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The hydrocarbon source rocks of the Pliensbachian (Early Jurassic) in the Asturian Basin (northern Spain): Their relationship with the palaeoclimatic oscillations and gamma-ray response

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Abstract

Deposition of black shale facies, one of the main contributors for hydrocarbon production, is commonly assumed to be linked to Oceanic Anoxic Events (OAEs), which are supposed to be generated during warm palaeoclimates. This assumption could bias the exploration for hydrocarbon source rocks preferentially towards sediments deposited under warm palaeonvironments, as a preferential guide for hydrocarbon exploration. As a consequence, the establishment of the links between palaeotemperature and the formation of organic-rich deposits is of primary importance. For this purpose, the Upper Sinemurian, Pliensbachian and Lower Toarcian (Lower Jurassic) deposits of the Asturian Basin in northern Spain, including more than 100 m thick succession containing organic-rich and black shale deposits, have been studied. Correlation between palaeoclimatic data, previously obtained from oxygen isotopes, and the TOC content reveals that black shales and organic-rich sediments were deposited not only during warming intervals but also during a prominent cooling event that occurred at the Late Pliensbachian. This cooling period has been pointed out as one of the main intervals to have developed ice caps in the poles during the Jurassic. On the contrary, no black shales were generated during the postulated Early Toarcian OAE, which coincides with a superwarming interval. Additionally, the study of the facies cycles and the measurement of gamma-ray in outcrops and its correlation with TOC content provides data on the use of natural radioactivity and sea level changes as a proxy for preliminary organic matter richness evaluation.

Keywords: Organic-rich deposits, Climatic change, Oxygen isotopes, Carbon isotopes, Gamma ray, Sea level changes

Resumen

Normalmente se asume que la sedimentación de las facies de black shales, uno de los principales contribuyentes a la generación de hidrocarburos, está ligada a los Eventos Oceánicos Anóxicos (OAEs) y que éstas facies se formaron durante paleoclimas cálidos. Esta suposición puede orientar a la exploración de rocas madre de hidrocarburos preferentemente hacia los sedimentos depositados bajo paleoambientes cálidos. En consecuencia, el establecimiento de la relación entre paleotemperaturas y la formación de depósitos ricos en materia orgánica resulta de gran importancia para encontrar argumentos sobre este tema, aplicables a la exploración de hidrocarburos. Con este propósito se han estudiado los sedimentos del Sinemuriense Superior, Pliensbachiense y Toarciense Inferior (Jurásico Inferior) de la Cuenca de Asturiana, que incluyen más de 100 m de espesor de depósitos conteniendo facies con materia orgánica y black shales. La correlación entre los datos paleoclimáticos, obtenidos previamente a partir de isótopos de oxígeno, y el contenido de Carbono Orgánico Total (TOC) revela que los black shales y los sedimentos ricos en materia orgánica se depositaron no solo durante los intervalos cálidos sino también durante un destacado evento frío que se desarrolló durante el Pliensbachiense Superior. Este intervalo frío ha sido señalado como uno de los principales candidatos en los que se podrían haber desarrollado casquetes polares durante el Jurásico. Por el contrario, no se depositaron black shales durante el postulado OAE del Toarciense Inferior, que coincide con un intervalo de supercalentamiento. Además, el estudio de los ciclos de facies y la medida de la radioactividad natural (rayos gamma) en afloramiento, y su correlación con el contenido en TOC, aporta datos sobre el uso de los logs de rayos gamma y los cambios del nivel del mar como proxy para la evaluación preliminar de la riqueza en materia orgánica.

Palabras clave: Depósitos organógenos, Cambio climático, Isótopos de oxígeno, Isótopos de carbono, Rayos gamma, Cambios eustáticos

1. Introduction

Some of the main intervals of hydrocarbon source rocks are supposed to be linked to the postulated Oceanic Anoxic Events (OAEs), which have been defined (Jenkyns and Clayton, 1986, 1997) on the basis of the presence of black shale facies (>5wt.%TOC; Bates and Jackson, 1987) worldwide. The major forcing event behind these OAEs (Jenkyns *et al.*, 2002), has been attributed to abrupt rises in temperature, induced by rapid influx of CO_2 into the atmosphere from volcanogenic and/or methanogenic sources (Jenkyns, 2010). Following these ideas, palaeoclimatological studies, oriented to search for source rocks linked to warming periods could be used as an additional tool to the commonly used in hydrocarbons exploration.

The Rodiles section of the Asturian Basin in northern Spain (Fig. 1), which shows a succession of Upper Sinemurian, Pliensbachian and Lower Toarcian (Lower Jurassic) deposits, offers an excellent opportunity to asses this statement, as several climatic oscillations have been identified (Gómez *et al.*, 2016) and the record of the TOC content of the succession reveals the presence of several intervals of organic-rich and black shale deposits.

Comparison of the recorded changes in seawater palaeotemperature, using the $\delta^{18}O_{bel}$ from diagenetically screened belemnite calcite as a proxy, and the $\delta^{18}O_{bel}$ records obtained in several European sections has allowed the characterization of several climatic intervals probably of global extent (Gómez *et al.,* 2016). A warming interval which partly coincides with a negative $\delta^{13}C_{bel}$ excursion was recorded at the Late Sinemurian. An interval of "normal" temperature, with values close to the average temperature recorded in the studied period, is followed by another warming interval that contains a short lived positive $\delta^{13}C_{bel}$ peak, developed at the Early Pliensbachian. The Late Pliensbachian represents an outstanding cooling interval containing a positive $\delta^{13}C_{bel}$ excursion interrupted by a small negative $\delta^{13}C_{bel}$ peak, and finally, the Early Toarcian represented an exceptional superwarming period pointed as the main cause of a prominent mass extinction (Gómez and Goy, 2011).

The presence of organic-rich and black shale facies in the Pliensbachian deposits of northern Spain and the Lusitanian Basin of Portugal, which are considered one of the main targets for oil and gas exploration in these areas (Suárez-Ruiz, 1987; Suárez-Ruiz and Prado, 1995; Duarte *et al.*, 2010, 2014; Silva, 2013; Silva and Duarte, 2015), conducted to Borrego *et al.* (1996) to identify, on the basis of the OAEs definition by Jenkyns and Clayton (1986,1997) the presence of an "anoxic" event of Pliensbachian age in the Asturian Basin.

The objectives of this work are to provide data on the link between the evolution of seawater palaeotemperatures and the presence of organic-rich and black shale facies as well as the correlation between these facies and the deepening–shallowing cycles and the gamma-ray log. For these purposes, detailed measurement bed by bed of the lithological succession, ammonite-based biochronostratigraphical studies, coupled with stable isotope analysis of diagenetically screened belemnite calcite, and total organic carbon (TOC) analysis, have been performed.

The correlation between the occurrence of organic-rich deposits and the climatic, and sea level changes, allows to analyze the current criteria used to define the postulated Oceanic Anoxic Events and apply them as a guide for hydrocarbon exploration. The correlation between the gamma-ray measurements and the obtained TOC values allows evaluation of this tool to contribute in the assessment of the hydrocarbon potential of one area in the subsurface, on the basis of the available gamma-ray logs from previous wells.

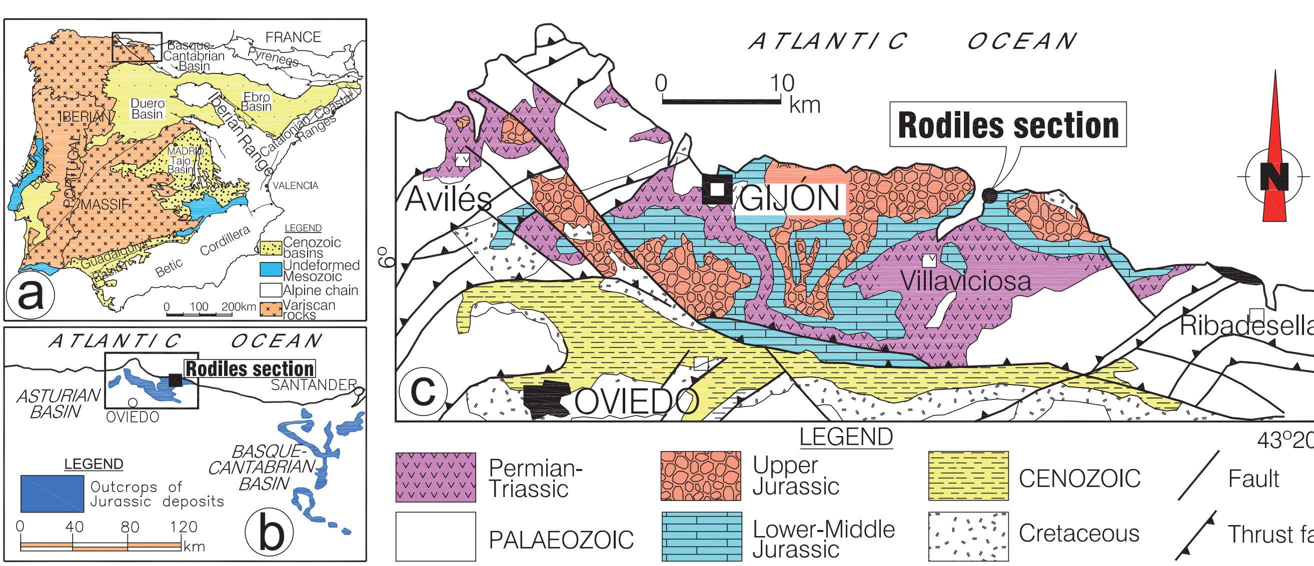


Fig. 1.- Maps showing the location of the Rodiles section. (a): Sketched map of the geology of Spain and Portugal showing the position of the Asturian Basin. (b): Outcrops of the Jurassic deposits in the Asturian and the western part of the Basque-Cantabrian Basin, as well as the position of the Rodiles section. (c): Sketched geological map of the Asturian Basin showing the location of the Rodiles section.

Fig. 2.- View of the Rodiles section in the coastal cliffs of eastern Asturias, were the uppermost Sinemurian, Pliensbachian and Lower Toarcian deposits are cropping out.

2. Materials and methods

The 110 m thick Rodiles section shows a well exposed Upper Sinemurian, Pliensbachian and Lower Toarcian (Lower Jurassic) succession (Fig. 2). A total of 191 analyses of stable isotopes were performed on diagenetically screened belemnite calcite samples to determine the seawater palaeotemperatures and the carbon isotope variations in the time interval studied (see Gómez *et al.*, 2008; Gómez and Goy, 2011 for the latest Pliensbachian and the Early Toarcian, and Gómez *et al.*, 2016, for the all studied interval). In addition, a total of 146 samples were analyzed for TOC content and radioactivity (gamma-ray) of the rocks was measured bed by bed along the whole section.

Belemnite calcite was processed in the stable isotope labs of the Michigan University (USA) following the methods described in Gómez and Goy (2011). TOC analyses have been performed in the Centro de Espectrometría Atómica of the Universidad Complutense of Madrid using a Shimadzn TOC-V analyzer for solid samples (SSM-5000 A). One sample of standard NIST 1944 was analyzed every four samples of rock to control the total carbon values and bicarbonate of soda for the inorganic carbon. Analytical error was better than ±0.7%. Gamma ray values were measured in the field in a total of 562 layers with a portable scintillation counter Exploranium Geometrics GRS101.

3. Results

The well exposed Upper Sinemurian, Pliensbachian and Lower Toarcian deposits cropping out in the coastal cliffs of the eastern part of the Asturias region in northern Spain, are represented by a succession of alternating lime mudstone to bioclastic wackestone and marl (Fig. 2) belonging to the Santa Mera Member of the Rodiles Formation (Valenzuela, 1988).

The lithological succession, sequence stratigraphy, curve of the gamma-ray measured figures, profiles of the $\delta^{18}O_{bel}$ and $\delta^{13}C_{bel}$ values obtained from belemnite calcite and the curve of Total Organic Carbon (TOC) variations have been plotted against the 562 measured beds of the Rodiles section (Fig. 3).

3.1. Lithology

The Upper Sinemurian, Pliensbachian and Lower Toarcian deposits of the Rodiles section are constituted by couplets of bioclastic lime mudstone to wackestone, occasionally containing bioclastic packstone facies commonly concentrated in gutters, and grey to black marls, deposited in an open marine external platform environment.

Pliensbachian organic-rich deposits include a wide variety of facies. They are represented by medium to dark grey shales as well as black shales, rarely maroon probably due to weathering. A few of these intervals are laminated, but very often shales are massive and bioturbated. In many cases the massive aspect is probably due to homogenization derived from intense bioturbation. Some of the massive marly levels also show evidences of reworking, supported by the presence of bioclasts and/or reworked fossils, mainly of brachiopods, belemnites, bivalves, crinoids and ammonites, which are in cases concentrated in bioclastic rills. In some layers, especially of the Early Pliensbachian Jamesoni Chronozone, the reworked hollow brachiopods contain crude oil, introduced during early diagenesis, before the internal pore space of the brachiopod was completely filled by the blocky generation of calcite. Many of the organic-rich intervals show a multi-episodic origin, indicated by the presence of more calcareous horizons and surfaces which were colonized mainly by *Chondrites, Thalassinoides* and *Phymatoderma*. Pyrite is common as crystals or small nodules, framboids or replacement of macrofauna (mainly ammonites). Deposition of the carbonates has been interpreted as the result of storm-density currents, and the marls as the advention of continental mud deposited in a temporary oxygen-deficient basin (laminated facies) or well-oxygenated seafloor (bioturbated facies) (Valenzuela, 1988; Valenzuela *et al.*, 1985, 1986, 1989; Borrego *et al.*, 1996; Bádenas *et al.*, 2012).

3.2. Sequence stratigraphy

The limestone–marl couplets are organized in small-scale shallowing and deepening upward cycles. The shallowing upward sequences are characterized by a succession of couplets, on which carbonates are thickening upward, while marls are commonly thinning upwards. On the contrary, in the deepening upward elemental sequences, marls show a thickening upward trend, indicating increasing accommodation space, while carbonates tend to be generally thinner. These elemental sequences have been grouped into higher order cycles, constituted by the stacking of several shallowing or deepening upward sequences.

In the Rodiles section, the Upper Sinemurian deposits show a shallowing upward trend, followed by a brief deepening interval containing the Sinemurian–Pliensbachian boundary (Fig 3). This deepening tendency is followed by a short episode of shallowing upward deposits developed within the earliest Pliensbachian Taylori–Polymorphus subchronozones. One of the longest-lasting deepening upwards intervals develops in most of the Early Pliensbachian. The Late Pliensbachian starts with a more calcareous shallowing upward cycle, and a deepening upward interval recorded in the Subnodosus–Gibbosus subchronozones of the Margaritatus Chronozone. The remaining Upper Pliensbachian deposits are mainly constituted, by a succession of shallowing upward sequences. After short episodes of alternating shallowing and deepening sequences, the generalized Early Toarcian deepening represents the initiation of the main global Early Toarcian transgression (Hallam, 1997; Gómez and Goy, 2000).

3.3. Gamma-ray log

Gamma-ray logs have commonly been applied in the studies of sequence stratigraphy (i.e. van Buchem *et al.*, 1992; Gómez and Goy, 2000; Pawellek and Aigner, 2003; Correia *et al.*, 2012). Obtained gamma-ray log in the Rodiles section (Fig. 3) supports the sequence stratigraphy recognizable in the field. The marly-rich deepening upward episodes show generally higher values of radioactivity; mainly due to the higher proportion of marls, than the relatively more calcareous shallowing upward intervals. This fact is a quite common feature as indicated by several works concerning the Lower Jurassic of the Cleveland Basin in the UK (van Buchem *et al.*, 1992) and in the Lusitanian Basin of Portugal (Correia *et al.*, 2012). No geochemical analysis to determine if the main source of the radioactivity is U, Th or K have been performed, but in deposits of similar age studied in the Lusitanian Basin, correlation coefficient is slightly higher with K (0.64) than with Th (0.56) and with U (0.47) (Correia *et al.*, 2012).

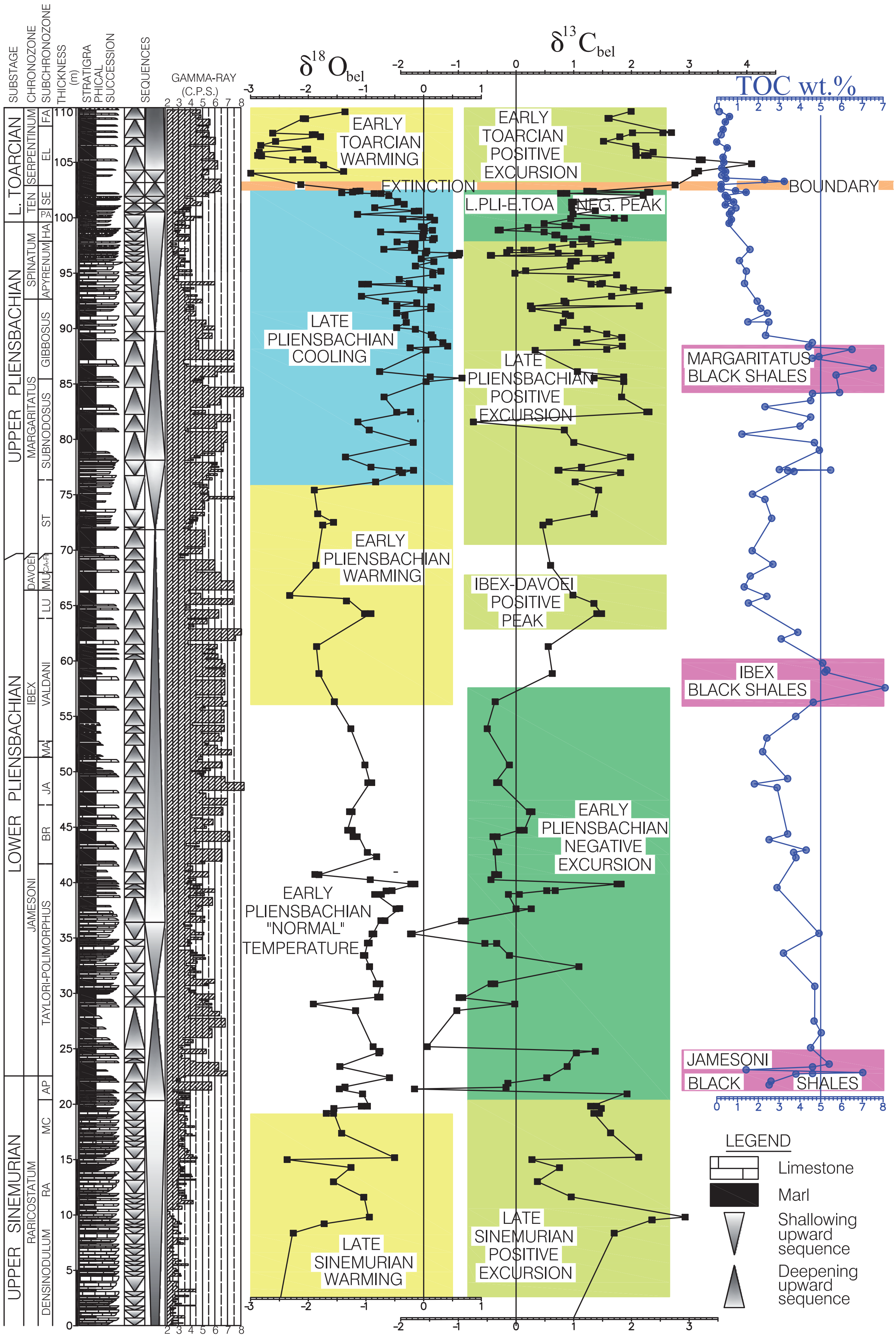
3.4. Biochronostratigraphy

The ammonite-based biochronostratigraphical subdivisions of these deposits in the Asturian Basin have been carried out by Suárez-Vega (1974), Gómez *et al.* (2008), Goy *et al.* (2010a, b), Comas-Rengifo and Goy (2010) and Gómez *et al.* (2016) which are the subdivisions used in this work.

3.5. Oxygen isotopes and palaeotemperatures

Oxygen isotopes record several oscillations in the studied interval (Fig. 3) (Gómez *et al.*, 2016). A negative $\delta^{18}O$ excursion developed during the Late Sinemurian. The earliest Pliensbachian represents an interval of the average values of $\delta^{18}O$ of the interval studied, and another negative $\delta^{18}O$ excursion was recorded at the Early–Late Pliensbachian transition. The Late Pliensbachian is represented by a remarkable long-term positive $\delta^{18}O$ excursion, and the Early Toarcian coincides with a highly negative $\delta^{18}O$ excursion.

Fig. 3.- (next page) Stratigraphical succession of the Upper Sinemurian, Pliensbachian and Lower Toarcian deposits of the Rodiles section, showing the lithological column, the sequence stratigraphy, the gamma-ray log, the ammonite taxa distribution, the profiles of the $\delta^{18}O_{bel}$ and $\delta^{13}C_{bel}$ values obtained from belemnite calcite and the Total Organic Carbon (TOC) content. The climatic intervals, the carbon isotope excursions and the black shale intervals have been highlighted. Chronozones abbreviations: TEN: Tenuicostatum. Subchronozones abbreviations: RA: Raricostatum. MC: Macdonnelli. AP: Aplanatum. BR: Brevispina. JA: Jamesoni. MA: Masseanum. LU: Luridum. MU: Maculatum. CA: Capricornus. FI: Figulinum. ST: Stokesi. HA: Hawskerense. PA: Paltum. SE: Semicelatum. EL: Elegantulum. FA: Falciferum.



SUBSTAGE
CHRONOZONE
SUBCHRONOZONE
THICKNESS (m)
STRATIGRAPHICAL SUCCESSION
SEQUENCES
GAMMA-RAY (C.P.S.)
$\delta^{18}O_{bel}$
$\delta^{13}C_{bel}$
TOC wt.%
L. TOARCIAN
UPPER PLIENSBACHIAN
LOWER PLIENSBACHIAN
UPPER SINEMURIAN
SERPENTINUM
SPINATUM
MARGARITATUS
DAVOEI
IBEX
JAMESONI
RARICOSTATUM
EARLY TOARCIAN WARMING
EXTINCTION
LATE PLIENSBACHIAN COOLING
EARLY PLIENSBACHIAN WARMING
EARLY PLIENSBACHIAN "NORMAL" TEMPERATURE
LATE SINEMURIAN WARMING
EARLY TOARCIAN POSITIVE EXCURSION
L.PLI-E.TOA NEG. PEAK
LATE PLIENSBACHIAN POSITIVE EXCURSION
IBEX-DAVOEI POSITIVE PEAK
EARLY PLIENSBACHIAN NEGATIVE EXCURSION
LATE SINEMURIAN POSITIVE EXCURSION
BOUNDARY
MARGARITATUS BLACK SHALES
IBEX BLACK SHALES
JAMESONI BLACK SHALES
LEGEND
Limestone
Marl
Shallowing upward sequence
Deepening upward sequence

3.6. Carbon isotopes

The $\delta^{13}C_{bel}$ carbon isotope curve found in the Asturian Basin (Fig. 3) also reflects several carbon isotope excursions (CIEs) (Gómez *et al.*, 2016). From bottom to top the Late Sinemurian positive CIE, the Early Pliensbachian negative excursion, the Early Pliensbachian Ibex–Davoei positive peak, the Late Pliensbachian positive excursion, the Late Pliensbachian–Early Toarcian negative peak and the Early Toarcian positive CIE.

3.7. Total Organic Carbon (TOC) content

Virtually all the Pliensbachian assayed samples, yielded values above 1wt.%TOC, while most of the Lower Toarcian samples show values below this figure (Fig. 3). Average TOC content over the 110 m of measured section is 2wt.%. Following the classification of Peters and Cassa (1994), most of the Pliensbachian shales have good petroleum potential (1–2wt.%TOC), with intervals of organic-rich shales (2–4wt.%TOC), and black shales, containing over 5wt.%TOC, considered as rocks with excellent petroleum potential. Here we have labelled organic-poor facies to the deposits containing 0 to 2.5wt.%TOC, organic-rich deposits to the marls containing between 2.5 and 5wt.%TOC, and black shales to the deposits containing more than 5wt.%TOC.

Within the Pliensbachian, three main intervals with high TOC content can be distinguished (Fig. 3). The earliest interval extends along the latest Sinemurian and the Early Pliensbachian Jamesoni Chronozone, where most of the marly levels are organic-rich, with values above 2.5wt.% TOC. This interval contains black shales assaying up to 7wt.%TOC in the early Jamesoni Chronozone.

The middle interval is located in the Ibex Chronozone and contains several beds of black shales with TOC values slightly above 5wt.%. The upper organic-rich interval is mainly located in the Margaritatus Chronozone, which contains several episodes of black shale facies yielding up to 7.5wt.%TOC. Additional thin organic-rich intervals have been recorded in the Davoei Chronozone of the Early Pliensbachian and in the Early Toarcian, near the boundary between the Tenuicostatum and the Serpentinum chronozones. However, TOC values theoretically representatives of the postulated Toarcian Oceanic Anoxic Event, defined by the deposition of black shale facies (Jenkyns and Clayton, 1986, 1997; Jenkyns *et al.*, 2002; Jenkyns, 2010), are generally below 1wt.% and do not surpass 3.2wt.%TOC in a thin interval (Fig. 3).

4. Discussion

The studied Upper Sinemurian, Pliensbachian and Lower Toarcian section of the Asturian Basin can be correlated with other successions of similar age in terms of sequence stratigraphy, TOC content as well as climate oscillations inferred from the $\delta^{18}O$ values and changes in $\delta^{13}C$.

4.1. Sequence stratigraphy and TOC content

Comparison between the succession of shallowing and deepening upward sequences obtained in the Rodiles section

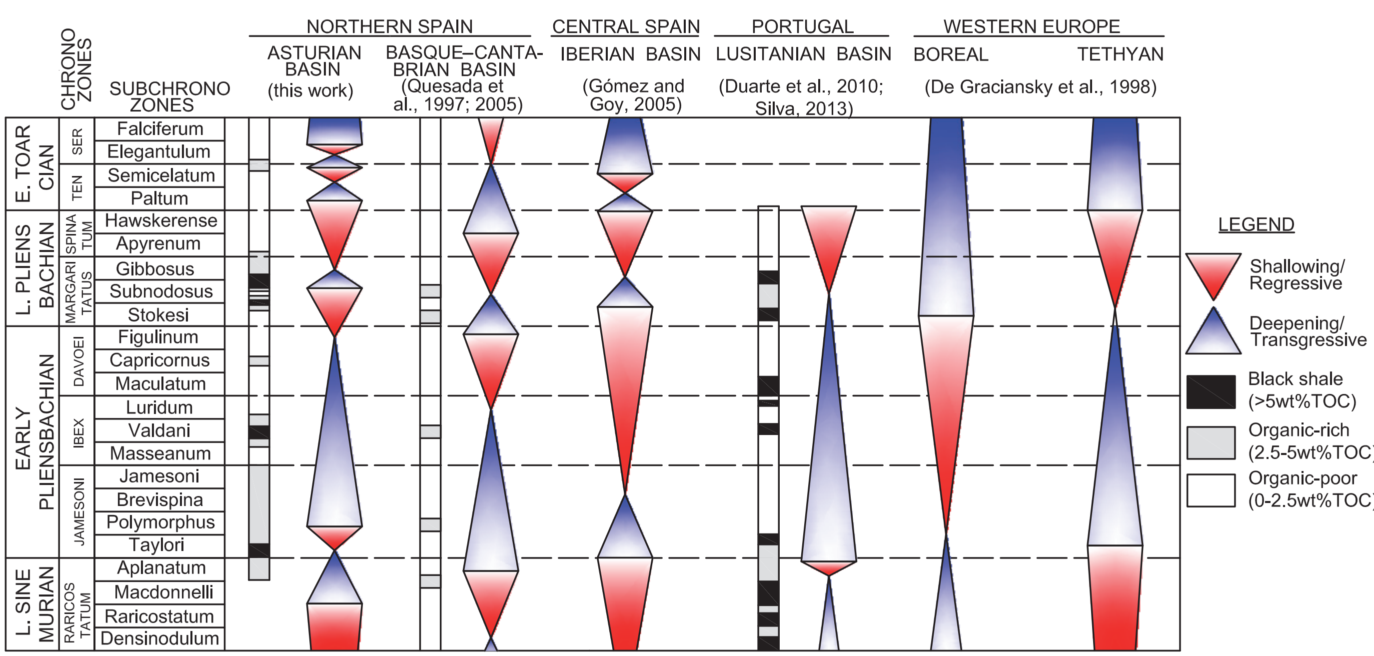


Fig. 4.- Correlation between the succession of shallowing and deepening upward sequences obtained in the Asturian, Basque-Cantabrian, Iberian and Lusitanian basins and in Western Europe, as well as the stratigraphical distribution of the organic-poor, organic-rich and black shales deposits in each basin

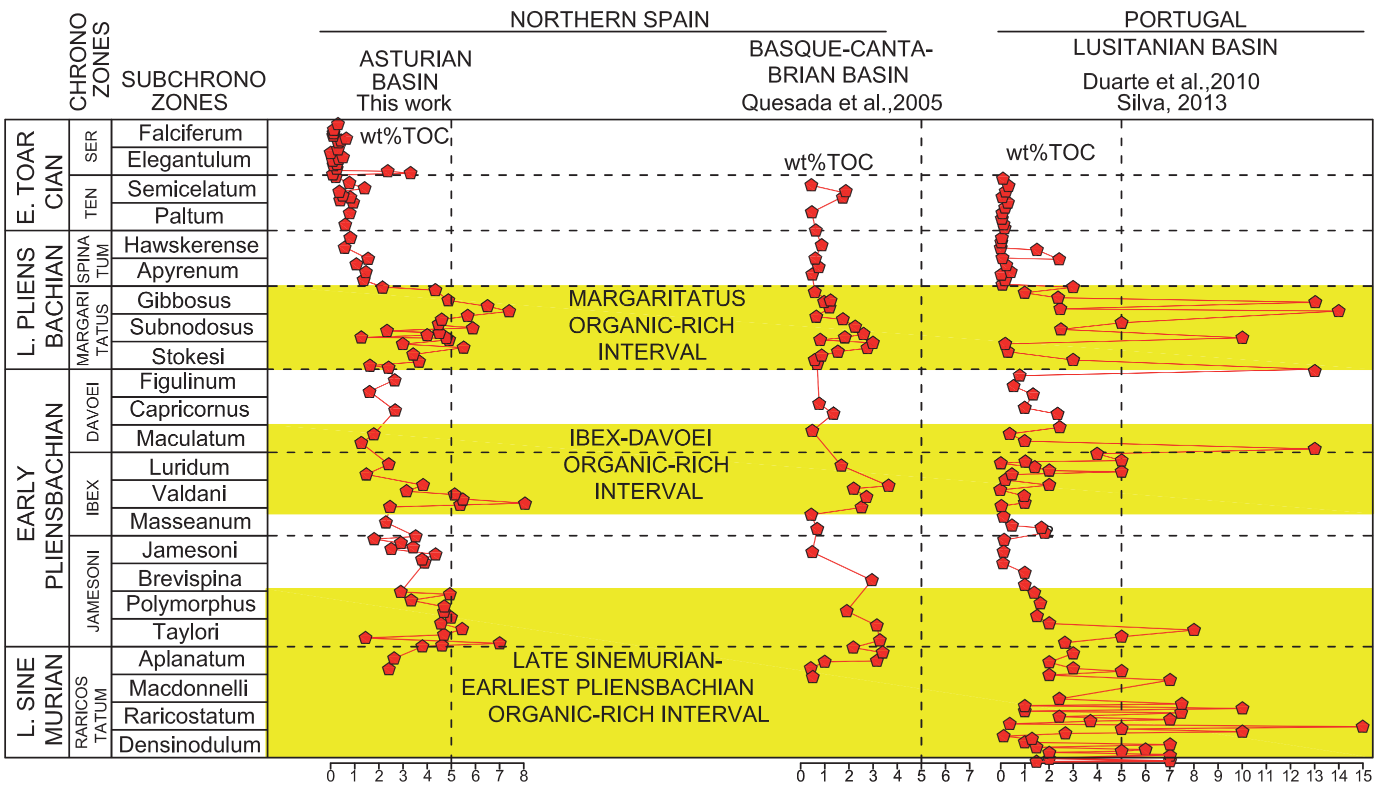


Fig 5.- Curves showing the TOC wt.% values obtained in the Asturian, Basque-Cantabrian and Lusitanian basins against the ammonite chronozones and subchronozones. The ages of these potential hydrocarbon source rocks are quite consistent in the represented areas. The Upper Sinemurian–Lowermost Pliensbachian organic-rich interval is especially well represented in the Lusitanian Basin. Additional organic-rich intervals occur at the Ibex–Davoei chronozones of the Early Pliensbachian and at the Margaritatus Chronozone of the Late Pliensbachian.

and the sequences obtained in contemporaneous deposits of other areas, as well as the stratigraphical distribution of the organic deposits in each area, is represented in figure 4.

In the Asturian Basin, almost the whole black shale and organic-rich intervals coincide with the development of deepening upward sequences, except for the thin interval in the transition between the Stokesi and the Subnodosus subchronozones of the Late Pliensbachian Margaritatus Chronozone, which was developed in a shallowing upward sequence.

In the neighbour Basque-Cantabrian Basin no real black shales with TOC values higher than 5wt.% have been reported, but several organic-rich intervals have been assayed by Quesada *et al.* (1997, 2005). Almost all these intervals coincide with transgressive facies cycles, except for the Late Sinemurian interval that coincides with a regressive hemicycle. In the Iberian Range of Central Spain, Sinemurian and Pliensbachian deposits are mainly represented by organic-poor shallow platform carbonate facies with minor transgressive marls (Gómez and Goy, 2005) but many of the recognized cycles have similar ages to the cycles found in the Asturian Basin.

Organic-rich deposits and black shales have also been recorded in the Portuguese Lusitanian Basin (Duarte *et al.*, 2010, 2014; Silva, 2013; Boussaha *et al.*, 2014). The richest interval in this area corresponds to the Late Sinemurian, coinciding with a transgressive hemicycle. Additional black shale and organic-rich deposits coinciding with the Early Pliensbachian transgressive hemicycle are also present. However, higher in the section, a part of the black shales and organic-rich deposits of the Late Pliensbachian seem to be deposited in a regressive hemicycle. Correlation of the facies cycles in the different considered areas is difficult; probably because of some of them are the results of the local and/or regional tectonic evolution. Nevertheless, some features like the change in tendency from deepening to shallowing trends recorded in the Late Pliensbachian Margaritatus Chronozone (except for the Boreal realm), and the Early Toarcian transgressive trend, observed in most of the mentioned areas, have been generally considered as probable global events.

4.2. Organic-rich deposits

Hydrocarbon source rocks of Pliensbachian age are not unique of the Asturian Basin. As mentioned before, they have also been reported in the Basque-Cantabrian and in the Lusitanian basins. As a result, Borrego *et al.* (1996), following the definition of Oceanic Anoxic Events enounced by Jenkyns and Clayton (1986, 1997), defined the presence of an "anoxic" event in the Pliensbachian of Asturias, based on the presence of black shale facies in this area.

Plotting of the TOC wt.% values obtained in the Asturian, Basque-Cantabrian and Lusitanian basins against the ammonites chronozones and subchronozones, allows correlation of the organic deposits and black shale facies between the three basins (Fig. 5). The ages of these hydrocarbon main source rocks are quite consistent in the mentioned areas. They are mainly constrained to the earliest part of the Jamesoni Chronozone and to the Ibex and the base of the Davoei chronozones of the Early Pliensbachian as well as the Margaritatus Chronozone of the Late Pliensbachian. The richest Late Sinemurian intervals of the Lusitanian Basin of Portugal (Duarte *et al.*, 2010, 2014; Silva 2013; Boussaha *et al.*, 2014; Silva and Duarte, 2015) have not been recorded in the Spanish basins because deposits of this age are represented by shallow platform carbonates.

Characterization of the organic matter in the Pliensbachian deposits of the Asturian Basin show a typical marine assemblage, dominated by amorphous organic matter and liptodetrinite, with increasing thermal maturation eastwards, from <0.5% VR_r to 1.5% VR_r (Suárez-Ruiz, 1987; Suárez-Ruiz and Prado, 1995; Borrego *et al.*, 1996).

Around the Ayoluengo oil field, located in the western Basque-Cantabrian Basin, organic geochemistry shows that Pliensbachian source rocks contains a type II kerogen with average TOC content of 3.2wt.% over a 42 m thick interval with average HI of 500 mgHC/g organic carbon and T_{max} indicating that source rocks are immature (424 to 430ºC), mature (435 to 450ºC) and post mature in the centre of the basin (Quesada *et al.*, 1995, 1996, 1997; Beroiz and Permanyer, 2011). In the Lusitanian Basin, kerogen assemblages are dominated by marine amorphous organic matter, with Rock-eval pyrolysis having S2 values >10 mg HC/g rock, Hydrogen Index averaging 355 mg HC/g TOC but the sampled rocks have T_{max} below 437ºC and average vitrinite reflectance of 0.43% R_o, indicating that they are thermally immature or very early mature (Duarte *et al.*, 2012).

Potential hydrocarbon source rocks of Pliensbachian age have also been described in other parts of the world. In the Middle Atlas of Morocco, Sachse *et al.* (2012) reported the presence of a predominantly algal-derived organic matter with minor input of woody terrestrial material source rock, with values between 1.9 and 3.9 wt.% TOC, mean HI values of 450 mg HC/g C_{org} and T_{max} between 431 and 495ºC. In the western Canada Basin, also Pliensbachian organic-rich deposits containing 5–10wt.% TOC have been mentioned. This kerogen, which is Type I/II, with HI up to 800 mg HC/g TOC, have entered the oil window (Riediger, 2002).

Depositional environments of organic-rich deposits in the Asturian Basin, as in many other areas, have been related with oxygen depleted conditions (Borrego *et al.*, 1996; Bádenas *et al.*, 2012). Laminated facies were most probably deposited during periods of seawater stratification, leading to restricted circulation and decline of bottom water oxygen (Wignall, 1991). However, in the Asturian Basin no evidences supporting long periods of anoxia have been documented. Laminated facies are rare and there are no evidences of significant faunal turnovers in conjunction with oxygen-deficient bottom water. The study of the Pliensbachian brachiopods of the Asturian Basin carried out by Comas-Rengifo *et al.* (2008) and the study of the distribution of nannofossils performed by Fraguas (2010) show that neither the benthic nor the nektonic organisms were significantly affected in their vertical distribution by periods of deficiency in oxygen. This fact, together with the widespread presence of bioturbation in the organic-rich deposits (Armendáriz *et al.*, 2012) indicates that these environmental conditions were only occasionally reached and that they were not severe and long enough to produce major turnovers in the populations. In fact, in the case of the Lower Toarcian of Northwestern Europe, deposition of black shale facies, representatives of the postulated Toarcian Oceanic Anoxic Event (TOAE), coincides with the repopulation interval, after the major extinction event (Gómez and Goy, 2011) and not with the extinction event. Alternation of anoxia–euxinia and oxygenated bottom waters in several of the so-called "anoxic" events, like in the Toarcian Oceanic Anoxic Event is indicated by the presence of abundant bivalves in some levels (Röhl *et al.*, 2001) and the presence of currents (Trabucho-Alexandre *et al.*, 2012) in the German black shale deposits. This conclusion has also been reached after the study of other black shale facies like the Oxford Clay (Kenig *et al.*, 2004).

4.3. Correlation between organic deposits and gamma ray

Some organic-rich rocks are enriched in authigenic uranium and hence they can be more radioactive (Schmoker, 1981; Meyer and Nederlof, 1984; Mann *et al.*, 1986; Wignall and Myers, 1988; Stocks and Lawrence, 1990; Lüning and Kolonic, 2003). As a consequence, a good correlation between TOC values and U concentration, and hence in radioactivity, can be established in some organic-rich and black shale facies. In those areas, U (natural radioactivity) can be used as a proxy to predict the TOC content of the rocks. This correlation is especially useful when exploring in the subsurface, where gamma ray logs from previously drilled wells are available, but not cores or TOC analysis have been performed.

The U/TOC ratio varies, depending on many factors such as the primary concentration of organic matter and U in the water body, the lithological composition, the rate of deposition, the duration of anoxia, etc. (see Lüning and Kolonic, 2003). In the Western Europe Lower Jurassic black shales, the quality of U and TOC relationship varies from good, like in the Posidonienschiefer of northern Germany (Mann *et al.*, 1986) and in the Sinemurian–Pliensbachian of the Lusitanian Basin (Correia *et al.*, 2012), to moderate like in the Lower Jurassic

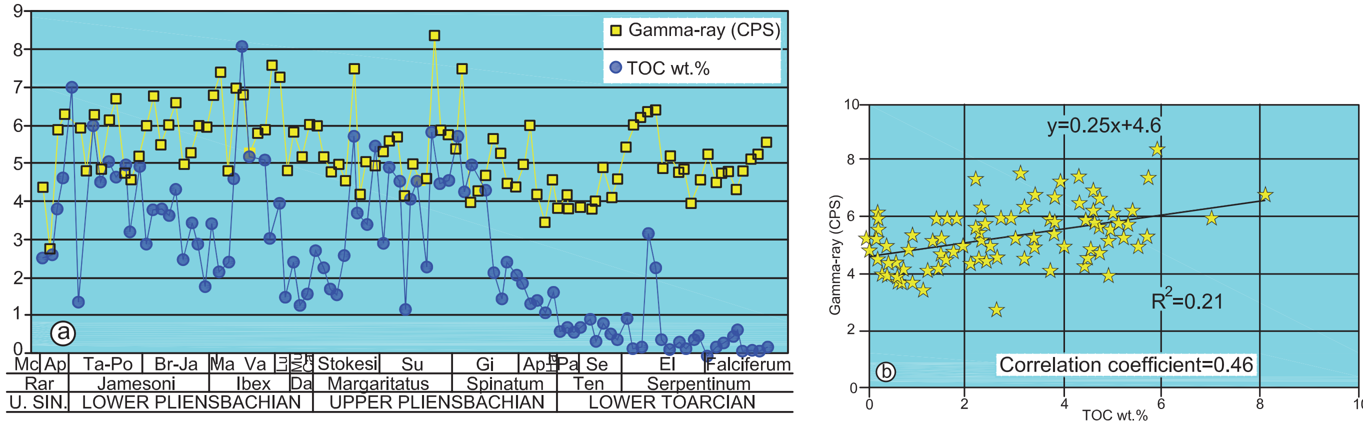


Fig. 6.- (a): Plot of obtained TOC and gamma-ray values of the Rodiles section, against the chronostratigraphical units. TOC and gamma ray values tend to follow similar trends in some stratigraphic intervals, while values are even contradictory in some other intervals. (b): Plot of gamma-ray values against TOC values. Obtained correlation coefficient of both parameters (0.46) can be considered as middling. Chronozones abbreviations: Rar.: Raricostatum. Da: Davoei. Ten.: Tenuicostatum. Subchronozones abbreviations: Mc: Macdonnelli. Ap: Aplanatum. Ta: Taylori. Po: Polymorphus. Br: Brevispina. Ja: Jamesoni. Ma: Masseanum. Va: Valdani: Lu: Luridum. Mu: Maculatum. Ca: Capricornus. Su: Subnodosus. Gi: Gibbosus. Ap:Apyrenum. Ha: Hawskerense. Pa: Paltum. Se: Semicelatum. El: Elegantulum.

of NE England (Wignall and Myers, 1988; van Buchem *et al.*, 1992) and poor, like in the subsurface of the Netherlands, where the bituminous Posidonienschiefer does not correlate with any significant increase in gamma ray activity (Meyer and Nederlof, 1984).

Measurements of gamma ray and TOC values in the same strata in the Rodiles section allowed correlation between these two parameters. Tendencies of TOC and gamma ray curves coincide in some stratigraphic intervals, but values are even contradictory in some others (Fig. 6a). For instance, the substantial decrease in TOC recorded in the uppermost Pliensbachian and the Lower Toarcian deposits, is not reflected in a significant decrease in the gamma ray values. In addition, the correlation coefficient of both parameters is quite low (0.46) (Fig. 6b), suggesting that, based on current data, radioactivity can be pointed as a partially reliable proxy to estimate the presence of source rocks in the subsurface of the Asturian Basin.

4.4. Correlation between the carbon isotope curve and the TOC content

Correlation between the $\delta^{13}C_{bel}$ data and the presence of organic-rich and black shale deposits shows that the Late Sinemurian positive excursion contains organic-poor deposits in the Asturian Basin, but organic-rich and black shale facies in the Lusitanian Basin (Fig. 7). Higher in the section, the Early Pliensbachian negative $\delta^{13}C$ excursion coincides with the thickest recorded organic-rich interval in the Rodiles section, which includes black shale facies. In the Basque-Cantabrian Basin, this negative $\delta^{13}C_{bel}$ excursion coincides with the interval where organic-rich facies are more abundant and in the Lusitanian Basin it partly coincides with the richest interval in organic matter (Duarte *et al.*, 2010, 2013; Silva, 2013).

Many papers argue that these periods of rapid burial of large amounts of organic matter, like the above mentioned Early Pliensbachian interval, are associated with positive $\delta^{13}C$ excursions, because the buried organic carbon is rich in ^{12}C, leading to enrichment of ^{13}C (Jenkyns and Clayton, 1986, 1997; Schouten *et al.*, 2000). Nevertheless, in this case, the recorded enrichment of organic matter in sediments is linked not to a positive excursion, but to a well marked and extensive negative $\delta^{13}C$ excursion. In other cases, like in the Early Toarcian, where a positive $\delta^{13}C$ excursion can include generally ephemeral negative excursions, the occurrence of an input of isotopically light carbon due to large-scale venting of volcanogenic CO_2 and/or dissociation of gas hydrate and /or thermal metamorphism of coals has been invoked (i.e. Hesselbo *et al.*, 2000; Jenkyns, 2003, 2010; McElwain *et al.*, 2005).

Coinciding with the Ibex–Davoei positive $\delta^{13}C_{bel}$ peak, organic-rich deposits have been described in the Basque-Cantabrian Basin and black shales in the Lusitanian Basin, but mainly organic-poor deposits are present in the Asturian Basin. The following $\delta^{13}C_{bel}$ excursion is an about 1.5–2‰ positive excursion, well recorded in the correlated Upper Pliensbachian sections (the Late Pliensbachian positive excursion in figure 7). Associated with the earliest part of this positive $\delta^{13}C_{bel}$ excursion, organic-rich and black shale deposits, mainly constrained to the Margaritatus Chronozone, have been found in the northern Spain sections (Quesada *et al.*, 2005; this work) and in the Lusitanian Basin (Duarte *et al.*, 2010, 2014). Several negative $\delta^{13}C_{bel}$ peaks have been recorded in the latest Pliensbachian Spinatum Chronozone in the Asturian Basin (Fig. 3). As an hypothesis, the youngest peak, here called the Late Pliensbachian–Early Toarcian peak, could be correlated with the negative CIE located around the Pliensbachian–Toarcian boundary that was described by Hesselbo *et al.* (2007) in bulk rock samples in

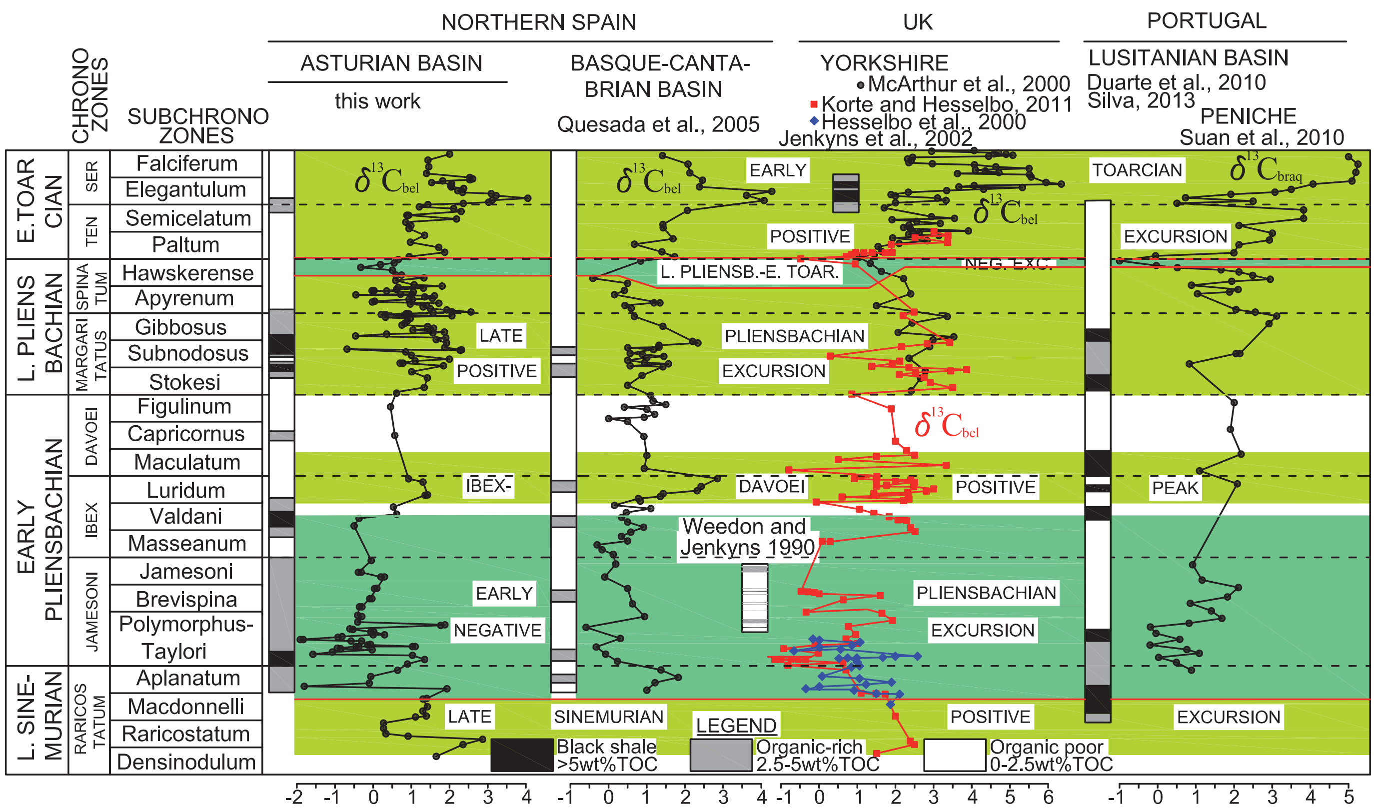


Fig. 7.- Correlation chart of the belemnite calcite-based $\delta^{13}C$ sketched curves and the presence of organic-rich and black shale deposits across Western Europe. The Late Sinemurian–Early Pliensbachian negative $\delta^{13}C$ excursion coincides with the presence of organic deposits in Northern Spain and in Portugal. The Ibex–Davoei positive peak contains organic-rich deposits especially in the Lusitanian Basin. The Late Pliensbachian positive $\delta^{13}C$ excursion is linked to the presence of organic-rich deposits and black shales in Northern Spain and in Portugal. A generally modest negative $\delta^{13}C$ peak, located around the Pliensbachian–Toarcian boundary, can be followed in all the areas. Finally, a new positive $\delta^{13}C$ excursion which can be extended to other localities, is recorded in the Early Toarcian of the considered areas.

Portugal, and later tested by Suan *et al.* (2010) in the same basin and extended to the Yorkshire (UK) by Korte and Hesselbo (2011). However, this excursion seems to be slightly diachronic respect to the ammonites chronozones and subchronozones. In Asturias and in the Basque-Cantabrian Basin (Quesada *et al*., 2005) is latest Pliensbachian Hawskerense Subchronozone in age (Fig. 7), in the Yorkshire (UK) virtually coincides with the Pliensbachian–Toarcian boundary (Korte and Hesselbo, 2011), in Peniche (Portugal) has been located in the earliest Toarcian (Hesselbo *et al*., 2007), around the Pliensbachian–Toarcian boundary (Suan *et al*., 2010) or in the latest Pliensbachian (Litter *et al*., 2010), and in Katsuyama (Japan) a small negative peak has been detected around the Pliensbachian–Toarcian boundary (Gröcke *et al*., 2011). Nevertheless, in some other sections like in Sancerre, in the southern Paris Basin (Hermoso *et al*., 2009, 2012), in Dotternhausen in Germany (Rhöl *et al*., 2001), in Brody-Lubienia in the Polish basin (Hesselbo and Pienkowsky, 2011), in Arroyo Lapa in Argentina (Al-Suwaidi *et al*., 2010) and the polar sections studied in northern Siberia (Suan *et al*., 2011) this negative $\delta^{13}C_{bel}$ peak has not been clearly evidenced.

The Early Toarcian is characterized by a prominent positive $\delta^{13}C_{bel}$ excursion, detected in all the considered sections, which virtually represents a continuation of the Late Pliensbachian positive CIE. As mentioned for the Early Pliensbachian, the origin of this positive excursion has been interpreted by some authors as the response of water masses to excess and rapid burial of large amounts of organic matter rich in ^{12}C, which led to enrichment in ^{13}C of the sediments (Jenkyns and Clayton, 1997; Schouten *et al.*, 2000). This explanation implies that this positive $\delta^{13}C$ excursion is linked to the presence of black shale and/or organic-rich deposits. However, in the surveyed area, as well as in many other sections, this pervasive positive CIE is not associated with the presence of large amounts of organic matter in the sediments. As mentioned above, the TOC content of the deposits recording the positive $\delta^{13}C_{bel}$ excursion in the studied sections is generally lower than 1wt.% with a thin ephemeral peak up to 3.2wt.%TOC (Gómez *et al.*, 2008) and neither in Spain nor in Portugal (Hesselbo *et al.*, 2007), Italy (Perilli *et al.*, 2009; Sabatino *et al.*, 2009), or Morocco (Bodin *et al.*, 2010) this positive $\delta^{13}C$ excursion is associated with the presence of black shale facies. In addition, the positive $\delta^{13}C$ excursion is not clearly recorded neither in the High Atlas of Morocco (Bodin *et al.*, 2010) nor in Canada (Caruthers *et al.*, 2011), indicating a probably regional, but not global, extent of this CIE.

4.5. Correlation between the palaeotemperature oscillations and the TOC content

Several palaeoclimatic events along the latest Sinemurian, Pliensbachian and Early Toarcian from the correlation of the belemnite calcite-based $\delta^{18}O_{bel}$ curves obtained in different areas of Western Europe are shown in Fig.8. The earliest event is a negative $\delta^{18}O_{bel}$ excursion, marking the Late Sinemurian Warming, recorded in different sections of Western Europe (Gómez *et al.*, 2016). Associated with this warming interval, the presence of black shale and organic-rich facies in the Asturian Basin as well as in the Basque-Cantabrian and the Lusitanian basins have been recorded (Fig. 8).

Up in the section, an interval of $\delta^{18}O_{bel}$ corresponding to "normal" or slightly negative marine values was developed throughout most of the Jamesoni Chronozone and the earliest part of the Ibex Chronozone. This marks the Early Pliensbachian "normal" temperature interval, on which average calculated temperatures (16ºC) are very close to the average seawater temperatures of the all studied Late Sinemurian, Pliensbachian and Early Toarcian interval. Coinciding with the Early Pliensbachian Warming interval, black shale facies were deposited in the Asturian and in the Lusitanian basins, as well as organic-rich marls in the Basque-Cantabrian Basin.

The outstanding Late Pliensbachian $\delta^{18}O_{bel}$ positive excursion represents one of the most significant palaeoclimatic features of the Early Jurassic, documenting one of the most

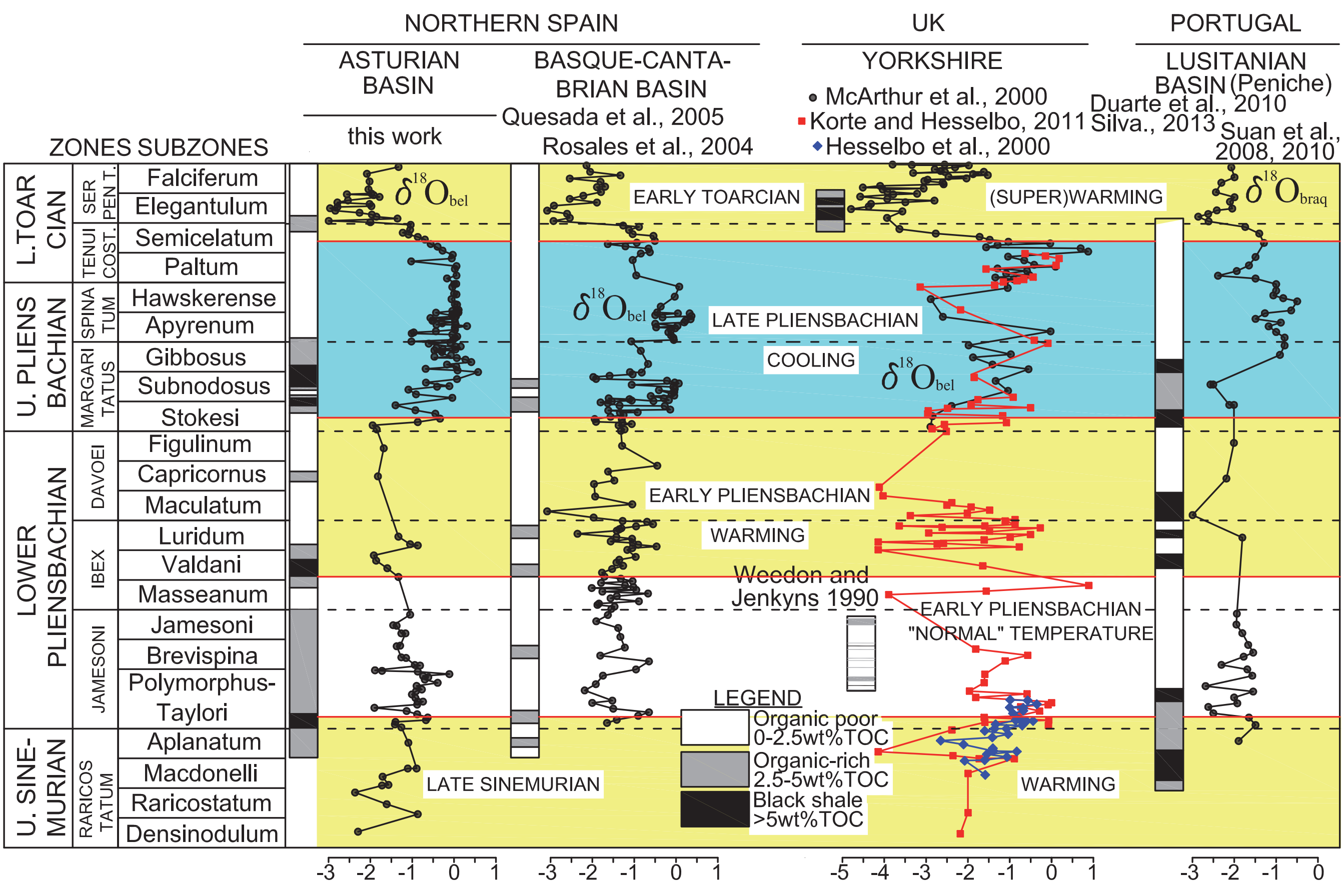


Fig. 8.- Correlation chart of the belemnite calcite-based $\delta^{18}O$ sketched curves and the presence of organic-rich and black shale deposits obtained in different areas of Western Europe. Several isotopic events along the latest Sinemurian, Pliensbachian and Early Toarcian can be recognized. The earliest event is a negative $\delta^{18}O$ excursion developed in the Late Sinemurian Raricostatum and the Early Pliensbachian Jamesoni chronozones, marking the Late Sinemurian Warming. Organic-rich intervals are recorded in the Asturian, Basque–Cantabrian and Lusitanian basins and black shale facies in the Asturian and the Lusitanian basins. After an interval of "normal" $\delta^{18}O$ values developed in most of the Jamesoni Chronozone and the earliest part of the Ibex Chronozone, containing substantial organic-rich deposits in the Asturian Basin and scarce organic-rich deposits and thin black shale facies in the Basque–Cantabrian and the Lusitanian basins, another negative $\delta^{18}O$ excursion representing the Early Pliensbachian Warming was developed in the Ibex, Davoei and earliest Margaritatus chronozones. Several episodes of organic-rich and black shales deposition were recorded at this interval in the Asturian, Basque–Cantabrian and Lusitanian basins. A main positive $\delta^{18}O$ excursion is recorded at the Late Pliensbachian and the earliest Toarcian in all the correlated localities, and another prominent negative shift in the $\delta^{18}O$ values is recorded in the Early Toarcian. Values are progressively more negative in the Tenuicostatum Chronozone and suddenly decrease around the Tenuicostatum–Serpentinum zonal boundary, delineating the Early Toarcian negative $\delta^{18}O$ excursion, which represents the Early Toarcian superwarming interval.

important cooling intervals of the Mesozoic. Associated with this cooling interval, organic-rich facies were recorded in the Asturian, Basque-Cantabrian and Lusitanian basins, including black shale facies in the Asturian and in the Lusitanian areas. The fact that the Pliensbachian represents the minimum pCO_2 values of the Jurassic, as documented by the GEOCARB II (Berner, 1994), in the GEOCARB III (Berner and Kothavala, 2001), and in the GEOCARBSULF (Berner, 2006a, b) curves, supported by the Steinthorsdottir and Vajda (2015) data for the Early Jurassic, do not support the idea that black shale deposits characterizing the OAEs were linked to warming intervals, and that those were induced by rapid influx of CO_2 into the atmosphere, from volcanogenic and/or methanogenic sources, as postulated by Jenkyns (2010).

A prominent negative shift in the $\delta^{18}O$ values, marks the Early Toarcian (super)Warming interval. Seawater temperatures progressively increase in the Tenuicostatum Chronozone and suddenly increase around the Tenuicostatum–Serpentinum zonal boundary, coinciding with the well known Early Toarcian mass extinction boundary (Gómez *et al.*, 2008; Gómez and Arias, 2010; Gómez and Goy, 2010, 2011; García Joral *et al.*, 2011; Fraguas *et al.*, 2012; Clémence *et al.*, 2015; Baeza-Carratalá *et al.*, 2015). The origin of this intense and rapid warming could be due to rise in atmospheric CO_2 concentration during the Early Toarcian that probably doubled from ~1000 ppm to ~2000 ppm (i.e. Berner, 2006a, b; Retallack, 2009; Steinthorsdottir and Vajda, 2015).

Lower Toarcian black shale facies are present in Western Europe (i.e. the Cleveland Basin of the UK, the Posidonia Shale of Germany, the Paris Basin in France) restricted to the Western Europe Euxinic Basin (WEEB) (Gómez and Goy, 2011). However, in the Lower Toarcian of the Asturian Basin, only a thin interval of organic-rich deposits is present, and organic-rich facies are absent in the rest of the Spanish sections, as well as in many other parts of the World.

5. Conclusions

Three main episodes of organic-rich and black shale facies have been documented in the Late Sinemurian–Pliensbachian–Early Toarcian interval of the Rodiles section in the Asturian Basin (northern Spain). The earliest interval was deposited at the Early Pliensbachian Jamesoni Chronozone. The middle interval corresponds with the Ibex Chronozone of the Early Pliensbachian, and the latest corresponds to the Margaritatus Chronozone of the Late Pliensbachian. These three intervals can also be recognized in the neighbour Basque–Cantabrian Basin and in the Lusitanian Basin of Portugal, delineating the palaeogeographical connection between these three basins during this period.

Against previous postulates, deposition of organic-rich and black shale facies are not restricted to the warming intervals. The presence of these types of deposits in the Margaritatus Chronozone of the Late Pliensbachian that were deposited during the outstanding Late Pliensbachian Cooling interval, clearly contradicts the idea that deposition of black shale facies characterizing the Oceanic Anoxic Events are due to abrupt rises in temperature and pCO_2 (i.e. Jenkyns, 2010). In northern Spain the presence of black shales is also linked to cooling periods coinciding with low pCO_2 intervals.

In most cases, deposition of black shale and organic-rich facies coincide with the development of deepening upward sequences, but some exceptions on which the organic-rich facies were developed in shallowing upward sequences have been evidenced.

Measurements of gamma ray and TOC values in the same strata in the Rodiles section allowed correlation between these two parameters. Tendencies of TOC and gamma-ray curves coincide in some stratigraphic intervals, but in some others the values are even contradictory. Correlation coefficient of both parameters is quite low (0.46), suggesting that, with current data, radioactivity can be evaluated as a poor proxy to estimate the presence of Jurassic source rocks in the subsurface of the Asturian Basin.

In addition, organic-rich and black shale deposits are not only linked to the positive $\delta^{13}C$ excursions, like in the Late Sinemurian, Late Pliensbachian and Early Toarcian, but they are also linked to prominent negative CIEs like in the case of the Early Pliensbachian negative $\delta^{13}C$ excursion, where organic-rich and black shale facies are present in the Asturian, as well as in the Basque-Cantabrian and in the Lusitanian basins.

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References

Al-Suwaidi, A.H., Angelozzi, G.N., Baudin, S.E., Damborenea, S.E., Hesselbo, S.P., Jenkyns, H.C., Manceñido, M.O., Riccardi, A.C., (2010): First record of the Early Toarcian Oceanic Anoxic Event from the Southern Hemisphere, Neuquén Basin, Argentina. *Journal of the Geological Society, London* 167: 633–636. doi:10.1144/0016-76492010-025.

Armendáriz, M., Rosales, I., Bádenas, B., Aurell, M., García-Ramos, J.C., Piñuela, L. (2012): High-resolution chemostratigraphic record from Lower Pliensbachian belemnites: Palaeoclimatic perturbations, organic facies and water mass Exchange (Asturian basin, northern Spain). *Palaeogeography, Palaeoclimatology, Palaeoecology* 333–334: 178–191. doi:10.1016/j.palaeo.2012.03.029

Bádenas, B., Aurell, M., Armendáriz, M., Rosales, I., García-Ramos, J.C., 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. doi.org/10.1016/j.sedgeo.2012.08.010

Baeza-Carratalá, J.F., García Joral, F., Giannetti, A. and Tent-Manclús, J.E. (2015): Evolution of the last koninckinids (Athyrida, Koninckidae), a precursor signal of the early Toarcian mass extinction event in the Western Tethys. *Palaeogeography, Palaeoclimatology, Palaeoecology* 429: 41–56. doi.org/10.1016/j.palaeo.2015.04.004

Bates, R.L., Jackson, J.A. (Eds.) (1987): *Glossary of geology*. A. Geol. Inst. Alexandria, Virginia, USA.

Berner, R.A. (1994). GEOCARB II: A revised model of atmospheric CO2 over Phanerozoic time. Am. J Sci. 249, 56–41, 1994. A revised model of atmospheric CO2 over Phanerozoic time. *American Journal of Science* 249: 56–41.

Berner, R.A. (2006a): GEOCARBSULF: a combined model for Phanerozoic atmospheric O_2 and CO_2, *Geochimica and cosmochimica Acta* 70, 5653–5664. doi:10.1016/j.gca.2005.11.032

Berner, R.A (2006b): Inclusion of the weathering of volcanic rocks in the GEOCARBSULF Model. *American Journal of Science* 306(5): 295–302..doi:10.2475/05.2006.01

Berner, R.A., Kothavala, Z. (2001): GEOCARB III. A revised model of atmospheric CO2 over Phanerozoic time. *American Journal of Science* 301: 182–204. doi:10.2475/ajs.301.2.182

Beroiz, C., Permanyer, A. (2011): Hydrocarbon habitat of the Sedano trough, Basque-Cantabrian Basin, Spain. *Journal of Petroleum Geology* 34: 387–410.

Bodin, S., Mattioli, E., Fröhlich, S., Marshall, J.D., Boutib, L., Lahasini, S., Redfern, J. (2010): Toarcian carbon isotope shifts and nutrient changes from the Northern margin of Gondwana (High Atlas, Morocco, Jurassic): palaeoenvironmental implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* 297: 377–390. doi:10.1016/j.palaeo.2010.08.018

Borrego, A.G., Hagemann, H.W., Blanco, C.G., Valenzuela, M., 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.

Boussaha, M., Pittet, B., Mattioli, E., Duarte, L.V. (2014): Spatial characterization of the late Sinemurian (Early Jurassic) palaeoenvironments in the Lusitanian Basin. *Palaeogeography, Palaeoclimatology, Palaeoecology* 409: 320–339. http://dx.doi.org/10.1016/j.palaeo.2014.05.023

Caruthers, A.H., Gröcke, D.R., Smith, P.L. (2011): The significance of an Early Jurassic (Toarcian) carbon-isotope excursion in Haida Gwaii (Queen Charlot Islands) British Columbia, Canada. *Earth and Planetary Science Letters* 307: 19−26. doi.org/10.1016/j.epsl.2014.04.023

Clémence, M.E., Gardin, S., Bartolini A (2015): New insights in the pattern and timing of the Early Jurassic calcareous nannofossil crisis, *Palaeogeography, Palaeoclimatology, Palaeoecology* 427: 100–108. doi.org/10.1016/j.palaeo.2015.03.024

Comas-Rengifo, M.J., García Joral, F., Goy, A., Rodrigo, A. (2008): Los Rhynchonellida (Brachiopoda) del Jurásico Inferior en la costa de Asturias (España). In: J.I. Ruiz-Omeñaca, L. Piñuela, J.C. García-Ramos (Eds.). *Libro de resúmenes XXIV Jornadas S.E.P. Museo del Jurásico de Asturias (MUJA), Colunga*, pp. 261–262.

Comas-Rengifo, M.J., Goy, A. (2010): Caracterización biocronoestratigráfica del Sinemuriense Superior y el Pliesnbachiense entre los afloramientos de Playa de Vega y de Lastres (Asturias). In: J.C. García-Ramos (Coord.). Las sucesiones margo-calcáreas marinas del Jurásico Inferior y las series fluviales del Jurásico Superior. Acantilados de Playa de Vega (Ribadesella). *V Congreso Jurásico de España. MUJA.* 9−18.

Correia, G.G., Duarte, L.V., Pereira, A., 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. doi.org/10.5209/rev_JIGE.2012.v38.n2.40464

De Graciansky, P.C., Jacquin, T., Hesselbo, S.P. (1998): The Ligurian Cycle: an overview of Lower Jurassic 2nd-order transgressive-regressive facies cycles in western Europe. In: P.C. de Graciansky, J. Hardenbol, P.R. Vail, (Eds.). Mesozoic and Cenozoic Sequence Stratigraphy of European Basins. *SEMP Special Publication* 60: 468–479.

Duarte, L.V., Silva, R.L., Oliveira, L.C.V., Comas-Rengifo, M.J., 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. doi:10.1344/105.000001536

Duarte, L.V., Silva, R.L., Mendonça Filho, J.G., Poças Ribeiro, N., Chagas, R.B.A. (2012): High-resolution stratigraphy, Palynofacies and source-rock potential of the Água de Madeiros Formation (Lower Jurassic), Lusitanian Basin, Portugal. *Journal of Petroleum Geology* 35: 105–126.

Duarte, L.V., Comas-Rengifo, M.J., Silva, R.L., Paredes, R., Goy, A. (2014): Carbon isotope stratigraphy and ammonite biochronostratigraphy across the Sinemurian–Pliensbachian boundary in the western Iberian margin. *Bulletin of Geosciences* 89, 4: 719–736. doi.10.3140/bull geosci.1476.

Fraguas, A. (2010): Late Sinemurian–Early Toarcian calcareous nannofossils from the Cantabrian Basin: spatial and temporal distribution. Ph.D. Thesis. University Complutense of Madrid. Madrid, Spain. ISBN: 978-84-694-2280-9

Fraguas, A., Comas-Rengifo, M.J., Gómez, J.J., Goy, A. (2012): The calcareous nannofossil crisis in Northern Spain (Asturias province) linked to the Early Toarcian warming-driven mass extinction. *Marine Micropaleontology* 94–95: 58–71. doi:10.1016/j.marmicro.2012.06.004.

García Joral, F., Gómez, J.J., Goy, A. (2011): Mass extinction and recovery of the Early Toarcian (Early Jurassic) brachiopods linked to climate change in northern and central Spain. *Palaeogeography, Palaeoclimatology, Palaeoecology* 302: 367–380. doi:10.1016/j.palaeo.2011.01.023

Gómez, J.J., Arias, C. (2010): Rapid warming and ostracods mass extinction at the Lower Toarcian (Jurassic) of central Spain. *Marine Micropaleontology* 74: 119−135. doi:10.1016/j.marmicro.2010.02.001.

Gómez, J.J., Goy, A. (2000): Definition and Organization of Limestone-Marl Cycles in the Toarcian of the Northern and East-Central Part of the Iberian Subplate (Spain). *GeoResearch Forum* 6: 301–310.

Gómez, J.J., Goy, A. (2005): Late Triassic and Early Jurassic palaeogeographic evolution and depositional cycles of theWesternTethys Iberian platform system (Eastern Spain). *Palaeogeography, Palaeoclimatology, Palaeoecology* 222: 77−94. doi:10.1016/j.palaeo.2005.03.010

Gómez, J.J., Goy, A. (2010): Early Toarcian (Early Jurassic) mass extinction linked to warming in northern and central Spain. Comparison with other sections of Western Europe. *Earth Sciences Frontiers, Special Publication* 17: 374−375.

Gómez, J.J., Goy, A. (2011): Warming-driven mass extinction in the Early Toarcian (Early Jurassic) of northern Spain. Correlation with other time-equivalent European sections. *Palaeogeography, Palaeoclimatology, Palaeoecology* 306: 176−195. doi:10.1016/j.palaeo.2011.04.018

Gómez, J.J., Goy, A., Canales, M.L. (2008): Seawater temperature and carbon isotope variations in belemnites linked to mass extinction during the Toarcian (Early Jurassic) in Central and Northern Spain. Comparison with other European sections. *Palaeogeography, Palaeoclimatology, Palaeoecology* 258: 28−58. doi:10.1016/j.palaeo.2007.11.0

Gómez, J.J., Comas-Rengifo, M.J., Goy, A. (2016): Palaeoclimatic oscillations in the Pliensbachian (Early Jurassic) of the Asturian Basin (Northern Spain). *Climate of the Past* 12, 1199–1214. doi:10.5194/cp-12-1199-2016.

Goy, A., Comas-Rengifo, M.J., García-Ramos, J.C., Gómez, J.J., Herrero, C., Suárez-Vega, L.C., Ureta, M. (2010a): The Toarcian Stage in Asturias (North Spain): Amonite record, stratigraphy and correlations. *Earth Sciences Frontiers, Special Publication* 17: 38−39.

Goy, A., Comas-Rengifo, M.J., Gómez, J.J., Herrero, C., Suárez-Vega, L.C., Ureta, M. (2010b): Biohorizontes de ammonoideos del Toarciense en Asturias. In: J.J. Ruiz Omeñaca, L. Piñuelas, J.C. García-Ramos (Eds.). *Comunicaciones V Congreso Jurásico de España. MUJA.* 94−102.

Gröcke, D.R., Hori, R.S., Trabucho-Alexandre, J., Kemp, D.B., Schwark, L. (2011): An open marine record of the Toarcian oceanic anoxic event. *Solid Earth* 3: 385–410. doi:10.5194/sed-3-385-2011.

Hallam, A., (1997): Estimates of the amount and rate of sea-level change across the Rhaetian–Hettangian and Pliensbachian–Toarcian boundaries (latest Triassic to early Jurassic). *Journal of the Geological Society of London* 154, 773–779.

Hermoso, M., Minoletti, F., Le Callonnec, L., Jenkyns, H.C., Hesselbo, S.P., Rickaby, M., Rafélis, M., Emmanuel, L., (2009): Global and local forcing of Early Toarcian seawater chemistry: A comparative study of different paleoceanographic settings (Paris and Lusitanian basins). *Paleoceanography* 24. PA4208. doi:10.1029/2009PA001764.

Hermoso, M., Minoletti, F., Rickaby, R.E.M., Hesselbo, S.P., Baudin, F., Jenkyns, H.C. (2009): Dynamics of a stepped carbon-isotope excursion: Ultra-high resolution study of Early Toarcian environmental change. *Earth and Planetary Science Letters* 319-320: 45−54. http://dx.doi.org/10.1016/j.epsl.2014.04.023

Hesselbo, S.P., Pienkowski, G. (2011): Stepwise atmospheric carbon-isotope excursion during the Toarcian Oceanic Anoxic Event (Early Jurassic, Polish Basin). *Earth and Planetary Science Letters* 301: 365−37. doi:10.1016/j.epsl.2010.11.021

Hesselbo, S.P., Gröcke, D.R., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Morgans Bell, H.S., Green, O.R. (2000): Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* 406: 392−395. doi :10.1038/35019044

Hesselbo, S.P., Jenkyns, H.C., Duarte, L.V., 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. doi.org/10.1016/j.epsl.2006.11.009

Jenkyns, H.C. (2003): Evidence for rapid climate change in the Mesozoic-Palaeogene greenhouse world. *Philosophical Transactions of the Royal Society of London A* 361: 1885−1916.

Jenkyns, H.C. (2010): Geochemistry of oceanic anoxic events. *Geochemistry, Geophysics, Geosystems* 11, Q03004, doi: 10.1029/2009GC0022788.

Jenkyns, H.C., Clayton, C.J. (1986): Black shales and carbon isotopes in pelagic sediments from the tethyan Lower Jurassic. *Sedimentology* 33: 87–106.

Jenkyns, H.C., Clayton, C.J. (1997): Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology* 44: 687−706.

Jenkyns, H.C., Jones, C.E., Gröcke, D.R., Hesselbo, S.P., 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.

Kenig, F., Hudson, J.D., Sinninghe Damsté, J.S., Popp, B.N. (2004): Intermittent euxinia: Reconciliation of a Jurassic black shale with its biofacies. *Geology* 32: 421–424. doi:10.1130/G20356.1

Korte, C., Hesselbo, S.P. (2011): Shallow marine carbon and oxygen isotope and elemental records indicate icehouse–greenhouse cycles during the Early Jurassic. *Paleoceanography* 26, 4, doi: 10.1029/2011PA002160

Litter, K., Hesselbo, S.P., Jenkyns, H.C. (2010): A carbon-isotope perturbation at the Pliensbachian–Toarcian boundary: evidence from the Lias Group, NE England. *Geological Magazine* 147(2): 181–192. doi:10.1017/S001675680999045.

Lüning, S., Kolonic, S. (2003): Uranium spectral gamma ray response as a proxy for organic richness in black shales: applicability and limitations. *Journal of Petroleum Geology* 26: 153–174. doi: 10.1111/j.1747-5457.2003.tb00023.x

McArthur, J.M., Donovan, D.T., Thirlwall, M.F., Fouke, B.W., 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. doi: 10.1016/S0012-821X(00)00111-4

Mann, U., Leythaeuser, D., Müller, P.J. (1986): Relation between source rock properties and wireline log parameters. An example from Lower Jurassic Posidonia Shale, NW-Germany. In: D. Leythaeuser and J. Rullkötter (Eds.). *Advances in Organic Geochemistry 1985*, Oxford (Pergamon Press), pp. 1105–1112.

McElwain, J.C., Wade-Murphy, J., Hesselbo, S.P. (2005): Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature* 435: 479−482. doi:10.1038/nature03618

Meyer, B.L., Nederlof, M.H. (1984): Identification of source rocks on wireline logs by density/resistivity and sonic transit time/resistivity crossplots. *AAPG Bulletin* 68: 121–129.

Pawellek, T., Aigner, T. (2003): Stratigraphic architecture and gamma ray logs of deeper ramp carbonates (Upper Jurassic, SW Germany). *Sedimentary Geology* 3–4: 203–240. doi:10.1016/S0037-0738(02)00319-6

Perilli, N., Rodrigues, R., Veiga de Oliveira, L.C., Catanzariti, R. (2009): Lower Toarcian organic-rich sediments from the Tuscan Succession (Northern Apennines, Italy): preliminary results. *Volumina Jurassica* 7: 55–65.

Peters, K.E., Cassa, M.R. (1994): Applied Source Rock Geochemistrty. In: Magoon, L. B., Dow W. G. (Eds.). *The petroleum system–from source to trap. AAPG Memoir* 60, 93–119.

Quesada, S., Dorronsoro, C., Robles, S. (1995): Genetic relationship between the oil of the Ayoluengo field and the Early Jurassic source-rock of the Southwestern Basque-Cantabrian Basin, Northern Spain. In: J.O. Grimalt and C. Dorronsoro (Eds.), *Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History*, A.I.G.O.A.; Donostia–San Sebastian, 461–463.

Quesada, S., Robles, S., Dorronsoro, C. (1996): Caracterización de la roca madre del Lias y su correlación con el petróleo del Campo de Ayoluengo en base a análisis de cromatografía de gases e isótopos de carbono, Cuenca Vasco–Cantábrica, España. *Geogaceta* 20: 176–179.

Quesada, S., Dorronsoro, C., Robles, S., Chaler, R., Grimalt, J.O. (1997): Geochemical correlation of the oil from the Ayoluengo field to Early Jurassic Black shales units in the Southwestern Basque-Cantabrian Basin, Northern Spain. *Organic Geochemistry* 27: 25–40. doi: 10.1016/S0146-6380(97)00045-4

Quesada, S., Robles, S., 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.doi: 10.1144/0016-764903-04.

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. doi: 10.2113/50.2.263

Röhl, H.J., Schmid-Röhl, A., Oschmann, W., Frimmel, A., Schwark, L. (2001): The Posidonia Shale (Lower Toarcian) of SW-Germany: an oxygen-depleted ecosystem controlled by sea level and palaeoclimate. *Palaeogeography, Palaeoclimatology, Palaeoecology* 165: 27−52. doi: 10.1016/S0031-0182(00)00152-8

Rosales, I., Quesada, S., Robles, S. (2004): Paleotemperature variations of Early Jurassic seawater recorded in geochemical trends of belemnites from the Basque−Cantabrian basin, northern Spain. *Pa-*

laeogeography, Palaeoclimatology, Palaeoecology 203: 253−275. doi:10.1016/S0031-0182(03)00686-2

Sabatino, N., Neri, R., Bellanca, A., Jenkyns, H.C., Baudin, F., Parisi, G., Masetti, D. (2009): Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria–Marche Appenines) and Monte Mangart (Julian Alps) section: paleoceanographic and stratigraphic implications. *Sedimentology* 56: 1307–1328. doi: 10.1111/j.1365-3091.2008.01035.x

Sachse, V.F., Leythaeuser, D., Grobe, A., Rachidi, M., Littke, R. (2012): Organic geochemistry and petrology of a Lower Jurassic (Pliensbachian) petroleum source rock from Aït Moussa, Middle Atlas, Morocco. *Journal of Petroleum Geology* 35: 5–24. doi: 10.1111/j.1747-5457.2012.00516.x

Schmoker, J.W. (1981): Determination of organic-matter content of Appalachian Devonian shales from gamma-ray logs. *AAPG Bulletin* 65: 1285−1298.

Schouten, S., van Kaam-Peters, H.M.E., Rijpstra, W.I.C., Schoell, M., Sinninghe Damste, J.S. (2000): Effects on an oceanic anoxic event on the stable carbon isotopic composition of Early Toarcian carbon. *American Journal of Science* 300: 1−22. doi: 10.2475/ajs.300.1.1

Silva, R. (2013): Series carbonatadas ricas em materia orgánica do Jurássico da Bacia Lusitânica (Portugal): Sedimentologia, Geoquímica e interpretação paleoambiental. *Ph D Thesis. Universidad de Coimbra*. 224 p.

Silva, R., Duarte, L.V. (2015): Organic matter production and preservation in the Lusitanian Basin (Portugal) and Pliensbachian climatic hot snaps. *Global and Planetary Change* 131: 24−34. doi.org/10.1016/j.gloplacha.2015.05.002

Steinthorsdottir, M. and Vajda, V. (2015): Early Jurassic (late Pliensbachian) CO_2 concentrations based on stomatal analysis of fossil conifer leaves from eastern Australia, *Gondwana Research* 27, 932–939. doi.org/10.1016/j.gr.2013.08.021

Stocks, A.E., Lawrence, S.R. (1990): Identification of source rocks from wireline logs. In: Hurst, A., Lovell, M. A. and Morton, A. C. (Eds), *Geological applications of wireline logs*. *Geological Society. Special Publication* 48: 241–252.

Suan, G., Mattioli, E., Pittet,B., Maillot, S., Lécuyer, 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, PA 1202. doi: 10.1029/2007PA001459.

Suan, G., Mattioli, E., Pittet,B., Lécuyer, C., Suchéras-Marx, B., Duarte, L.V., Philippe, M., Reggiani, F., Martineau, F. (2010): Secular environmental precursor to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* 290: 448–458. doi:10.1016/j.epsl.2009.12.047

Suan, G., Nikitenko, B.L., Rogov, M.A., Baudin, F., Spangenberg, J.E., Knyazev, V.G., Glinskikh, L.A., Goryacheva, A.A., Adatte, T., Riding, J.B., Föllmi, K.B., Pittet,B., Mattioli, E., Lécuyer, C., (2011): Polar record of Early Jurassic massive carbon injection. *Earth and Planetary Science Letters* 312: 102–113. doi:10.1016/j.epsl.2011.09.050

Suárez-Ruiz, I. (1987): Caracterización, clasificación y estudio de la evolución de la materia orgánica dispersa en el Jurásico de Asturias y Cantabria. *Ph.D. Thesis, Universidad de Oviedo*, Spain.

Suárez-Ruiz, L., Prado, J.G. (1995): Characterization of Jurassic black shales from Asturias (Northern Spain): evolution and petroleum potential. In: C. Snape, (Ed.), *Composition, Geochemistry and conversion of Oil Shales*. Kluwer Academic Publications, pp. 387−393.

Suárez-Vega, L.C. (1974): Estratigrafía del Jurásico en Asturias. *Cuadernos de Geología Ibérica* 3: 1−369.

Trabucho-Alexandre, J., Dirks, R., Veld, H., Klaver, G., de Boer, P.L. (2012): Toarcian black shales in the Dutch Graben: Record of energetic, variable depositional conditions during an Oceanic Anoxic Event. *Journal of Sedimentary Research* 82: 104–120.doi. 10.2110/jrs.2012.5.

Valenzuela, M. (1988): Estratigrafía, sedimentología y paleogeografía del Jurásico de Asturias. *Ph. D. Thesis, Universidad de. Oviedo*, Spain.

Valenzuela, M., García-Ramos, J.C., González Lastra, J.A., Suárez de Centi, C. (1985): Sedimentación cíclica margo-calcárea de plataforma en el Lías de Asturias. *Trabajos de Geología* 15: 45−52.

Valenzuela, M., García-Ramos, J.C., Suárez de Centi, C. (1986): The Jurassic sedimentation in Asturias (N Spain). *Trabajos de Geología* 16: 121–132.

Valenzuela, M., García-Ramos, J.C., Suárez de Centi, C. (1989): La sedimentación en una rampa carbonatada dominada por tempestades, ensayos de correlación de ciclos y eventos de la ritmita margo-calcárea del Jurásico de Asturias. *Cuadernos de Geología Ibérica* 13: 217–235.

van Buchem, F.S.P., Melnyk, D.H., McCave, I.N. (1992): Chemical cyclicity and correlation of Lower Lias mudstones using gamma ray logs, Yorkshire, UK. *Journal of the Geological Society of London* 149: 991−1002.

Weedon, G.P., Jenkyns, H.C. (1990): Regular and irregular climatic cycles and the Belemnite Marls (Pliensbachian, Lower Jurassic, Wessex Basin). *Journal of the Geological Society of London* 147: 915−918.

Wignall, P.B. (1991): Model for transgressive black shales?. *Geology* 19: 167–170.

Wignall, P.B., Myers, K.J. (1988): Interpreting benthic oxygen levels in mudrocks: a new approach. *Geology* 16: 452–455.