Carbon isotope stratigraphy and ammonite biochronostratigraphy across the Sinemurian–Pliensbachian boundary in the western Iberian margin

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Here, we present an integrated stratigraphical study across the Sinemurian–Pliensbachian interval cropping out into the Portuguese reference section of S. Pedro de Moel (Lusitanian Basin). Characterized by marl-limestone alternations of the Água de Madeiros Formation (subdivided into Polvoeira and Praia da Pedra Lisa members), this succession is particularly dominated by organic-rich facies (black shales) and contains a diverse fauna of benthic and nektonic macrofossils. This stratigraphic and sedimentary setting is the basis for a high-resolution carbon isotope study, constrained by new ammonite biochronostratigraphic determinations and other palaeontological data. The new ammonite collections characterize the Oxynotum and Raricostatum chronozones and the Raricostatum, Macdonnelli and Aplanatum subchronozones, and accurately identify the Sinemurian–Pliensbachian boundary in this western Iberian margin setting. Carbon isotope measurements were made from bulk carbonate ($\delta^{13}C_{carb}$) from 351 samples, representing the Oxynotum to earliest Jamesoni (early Taylori) Chronozone intervals. The carbon isotope values exhibited a large range, varying between +2.85‰ in the Oxynotum Subchronozone to very negative values observed in some limestone beds from the Raricostatum Subchronozone (lowest reaching –6.7‰), a variation clearly controlled by lithological and facies changes. Despite these strong anomalous isotopically light values (below –2‰), which are clearly associated with organic matter degradation and early diagenesis, the $\delta^{13}C_{carb}$ curve shows a long-term negative trend across the Oxynotum to the early Taylori Subchronozone interval. This tendency is reversed around 5 m above the Sinemurian–Pliensbachian boundary, and the $\delta^{13}C_{carb}$ values become positive correlative with an absence of organic matter and argillaceous sediments in the limestone beds of Praia da Pedra Lisa Member. Although the $\delta^{13}C$ data recorded across the Sinemurian–Pliensbachian of the Lusitanian Basin had been controlled by internal depositional conditions, the general evolution of carbon isotopes agrees with the trend recognized in other basins. • Key words: carbon isotopes, ammonite biochronostratigraphy, organic-rich marly limestone, Sinemurian–Pliensbachian boundary, Portugal.

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The Lusitanian Basin (LB), located on the western Iberian passive margin of the Atlantic (Fig. 1A), provides an excellent record of the Early Jurassic time interval. Primarily comprising thick marine carbonate deposits, part of this succession, namely the Upper Sinemurian–Pliensbachian interval, is composed of hemipelagic marl-limestone alternations (*e.g*. Soares *et al*. 1993; Azerêdo *et al*. 2003; Duarte *et al.* 2004b, 2010; Duarte 2007), biostratigraphically

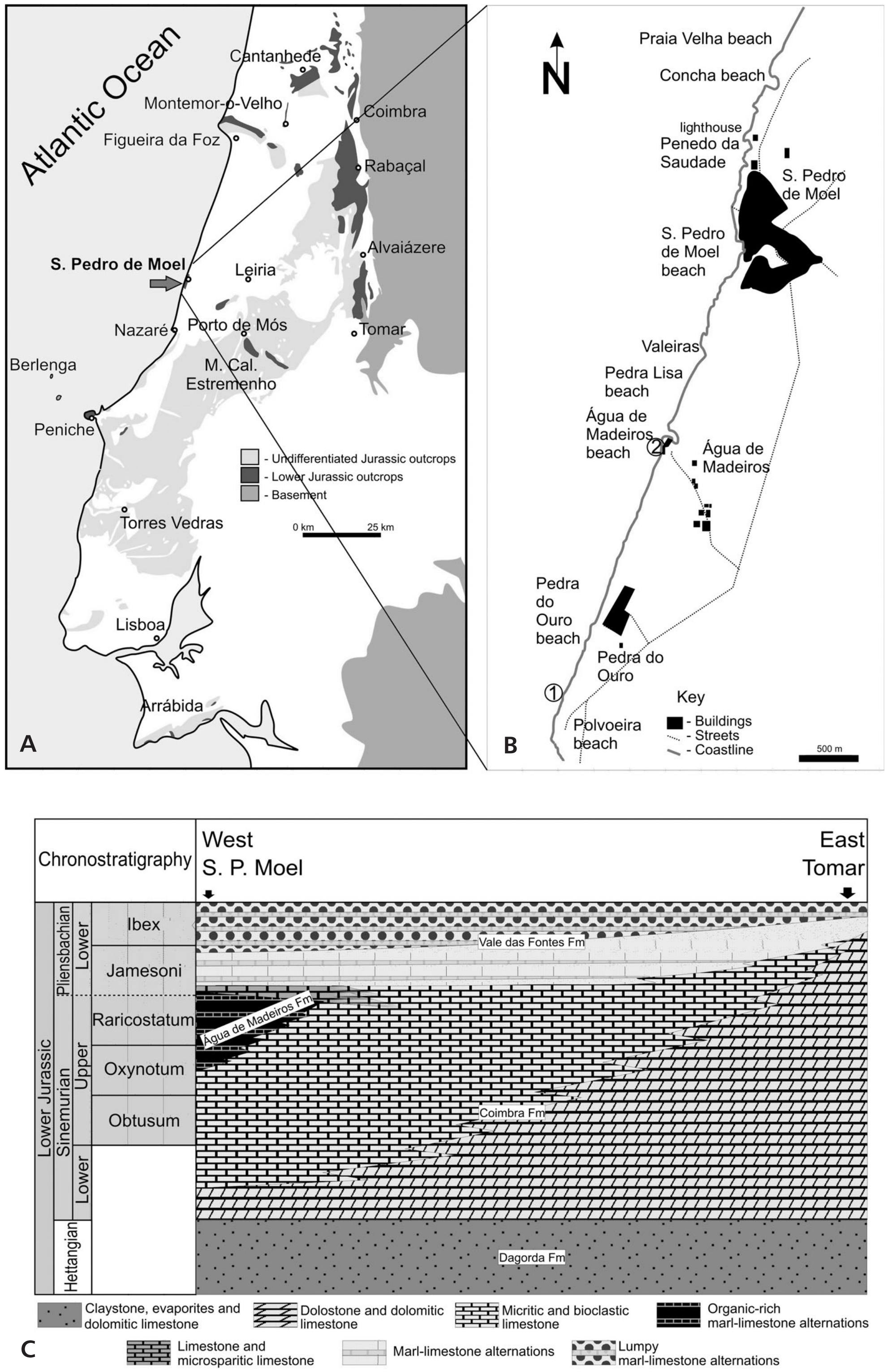


Figure 1. A – simplified geological map of the central-northern part of the Lusitanian Basin (Portugal) with the location of the main Lower Jurassic hemipelagic deposits. • B – sketch map of coastal area of S. Pedro de Moel with the location of the two studied sections: 1 – Polvoeira; 2 – Água de Madeiros. • C – generic facies and stratigraphic chart for the Hettangian–Lower Pliensbachian interval of the Lusitanian Basin (adapted from Duarte *et al.* 2010).

well controlled through accurate ammonite determinations (*e.g.* Mouterde 1967a, Phelps 1985, Dommergues 1987, Comas-Rengifo *et al.* 2013, and references therein) and calcareous nannofossils (Oliveira *et al.* 2007, Regianni *et al.* 2010, Mattioli *et al.* 2013). A characteristic feature of the Upper Sinemurian and Pliensbachian sedimentation in the LB is the richness in organic matter, making it one of the most important stratigraphic intervals of hydrocarbon source rocks (*e.g.* Oliveira *et al.* 2006; Duarte *et al.* 2010, 2012; Silva *et al.* 2011, 2012; Correia *et al.* 2012; Poças

Ribeiro *et al.* 2013; Silva 2013). Here, we present a high-resolution integrated stratigraphic study of the Upper Sinemurian–lowermost Pliensbachian carbonate deposits (Água de Madeiros Formation), cropping out into the S. Pedro de Moel area (Fig. 1A, B). This work comprises a carbon isotope analysis of this interval in the westernmost European domain, supported through new biostratigraphic interpretations, considered together with other previously published lithostratigraphic, palaeontological (benthic macrofauna) and geochemical (total organic carbon, TOC) data. The S. Pedro de Moel section presents the most complete record of Sinemurian and Lower Pliensbachian ammonites of the LB (*e.g.* Pompeckj 1898, 1906; Choffat 1903–1904; Mouterde 1967b; Antunes *et al.* 1981; Mouterde *et al.* 1981; Dommergues 1987; Dommergues *et al.* 2004, 2010; Duarte *et al.* 2010; Meister *et al.* 2012; Comas-Rengifo *et al.* 2013). In this study, we present new precise biostratigraphic determinations, particularly in terms of the definition of some zonal and subzonal boundaries of the Late Sinemurian (Oxynotum and Raricostatum chronozones). This improved biochronostratigraphic zonation will be useful in future stratigraphic correlation and palaeoenvironmental studies involving this interval in the Iberia margin. In addition, our high-resolution carbon isotope data build on and extend the conclusions of the recent chemostratigraphic studies of Korte & Hesselbo (2011), Riding *et al.* (2012) and Jenkyns & Weedon (2013). Developed in different geological contexts of UK Jurassic basins, the cited studies suggest that carbon isotope evolution during the Late Sinemurian (since the Oxynotum Chronozone) to earliest Pliensbachian is marked by global scale geochemical events (see Korte & Hesselbo 2011, Riding *et al.* 2012).

Geological setting

The LB is a narrow and small north-south elongated basin, bordered in the east by the Iberian Massif and to the west by the Variscan (granitic and metamorphic) Berlenga Horst (Fig. 1A). This basin originated during the Triassic, resulting from an extensional phase that preceded the opening of the Central Atlantic Ocean. From the Jurassic to late Cretaceous, the sedimentary infill records a great variety of sediments and facies that reflect palaeoenvironmental changes. In terms of the LB sedimentary evolution, several phases have been identified, each bounded by regional unconformities (*e.g.* Wilson *et al.* 1989, Alves *et al.* 2002, among others). The first cycle, ranging from the Triassic to the Middle Jurassic (Callovian) (Soares *et al.* 1993, Azerêdo *et al.* 2003), includes the stratigraphic interval presented and discussed in the present study (Fig. 1C).

In the LB, the Lower Jurassic generally comprises marine carbonate deposits (see Soares *et al.* 1993, Azerêdo *et al.* 2003, Duarte *et al.* 2004b). The base of the Jurassic

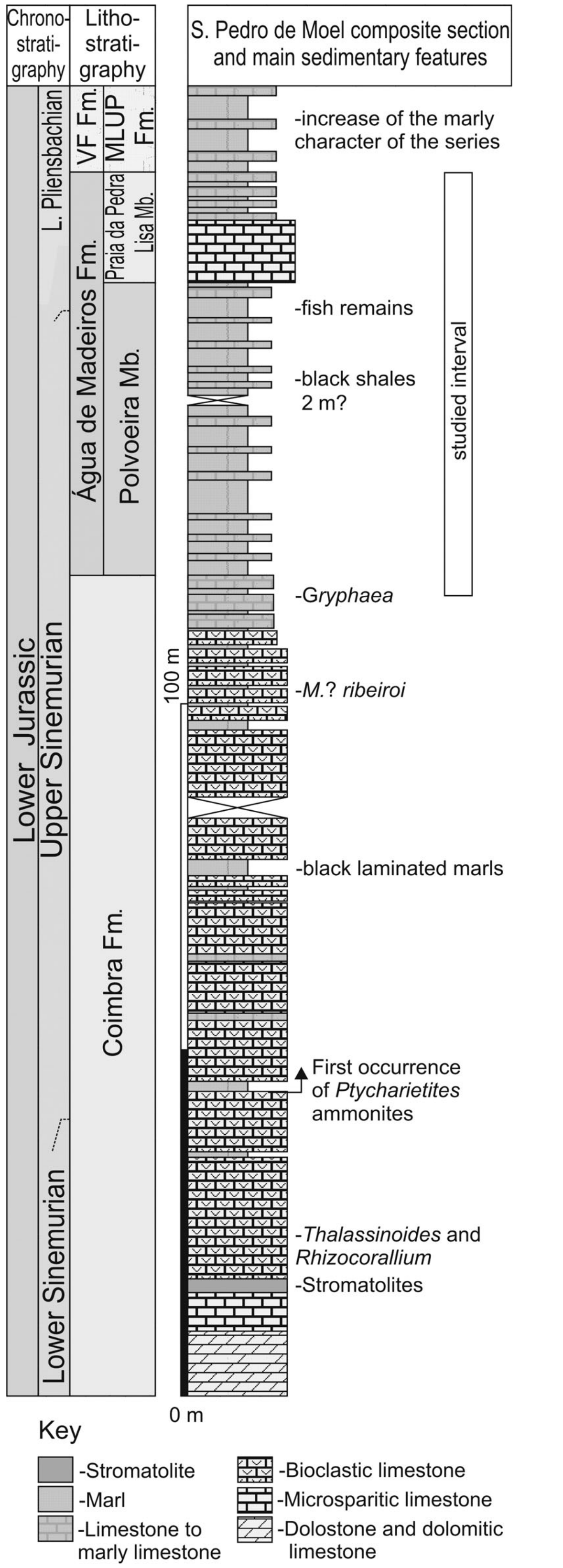


Figure 2. Synthetic stratigraphic log of the Sinemurian–Lower Pliensbachian succession in the S. Pedro de Moel area (adapted from Duarte *et al.* 2008, 2012; Azerêdo *et al.* 2010).

succession, probably Hettangian, is marked by a fine-grained, primarily siliciclastic sediments with some dolomitic and evaporitic intercalations (Dagorda Fm.). The first predominantly carbonate unit represented at a basinal scale, the Coimbra Fm. (Sinemurian), overlies the Dagorda Fm. (Fig. 1C). The Coimbra Fm. comprises a succession of dolostone and limestone, with the latter lithotype better expressed at the top of the unit and in the most western sectors. This lithotype corresponds to a marginal-marine palaeoenvironmental setting (Azerêdo *et al.* 2010). During the Late Sinemurian, particularly in the western part of the basin (Peniche, S. Pedro de Moel and Figueira da Foz localities, Fig. 1A), the succession is characterized by marl–limestone alternations with common ammonites and black shale, belonging to the Água de Madeiros Fm. This unit marks the onset of the development of open marine conditions in the basin and is subdivided into the Polvoeira and Praia da Pedra Lisa members (Duarte & Soares 2002). This fine-grained sedimentation extends throughout the basin in the Lower Pliensbachian–Upper Toarcian interval, corresponding to the Vale das Fontes, Lemede and S. Gião formations (Duarte & Soares 2002; Duarte *et al.* 2004b, 2010; Duarte 2007).

The Lower Jurassic at S. Pedro de Moel

S. Pedro de Moel is a small town located on the coast approximately 110 km north of Lisbon (Fig. 1A). In this area, the Lower Jurassic carbonate outcrops are restricted to the coastline (Fig. 1B), including the Lower Sinemurian to Middle Toarcian interval, in an intensely folded and faulted succession (see Duarte *et al.* 2008, 2012). Despite this complex structural setting the Sinemurian record in these exposures is particularly important. In the present study we observed the best and most continuous succession of the Coimbra Fm., the type-section of the Água de Madeiros Fm. and its two members (*e.g.* Duarte & Soares 2002; Duarte *et al.* 2008, 2010, 2012; Azerêdo *et al.* 2010) (Fig. 2). The occurrence of ammonites from the Obtusum Chronozone of S. Pedro de Moel, the oldest known record in the LB, allowed dating the succession from the middle part of the Coimbra Fm. upwards (Dommergues *et al.* 2004, 2010).

Material and methods

Although this study makes use of stratigraphic and sedimentological data from other locations within the LB (Fig. 1A), the study was primarily centered in the S. Pedro de Moel region, where there are two complementary sections of the Upper Sinemurian to Lower Pliensbachian, cropping out at the Polvoeira and Água de Madeiros beaches (Figs 1B and 3). These two localities, considered as type-sections of the Polvoeira and Praia da Pedra Lisa members (Duarte & Soares 2002), have been studied in detail in terms of lithostratigraphy, high-resolution ammonite biostratigraphy and carbon stable isotopes. In addition to lithology, ammonite biostratigraphy and carbon isotopes, other data were also considered, such as the benthic macrofauna record (*e.g.* Paredes *et al.* 2013a, b) and the previously published total organic carbon values (see Duarte *et al.* 2012).

Biochronostratigraphy. – The new biochronostratigraphic determinations were based on the sampling and examination of more than 800 ammonite specimens. These data were complemented using other palaeontological information, *e.g.* the occurrence of benthic macrofauna (bivalves and brachiopods), recorded in the studied succession.

Carbon and oxygen stable isotopes in bulk carbonate. – A total of 351 samples of bulk carbonate ($\delta^{13}C_{carb}$) were collected from the top of Coimbra Fm. and through the whole Água de Madeiros Fm. (Oxynotum to early Jamesoni chronozones interval). Approximately 275 of these samples are from an interval of 29 m in thickness, with a sampling spacing average of 10 cm. The $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ measurements were performed in a stable isotope laboratory at Cardiff University, using a Thermo Electron Delta V Advantage mass spectrometer with an automated carbonate preparation device (GasBench III). The isotope values are presented in per mil relative to the PDB standard and calibrated using a routine preparation and analysis of the carbonate standard NBS-19. The analytical precision is generally better than 0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$.

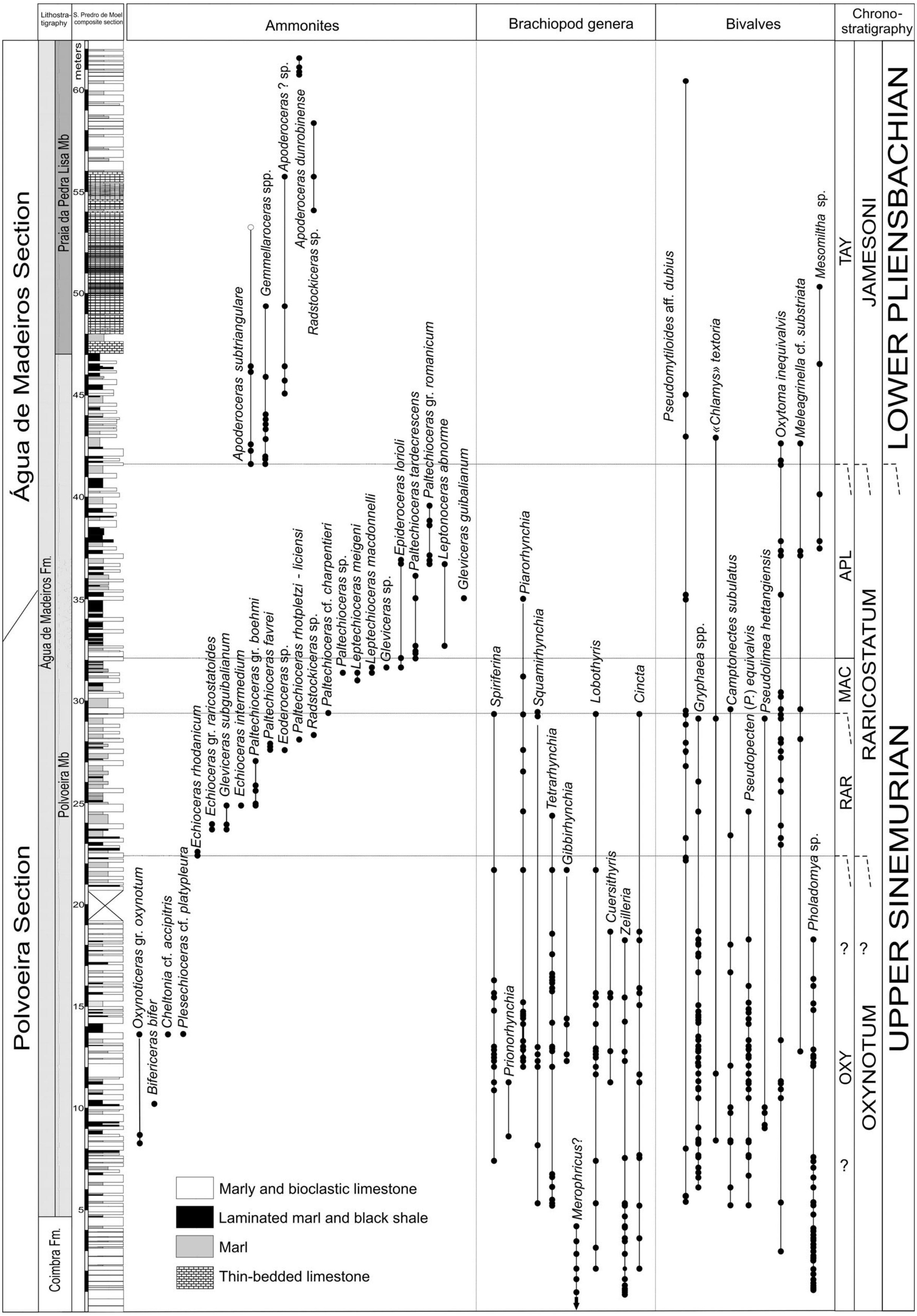
Results

Lithostratigraphy and ammonite biochronostratigraphy

The Polvoeira Section

This section is located at approximately 4 km south of S. Pedro de Moel (39°43´ 18˝ N; 9°02´ 56˝ W), presenting a continuous succession from the top of Coimbra Fm. to the middle-top part of the first member (Polvoeira Mb.) of

Figure 3. Lithostratigraphy, ammonite distribution, and main benthic faunal occurrences across the uppermost Sinemurian to lowermost Pliensbachian (Água de Madeiros Fm.) of S. Pedro de Moel composite section. Abbreviations: OXY – Oxynotum; RAR – Raricostatum; MAC – Macdonnelli; APL – Aplanatum; TAY – Taylori.


Polvoeira Section
Água de Madeiros Section
Lithostratigraphy
S. Predro de Moel composite section
meters
Coimbra Fm.
Água de Madeiros Fm.
Polvoeira Mb
Praia da Pedra Lisa Mb
Ammonites
Brachiopod genera
Bivalves
Chronostratigraphy
Oxynoticeras gr. oxynotum
Bifericeras bifer
Cheltonia cf. accipitris
Plesechioceras cf. platypleura
Echioceras rhodanicum
Echioceras gr. raricostatoides
Gleviceras subguibalianum
Echioceras intermedium
Paltechioceras gr. boehmi
Paltechioceras favrei
Eoderoceras sp.
Paltechioceras rhotpletzi - liciensi
Radstockiceras sp.
Paltechioceras cf. charpentieri
Paltechioceras sp.
Leptechioceras meigeni
Leptechioceras macdonnelli
Gleviceras sp.
Epideroceras lorioli
Paltechioceras tardecrescens
Paltechioceras gr. romanicum
Leptonoceras abnorme
Gleviceras guibalianum
Apoderoceras subtriangulare
Gemmellaroceras spp.
Apoderoceras ? sp.
Apoderoceras dunrobinense
Radstockiceras sp.
Spiriferina
Prionorhynchia
Piarorhynchia
Squamirhynchia
Tetrarhynchia
Gibbirhynchia
Merophricus?
Lobothyris
Cuersithyris
Zeilleria
Cincta
Pseudomytiloides aff. dubius
Gryphaea spp.
«Chlamys» textoria
Camptonectes subulatus
Pseudopecten (P.) equivalvis
Pseudolimea hettangiensis
Oxytoma inequivalvis
Meleagrinella cf. substriata
Pholadomya sp.
Mesomiltha sp.
OXY
RAR
MAC
APL
TAY
OXYNOTUM
RARICOSTATUM
JAMESONI
UPPER SINEMURIAN
LOWER PLIENSBACHIAN
Marly and bioclastic limestone
Laminated marl and black shale
Marl
Thin-bedded limestone

Água de Madeiros Fm. (Fig. 3). This locality is the only place where a continuous sedimentation between these two formations can be observed.

The Coimbra Fm. primarily comprises bioclastic limestone (wackestone to grainstone) and rare intercalations of greyish marl and bioclastic marlstone in excess of approximately 26 m (in Fig. 3 only the upper 4.5 m are illustrated). This part of the Coimbra Fm. is rich in benthic fauna, including brachiopods [primarily terebratulids, such as *Merophricus*? *ribeiroi* (Choffat) and *Zeilleria quiaosensis* (Choffat)], infaunal (*e.g. Pholadomya*) and epifaunal (*Gryphaea*) bivalves, gastropods and ahermatipic corals. *Rhizocorallium* and *Thalassinoides* trace fossils are particularly abundant and nektonic fossils are absent.

The Polvoeira Mb. (approximately 31 m thick) comprises organic-rich marl-limestone alternations, more bioclastic at the base, becoming progressively more argillaceous and rich in black shale in the uppermost part. Compared with the top of the Coimbra Fm., the base of the Polvoeira Mb. shows continuous deposition, with similar limestone facies and abundant and diversified macrofauna. Organic-rich facies occur in several levels, preferentially in marly beds, most of which exhibit fine lamination. The thickness of these beds is generally less than 10 cm, with the thickest black shale level (50 cm) observed in the middle of the succession. This sedimentary variation is coupled with the occurrence of rare nektonic macrofossils, but some discrete levels with *Oxynoticeras* gr. *oxynotum* (Quenstedt), *Bifericeras bifer* (Quenstedt), *Plesechioceras* cf. *platypleura* Dommergues & Meister and *Cheltonia* cf. *accipitris* (Buckman) have been identified (Figs 3 and 4A). In the upper part of this section the succession is more argillaceous (Fig. 4B) and enriched in organic matter (medium grey to dark grey marl, thin laminated limestone and black shale), coupled with an increase of nektonic invertebrate fauna (ammonites and belemnites), fossil fish and wood remains. Some levels are particularly rich in ammonites, such as oxynoticeratids and echioceratids, occurring in succession typical of the Raricostatum Chronozone: *Echioceras rhodanicum* (Dumortier), *Echioceras* gr. *raricostatoides* (Vadasz), *Gleviceras subguibalianum* (Pia), *Paltechioceras* gr. *boehmi* (Hug), *Paltechioceras favrei* (Hug), *Paltechioceras rhotpletzi* (Böse), *Paltechioceras* cf. *charpentieri* (Schafhautl), *Leptechioceras meigeni* (Hug), *Leptechioceras macdonnelli* (Portlock), *Paltechioceras tardecrences* (Hauer) (Fig. 4C), *Gleviceras guibalianum* (d'Orbigny) and *Paltechioceras romanicum* (Uhlig). The later three taxa occur abundantly in the upper studied level of the Polvoeira section (Fig. 4B).

As in the top of Coimbra Fm., benthic macrofauna (brachiopods and bivalves) are abundant in the lower portion of the Polvoeira Mb. Brachiopods are particularly abundant in the Oxynotum Chronozone, which include the *Spiriferina* genus, terebratulids (*Lobothyris*, *Cuersithyris*) and zeilleriids (*Zeilleria*, *Cincta*), while rhynchonellids and tetrarhynchiids dominate the assemblages (*Tetrarhynchia*, *Squamirhynchia*, *Prionorhynchia*, *Gibbirhynchia*, *Piarorhynchia*), with rhynchonellids becoming exclusive in the lower part of the Raricostatum Subchronozone. Among bivalves, *Pholadomya* and *Gryphaea* associations dominate up to the top of Oxynotum Chronozone. In the Raricostatum Chronozone, these associations are replaced by *Pseudomytiloides* aff. *dubius* Sowerby (Fig. 4D), and two different species of Oxytomidae, *Oxytoma inequivalvis* Sowerby and *Meleagrinella* aff. *substriata* (Münster), particularly in the upper part of Raricostatum Chronozone. Some Pectinoida are occasionally present, such as "*Chlamys*" *textoria* (Schlotheim), *Camptonectes subulatus* (Münster), *Pseudopecten* (*Ps.*) *equivalvis* Sowerby and *Pseudolimea hettangiensis* (Terquem).

The Água de Madeiros Section

The Água de Madeiros section is located approximately 1.5 km south of S. Pedro de Moel (39°44´ 27˝ N; 9°02´ 20˝ W), and displays a continuous succession of approximately 30 m in thickness, including the top of Polvoeira and the Praia da Pedra Lisa members of Água de Madeiros Fm. (Figs 3, 4E, 4F). At the base, this section shows the upper part of the Polvoeira Mb., with marl-limestone alternations approximately 14 m thick, organic-rich levels (black shale) and wood fragments of decimetric sizes (see Silva *et al.* 2013). Marlstones are grey to black, occasionally laminated, and rich in disseminated organic matter, while limestone is generally in decimetric beds of fossiliferous wackestone, often with abundant ostracods and mollusks.

Belemnites and ammonites are particularly abundant in the lower part of the studied section, showing several levels with abundant *Paltechioceras tardecrescens* (Hauer), *Paltechioceras romanicum* (Uhlig), some *Leptonoceras abnorme* (Hauer) and *Epideroceras lorioli* (Hug), a typical ammonite association of the Raricostatum Chronozone (Aplanatum Subchronozone) (Fig. 4E).

Upwards, the top of Polvoeira Mb. shows a significant change in the ammonite record. After the disappearance of echioceratids (Fig. 4E), *Gemmellaroceras* spp. and *Apoderoceras subtriangulare* (Young & Bird) appear marking the base of the Pliensbachian (see discussion below). Despite the relative abundance of ammonites in several levels, the specimens are tiny and/or poorly preserved. In the upper part of the Polvoeira Mb., brachiopods are practically absent and bivalves are restricted to sporadic occurrences of *Mesomiltha* sp., *Oxytoma inequivalvis* Sowerby and *Meleagrinella* aff. *substriata* (Münster).

The Praia da Pedra Lisa Mb. is predominantly calcareous (mainly mudstone and wackestone), beginning with approximately 9 m of decimetre- to centimetre-thick

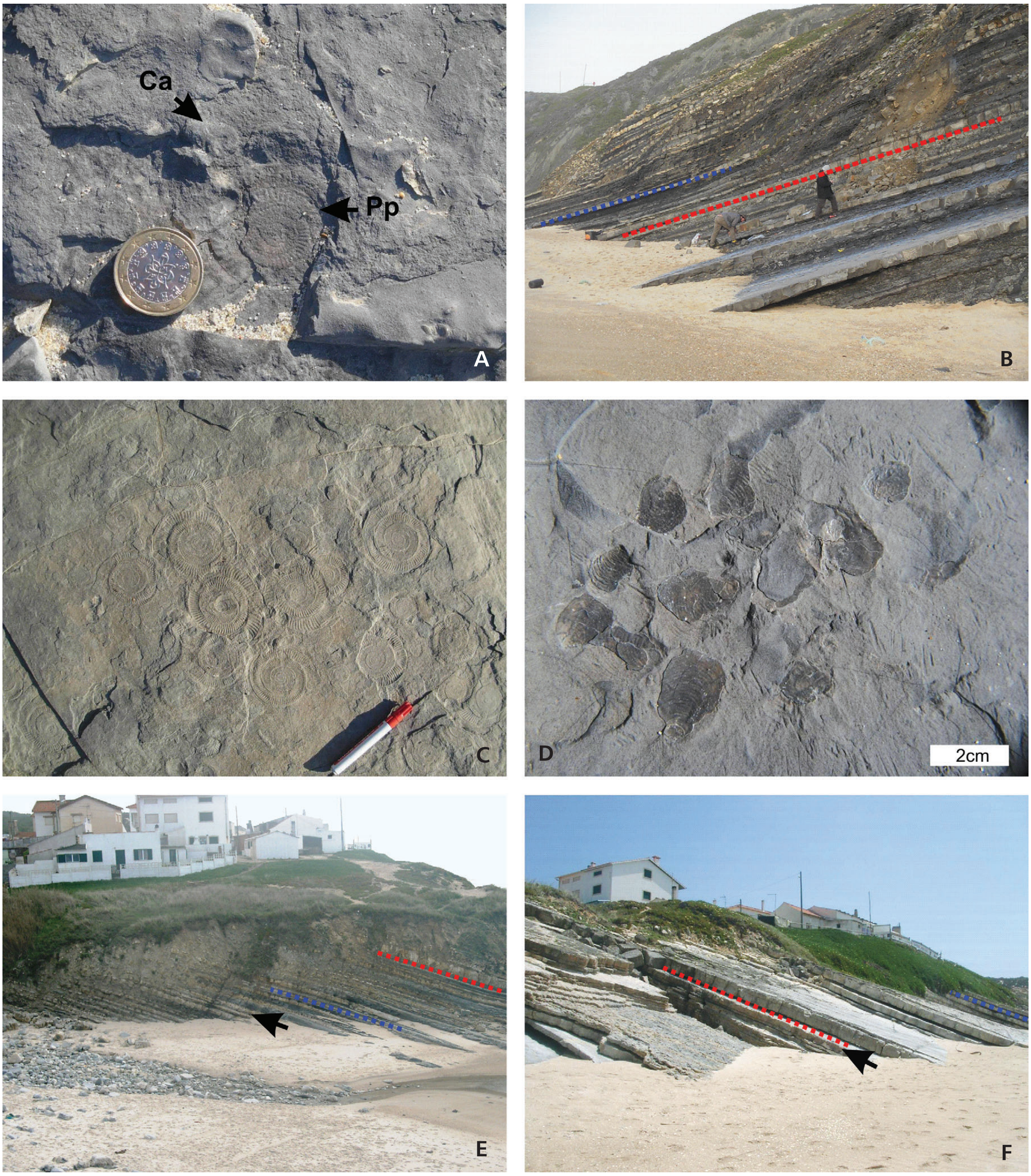


Figure 4. Biostratigraphically significant fossils and details of lithostratigraphy in the Oxynotum-Jamesoni chronozones interval (Água de Madeiros Fm.) in the studied area. • A – *Cheltonia* cf. *accipitris* (Ca) and *Plesechioceras platypleura* (Pp) recorded ~13.7 m of the Polvoeira section (see Fig. 3). This ammonite association is typical of the Oxynotum Chronozone (Oxynotum Subchronozone). • B – upper part of the middle Polvoeira Mb. observed in the top of Polvoeira section. Red line: Raricostatum-Macdonnelli subchronozones boundary; blue line: Macdonnelli-Aplanatum subchronozones boundary. • C – bedding plane with abundant *Paltechioceras tardecrescens* (Aplanatum Subchronozone) observed in the Polvoeira section (~32.5 m in the Fig. 3). • D – some slightly disarticulated *Pseudomytiloides* bivalves with preserved shell and showing the characteristic ornamental folds. Typical record of top of Raricostatum and base of Macdonnelli subchronozones from the Polvoeira section (~29.4 m in the Fig. 3; Macdonellli Subchronozone). • E – lower part of the Água de Madeiros section showing the transition between the two members of the Água de Madeiros Fm. (red line). The arrow marks the uppermost level with echioceratids and the blue line corresponds to the first *Apoderoceras subtriangulare* (proposed Sinemurian–Pliensbachian boundary). • F – middle-upper part of the Praia da Pedra Lisa Mb. in the Água de Madeiros section. Red line: change of facies observed in the middle part of the member (see text); arrow: reference level with *Radstockiceras*; blue line: first occurrence of *Apoderoceras dunrobinense* (according to Meister *et al.* 2012).

microspar limestone, occasionally showing lamination and irregular stratification. Benthic and nektonic macrofauna are scarce; however, some levels yield tiny *Gemmellaroceras* sp. (?) and *Radstockiceras* sp. (Fig. 4F). Despite the occurrence of *Rhizocorallium* and *Thalassinoides* trace fossils, benthic macrofauna is practically absent.

The upper part of the studied member, approximately 7 m thick, is characterized by a gradual increase in interbedded centimetre-scale grey to dark grey marl and a marked thickening of the limestone beds. Some marly intervals show lamination, corresponding to organic-rich facies. Limestone consists of fossiliferous micrite to biomicrite/wackestone with mollusks and ostracods. Benthic macrofauna are rare, represented by the reappearance of *Pseudomytiloides* aff. *dubius* Sowerby and some disarticulated valves of *Praechlamys rollei* (Stoliczka), but belemnites and ammonites are occasionally identified in the limestone facies. Large specimens of *Apoderoceras* are frequent in the upper limestone levels of the member. Mouterde (1967b) and Antunes *et al.* (1981) assigned these levels to the Upper Sinemurian (Raricostatum Chronozone), but Duarte *et al.* (2010) suggested that these levels belong to Lower Pliensbachian (Jamesoni Chronozone, Taylori Subcronozone). This view was corroborated recently by Meister *et al.* (2012), who identified in these last levels the occurrence of *Apoderoceras dunrobinense* Spath, *Tragophylloceras numismale* (Quenstedt) and *Vicininodiceras* aff. *mouterdei* Donovan (Fig. 4F).

Carbon and oxygen isotopes

The $\delta^{13}C_{carb}$ determined across the studied section shows a very large variation, between –6.7‰ and +2.85‰ (Fig. 5; and supplementary data table). The carbon isotope values generally decrease upward through the Polvoeira Mb., exhibiting the maximum values (above +2‰) at the base of the studied succession (Oxynotum Chronozone). Strong negative values (below –2‰) are exclusive to nine limestone beds recorded above the first occurrence of genus *Echioceras* (Raricostatum Subchronozone) until the top of the member. Across the boundary between the two members of the Água de Madeiros Fm., with the interruption of organic-rich facies in the succession, the $\delta^{13}C_{carb}$ increases to approximately +1‰. In addition to these general characteristics, other features in the carbon isotopic curve are notable (Fig. 5): 1) An important negative shift (~1‰) in the $\delta^{13}C_{carb}$ from values clearly above 2‰ over the reference level with *Bifericeras* to values of approximately 1.5‰ (between ~10 m and ~28 m; see also Fig. 3). Despite this evolution some organic levels reach values below 0‰; 2) a negative shift is recorded around the levels with *Paltechioceras tardecrences*, *Gleviceras guibalianum* and *Paltechioceras romanicum* (~32.5 m; see also Fig. 3) showing values consistently below 1‰, with an average of 0.5‰; and 3) despite the increase in $\delta^{13}C_{carb}$ at the base of the Praia da Pedra Lisa Mb. to values of approximately +1‰, the carbon isotopic curve shows a slight decline across this member, after reaching a maximum value of +1.34‰.

The oxygen isotope values in bulk carbonate ($\delta^{18}O_{carb}$) vary between –5.61‰ and –1.39‰. This variation across the studied succession of S. Pedro de Moel is clearly more irregular than that of the $\delta^{13}C_{carb}$ values (Fig. 5). Besides the low correlation observed between $\delta^{18}O_{carb}$ and $\delta^{13}C_{carb}$ (R_2= –0.25; Fig. 6) there is a large contrast in the oxygen isotope signal between limestones and marls, and strong positive values are associated with most $\delta^{13}C_{carb}$ negative ones. Despite these geochemical data, similar to $\delta^{13}C_{carb}$, a large negative trend is also observed for the $\delta^{18}O_{carb}$ of bulk carbonate across the Late Sinemurian.

Discussion

Biochronostratigraphy

The lithological equivalence, facies and ammonite record were used to establish a correlation between the two sections studied and present a detailed composite section for the uppermost Sinemurian to lowermost Pliensbachian in the S. Pedro de Moel region. The studied formation is 58 m thick, with 42 m corresponding to the Polvoeira Mb. (Fig. 3). As previously demonstrated by Duarte *et al.* (2010, 2012) the most continuous succession corresponding to the uppermost Sinemurian–lower Pliensbachian is observed at S. Pedro de Moel, the only location within the basin presently well controlled by ammonites. Building on several studies concerning ammonites and the biostratigraphy of the Água de Madeiros section (*e.g.* Mouterde 1967b, Antunes *et al.* 1981, Meister *et al.* 2012), the data presented in this study provide a more detailed biostratigraphic resolution for the Oxynotum-Raricostatum chronozones interval, and new evidence for the Sinemurian–Pliensbachian boundary.

The ammonite record is facies dependent, showing scattered and isolated occurrences in the lower part of the Polvoeira and Praia da Pedra Lisa members (associated with shallower conditions; see Duarte *et al.* 2010), a fact that creates some uncertainties in the definition of some biochronostratigraphic boundaries. The taxa *Oxynoticeras* gr. *oxynotum*, *Bifericeras bifer*, *Plesechioceras* cf. *platypleura* and *Cheltonia* cf. *accipitris* at the base of the Polvoeira Mb. characterize the Oxynotum Chronozone (Oxynotum Subchronozone) (see Corna *et al.* 1997, Page 2003, Meister 2010), but the placement of the lower boundary of this Subchronozone is unknown. Despite the occurrence of several levels with ammonites from the Obtusum Chronozone (including endemic species of *Epophio-*

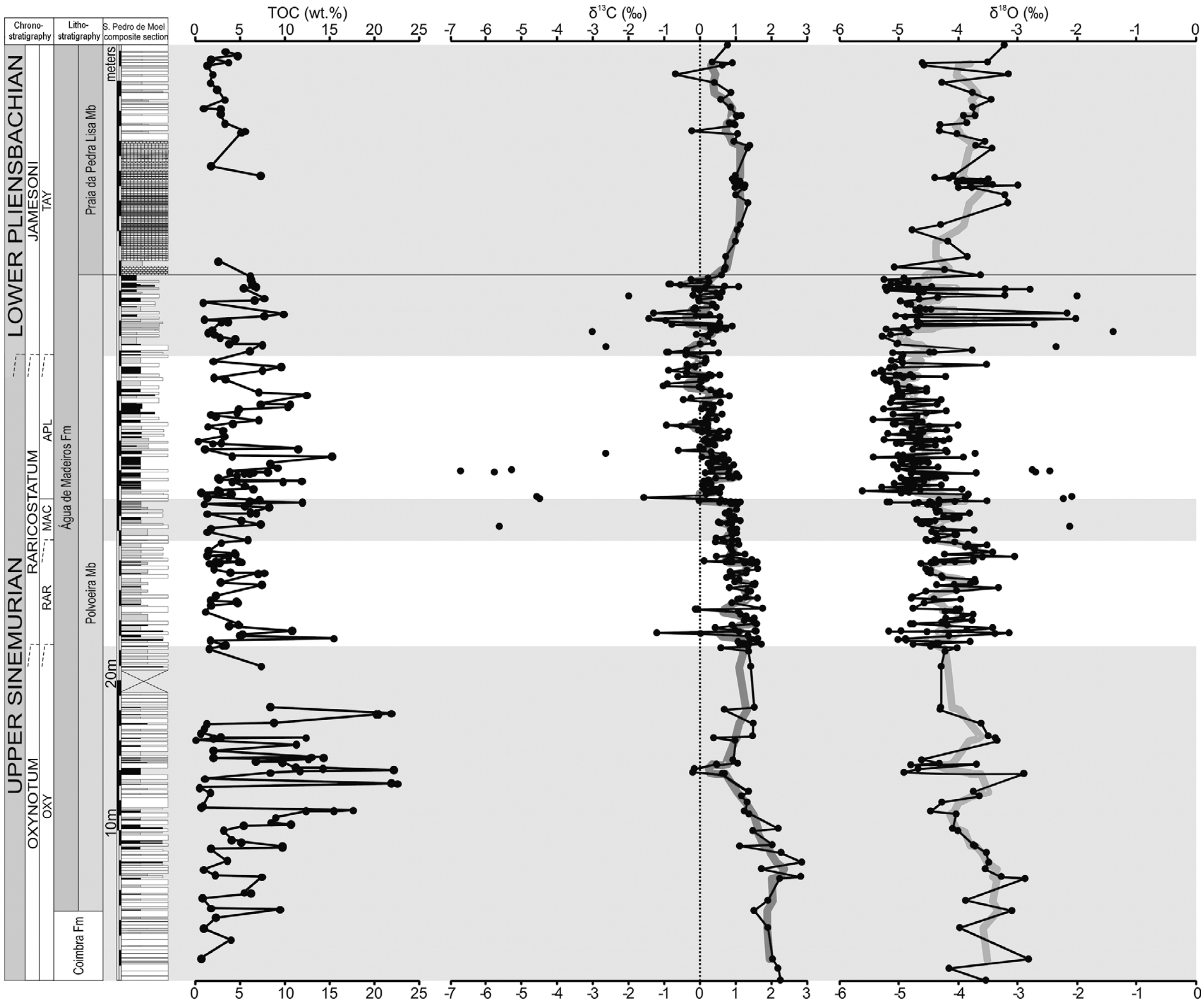


Figure 5. $\delta^{13}C_{carb}$ evolution across the Oxynotum-earliest Jamesoni chronozone interval at S. Pedro de Moel. Variations in the TOC content from Duarte *et al.* (2012). Abbreviations: OXY – Oxynotum; RAR – Raricostatum; MAC – Macdonnelli; APL – Aplanatum; TAY – Taylori.

ceroides and *Ptycharietites*; Dommergues *et al.* 2010) observed in the middle part of Coimbra Fm. cropping out into the northern S. Pedro de Moel area (Concha beach and Penedo da Saudade; Figs 1B, 2), the base of the Oxynotum Chronozone is difficult to determine precisely in S. Pedro de Moel. Indeed, ammonites are absent in the bioclastic facies (wackestone-packestone) characterizing the upper part of the Coimbra Fm., which is more than 40 m thick. In addition, according to our knowledge about the lateral facies variation in the basin (dolostone dominates in the eastern part) and previously published data (see Mouterde *et al.* 1981), the fauna observed in the upper part of the Oxynotum Chronozone has not been identified in other locations within the LB.

The succession of taxa observed in the middle part of the Polvoeira Mb., with a great abundance of echioceratids and oxynoticeratids, facilitate the first detailed characterization of the Raricostatum Chronozone in Portugal (Comas-Rengifo *et al.* 2013). The occurrence of *Echioceras rhodanicum*, *Paltechioceras* cf. *charpentieri*, *Leptechioceras meigeni*, *Paltechioceras tardecrescens* and *Paltechioceras romanicum* in a continuous succession, rich in ammonites (Fig. 3), allows the recognition of Raricostatum, Macdonnelli and Aplanatum subchronozones, respectively (see Corna *et al.* 1997, Blau & Meister 2000, Page 2003, Meister 2010) (Figs 3, 4C, E). However, the absence of an ammonite record between the last horizon with *Plesechioceras platypleura* and *Cheltonia* cf. *accipitris* of the Oxynotum Subchronozone and the first occurrence of *Echioceras* species (in an interval more than 8 m thick) makes the definition of the Oxynotum-Raricostatum chronozone boundary uncertain and difficult the identification of index ammonites from the Densinodulum Subchronozone.

Moreover, it has been difficult to define the base of the Pliensbachian Stage in S. Pedro de Moel area (*e.g.* Duarte *et al.* 2010, Meister *et al.* 2012), as is the case in other Tethyan and northwest European basins, due to the worldwide rarity of good sections with ammonites, frequent condensation, and endemism (Meister 2010). In the studied area, the absence of *Bifericeras donovani* Dommergues & Meister, that allowed definition of the Pliensbachian GSSP (base of Jamesoni Chronozone) in Robin Hood's Bay (see Meister *et al.* 2003, 2006), the facies change between the two members of the Água de Madeiros Fm. and the scarcity of the ammonite record make it difficult to identify the early Jamesoni Chronozone index ammonites. According to the criteria of Meister (2010) for the LB, the Sinemurian–Pliensbachian boundary should be located between the last horizon with *Paltechioceras* and the first occurrence of *Apoderoceras dunrobinense* Spath, as Meister *et al.* (2012) recently identified in the Água de Madeiros section (Fig. 4F) corresponding to the lower part of the Jamesoni Chronozone (lower to middle Taylori Subchronozone). Based on the palaeontological information shown in Fig. 3, the interval of incertitude is approximately 19 m thick. However, based on our recent data, the occurrence of *Apoderoceras subtriangulare* (Figs 3, 4E) 2.2 m above the last level with echioceratids, represents the best marker for the definition of the base of the Jamesoni Chronozone. These levels with *Apoderoceras* and *Gemmellaroceras*, recorded in the uppermost part of the Polvoeira Mb. and in some levels of the base of Praia da Pedra Lisa Mb., confirm an association very different from *Apoderoceras dunrobinense* identified by Meister *et al.* (2012) in the upper part of the studied section (see Figs 3, 4F). Moreover, based on the criteria of Meister (2010), the association of *Apoderoceras* with *Gemmellaroceras* in the Água de Madeiros section could be important for extra-basinal correlations. Indeed, these data are practically the same as those of Comas-Rengifo *et al.* (2010) in Asturias (northern Spain), which also show the absence of *Bifericeras donovani*. The recognition of *Gemmellaroceras* in several levels above the last occurrence of *Paltechioceras tardecrescens* in Asturias (see Comas-Rengifo *et al.* 2010), similar to S. Pedro de Moel, could be a good indicator in terms of biochronology of the lowermost Pliensbachian in Iberia.

Interpretation of stable isotope data

Palaeoenvironmental interpretation and diagenesis

The studied carbonate succession is dominated by marl-limestone alternations with significant organic matter accumulation, materialized in high TOC (Fig. 5), a characteristic exclusive to the western portion of the LB and particularly well developed in the studied area (Duarte *et al.* 2012). As demonstrated by Duarte *et al.* (2010), these organic-rich facies disappear laterally in the Upper Sinemurian (Fig. 1C) and in the eastern part of the basin the series are dominated by dolostone and dolomitic limestone. The role of organic matter is important in the palaeoenvironmental discussion and the vertical variation of $\delta^{13}C_{carb}$ recorded at S. Pedro de Moel.

At S. Pedro de Moel, the benthos-rich fossil community is associated with calcareous facies in the Oxynotum Chronozone, suggesting a palaeoenvironment dominated by shallow marine conditions with normal oxygen levels. This carbonate-rich sedimentation was interrupted by some phases of organic accumulation, in centimetric black shale intervals, reaching up to 22 wt.% TOC (Fig. 5; Duarte *et al.* 2012). Despite the high abundance of benthic macrofossils, including endobenthonics such as *Pholadomya*, this group is absent in TOC-rich levels (above 4 wt.%), suggesting dysoxic (perhaps anoxic) phases. The kerogen type described in several samples from the Oxynotum Chronozone by Duarte *et al.* (2012) and Poças Ribeiro *et al.* (2013) indicates some palaeoenvironmental restriction, with a clear dominance of amorphous organic matter and a low contribution of palynomorphs and phytoclasts. In this context, the carbon isotope signal observed in this part of the succession, sometimes above +2‰, is typical of a normal marine environment. The secular negative trend observed in the top of Oxynotum Chronozone is clearly influenced by the increase of organic matter of black shales in this part of the succession, such as confirmed by the TOC curve (Fig. 5).

The sedimentary conditions changed significantly in the Raricostatum to base of the Jamesoni chronozones interval. Indeed, an increase in clay is observed in the succession from the Raricostatum Subchronozone, together with enhanced organic-rich deposition, better developed than that in the Oxynotum Subchronozone (despite the fact that highest values above 20 wt.% here observed), confirmed through the high TOC content through multiple levels (Fig. 5). According to Duarte *et al.* (2012) the TOC background in the marly facies of upper Sinemurian to lowermost Pliensbachian interval is generally greater than 2 wt.%, with several (thicker) levels near 10 wt.%. In addition, the kerogen assemblages are rich in amorphous organic matter through the upper part of the Polvoeira Mb. (Raricostatum-extreme base of Jamesoni chronozones interval), but a slight increase in palynomorphs and phytoclasts is observed (see Duarte *et al.* 2012). Moreover, the succession (Raricostatum Chronozone) becomes enriched in nektonic fauna (principally ammonites, with occurrence of the first echioceratids, and belemnites), while the benthic fossil content abruptly decreases. An exception is an interesting fauna of *Pseudomytiloides* and *Oxytoma* *inequivalvis* (Paredes *et al.* 2013a, b), a fauna that has been associated with oxygen-deficient waters of northwestern European Early Toarcian (*e.g.* Schmid-Rohl *et al.* 2002, Wignall *et al.* 2005, Caswell *et al.* 2009). Thus, the sedimentary evidence identified in the Raricostatum Chronozone is correlated with a major transgressive event, observed in other points of the basin, such as Peniche, Figueira da Foz and Montemor-o-Velho (Fig. 1A; see Duarte *et al.* 2010). In this sedimentary context, we observe a drop in $\delta^{13}C_{carb}$, compared with the previous Oxynotum Chronozone (Fig. 5). A slight negative carbon-isotope trend is evident across the Polvoeira Mb., *i.e.*, between the Oxynotum Subchronozone and the earliest Jamesoni Chronozone. In addition to the negative trend of carbon-isotope curve, strongly anomalous negative $\delta^{13}C_{carb}$ values (between –7 and –2‰) have been recorded in several carbonate-enriched horizons, which are poor in TOC (calcareous facies with TOC <1 wt.%). Considering the organic rich-facies dominance of this part of the succession, including the entire Raricostatum Chronozone, these sudden variations are likely associated with the oxidation of organic matter responsible for the occurrence of isotopically light dissolved inorganic carbon at the sea floor (*e.g.* von Breymann *et al.* 1991, Marshall 1992). In addition, sedimentological data suggest that the limestone underwent diagenetic effects, such as rapid lithification and early cementation. Indeed, lighter carbon isotope values, corresponding to highest oxygen isotopic values, have been observed in non-compacted limestone lithotypes, evidenced in some beds through taphonomic criteria, such as the preserved volume of ammonite shells, filled with calcite spar cements (see Duarte *et al.* 2004b). Silva *et al.* (2011) discussed similar features as observed in the $\delta^{13}C_{carb}$ record of the Pliensbachian (Ibex-Margaritatus chronozones) marl-limestone series at Peniche. It is possible that early cementation, associated with the microbial processes of organic matter decay and/or marine cementation, might have been the cause for the observed scatter of $\delta^{13}C$ data (Silva *et al.* 2011 and references therein). These geochemical anomalies, observed through the Raricostatum Chronozone, are clearly controlled by diagenesis, showing the complexity of the geochemical processes associated with organic matter and carbonate deposition.

The major change in the sedimentation occurred with the deposition of limestone corresponding to the base of the Praia da Pedra Lisa Mb. This vertical change, characterized by the abrupt disappearance of clay and organic matter, is particularly evident in other parts of the basin, suggesting that a regressive event occurred in the LB during the earliest Pliensbachian. The $\delta^{13}C_{carb}$ values stabilized across the calcareous facies of this member, showing values around +1‰. However, the slight negative trend of carbon isotopes observed in the top of the studied succession (Fig. 5) might reflect an increase in organic matter, confirmed by the TOC curve of Duarte *et al.* (2012).

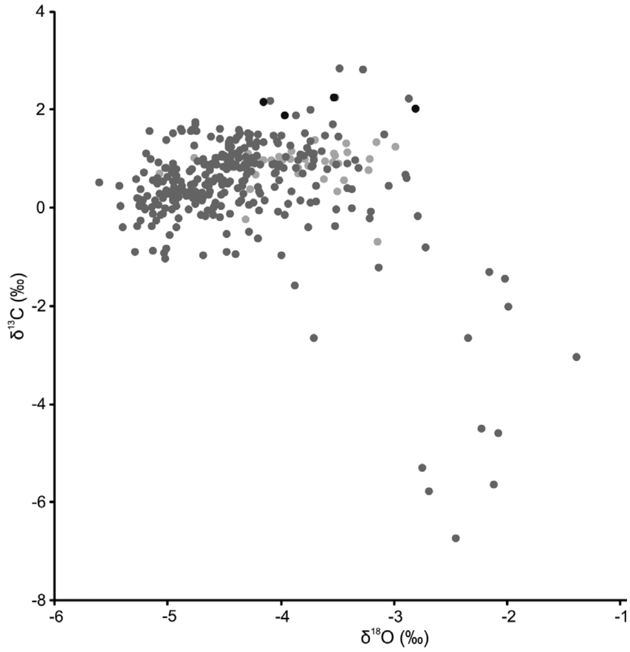


Figure 6. Cross plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ from the Oxynotum-earliest Jamesoni chronozone interval at S. Pedro de Moel. ● – Praia da Pedra Lisa Mb., ● – Polvoeira Mb., ● – Coimbra Formation.

Global isotope events in the Late Sinemurian and at the Sinemurian/Pliensbachian boundary?

The Lower Jurassic marly limestones of the LB have been the focus of several studies associated with stable isotope geochemistry and chemostratigraphy (*e.g.* Duarte *et al.* 2004a, 2007; Oliveira *et al.* 2006, 2009; Hesselbo *et al.* 2007; Suan *et al.* 2008a, 2010; Silva *et al.* 2011, 2013; Pittet *et al.* 2014). Some of these studies were based on high-resolution data obtained from bulk carbonate, brachiopods, belemnites, bulk organic matter, and fossil wood, generated in the context of an accurate ammonite biostratigraphy. Concerning carbon isotopes, several geochemical events have been identified in the Pliensbachian–Toarcian interval of the basin, particularly those in association with the Toarcian Oceanic Anoxic Event (T-OAE) (*e.g.* Hesselbo *et al.* 2007; Suan *et al.* 2008a, b, 2010; Littler *et al.* 2010; Pittet *et al.* 2014).

Considering the Sinemurian record and the Sinemurian–Pliensbachian boundary, this interval has not yet been sufficiently studied and clarified in terms of stable isotopes, despite the significant contributions of Hesselbo *et al.* (2000), Jenkyns *et al.* (2002), Morettini *et al.* (2002), van de Schootbrugge *et al.* (2005), Korte & Hesselbo (2011), Riding *et al.* (2013) and Jenkyns & Weedon (2013). Consistent with different parameters and

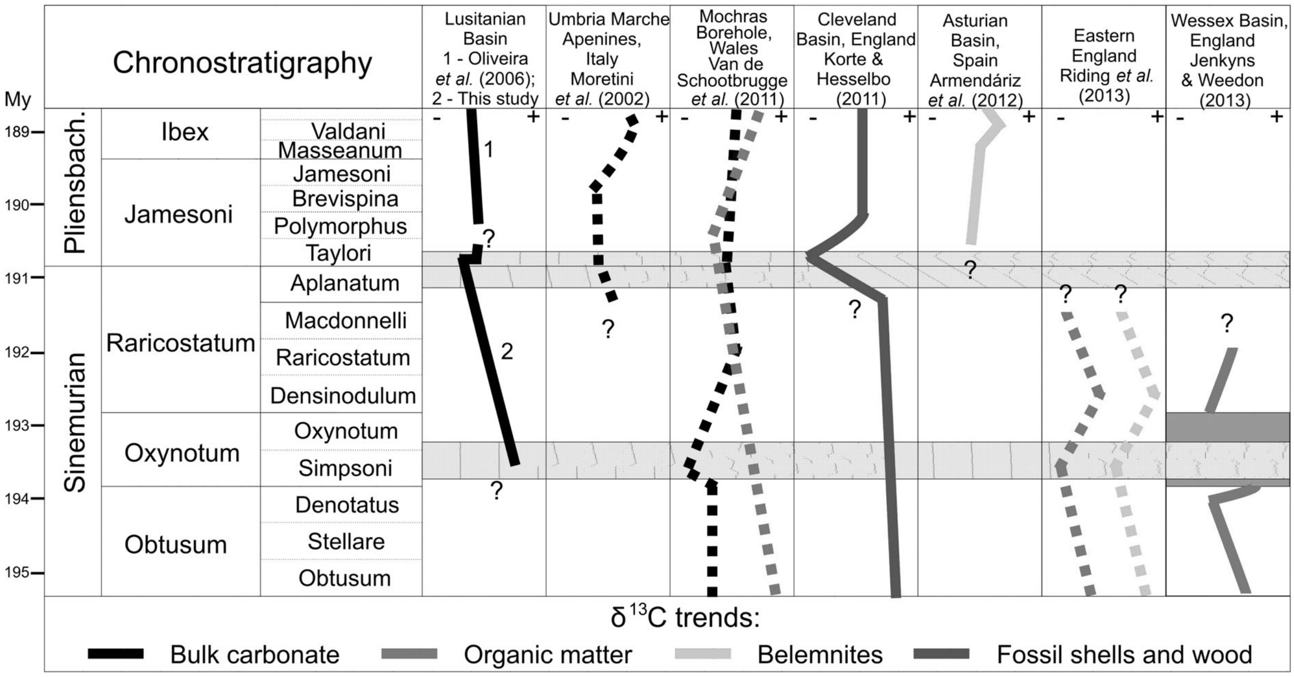


Figure 7. Correlation of the bulk carbonate C-isotope curve from Portugal and other C-isotope secular trends from other European basins across the Sinemurian–Pliensbachian boundary. Ammonite chronostratigraphy data from Ogg & Hinnov (2012). Continuous lines: high-resolution analysis; dashed lines: low-resolution analysis. Dark gray shading: hiatus; light gray shading indicates the two global C-isotopic events suggested by Riding *et al.* (2013) (Oxynotum Chronozone) and Korte & Hesselbo (2011) (Sinemurian–Pliensbachian boundary).

stratigraphic resolutions, Riding *et al.* (2013) and Korte & Hesselbo (2011) recently reported two negative carbon-isotope excursions from the Oxynotum Chronozone and at the Sinemurian–Pliensbachian boundary, respectively (Fig. 7). The last one was evidenced, for the first time, by Jenkyns *et al.* (2002), based on scattered belemnite data from Central and Western Europe. From a large data set of analyzed materials (belemnites, bivalves, brachiopods and fossil wood fragments) across the base Pliensbachian GSSP at Robin Hood's Bay, England (Fig. 7; see also Hesselbo *et al.* 2000, Meister *et al.* 2006), Korte & Hesselbo (2011) demonstrated a drop of ~2‰ in the carbon-isotope record around the cited boundary, interpreted by these authors as a major carbon isotope event, similar to that observed in the Early Toarcian (Polymorphum-Levisoni Chronozone boundary).

Although the Oxynotum negative carbon isotope excursion is not corroborated by our results, perhaps due to the absence of isotopic data below the Oxynotum Chronozone, a negative carbon-isotope trend (greater than 2.5‰; Fig. 5) is observed in the S. Pedro de Moel section, in bulk carbonates between the Oxynotum Chronozone and the first levels with *Gemmellaroceras* and *Apoderoceras* (indicators of earliest Pliensbachian). This chemostratigraphic event seems to be correlative with $\delta^{13}C$ negative excursion recorded at Robin Hood's Bay (see Korte & Hesselbo 2011; Fig. 7). However, no sudden negative excursion is recorded in the Portuguese series, unlike observed at Robin Hood's Bay. At S. Pedro de Moel, the $\delta^{13}C_{carb}$ curve shows a slight increase across the levels with *Radstockiceras* sp. and *Apoderoceras dunrobinense* (Taylori Subchronozone; see Meister *et al.* 2012), with values around +1‰ (Fig. 5). This trend precedes a slight drop in $\delta^{13}C_{carb}$, observed across the Jamesoni Chronozone in the carbon isotopic data presented by Oliveira *et al.* (2006) for the Pliensbachian of the Peniche reference section (Fig. 7). At a regional scale, although examples of high-resolution stratigraphic analysis are limited (exception of Korte & Hesselbo 2011, Armendáriz *et al.* 2012), the early Pliensbachian carbon isotope evolution recorded in the LB is not consistent with those observed in Northern Spain (Asturian and Basque-Cantabrian basins), Central Italy (Umbria-Marches Apeninnes) or England (*e.g.* Morettini *et al.* 2002, van de Schootbrugge *et al.* 2005, Rosales *et al.* 2006, Korte & Hesselbo *et al.* 2011, Armendáriz *et al.* 2012), particularly during the Ibex Chronozone, as presented in Fig. 7 (see also Silva *et al.* 2011).

Considering the sedimentary characteristics of the studied succession, which comprises different carbonate units with several lateral and vertical facies changes, the $\delta^{13}C_{carb}$ curve across the Sinemurian–Pliensbachian of S. Pedro de Moel is strongly influenced by the role of organic matter during sedimentation. Similarly to the case documented recently by Jenkyns & Weedon (2013) for Southwest England, the regional occurrence of organic matter around the western and northern Iberia Peninsula during the Late Sinemurian to Early Pliensbachian (see Duarte *et al.* 2010, 2012, and references therein) could be an important factor in the control of the global seawater carbon-isotope composition.

Conclusions

In the LB, the Sinemurian comprises thick carbonate deposits, showing great lateral facies differentiation from eastern dolostones and dolomitic limestones to western distal ramp limestones and marly limestones. In this region of the basin, the Upper Sinemurian (Oxynotum-Raricostatum chronozones) is characterized by organic-rich facies with a good record of ammonites. The S. Pedro de Moel composite section constitutes the most continuous and biostratigraphically well constrained succession in the basin for the Upper Oxynotum Chronozone to the Lower Jamesoni Chronozone. The following conclusions are derived from the high-resolution stratigraphic analysis of this reference section in terms of ammonite biochronostratigraphy and carbon isotope evolution:

1) A detailed ammonite biostratigraphic characterization of the Oxynotum and Raricostatum chronozones (and subchronozones) is presented for the first time in the LB, supported by a high-resolution bed-by-bed sedimentological and geochemical (TOC) analysis of the succession. The occurrence of *Apoderoceras* ~2.2 m above the last *Paltechioceras* level allows precise the identification of the Sinemurian–Pliensbachian boundary.

2) Across the Oxynotum to lowermost Jamesoni chronozones the carbon isotope data from bulk carbonate show a significant negative trend (from values of +2.85‰ to around 0‰), with very negative values (between –2‰ and –6.7‰) recorded particularly in some calcareous levels of the Raricostatum to earliest Jamesoni chronozones. The isotopic signal is clearly correlated with facies changes, and the most negative values are particularly influenced by organic matter in the depositional environment. However, despite these sedimentary characteristics, the negative trend of $\delta^{13}C_{carb}$ ended in the earliest Pliensbachian, showing similarities to the negative carbon isotope excursion recently identified in the Cleveland Basin.

3) In the present study, using the most recent data obtained in the S. Pedro de Moel region, we emphasize the importance of this area as the main stratigraphic reference of the Sinemurian in the whole western Iberia margin. Considering the organic nature of the sedimentation, all these geochemical trends would be confirmed through the carbon isotope analyses in bulk organic matter, to develop in a future work.

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Appendix

Lithostratigraphic references: [1] – top of Coimbra Formation; [2] – base of Polvoeira Member; [3] – top of Polvoeira Member; [4] – base of Praia da Pedra Lisa Member.

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
2.00	2.25	–3.53
81.50	2.18	–4.15
143.00	2.03	–2.81
352.00	1.90	–3.97 [1]
465.50	1.51	–3.09 [2]
533.00	1.90	–3.87
679.50	2.23	–2.87
693.00	2.82	–3.27
744.50	1.72	–3.54
788.00	2.85	–3.48
853.00	2.27	–3.52
896.00	1.11	–3.71
904.00	2.02	–3.74
998.00	1.48	–4
1013.50	2.19	–4.09
1109.00	1.37	–4.03
1129.00	1.24	–4.46
1188.00	1.32	–4.27
1230.00	1.16	–3.64

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
1260.00	1.36	–3.74
1379.00	0.63	–2.89
1379.00	0.69	–2.89
1386.00	–0.21	–4.91
1411.00	–0.16	–4.67
1441.00	0.46	–3.69
1437.00	0.47	–4.79
1446.50	1.05	–4.31
1469.50	0.92	–4.61
1599.00	0.98	–3.34
1617.00	0.38	–3.37
1630.00	1.47	–3.49
1714.00	1.49	–3.61
1806.00	0.68	–4.30
1820.00	1.52	–4.29
2092.00	1.42	–4.28
2193.00	1.36	–4.22
2215.50	0.58	–4.01
2227.00	1.34	–4.46

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
2236.00	1.12	–4.43
2240.00	1.72	–4.75
2246.00	1.24	–4.32
2246.00	1.20	–4.36
2258.00	1.07	–3.79
2268.00	1.58	–4.87
2271.00	1.40	–5.01
2277.00	1.62	–4.88
2297.00	1.34	–4.15
2311.00	0.01	–3.38
2316.00	–1.21	–3.14
2323.00	1.10	–4.52
2327.00	1.57	–5.16
2329.00	1.54	–4.96
2335.00	0.98	–3.85
2350.00	0.43	–3.42
2368.00	0.90	–4.18
2376.00	1.57	–4.80
2376.00	1.59	–4.75

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
2386.00	1.51	–4.27
2399.00	1.24	–3.76
2414.00	1.52	–4.20
2429.00	1.29	–3.92
2439.00	1.13	–3.74
2459.00	1.07	–4.21
2474.00	–0.07	–4.03
2474.00	–0.13	–3.97
2479.00	1.75	–4.76
2515.00	0.89	–4.57
2540.00	1.06	–3.95
2542.00	1.12	–4.40
2547.00	1.61	–4.78
2554.50	1.28	–4.77
2592.50	1.42	–4.54
2597.00	1.33	–4.02
2617.00	0.82	–3.32
2636.00	1.53	–4.36
2638.00	1.48	–4.06
2644.00	1.54	–3.79
2655.00	0.97	–3.71
2670.00	1.09	–3.72
2684.00	0.75	–4.26
2694.00	0.91	–4.28
2713.00	1.29	–4.46
2723.00	0.84	–4.51
2733.00	1.31	–4.46
2743.00	1.62	–4.54
2778.00	1.47	–4.62
2780.00	1.25	–4.44
2784.00	1.39	–4.40
2784.00	1.40	–4.45
2786.00	1.60	–4.37
2788.00	1.47	–4.38
2789.00	0.84	–4.41
2789.00	0.91	–4.23
2790.00	0.72	–4.05
2795.00	0.11	–3.74
2803.00	1.45	–4.39
2822.00	0.81	–3.59
2825.00	0.46	–3.05
2839.50	1.26	–4.23
2853.00	0.92	–3.41
2872.00	0.87	–3.72
2888.00	0.84	–3.87
2901.00	0.89	–3.51
2905.00	1.09	–3.83
2921.00	0.43	–4.05
2930.00	1.06	–4.51
2931.00	0.90	–4.40

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
2937.00	0.64	–4.54
2947.00	0.45	–4.34
2971.00	0.91	–4.05
2971.00	0.89	–4.02
2981.00	1.02	–4.37
2991.00	0.93	–4.44
3001.00	0.86	–3.73
3007.00	1.03	–4.25
3025.00	–5.62	–2.12
3042.00	0.89	–4.60
3045.00	0.77	–4.63
3048.00	0.57	–4.51
3048.00	0.56	–4.53
3053.00	0.52	–4.47
3063.00	1.12	–4.38
3070.00	1.00	–4.69
3076.00	0.89	–4.08
3084.00	0.84	–4.02
3084.00	0.83	–3.98
3091.00	0.95	–4.24
3113.00	0.71	–3.80
3120.00	0.82	–4.36
3126.00	0.82	–4.31
3138.00	1.02	–4.37
3172.00	1.05	–4.51
3176.00	0.88	–4.32
3176.00	0.87	–4.42
3178.50	0.96	–4.73
3181.00	0.84	–4.45
3183.50	0.88	–4.66
3184.00	0.55	–4.45
3187.00	1.00	–5.15
3187.00	1.13	–5.19
3189.00	0.86	–4.47
3191.00	0.71	–4.05
3195.50	–0.02	–3.51
3201.00	0.58	–4.32
3210.00	–4.49	–2.22
3217.00	–1.57	–3.87
3224.00	–4.58	–2.08
3239.00	0.17	–3.82
3247.00	0.55	–4.95
3252.00	0.27	–4.82
3261.00	0.52	–5.61
3267.00	0.54	–4.63
3272.00	0.10	–3.93
3280.00	0.10	–4.76
3285.00	0.59	–5.28
3300.00	0.07	–4.28
3310.00	0.31	–5.07

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
3326.00	0.11	–4.57
3335.50	0.23	–4.90
3346.00	0.44	–4.21
3349.00	0.91	–4.96
3351.50	0.80	–4.48
3354.00	1.08	–4.50
3356.00	0.84	–4.42
3359.00	0.97	–4.47
3359.00	0.98	–4.46
3364.00	1.01	–4.29
3371.00	1.03	–4.57
3373.00	1.02	–4.58
3376.50	0.79	–4.78
3381.00	0.15	–3.69
3386.00	–5.76	–2.69
3394.00	0.34	–4.76
3394.00	–6.71	–2.45
3402.00	–5.28	–2.75
3408.00	0.82	–5.01
3419.00	0.30	–4.33
3434.00	0.94	–5.08
3444.00	0.23	–4.75
3449.00	0.32	–4.50
3452.00	0.33	–4.69
3452.00	0.36	–4.63
3459.00	0.73	–4.96
3459.00	0.69	–4.94
3463.00	0.48	–4.52
3467.00	0.79	–4.95
3476.00	0.51	–4.76
3486.00	0.34	–3.91
3486.50	0.06	–5.42
3491.00	0.34	–4.99
3499.00	0.67	–4.92
3499.00	0.63	–5.00
3511.00	–2.64	–3.71
3521.00	0.31	–4.18
3531.00	–0.61	–4.21
3538.00	0.09	–4.76
3555.00	–0.01	–4.60
3565.00	0.41	–4.38
3576.00	0.29	–4.70
3578.00	0.22	–4.95
3578.00	0.27	–5.03
3595.00	0.13	–4.24
3598.00	0.11	–4.37
3603.00	0.38	–5.24
3607.00	0.16	–4.15
3612.00	0.60	–4.74
3615.00	0.50	–4.64

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
3620.00	0.76	–4.81
3628.00	0.50	–4.64
3632.00	0.47	–4.66
3643.00	0.26	–5.18
3653.00	0.06	–4.59
3656.00	0.80	–4.93
3659.00	0.56	–4.60
3666.00	–0.04	–4.19
3681.00	0.22	–4.77
3693.00	–0.52	–4.48
3699.00	–0.94	–4.00
3707.00	0.22	–5.05
3708.00	0.06	–5.09
3722.00	–0.14	–4.60
3737.00	0.46	–5.43
3745.00	0.17	–4.69
3760.00	0.22	–4.69
3772.00	0.62	–5.09
3780.00	0.27	–4.53
3794.50	0.34	–4.20
3807.00	0.05	–5.25
3815.00	0.37	–4.91
3838.50	0.16	–4.35
3850.00	0.57	–5.13
3869.00	–0.47	–4.28
3879.00	–0.25	–5.10
3894.00	0.82	–5.02
3899.00	0.57	–4.94
3909.00	0.44	–4.94
3923.50	0.57	–4.53
3933.00	0.30	–5.01
3943.50	0.05	–4.53
3954.00	–0.03	–4.82
3961.00	–1.03	–5.02
3974.00	–0.92	–5.03
3989.00	0.03	–5.14
3999.00	0.02	–5.21
4009.00	0.18	–5.25
4014.00	0.06	–5.25
4017.00	0.05	–4.92
4021.00	0.16	–4.75
4023.00	–0.62	–4.21
4029.00	0.32	–4.97
4033.00	0.55	–5.04
4036.00	0.26	–4.80
4044.00	–0.38	–5.40
4054.00	–0.37	–5.27
4064.00	–0.88	–5.29

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
4082.00	–0.35	–5.15
4087.00	–0.13	–5.06
4104.00	–0.36	–3.52
4114.00	0.13	–4.93
4129.00	0.17	–5.12
4144.00	0.16	–4.95
4168.00	–0.39	–4.92
4181.00	0.52	–5.09
4185.00	–0.88	–4.48
4185.00	–0.93	–4.40
4199.00	–0.38	–3.76
4222.00	–2.64	–2.35
4240.00	0.00	–5.02
4245.00	0.37	–5.01
4291.00	0.22	–5.27
4303.00	–0.10	–5.13
4313.00	0.29	–4.83
4322.00	–3.02	–1.39
4331.00	0.46	–4.87
4339.00	0.72	–5.21
4348.00	0.29	–4.91
4358.50	0.90	–4.68
4369.50	–0.79	–2.72
4380.00	0.55	–4.64
4396.00	–0.96	–4.69
4409.00	–1.44	–2.02
4421.00	0.56	–4.88
4428.00	–0.11	–5.04
4435.00	0.27	–4.63
4445.50	–1.30	–2.16
4461.00	–0.14	–4.71
4471.00	–0.12	–4.45
4471.00	–0.18	–4.54
4481.00	0.45	–4.64
4505.00	0.34	–4.85
4505.00	0.37	–4.79
4525.50	–0.03	–4.97
4538.50	–0.04	–4.65
4550.00	0.56	–4.34
4560.00	–2.00	–1.99
4565.00	–0.19	–3.21
4581.00	0.45	–4.65
4586.00	0.62	–4.58
4596.00	–0.01	–5.20
4604.00	–0.15	–2.79
4608.00	–0.06	–3.20
4618.00	0.15	–5.22
4622.00	1.08	–4.44

Cumulative thickness (cm)	$\delta^{13}C_{(PDB)}$‰	$\delta^{18}O_{(PDB)}$‰
4625.00	0.69	–4.67
4634.00	–0.55	–4.99
4639.00	–0.82	–5.01
4639.00	–0.87	–5.13
4653.00	0.25	–4.84
4670.00	–0.25	–5.24
4680.00	0.23	–4.91 [3]
4700.00	0.60	–3.62 [4]
4735.00	0.68	–4.22
4752.00	0.71	–5.07
4822.00	0.72	–3.84
4924.00	0.99	–4.17
5000.00	1.04	–4.77
5035.00	1.13	–4.29
5180.00	1.34	–3.16
5234.00	1.00	–3.21
5282.00	1.24	–3.77
5282.00	0.98	–3.99
5291.00	1.02	–3.79
5298.00	1.26	–2.99
5302.00	1.14	–3.42
5312.00	1.08	–3.52
5316.00	1.06	–4.01
5324.00	1.12	–3.53
5324.00	0.95	–3.61
5332.00	1.01	–3.92
5340.00	0.91	–3.49
5344.00	0.97	–4.15
5348.00	0.99	–4.39
5363.00	0.99	–4.08
5544.00	1.33	–3.43
5562.00	1.39	–3.70
5589.00	0.95	–3.55
5640.00	1.05	–4.02
5660.00	–0.23	–4.31
5700.00	0.98	–4.30
5713.00	0.82	–3.85
5762.00	1.16	–3.91
5762.00	1.02	–3.71
5817.00	0.86	–3.75
5869.00	0.58	–3.44
5915.00	0.87	–3.76
5982.00	0.40	–4.27
6039.00	–0.69	–3.15
6097.00	0.62	–4.57
6113.00	0.91	–4.60
6118.00	0.34	–3.50
6232.00	0.77	–3.22