasts, cuticles, membranes, pollen grains, spores and *Botryococcus* sp., punctuated by minor events of marine influenced material (extremely rare occurrence of *Prasinophyta* phycomata, acritarcs and dinoflagellate cysts in palynofacies preparations; see palynological data from Barrón and Azerêdo, 2003). An upward increase of AOM is also recorded. From sample P9 to P12 (Figs 5.1.10c and 5.1.10d) a marked change in the kerogen assemblage is seen. The phytoclast content increases from about 66 % to about 95 % with a concomitant decrease of AOM and palynomorphs. The sample P9 contains very rare marine palynomorphs. The sample P13 represents the return of more diversified kerogen assemblages (Fig. 5.1.10e). From sample P16 to P18, the phytoclast content of the kerogen assemblages decreases (from ~90% to ~40%) and AOM tends to increase (Fig. 5.1.10f). Palynomorphs also present major changes. An increase of sporomorphs and *Botryococcus* sp. are observed. From sample P18 to P20 the kerogen trend is reversed, with a sharp increase of phytoclast particles to about 95% in sample P20.

At Vale de Ventos (Table 5.1.2, Fig. 5.1.7), the kerogen assemblages are almost exclusively of terrestrial origin, mainly phytoclasts and amorphous products (Fig. 5.1.10g and 5.10h). Palynomorphs are rare, reaching up to 6% in sample VV1. From the base to the top, there is an increase of opaque and a decrease of non-opaque phytoclasts. The phytoclasts of the lowermost samples tend to present a more diversified set of preservation conditions of the components (not degraded, gelified and pseudoamorphized particles). On the other hand, the topmost sample (VV6) presents an increase of opaque (equidimentional) phytoclasts and a decrease of non-opaque particles, cuticles and AOM.


a)
200 µm
b)
200 µm
c)
Phy
Sporomorph
GPhy
Memb
200 µm
d)
200 µm
e)
Phy
Cuticles
Sporomorph
200 µm
f)
Cuticles
Spore
AOM M
Phy
200 µm
g)
Phy
Palynomorph
AOM M
200 µm
h)
200 µm

5.1.6. Discussion

5.1.6.1. Cabo Mondego Formation: the latest record of Middle Jurassic marine environments and the late Callovian forced regression

The analysed portions of the Cabo Mondego Formation (Fig. 5.1.3) at Figueira da Foz and Pedrógão (Fig. 5.1.5) show that the basal deposits of the sampled interval (Upper Callovian, Cabo Mondego Formation) have kerogen assemblages characteristic of marine environments. In addition to the general lithological context of this part of the series, it contains a diversified array of marine palynomorphs (e.g. acritarcs, dinoflagellate cysts, *Prasinophyta* phycomata) and AOM *s.s.*, derived from plankton (see Tyson, 1995; Mendonça Filho et al., 2011). Upwards, the variation of kerogen assemblages at Pedrógão and Figueira da Foz are evidence of an overall regressive trend, which is clearer at Figueira da Foz than at Pedrógão. The former presents more contrasting palynofacies, from high preservation environments to high energy deposition. Taking into consideration the general sedimentological framing of the studied series (i.e. Azerêdo et al., 2002a), the lowermost samples of each section (P1, P2, P3 and CM1) are characteristic of relatively proximal open-marine (mid-outer ramp) environments, as suggested from the wide occurrence of marine palynomorphs, lack of AOM (this feature suggests deposition under oxic environments) in Pedrógão samples and significant phytoclasts contribution (including translucent particles which indicate some degree of proximity) (see Tyson, 1995). The presence of AOM in the CM1 sample indicates good preservation conditions under oxygen deficient environments. The kerogen assemblages of the top of the sections are typical of marginal-marine environments (dominance of the phytoclast group), although with a marked difference in terms of energy levels. The presence of cuticles and membranes suggests proximity to the source area (Tyson, 1995; Mendonça Filho et al., 2011).

Azerêdo et al. (2002a), in a comprehensive paper about the Middle–Upper Jurassic transition in the Central-Northern sectors of the Lusitanian Basin, analysed in great detail these and other Lusitanian Basin sections and presented an integrated scenario on the development and evolution of the coeval depositional environments of the Late Callovian.

Previous page: Fig. 5.1.10. Particular aspects of the kerogen assemblage of the Cabaços Formation; a) and b) sample CM6 (Cabo Mondego section); c) sample P9 (Pedrógão section); d) sample P12 (Pedrógão section); e) sample P13 (Pedrógão section); f) sample P17 (Pedrógão section); g) and h) sample VV3 (Vale de Ventos section). Phy – phytoclast; GPhy – Gelified phytoclast; AOM M – amorphous organic matter, amorphous products of macrophyte tissues; Memb - Membrane. a), c), d), e), f) and g) fluorescent mode; b) and h) transmitted white light.

The authors demonstrate that the Middle–Upper Jurassic disconformity is preceded by a major forced regression, during which the open-marine series of the western parts of the basin, including the two studied sections, rapidly graded into more proximal sedimentary packages.

5.1.6.2. The Cabaços Formation: non-marine sedimentation and lateral variability of the depositional systems

The Cabaços Formation corresponds to the first sediments deposited after the aforementioned major tectonostratigraphic discontinuity at the Middle–Late Jurassic boundary, with widespread deposition of contrasting non-marine sediments, evolving into mixed non-marine and restricted-marine ones. Its variable palynofacies record reflects the high-frequency changes and complex interactions of the depositional settings established across this transitional interval.

Overall, the exemplary palynofacies data from Cabo Mondego suggest that deposition took place in increasingly calmer and proximal environments, very close to the source area (e.g. Tyson, 1995; Mendonça Filho et al., 2011). The abundance of the cuticle+innermost part of cuticle epidermis related particles implicates that deposition took place in a location extremely close to the source-area and in a calm high-preservation environment, reinforcing the former interpretations pointing to sedimentation related with embayments and lagoons with tributaries represented by small deltas (Wright, 1985; Azerêdo et al., 2002a; Azerêdo and Wright, 2004).

The palynofacies at Pedrógão also indicates that the particulate organic matter is mostly of continental origin (phytoclasts, cuticles, membranes, pollen grains, spores and *Botryococcus* sp.), but punctuated by minor events of marine influence (rare occurrence of *Prasinophyta* phycomata and dinoflagellate cysts; see also Barrón and Azerêdo, 2003). Excluding the lowermost sample and the two uppermost ones, the palynofacies shows a clear pattern of vertical facies variation, inferred to represent changes in the water column depth and/or periods of environmental restriction. The marked change in the kerogen assemblage from sample P9 to P12 (Figs 5.1.10c and 5.1.10d), with increasing phytoclast content and concomitant decrease of AOM and palynomorphs, coupled with very rare marine palynomorphs in P9, is interpreted as reflecting deposition in calm and oxygen deficient environments with sporadic marine influence (sample P9), grading upwards (sample P12) to more proximal, higher energy settings (cf. Tyson, 1995). The next sample, P13, represents the start of a new cycle with the return of more diversified kerogen assemblages (Fig. 5.1.10e). A full shallowing-deepening water column cycle and/or periods of changing environmental restriction conditions is inferred between samples P16 and P20, superimposed by other similar small scale cycles. This hypothesis is based on the decrease of phytoclast and increase of AOM and palynomorph (sporomorphs and *Botryococcus* sp.) groups content from sample P16 to P18. Part of this AOM is probably of vegetal origin (Fig. 5.1.10f), although reworked to a point where is classified as amorphous products from bacteria. These trends are thought to represent an interval of increasing water depth and/or increasing palaeoenvironmental restriction, promoting a higher degree of preservation. From sample P18 to P20 the kerogen trend is reversed, with a sharp increase of phytoclast related particles to about 95% in sample P20. This is thought to reflect a progressive increase of energy of the depositional environment, probably related with a shoreline location, as indicated by the presence of higher energy conditions and current activity, evidenced by the presence of cross lamination just above sample 20 (Fig. 5.1.5).

At Vale de Ventos (Table 5.1.2, Fig. 5.1.7), the kerogen assemblages are almost exclusively related to a terrestrial origin. From the base to the top, there is an increase of opaque versus a decrease of non-opaque phytoclasts, which shows an upward increase of the most resistant material.

Overall, it seems that these palynofacies reflect a "proximal to distal" distribution in relation to source area (e.g. Tyson, 1995; Mendonça Filho et al., 2011), which is in good agreement with the independently obtained sedimentological data and inferred depositional environments. In contrast to the marine carbonate deposits of Middle Jurassic age that precede it, the Cabaços Formation encompasses a wider range of depositional environments, a variability that is clearly reflected in the geochemical and palynofacies data presented in this study.

5.1.7. Singular kerogen particles and their role to the understanding of the palaeoenvironmental dynamics

5.1.7.1. Intraclasts: insights into the neighboring environments

In the present study, a few particles of the kerogen assemblages of the Pedrógão section do not fall within the traditional AOM, phytoclasts or palynomorphs groups (Table 5.1.2), but show morphological characteristics similar to those described from modern microbial mats of the Andros Island (e.g. Monty, 1972). The most striking feature is the presence of vertical tubes, which most likely represent impressions of filamentous cyanobacteria embedded in a "spongy" matrix lying in-between a more compact, faintly laminated (microbial biofilms?) organic matrix. This includes filamentous cyanobacteria in horizontal arrangement.

Figure 5.1.11 is a schematic representation and interpretation of the structures observed in one of these particles. This configuration bears remarkable similarities with the lower living part of a common type of microbial mat formed by cyanobacteria *Scytonema* Agardh ex Bornet et Flahault 1887 and *Schizothrix* Kützing ex Gomont 1892 genera (see Guiry and Guiry, 2013) in the fresh-water lakes of contemporary Andros Island.

The living portion of the mat is divided into two parts: the top corresponds to a spongy calcareous laminae made of long vertical bundles of calcified *Scytonema* and horizontal calcified film of *Schizothrix*, whereas the lower portion, mostly organic, consists of a loose green layer with erect non-calcified filaments of *Scytonema* intermingled with films and draperies of *Schizothrix,* delineating large vacuoles (Monty, 1972, 1976). The periodic differentiation of the cyanobacteria assemblage, forming an alternation of calcified and hyaline layers, is regarded as the response of the cyanobacteria community to the changing palaeoenvironmental conditions, namely salinity and moisture (Monty, 1976).

These particles correspond to the remnants of cohesive microbial mats, inclusively showing some structures resembling mat-forming filamentous cyanobacteria, an extremely rare occurrence in palynofacies studies (e.g. Traverse, 2007). These particles are probably related to the filaments category within the structured organic matter (STOM) group of Batten and Stead (2005), although we prefer to describe it as intraclasts. They represent a testimony of a complex association of cyanobacteria, formed in nearby depositional environment and subjected to erosion and redeposited to be finally incorporated in sediment. The term intraclast is used in parallelism with the same term used in sedimentology.

Importantly, these intraclasts highlight the complexity of the nearby palaeoenvironments during the Oxfordian in the Lusitanian Basin. For example, Martins et al. (2001) mention the significant presence of well developed cyanolites with *Scytonema* and *Schizothrix*-related structures at the base of the Cabaços Formation in the Sicó Massive (located about 35 kilometers to east of Pedrogão).

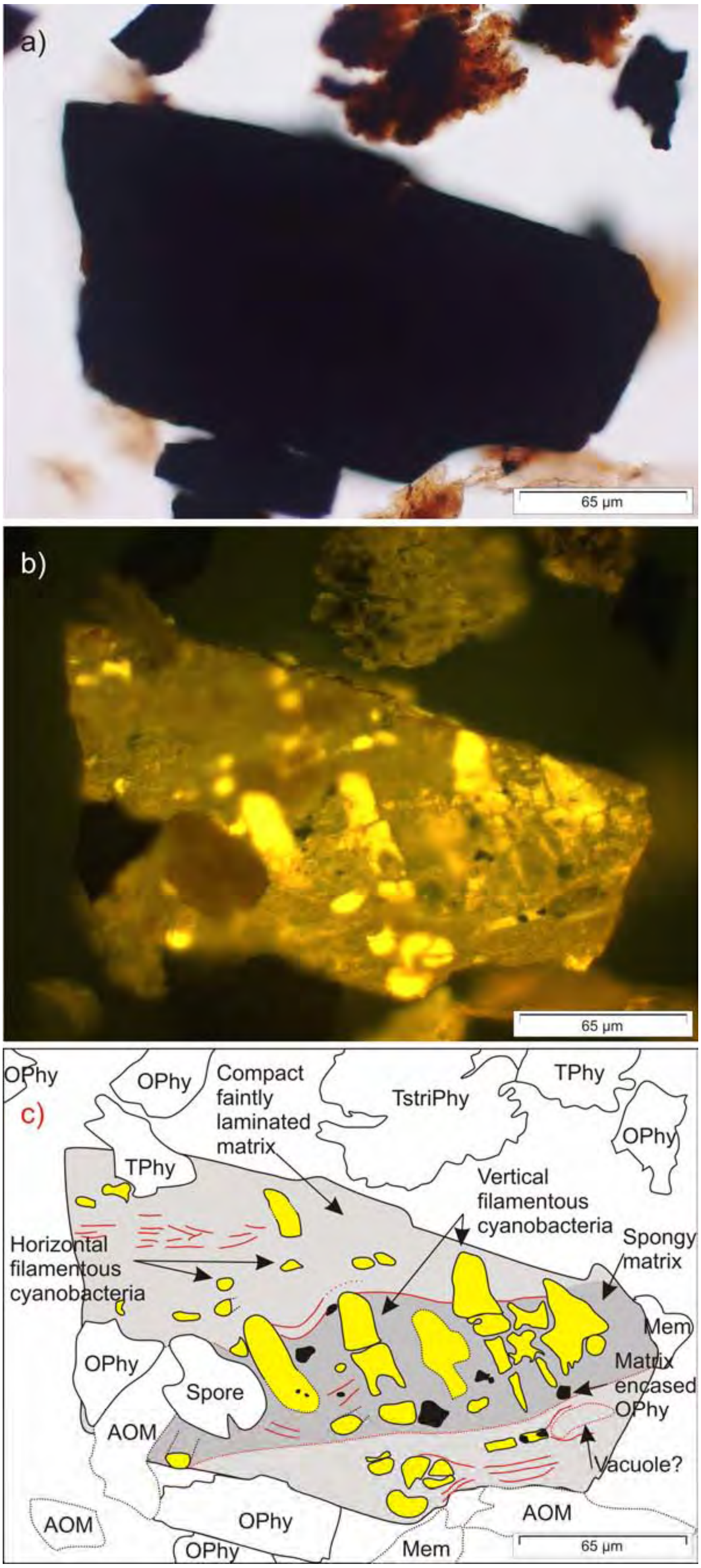


Fig. 5.1.11. Intraclast found in sample P9, Pedrógão section, and schematic interpretation of its inner structures. OPhy-opaque phytoclast; TstriPhy-non-opaque striate phytoclast; TPhy-translucent phytoclast; Mem-membrane; AOM; amorphous organic matter. a) transmitted white light; b) fluorescent mode.

In addition, Azerêdo et al. (2002a) recognized the occurrence of microbial laminite clasts in thin-sections from many of the locations they studied, besides microbialites; however, here we document much smaller particles, within the kerogen assemblage, hence the originality of the findings and of their preservation stage. Wright (1985), had already suggested some degree of similarity between the Upper Jurassic deposits of the Lusitanian Basin and the present-day algal marshes observed in parts of the Florida Everglades or in the interior of Andros Island, Bahamas, supported by the high abundance of porostromate tubes (calcified cyanobacteria), calcite rhombs and polyhedral crystals, associated with organic sheath material. This observation further attests our interpretation of an origin related to (redeposited) microbial mats as a plausible source for these exotic particles.

5.1.7.2. Botryococcus genus diversity as an indicator of degree of palaeoenvironmental stability

The *Botryococcus* genus, a planktonic microalga, is often regarded as an important kerogen group in petroleum exploration (e.g. Metzger and Largeau, 2005). This genus commonly thrives in continental, shallow and oxygenated freshwater lakes, ponds or other stagnant water bodies, although it can be found in a variety of depositional environments (mostly due to redeposition). It may inhabit oligo-to mesotrophic waters under various pH values (Wake and Hillen, 1980), although the optimal conditions are eutrophic and slightly acidic (e.g. Demetrescu, 1999).

In the Pedrógão section, the first and the last two samples of the Cabaços Formation present contents of *Botryococcus* sp. around 60% (P5) and 40% (P21and P22) of total kerogen. These samples also differ in the kerogen assemblages, the sample P5 being richer in continental palynomorphs and poorer in phytoclasts than the samples P21and P22 (see Table 5.1.2). These last two samples, besides other extremely rare fresh water palynomorphs (such as zygospores), also include marine (dinoflagellate cysts) palynomorphs and high amounts of AOM. It has been demonstrated that fossil *Botryococcus* sp. colonies are very useful when interpreting palaeoenvironments (e.g. Guy-Ohlson, 1992, 1998). It is generally suggested that *Botryococcus* genus occurrences comprising a diversified set of types of colony and developmental stages indicate contrasting seasonal conditions prior to, or contemporaneously with deposition, while low diversity indicates short but stable periods of growth (Guy-Ohlson, 1998; Demetrescu, 1999). In fact, sample P5 shows a lower *Botryococcus* sp. diversity, mainly skeleton matrix colony with empty mother-cell cups (Fig.

5.1.12a) than P21 and P22 samples which, in addition to a greater variation in size of skeleton matrix colonies (up to 200 µm), include unbranched compound colonies showing typical botryoidal form (Fig. 5.1.12b). This feature is in good agreement with the studies of Azerêdo et al. (1998, 2002a) where a change from humid to more seasonally contrasting semi-arid conditions, evidenced by the occurrence of evaporites and pedogenic carbonates, is suggested for the during the Middle–Late Jurassic transition period in the Lusitanian Basin.

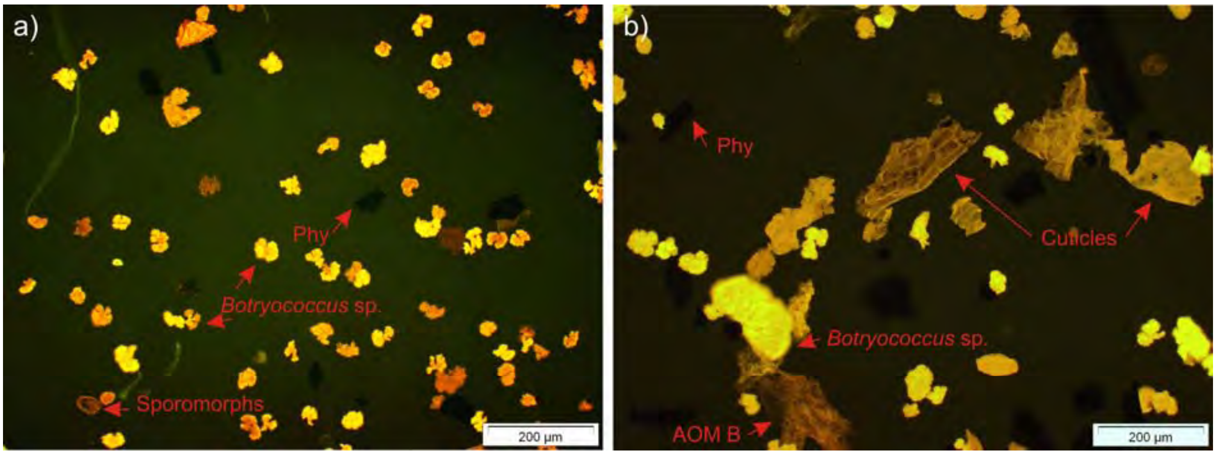


Fig. 5.1.12 *Botryococcus* sp. morphological diversity in the Cabaços Formation at Pedrógão; a) sample P5; b) sample P21. Phy – Phytoclast; AOM B – Amorphous organic matter, amorphous products of microbial origin. a) and b) fluorescent mode.

5.1.8. Possible hydrocarbon prospects in the Central-Northern sectors of the Lusitanian Basin

The stratigraphic record of the Lusitanian Basin includes two main intervals with a recognized potential for hydrocarbon generation, the Sinemurian–Pliensbachian Água de Madeiros and Vale das Fontes formations and the Oxfordian Cabaços Formation and its lateral equivalents (e.g. Duarte et al., 2010, 2012; Silva et al., 2011a, 2011b and references therein). Although these lithological units are of a basin-wide extent, their source-rock potential is usually thought to be roughly limited to the northern (Sinemurian–Pliensbachian) and southern (Oxfordian) parts of the basin (DGEG, 2012).

The lowermost sample of Cabo Mondego Formation at Figueira da Foz (Callovian) has a kerogen assemblage dominated by AOM *s.s.* (plankton derived) and abundant marine palynomorphs and TOC values reaching ~2 wt.%. Although only observed in one sample of this unit, the high organic content of this level and its AOM content suggest that this unit should be more deeply studied regarding its source rock potential.

As aforementioned, the Cabaços Formation is often neglected as a potential source rock in the northern sectors of the Lusitanian Basin (see DGEG 2012), mainly due to its continental character. In fact, most of the studied samples from the Vale de Ventos, Pedrógão and Cabo Mondego sections confirm its marginal value as a prospect, being dominated by woody particles with potential for gas generation (equivalent to Type III and IV kerogens, van Krevelen, 1961; Tissot et al., 1974; Tyson, 1995 and references therein). Nevertheless, a few samples have significant amounts of kerogen particles included in the kerogen groups Type I (e.g. *Botryococcus* genus) and Type II (e.g. leaf remains) (van Krevelen, 1961; Tissot et al., 1974; Tyson, 1995 and references therein) and, although spatially restricted, there are some indications of the existence of nearby environments dominated by microbial components (see also Spigolon et al. 2011 for Rock-Eval data from the Cabo Mondego section).

All these observations suggest that the studied units may be considered as potential source-rocks and this must be considered in future studies regarding the discrimination of the petroleum systems of the Lusitanian Basin.

5.1.9. Conclusions

The main results concerning a palynofacies and TOC survey of the Middle–Upper Jurassic transition units in the Central-Northern sectors of the Lusitanian Basin (Portugal) are:

-The uppermost Middle Jurassic series of the Cabo Mondego Formation (Callovian) have at its base kerogen assemblages characteristic of marine environments. The palynofacies tend to record more proximal/higher energy (costal) environments upwards in the section. The maximum TOC value determined in these deposits was 1.94 wt. % (Cabo Mondego section).

-The first deposits of Late Jurassic age, belonging to the Cabaços Formation (lower?/middle Oxfordian) present a great variety of organic content between the studied sections. The highest TOC value of 30.6 wt. % was determined in the Cabo Mondego section; in Vale de Ventos and Pedrógão sections TOC reaches up to 11.6 wt.% and 4.7 wt.%, respectively. The particulate organic matter is mostly of continental origin (phytoclasts and sporomorphs) punctuated by minor events of marine influence (rare occurrence of, for example, *Prasinophyta* phycomata and dinoflagellate cysts). The marine influence tends to decrease from Cabo Mondego (Figueira da Foz) to Vale de Ventos. Some of the analysed horizons show an important contribution from other components, such as amorphous organic matter and *Botryococcus* sp..

-The comparison of different studied sections shows TOC and palynofacies variations between relatively close settings and along narrow vertical intervals. This is in accordance with previously sedimentological and micropalaeontological studies, further attesting the high sedimentary dynamics that prevailed during the Middle–Late Jurassic transition in the Central-Northern sectors of the Lusitanian Basin.

References

ALMERAS, Y., RUGET, C., CARAPITO, M.C., CARIOU, E. and MOUTERDE, R., 1991. Biostratigraphie du Callovien de Pedrogão: le Portugal voie d'échanges fauniques au Callovien. Memórias e Notícias, 112, 239–246.

ALVES, T.M., GAWTHORPE, R.L., HUNT, D.W. and MONTEIRO, J.H., 2002. Jurassic tectono-sedimentary evolution of the Northern Lusitanian Basin (offshore Portugal). Marine and Petroleum Geology, 19, 727–754.

AZERÊDO, A.C., 2007. Formalização da litostratigrafia do Jurássico Inferior e Médio do Maciço Calcário Estremenho (Bacia Lusitânica). Comunicações Geológicas, 94, 29–51.

AZERÊDO, A.C. and CABRAL, M-C., 2004. Bio-sedimentary signatures of high-frequency salinity/subaerial exposure changes: Examples from the Oxfordian of Portugal (Cabaços Formation). Rivista Italiana di Paleontologia e Stratigrafia, 110, 231–238.

AZERÊDO, A.C., RAMALHO, M.M. and WRIGHT, V.P., 1998. The Middle-Upper Jurasscic disconformity in the Lusitanian Basin, Portugal: preliminary facies analysis and evidence for palaeoclimatic fluctuation. Cuadernos de Geología Ibérica, 24, 99–119.

AZERÊDO, A.C., WRIGHT, V.P. and RAMALHO, M.M., 2002a. The Middle-Late Jurassic forced regression and disconformity in central Portugal: eustatic, tectonic and climatic effects on a carbonate ramp system. Sedimentology, 49, 1339–1370.

AZERÊDO, A.C., CABRAL, M-C., RAMALHO, M.M. and PEREIRA, R., 2002b Overview of microfossil assemblages and palaeoecological signatures in the Middle-Upper Jurassic transitional successions from the Lusitanian Basin, Portugal. Comunicações do Instituto Geológico e Mineiro 89, 135–158.

AZERÊDO, A.C., DUARTE, L.V., HENRIQUES, M.H. and MANUPPELLA, G., 2003. Da dinâmica continental no Triásico aos mares do Jurássico Inferior e Médio. Cadernos de Geologia de Portugal. Instituto Geológico e Mineiro, Lisboa

AZERÊDO, A.C. and WRIGHT, V.P., 2004. Multi-scale signatures and events in carbonate systems (Middle to early Upper Jurassic, Lusitanian Basin). In: DUARTE LV and HENRIQUES MH (eds), Carboniferous and Jurassic Carbonate Platforms of Iberia, volume 1. 23rd IAS Meeting of Sedimentology Field Trip Guide Book, Coimbra, pp 75–91.

BARRÓN, E. and AZERÊDO, A.C., 2003. Palynology of the Jurassic (Callovian-Oxfordian) succession from Pedrógão (Lusitanian Basin, Portugal). Palaeoecological and palaeobiogeographical aspects. Neues Jahrbuch für Geologie und Paläontologie – Abhandlunge, 227, 259–286.

BATTEN, D.J., 1973. Use of palynologic assemblage-types in Wealden correlation. Palaeontology, 16, 1–40.

BATTEN, D.J., 1991. Reworking of plant microfossils and sedimentary provenance. In: MORTON, A.C., TOOLD, S.P., and HANGHAN, P.D.W., (eds) Geological Society Publications 57, pp. 79–90.

BATTEN, D.J., 1996. Palynofacies and palaeoenvironmental interpretation. In: JANSONIUS, J. and MCGREGOR, D.C., (eds) Palynology: principles and applications. American Association of Stratigraphic Palynologists Foundation, 3, pp. 1011–1064.

BATTEN, D.J. and STEAD, D.T., 2005. Palynofacies analysis and its stratigraphic application. In: KOUTSOUKOS, E.A.M., (ed.). Applied Stratigraphy. Springer, pp. 203–226.

BORNET, É. and FLAHAULT, C., 1886. Revision des Nostocacées hétérocystées contenues dans les principaux herbiers de France. Annales des Sciences Naturelles; Botanique, serie 7, 5, 51–129.

BUSTIN, R.M., 1988. Sedimentology and characteristics of dispersed organic matter in Tertiary Niger Delta: origin of source rocks in a deltaic environment. AAPG Bulletin, 72, 277–298.

CABRAL, M.C., AZERÊDO, A.C. and RAMALHO, M.M. 1998. Estudo preliminar dos Ostracodos de Pedrógão (passagem Dogger-Malm). Comunicações do Instituto Geológico e Mineiro, 84, A74–A77.

CABRAL, M.C., AZERÊDO, A.C. and RAMALHO, M.M., 1999. Les Ostracodes de Vale de Ventos (passage Dogger-Malm) – résultats préliminaires. Abstracts, European Palaeontological Workshop, Lisboa, pp 21–25.

CABRAL, M.C. and COLIN, J-P., 2002. Taxonomie et paléoécologie de nouveaux ostracodes limniques Candonidae dans l'Oxfordien (Jurassique supérieur) du Portugal. Geodiversitas, 24, 61–76.

CARAPITO KRAUSSHAR, C., 2008. Estratigrafia e Biostratigrafia do Batoniano-Oxfordiano do Cabo Mondego (Perfil da Praia). In: CALLAPEZ, P.M., ROCHA, R.B., MARQUES, J.F., CUNHA, L.S. and DINIS, P.M. (eds). A Terra, Conflitos e Ordem, Homenagem ao Professor Ferreira Soares. Museu Lab Mineral Geol Univ Coimbra, Coimbra, pp 187–195.

CHOFFAT, P., 1893. Sur les niveaux ammonitiques du Malm inférieur dans la contrée de Montejunto (Portugal). Phases peu connues du développement des mollusques. Comptes Rendus de l'Académie des Sciences Paris, 116, 833–835.

COLIN, J-P., CABRAL, M.C., DEPECHE F and METTE, W., 2000. *Sinuocythere* n. gen (Ostracoda, Limnocytheridea, Timiriaseviinae), a new genus of limnic ostracode from southern Tethyan Middle and Upper Jurassic. Micropalaeontology, 46, 123–134.

DEMETRESCU, E., 1999. The Chlorococcalean alga *Botryococcus* and its significance in hydrocarbons exploration. Geo-Eco-Marina, 4, 155–160.

DGEG, (2012). Direção-Geral de Energia e Geologia. Ministério da Economia, Governo Português. http://www.dgeg.pt/dpep/pt/petroleum_pt.htm. Accessed 2 of October of 2012

DROMART, G., GARCIA, J-P., GAUMET, F., PICARD, S., ROUSSEAU, M., ATROPS, F., LECUYER, C. and SHEPPARD, S.M.F., 2003a. Perturbation of the carbon cycle at the Middle/Late Jurassic transition: geological and geochemical evidence. American Journal of Science, 303, 667–707.

DROMART, G., GARCIA, J.-P., PICARD, S., ATROPS, F., LECUYER, C., SHEPPARD, S.M.F., 2003b, Ice age at the Middle–Late Jurassic transition? Earth and Planetary Science Letters, 213, 205–220.

DUARTE, L.V., SILVA, R.L., OLIVEIRA, L.C.V., COMAS-RENGIFO, M.J. and SILVA, F., 2010. Organic-rich facies in the Sinemurian and Pliensbachian of the Lusitanian Basin, Portugal: Total Organic Carbon distribution and relation to transgressive-regressive facies cycles. Geologica Acta, 8, 325–340.

DUARTE, L.V., SILVA, R.L., MENDONÇA, FILHO., J.G., POÇAS RIBEIRO, N. and CHAGAS, R.B.A., 2012. High-resolution stratigraphy, Palynofacies and source rock potential of the Água de Madeiros Formation (Upper Sinemurian) of the Lusitanian Basin, Portugal. Journal of Petroleum Geology, 35, 105–126.

GPEP, 1986. The petroleum potential of Portugal. Gabinete para a Pesquisa e Exploração de Petróleo, Lisbon, Unpublished report DGGE/DPEP, 62 pp..

GOMONT, M., 1892. Monographie des Oscillariées (Nostocacées homocystées). Annales des Sciences Naturelles; Botanique, serie 7, 15, 263–368.

GUIRY, M.D. and GUIRY, G.M., 2013. AlgaeBase. World-wide electronic publication, National University of Ireland, Galway. http://www.algaebase.org; searched on 04 February 2013.

GUY-OHLSON, D., 1992. *Botryococcus* as an aid in the interpretation of palaeoenvironment and depositional processes. Review of Palaeobotany and Palynology, 71, 1–15.

GUY-OHLSON, D., 1998. The use of the microalga *Botryococcus* in the interpretation of lacustrine environments at the Jurassic–Cretaceous transition in Sweden. Palaeogeography, Palaeoclimatology, Palaeoecology, 140, 347–356.

HOTTINGER, L., 1967. Foraminifères imperforés du Mésozoique marocain. Notes et Mémoires du Service Géologique du Maroc, 209, 1–168.

JONES C.E., JENKYNS, H.C., COE, A.L. and HESSELBO, S.P., 1994. Strontium isotopic variations in Jurassic and Cretaceous seawater. Geochimica et Cosmochimica Acta, 58, 3061–3074.

KÜTZING, F.T., 1849. Species algarum.. Lipsiae, FA Brockhaus

LEINFELDER, R.R., 1993. A sequence stratigraphic approach to the Upper Jurassic mixed carbonate-siliciclstic succession of the central Lusitanian Basin, Portugal. Profil, 5, 119–140

LEINFELDER, R.R., ERBENICH, A. and RAMALHO, M.M., 1988. Age and general facies development of the Ota Limestone (Estremadura, Portugal). Proceedings of the 2nd International Symposium on Jurassic Stratigraphy. Universidade Nova de Lisboa Press, pp. 917–932.

LEINFELDER, R.R. and WILSON, R.C.L., 1989. Seismic and sedimentologic features of Oxfordian-Kimmeridgian syn-rift sediments on the eastern margin of the Lusitanian Basin. Geologische Rundschau, 78, 81–104.

LEINFELDER, R.R. and WILSON, R.C.L., 1998. Third-order sequences in an Upper Jurassic rift-related second-order sequence, central Lusitanian Basin, Portugal. In: DE GRACIANSKY, P.C., HARDENBOL, J., JACQUIN, T. and VAIL, P. (eds). Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. SEPM Spec. Publ. 60, pp. 507–525.

LEWANDOWSKI, M., KROBICKI, M., MATYJA, B.A. and WIERZBOWSKI, A., 2005. Palaeogeographic evolution of the Pieniny Klippen Basin using stratigraphic and paleomagnetic data from the Veliky Kamenets section (Carpathians, Ukraine). Palaeogeography, Palaeoclimatology, Palaeoecology, 216, 53–72.

MARTÍN-CLOSAS, C, PERMANYER, A, VILA, M-J., 2005. Palynofacies distribution in a lacustrine basin. Geobios 38, 197–210.

MARTINS, J.M., AZERÊDO, A.C. and MANUPPELLA, G., 2001. Polymorphic oncoidal/cyanophyte structures in Middle to basal Upper Jurassic limestones from the Lusitanian Basin, Portugal: palaeoecological and regional cartographic significance. Comunicações do Instituto Geológico e Mineiro, 88, 99–126.

MENDONÇA FILHO, J.G., MENEZES, T.R. and MENDONÇA, J.O., 2011. Chapter 5: Organic composition (Palynofacies Analysis). In: FLORES, D. and MARQUES, M., (eds). ICCP Training Course on Dispersed Organic Matter. International Committee for Coal and Organic Petrology, Porto, pp 33–81.

MENDONÇA FILHO, J.G., MENEZES, T.R., MENDONÇA, J.O., OLIVEIRA, A.D., SILVA, T.F., RONDON, N.F. and DA SILVA, F.S., 2012. Organic Facies: Palynofacies and Organic Geochemistry approaches. In: PANAGIOTARAS, D., (ed). Geochemistry – Earth's System Processes. InTech, Rijeka, pp. 211–248.

MATYJA, B.A. and WIERZBOWSKI, A., 2006. The oceanic “Metis Geotectonic Event” (Callovian/Oxfordian) and its implications for the peri-Tethyan area of Poland. 7th International Congress on the Jurassic System, Volumina Jurassica, 4, 60–61.

METZGER, P. and LARGEAU, C., 2005. *Botryococcus braunii*: a rich source for hydrocarbons and related ether lipids. Applied Microbiology and Biotechnology, 66, 486–496.

MONTY, C.L.V., 1972. Recent algal stromatolitic deposits, Andros Islands, Bahamas. Preliminary report. Geologische Rundschau, 61, 742–783.

MONTY, C.L.V. 1976. The origin and development of cryptalgal fabrics. In: Walter MR (ed) Stromatolites, Developments in Sedimentology 20. Elsevier, New York, pp. 193–249.

MOUTERDE, R., ROCHA, R.B., RUGET, C. and TINTANT, H., 1979. Faciès, biostratigraphie et paléogéographie du Jurassique portugais. Ciências da Terra, 5, 29–52.

MULLER, J., 1959. Palynology of the recent Orinoco delta and shelf sediments: reports of the Orinoco Shelf Expedition. Micropaleontology, 5, 1–32.

PEREIRA, R., FEIST, M. and AZERÊDO, A.C., 2003. New charophytes from the Upper Jurassic of the Lusitanian Basin (Portugal). Journal of Micropalaeontology, 22, 113–126.

PIEŃKOWSKI, G. and WAKSMUNDZKA, M., 2009. Palynofacies in Lower Jurassic epicontinental deposits of Poland: tool to interpret sedimentary environments. Episodes, 32, 21–32.

PINHEIRO, L.M., WILSON, R.C.L., PENA DOS REIS, R., WHITMARSH, R.B. and RIBEIRO, A., 1996. The western Iberia margin: a geophysical and geological overview. In: WHITMARSH, R.B., SAWYER, D.S., KLAUS, A. and MASSON, D.G., (eds). Proceedings of the Ocean Drilling Program-Scientific Results, 149, 3–23.

RAIS, P., LOUIS-SCHMID, B., BERNASCONI, S.M. and WEISSERT, H., 2007. Palaeoceanographic and palaeoclimatic reorganization around the Middle–Late Jurassic transition. Palaeogeography, Palaeoclimatology, Palaeoecology, 251, 527–546.

RAMAJO, J. and AURELL, M., 2008. Long-term Callovian–Oxfordian sea-level changes and sedimentation in the Iberian carbonate platform (Jurassic, Spain): possible eustatic implications. Basin Research, 20, 163–184.

RAMALHO, M.M., 1970. *Cylindroporella lusitanica* n. sp., une nouvelle dasycladacée du Jurassique Supérieur portugais. Boletim da Sociedade Geológica de Portugal, 17, 123–127.

RAMALHO, M.M., 1971. Contribution à l'étude micropaléontologique et stratigraphique du Jurassique supérieur et du Crétacé inférieur des environs de Lisbonne (Portugal). Memórias dos Serviços Geológicos de Portugal, 19, 212 pp.

RAMALHO, M.M., 1981, Note préliminaire sur les microfaciès du Jurassique supérieur portugais. Comunicações dos Serviços Geológicos de Portugal, 67, 41–45.

RASMUSSEN, E.S., LOMHOLT, S., ANDERSEN, C. and VEJBÆK, O.V., 1998. Aspects of the structural evolution of the Lusitanian Basin in Portugal and the shelf and slope area offshore Portugal. Tectonophysics, 300, 199–225.

REY, J., DINIS, J.L., CALLAPEZ, P. and CUNHA, P.P., 2006. Da rotura continental à margem passiva. Composição e evolução do Cretácico de Portugal. Cadernos de Geologia de Portugal, Instituto Geológico e Mineiro, Lisboa

RUGET-PERROT, C., 1961. Études stratigraphiques sur le Dogger et le Malm inférieur du Portugal au Nord du Tage. Memórias dos Serviços Geológicos de Portugal, 7, 197 pp..

SCHNEIDER, S., FÜRSICH, F.T. and WERNER, W., 2009. Sr-isotope stratigraphy of the Upper Jurassic of central Portugal (Lusitanian Basin) based on oyster shells. International Journal of Earth Science, 98, 1949–1970.

SCHRODT, F., 1894. Das Vorkommen der Foraminiferen-Gattung *Cyclammina* im Oberen Jura. Zeit Deutsch Geol Ges 45:470–485.

SILVA, R.L., DUARTE, L.V., AZERÊDO, A.C. and MENDONÇA FILHO, J.G., 2011a. Contributos sedimentológicos e geoquímicos para a modelação dos sistemas petrolíferos portugueses: as séries jurássicas ricas em matéria orgânica da Bacia Lusitânica (Portugal). Modelação de Sistemas Geológicos, Laboratório de Radioactividade Natural da Universidade de Coimbra, Coimbra, pp. 383–391.

SILVA, R.L., DUARTE, L.V., COMAS-RENGIFO, M.J., MENDONÇA FILHO, J.G. and AZERÊDO, A.C. 2011b. Update of the carbon and oxygen isotopic records of the Early–Late Pliensbachian (Early Jurassic, ~187 Ma): Insights from the organic-rich hemipelagic series of the Lusitanian Basin (Portugal). Chemical Geology, 283, 177–184.

SILVA, R.L., MENDONÇA FILHO, J.G., DA SILVA, F.S., DUARTE, L.V., SILVA, T.F., FERREIRA. R. and AZERÊDO, A.C., 2012. Can biogeochemistry aid in the palaeoenvironmental/early diagenesis reconstruction of the ~187 Ma (Pliensbachian) organic-rich hemipelagic series of the Lusitanian Basin (Portugal)?. Bulletin of Geosciences, 87, 373–382.

SOARES, A.F., ROCHA, R.B., ELMI, S., HENRIQUES, M.H., MOUTERDE, R., ALMERAS, Y., RUGET, C., MARQUES, J., DUARTE, L.V., CARAPITO, C. and KULLBERG, J.C., 1993. Le sous-bassin nord-lusitanien (Portugal) du Trias au Jurassique moyen: histoire d'un "rift avorté". Comptes Rendus de l'Académie des sciences de Paris, 317, 1659–1666.

Spigolon, A.L.D., Pena dos Reis, R.P.B., Pimentel, N.L, Matos, V.G.A.E., 2011. Geoquímica orgânica de rochas potencialmente geradoras de petróleo no contexto evolutivo da Bacia Lusitânica, Portugal. Boletim Geociências da Petrobras 19, 131–162.

TRAVERSE, A., 1988. Paleopalynology, Unwin Hyman, Boston.

TRAVERSE, A., 2007. Paleopalynology (2^{nd} ed), Springer-Verlag.

TISSOT, B., DURAND, B., ESPITALIÉ, J., and COMBAZ, A., 1974. Influence of the nature and diagenesis of organic matter in the formation of petroleum. AAPG Bulletin, 58, 499–506.

TYSON, R.V., 1984. Palynofacies investigation of Callovian (Middle Jurassic) sediments from DSDP Site 534, Blake-Bahama Basin, western Central Atlantic. Marine Petroleum Geology, 1, 3–13.

TYSON, R.V., 1993. Palynofacies analysis. In: JENKINS, DG (ed) Applied Micropalaeontology, Kluwer Academic Publishers, Dordrecht, pp. 153–191.

TYSON, R.V., 1995. Sedimentary organic matter. Organic Facies and Palinofacies. Chapman & Hall, London.

VAN KREVELEN, D.W., 1961. Coal: Typology, Chemistry, Physics, Constitution. Elsevier Publishing Company.

WAKE, L.V. and HILLEN, L.W., (1980). Study of a "bloom" of the oil-rich alga *Botryococcus braunii* in the Darwin River Reservoir. Biotechnology and Bioengineering, 22, 1637–1656.

WILSON, R.C.L., HISCOTT, R.N., WILLIS, M.G. and GRADSTEIN, F.M., 1989. The Lusitanian Basin of west-central Portugal: Mesozoic and Tertiary tectonic, stratigraphic and subsidence history. In: Tankard AJ, Balkwill HR (eds) Extensional Tectonics and Stratigraphy of the North Atlantic Margins. AAPG Memoir, 46, 341–361.

WILLIAMS, G.L., 1992. Palynology as a palaeoenvironmental indicator in the Brent Group, northern North Sea In: MORTON AC, HASZELDINE RS, GILES MR and BROWN S. (eds) Geology of the Brent Group. Geological Society London Special Publications, 61, 203–212.

WITT, W.G., 1977. Stratigraphy of the Lusitanian Basin. Shell Prospex Portuguesa, Unpublished report, 61pp..

WRIGHT, V.P., 1985. Algal marsh deposits from the Upper Jurassic of Portugal In: TOOMEY, D.F. and NITECKI, M.H., (eds). Palaeoalgology: Contemporary Research and Applications. Springer-Verlag, New York, pp. 330–341.

ZAVATTIERI, A.M., ROSENFELD, U. and VOLKHEIMER, W., 2008. Palynofacies analysis and sedimentary environment of Early Jurassic coastal sediments at the southern border of the Neuquén Basin, Argentina. Journal of South American Earth Sciences, 25, 227–245.

Acknowledgements

Ricardo L. Silva thanks the FCT-MCTES for funding trough a PhD fellowship (SFRH/BD/47362/2008). We wish to thank LAFO-UFRJ team for all the technical support with sample preparation and organic petrography and Nuno Inês and Selma Lima for their valuable help in the field work at Pedrógão. We also acknowledge A.M. Zavattieri and P. Pieńkowski for the helpful comments and review of earlier versions of the manuscript. This work has been partially supported by project PTDC/CTE-GIX/098968/2008 - "High resolution stratigraphy of the Lower Jurassic organic-rich marine series in the Lusitanian Basin" (FCT-Portugal and COMPETE-FEDER) and project PEst-OE/CTE/UI0263/2011.

Capítulo 6 | Síntese final

O intervalo de tempo compreendido entre o Sinemuriano Superior e o Pliensbaquiano na Bacia Lusitânica (Portugal) é caracterizado pela ocorrência de diversos intervalos ricos em matéria orgânica, particularmente expressivos nos membros de Polvoeira da Formação de Água de Madeiros (Sinemuriano Superior-extrema base do Pliensbaquiano) e Margo-calcários com níveis betuminosos da Formação de Vale das Fontes, (Pliensbaquiano).

Na região de S. Pedro de Moel, a Formação de Água de Madeiros consiste numa sucessão de margas e calcários de origem marinha e rica em matéria orgânica, incluindo 3 litofacies caracterizadas pela sua riqueza em Carbono Orgânico Total: margas cinzentas escuras, *black shales* e calcários laminados. A pirólise *Rock-Eval* indica que o tipo de querogénio predominante é o do tipo 2 e que esta unidade possui um bom potencial para geração de óleo, embora seja termicamente imatura em afloramento. As assembleias de querogénio são dominadas pela ocorrência de Matéria Orgânica Amorfa (Membro de Polvoeira), embora a contribuição do grupo dos fitoclastos aumente para o topo em associação com as facies mais proximais (Membro de Praia da Pedra Lisa). Ao longo da secção observa-se alguma variabilidade morfológica no grupo da Matéria Orgânica Amorfa, em associação com mudanças da espessura da coluna de água e taxas de sedimentação.

No Membro de Polvoeira foram colhidas diversas amostras de madeira fóssil. Os dados obtidos, onde foi utilizada pela primeira vez a observação petrográfica e a determinação dos teores totais de C e N em adição à determinação do $\delta^{13}C$ e $\delta^{15}N$, sugerem que a composição isotópica dessas amostras foi afetada por diferentes processos sedimentares e diagenéticos (orgânicos e inorgânicos) ao longo da secção, impossibilitando o seu emprego em estudos de caracter paleoambiental.

O membro Margo-calcários com níveis betuminosos da Formação de Vale das Fontes consiste em alternâncias margo-calcárias hemipelágicas, ricas em matéria orgânica e com abundante fauna bentónica e nectónica. Os estudos sedimentológicos, estratigráficos e biostratigráficos de detalhe permitiram estabelecer uma correlação fina (camada a camada) entre diversos perfis estratigráficos desta unidade, a construção de um quadro de evolução sequencial de 3ª-ordem para este intervalo e melhorar os esboços paleogeográficos existentes. Foi ainda demostrada a grande semelhança entre o esquema sequencial de 3ª-ordem estabelecido para a Bacia Lusitânica com os de outras localizações europeias.

No perfil de referência de Peniche, demostrou-se também que existe uma relação entre os intervalos ricos em matéria orgânica caracterizados pela ocorrência de *black shales* com elevados teores de Carbono Orgânico Total e três excursões positivas $\delta^{13}C$, registadas em carbonatos e substratos orgânicos de natureza marinha e continental. Foi sugerido que a Zona Margaritatus corresponde a um evento (pelo menos regional) de preservação de matéria orgânica (Late Pliensbachian OMPI). Especula-se também que este evento, em última análise representando soterramento de carbono, pode ter condicionado o desenvolvimento do pequeno período de *ice-house?* que se infere que tenha ocorrido durante parte da Zona Spinatum.

Num trabalho inovador, desenvolvido à escala da bacia, foi mostrada a aplicabilidade de métodos biogeoquímicos no estudo de fácies ricas em matéria orgânica em séries sedimentares antigas. Foram determinados, nos principais intervalos de *black shales*, os teores de lípidos, hidratos de carbono e proteínas. Observou-se que as variações laterais e temporais das quantidades totais destas biomoléculas relacionam-se com as condições paleoceanográficas vigentes durante a deposição e diagénese.

A passagem Jurássico Médio–Superior corresponde a um hiato bacinal, precedido por uma regressão forçada complexa. Os primeiros sedimentos do Jurássico Superior pertencem à Formação de Cabaços e correspondem ao desenvolvimento de sistemas deposicionais do tipo lacustre, lagunar e marinho raso. Nas secções estudadas da região norte da Bacia Lusitânica, a matéria orgânica particulada é maioritariamente de origem continental (fitoclastos e esporomorfos), embora se observem pontualmente alguns elementos de origem marinha (como por exemplo, quistos de dinoflagelados). Nestas assembleias de querogénio, foi também identificada e descrita uma nova partícula da Palinofácies, denominada de intraclasto. Os estudos de distribuição do Carbono Orgânico Total e da Palinofácies permitiram demostrar a elevada variabilidade da natureza da matéria orgânica, relacionada com a elevada dinâmica sedimentar e paleoambiental referida em trabalhos anteriores.