Syndepositional processes in the pigmentation of oceanic red beds: evidence from the Basque–Cantabrian Basin (northern Spain)

Javier Elorza1,2, Juan José Gómez-Alday2 and Álvaro Jiménez Berrocoso3

1Dpto. Mineralogía y Petrología. Universidad del País Vasco. Apartado 644; 48080 Bilbao, Spain; 2Grupo Hidrogeología. IDR. Universidad Castilla-La Mancha. 02071 Albacete, Spain and 3Repsol Exploration, c/Méndez Álvaro 44, 28045 Madrid, Spain

Abstract
Oceanic red beds (ORBs) are present in Upper Cretaceous and Danian deep-marine deposits in the Basque–Cantabrian Basin of northern Spain. The presence and regularity of the succession of marl–limestone couplets is exceptional based on the macroscopic, microscopic and geochemical evidence collected. Five types of marl–limestone couplets are identified based on the colour, and a high maximum sedimentation rate (3.6 cm ka−1) is noted. The oxidizing activity of deep, cold-water masses is indicated by the oxygen isotope signal in the lower–upper Maastrichtian and Danian sections and the presence of the boreal inoceramid Spyridoceras tegulatus. In theory, the variation in colour from grey to greenish-yellow, purple and pink up to red tones correlates with the Fe3+/Fe2+ ratio. It is interpreted as the possible palaeoenvironmental transit of particles that sediment out slowly in oxic conditions when they circulate through cooler, oxidizing water masses. The colour is considered to be a depositional feature, and hematite, detected by X-ray diffraction, is the main staining agent, without discarding the possible redistribution of other factors such as a rise in sea level, weathered silicate rocks and/or nutrient sequestration by X-ray diffraction, is the main staining agent, without discarding the possible redistribution of other factors such as a rise in sea level, weathered silicate rocks and/or nutrient sequestration or the blocking of the ocean–climate system. These events are also characterized by positive carbon isotope (δ13C) excursions related to globally enhanced rates of organic carbon burial. The intervals between Cretaceous OAEs, albeit still greenhouse conditions, are considered to be normal periods of comparatively increased seawater oxygenation and temperature changes (Jenkyns, 2010; Robinson et al., 2017). However, it is generally recognized that the global temperature established in OAE2 (except for the Plenus Cold Event) was prevalent until the early Turonian Age due to the high CO2 content, meaning that the subsequent cooling required changes in other factors such as a rise in sea level, weathered silicate rocks and/or nutrient sequestration in black shales (Robinson et al., 2019).

In contrast to the Cretaceous OAEs, in subsequent periods oxic, deep-marine sediments were deposited in the world’s oceans, including red to pink to purple/green/yellow limestones, marlstones, claystones and cherts (Hu et al., 2005; Scott, 2009). These sediments have been called Cretaceous oceanic red beds (ORBs) (Wang et al., 2004, 2005; Hu et al., 2005) and, because they followed OAEs, many studies consider that their deposition was an inevitable consequence of OAE conditions (Wagreich et al., 2009; Wang et al., 2011). That is, continued organic-rich deposition during OAEs represented a CO2 sink, a situation that subsequently allowed both atmospheric oxygen and seawater-dissolved oxygen to increase, thus leading to the sedimentation of Cretaceous ORBs (Wagreich et al., 2009; Wang et al., 2011; Gambacorta et al., 2016).

1. Introduction

The geological history of the Cretaceous Period is marked by stages during which deep-marine environments underwent major deposition and burial of organic-rich, fine-grained sediments (referred to here as black shales) at regional to basin scales under the influence of low-to-absent dissolved oxygen in seawater (Hsu & Jenkyns, 1974; Schlanger & Jenkyns, 1976; Scholle & Arthur, 1980; Weissert et al., 1985; Jenkyns, 2010; Hünneke & Mulder, 2011). These periods have been called ocean anoxic events (OAEs), and it is generally accepted that at least five major OAEs occurred during the Cretaceous Period (Schlanger & Jenkyns, 1976; Jenkyns, 1980, 2010; Arthur et al., 1990; Wilson & Norris, 2001; Jarvis et al., 2006; Najarro et al., 2011; Beil et al., 2019). Cretaceous OAEs took place during greenhouse conditions (i.e. warm temperatures globally and high atmospheric pCO2), and their major significance is that they deeply perturbed the global carbon cycle through feedback mechanisms that controlled the evolution of the ocean–climate system. These events are also characterized by positive carbon isotope (δ13C) excursions related to globally enhanced rates of organic carbon burial. The intervals between Cretaceous OAEs, albeit still greenhouse conditions, are considered to be normal periods of comparatively increased seawater oxygenation and temperature changes (Jenkyns, 2010; Robinson et al., 2017). However, it is generally recognized that the global temperature established in OAE2 (except for the Plenus Cold Event) was prevalent until the early Turonian Age due to the high CO2 content, meaning that the subsequent cooling required changes in other factors such as a rise in sea level, weathered silicate rocks and/or nutrient sequestration in black shales (Robinson et al., 2019).
Along with oxygenated water masses, the main accepted conditions for the formation of Cretaceous ORBs are low sedimentation rates and oligotrophic conditions in seawater (Scott, 2009). In general, low sedimentation rates in an oxygenated water column would provide enough time for the oxidation of seawater Fe$^{2+}$ into Fe$^{3+}$ as the main colouring agent in ORBs, the precipitation of Fe$^{3+}$-rich oxides in the water column and/or within the sediments (surrounding other particles in both cases), and the incorporation of Fe$^{3+}$ into the crystal structure of carbonate minerals (e.g. calcite) (Jansa & Hu, 2009; Hu et al. 2012). Oligotrophic conditions, with a very low level of nutrients, imply that only small amounts of organic matter would reach the seafloor; this situation would promote its rapid degradation, reducing the likelihood of the creation of low-oxygen conditions in bottom waters and/or within the sediments.

The Upper Cretaceous and Paleocene sediments of the Basque–Cantabrian Basin in northern Spain are well suited for studying the origin of the colour variations within ORBs. Of particular interest are a series of short successions (2–5 m thick) from the lower Turonian, lower Maastrichtian, upper Maastrichtian and Danian sediments that were deposited in deep-marine environments, at a palaeodepth of at least 1500 m (Plaziat et al. 1998), in the Western Tethys facing the open North Atlantic. The sections are biostratigraphically complete with easily accessible outcrops that have traditionally provided a wealth of lithological, palaeontological, geochemical and cyclostratigraphic information (Gómez-Alday et al. 2004, 2008; Dinarès-Turrèl et al. 2013). Here, we describe the details of these colour variations, interpret their possible origin and discuss their palaeoceanographic significance. A broader impact of our work is that it may help to understand the products of the interaction between ocean and climate under greenhouse conditions, which has implications for our understanding of the evolution of our current climate.

2. Geological setting and antecedents

The Basque–Cantabrian Basin is located in the westernmost part of the Pyrenean chain, and its depositional history is connected to the opening of the Bay of Biscay (Fig. 1a–c). This basin constituted the most northerly part of the central North Iberian margin and occupied a latitude of c. 30°–35°N during most of the Late Cretaceous–Paleocene epochs (Rat et al. 1983; Plaziat, 1981; Floquet, 2004).

A deep-marine sector, the so-called Basque Arc Domain, with several sub-basins (e.g. the Plentzia and San Juan de Luz troughs) experienced a high rate of subsidence and the deposition of more than 4000 m of calcareous flysch during the Cenomanian (Mathey, 1987). The deep-marine sector was connected to platform materials by the Alpine Orogeny and make up the NE flank of the Biscay Synclinorium, with a local direction of N120°E. Palaeogeographic reconstructions situate the basin at latitude 30°–35°N. The Maastrichtian sediments of the Basque Arc Domain were deposited in the Orío trough, formed during the Campanian Age and limited by the North Iberian platform to the south and the Aquitaine platform to the north (see Plaziat, 1981; Mathey, 1987; Pujalte et al. 1998, 2000). Gypsium, clays and volcanic rocks (Keuper Facies, Triassic) are visible to a minor extent compared with the vast extent of carbonate sediments ordered by couplets of marls with either marly limestone or limestone, corresponding to the lower and upper Maastrichtian Stage, included in the Zumaya–Algorri Formation (Mathey, 1982) and differentiated into Members I–V (MacLeod & Ward, 1990; Ward & Kennedy, 1993). Although the lower and upper Maastrichtian couplets usually comprise subcouplets of marls and marly limestones, for the sake of simplicity we refer to these as marl–limestone couplets. Small sections of interest are found in the Sopelana beach cliffs (Figs 1, 3–6): the lower Maastrichtian, upper Maastrichtian and Danian sections.

3. Selected sections

Representative sections of red facies that emerge in the Basque Arc Domain (Fig. 1a, c) have been chosen: (1) the lower Turonian cliffs of Muriola beach (Fig. 2a); (2) five sections in the lower Maastrichtian (Fig. 3a) and upper Maastrichtian (Figs 4a and 5a) Sopelana beach cliffs; and (3) Danian materials (Fig. 6a).

3.3. Muriola beach cliffs: Lower Turonian section

The Muriola beach sea-cliff exposure (Barrika village, 20 km NE of Bilbao) covers less than 80 m and is assigned to the basalt Plentzia Formation (middle Cenomanian – uppermost Santonian; Mathey, 1982); it is well developed on the NE flank of the Biscay Synclinorium, with a local direction of N90°E (Fig. 1a, c). In general, the Plentzia Formation is formed of grey carbonate turbidites where the central part contains bedded and nodular chert in the Tb, Tc and Td intervals of the Bouma sequence (Elorza & Bustillo, 1989), but the Muriola beach section contains a dysoxic–anoxic event (1.40 m thick, expanded by 0.50 m of interbedded turbidites) that is the OAE2 itself or a local anoxic episode (Fig. 2a). Above and a short distance away, as a result of the presence of faults, a small deposit of reddish hemipelagic marls (＞2 m thick) has thin, interbedded grey turbidites that likely formed in a deep basin environment (Fig. 2b, c). Planktonic foraminifer species (Marginotruncana pseudolineatina, Marginotruncana renzi, Helvetoglobotruncana praehelvetica, Dicarinella hagni and Dicarinella canaliculata) date this section as early Turonian Age. The thin grey turbiditic beds include trace fossils at the base, but do not contain macrofossils such as ammonite moulds or inoceramid debris. The existence of small normal faults with reactivation structures, stylolites and extension veins are highlighted.
3.b.1. Lower Maastrichtian section

The materials of the lower Maastrichtian section are composed of grey marl–limestone couplets without turbiditic episodes and with a high rate of sedimentation per couplet (3 cm ka⁻¹); they were deposited in a deep basin environment (Gómez-Alday et al. 2004; Álvarez-Llano et al. 2006). The section belongs to the Gansserina gansseri biozone, in chron C31R prior to the latest Cretaceous regression. Macrofossils comprise thick, complete inoceramid shells (Ward et al. 1991; MacLeod, 1994; Gómez-Alday et al. 2004, 2008) and scarce ammonite moulds of different species (Ward & Kennedy, 1993), in addition to Zoophycos and Planolites as the dominant ichnofossils.

The object of our attention is a small section in the eastern part of Sopelana beach called El Peñón, where the carbonate marl–limestone couplets, inverted due to nearby diapiric activity, correspond to the lower Maastrichtian section of the Zumaya–Azgorri Formation (Fig. 3a). The marl–limestone couplets are mostly grey, with considerable large Platyceramus salisburgensis (Fugger & Kastner, 1885) (Fig. 3b) inoceramid shells. However, they evolve into greenish-yellow tones and then a greater prevalence of red tones (Fig. 3c, d). In these materials of greenish-yellow to reddish tones, inoceramid fragments, echinoids, trace fossils with numerous Zoophycos and later bleached fractures are preserved (Fig. 3b*, e–h).

3.b.2. Upper Maastrichtian section

Three small, complementary upper Maastrichtian sections have been chosen for this study. Section UM1 (2.67 m thick) is formed of six marl–limestone couplets of yellowish-grey shades in the limestones and slightly purple tones in the marls, arranged in normal position and belonging to the lower part of the upper Maastrichtian section (Fig. 4a, b). In the same Sopelana cliff, section UM1 has been complemented with another, smaller section, UM1*, of thicker couplets (two marl–limestone couplets, 1.39 m) with similar lithological characteristics and ichnofossil contents. Above, section UM2 (3.60 m thick) has five marl–limestone couplets of generally purple tones, both in marls and limestones (Fig. 4a, c, d). Both sections correspond to the Abathomphalus mayaroensis biozone, forming part of Member IV (Ward & Kennedy, 1993).
3.b.3. Danian section

The Paleocene sediments were deposited in slope-apron, basin-floor and deep-sea channel environments limited by the shallow limestones of the North Iberian platform to the south and the Aquitaine platform to the north. Neither purple nor intense red, the pink and white colour of the limestones is the most evident and defining characteristic in all recognized outcrops of Danian age (Sopelana, Zumaya, San Sebastián, Hendaye, Bidart sections) in the Basque Arc Domain (Fig. 1a). The small fragment of the stratigraphic record chosen in the Sopelana beach cliff belongs to the pinkish-white pelagic limestones and hemipelagic marls of the Danian (lower Palaeogene), located on the northeastern flank of the Biscay Synclinorium (Figs 1a, c, 4a, 6a, b).

The marl–limestone couplets are grouped in turn in sets in different ways (tight, amalgamated and open), without intervening turbiditic episodes or slides that would generate intraformational gaps. The depositional environment is deep basin and reaches the biozones of *Eoglobigerina pseudobulloides* and *Eoglobigerina trinidadensis* (Pujalte et al. 1998). The marl–limestone couplets are predominantly pink, but can change at the intrabed scale to white tones in both lithologies (Fig. 6c, e). Only crushed echinoid shells appear as macrofossils, and Zoophycos and Planolites are the predominant ichnofossils (Fig. 6g).

The limestone subcouplets have numerous sutured, irregular small stromatolites perpendicular to the stratification surface (Fig. 6h).

4. Methods

Detailed sedimentary logs, photographic documentation and a large sample set of bulk sediments and fossil shells from the sections studied...
were collected over several field seasons. We examined more than 50 thin-sections by standard microscopy methods, using Alizarin Red S and potassium ferricyanide staining (Dickson, 1965). All cathodoluminescence (CL) work employed a Technosyn Cold Cathode Luminescence system (model 8200 Mk II) mounted on an Olympus trinocular research microscope with a maximum magnification capability of 400×, using universal stage objectives. Standard operating conditions included an accelerating potential of 12 kV and a 0.5–0.6 mA beam current with a beam diameter of approximately 5 mm. For the intervals specifically addressed in this paper, sampling resolution was increased up to 2 cm per sample. Samples were collected using a portable drill and 6 mm bits on fresh surfaces of marls, marly limestones and limestones. The proportion of CaCO₃ (in percent) was measured on a split (90–150 mg) of each powdered sample using an automated calcimeter (Aquitaine Technique Innovation, Bordeaux, France) at the University of the Basque Country (Bilbao, Spain) following the method of Bernard (Allison & Moodie, 1965). The pressure of the evolved CO₂ gas was individually measured and converted to % CaCO₃. Analytical precision is better than 4% on the basis of replicate analyses. The stable isotope data were obtained from the same samples at the University of Missouri (USA) by reacting c. 50 μg of powder in 103% H₃PO₄ at 70°C in a Kiel III carbonate device. The δ¹³C and δ¹⁸O
of the evolved CO₂ was determined online in a Thermo Finnegan Delta Plus mass spectrometer. The results are normalized to the average of multiple analyses of the NBS-19 standard. The resulting corrections were small, and analytical precision, based on uncorrected values for NBS-19, was 0.02‰ and 0.05‰ for δ¹³C and δ¹⁸O, respectively. The isotope data are expressed in the standard δ-notation relative to the Vienna PDB standard.

A number of samples were selected and examined under a scanning electron microscope (SEM) and qualitatively determined (Al, Si, Fe, P, K, Ca) by energy-dispersive spectrometry (EDX) using a Jeol JSM6400 at the University of the Basque Country. X-ray diffractometry (XRD) analyses were performed with a Phillips PW1710 diffractometer using Cu Ka radiation monochromated by graphite with generator conditions of 40 kV, 20 mA, a step size of 0.02° (°2θ) and a time per step of 1 s.

5. Results

5.a. Lower Turonian section (Muriola beach cliff)

In the hemipelagic reddish marls of 2.35 m thickness, a total of 11 layers of grey carbonate turbidites Tb-1 to Tb-11 are intercalated, with parallel and cross laminations (Fig. 2b). The reddish marls are irregularly ‘bleached’ in contact with the grey turbidite beds (Fig. 2c). High-resolution calcimetric analyses (38 samples; c. 2–3 cm per sample) of the red hemipelagic marls reveal a mean value of 36% CaCO₃, whereas the mean value of the 23 samples of the grey carbonate turbidites is 75% CaCO₃ (Table 1).

In the turbidites Tb-3 and Tb-11, of medium thickness, a decrease in the concentration of CaCO₃ is observed towards the top (Fig. 2d). The analysis of red marls by XRD confirms that the minority mineral phases correspond to quartz, plagioclase, feldspar, micas and clays such as kaolinite and illite and/or smectite. The presence of hematite is recognized in the insoluble concentrate, as a result of the red marls having been attacked with dilute HCl. The chronostratigraphic and geochemical characteristics assign the reddish marls of Muriola beach to the Ca Cretaceous ORBs and as short-term Cretaceous ORBs of age < 1 Ma, according to the classification of Hu et al. (2012).

5.b. Lower Maastrichtian section (Sopelana beach cliff)

In El Peñón section, high-resolution calcimetric analysis provides a mean value across the five grey limestones of 79% CaCO₃ versus 60% for five grey marls; a mean value of 62% CaCO₃ for five greenish-yellow marls; 65% CaCO₃ for five red marls versus 87% for three red limestones; and a mean value of 91% CaCO₃ for three red
limestones with bleaching effect. These mean values indicate a high percentage of CaCO₃, although with a 20% difference between limestone versus marl values (Table 1). These compositional characteristics allow us to classify the reddish and greenish-yellow couplets of the lower Maastrichtian section as belonging to the Ca Cretaceous ORBs and as short-term Cretaceous ORBs of age < 1 Ma (Hu et al. 2012).

The δ¹⁸O‰ and δ¹³C‰ (V-PDB) values of the same samples in the grey and red facies were obtained to provide complementary data (Table 2). The δ¹⁸O in the grey limestone reaches a mean value of −2.32‰ compared with the mean value of −2.17‰ in the grey marls. In both the greenish-yellow marls and the red marls, the mean value of δ¹⁸O is −1.90‰. The analyses carried out in the contact zone between the red limestone and the bleached zones provide very similar mean values of 1.65‰ and 1.66‰, respectively.

The value obtained from a late calcite vein (100% CaCO₃) is δ¹⁸O = −4.02‰. The δ¹³C data exhibit stable values between a minimum of 1.93‰ and a maximum of 2.12‰. The mean value of δ¹⁸O in a single inoceramid shell in grey facies is 0.39‰, whereas the mean value in different inoceramid shells in red facies is 0.12‰. The δ¹³C data exhibit stable values with a slight decrease in the red facies (Table 2). The analysis of grey limestones and marls by XRD indicates that the minority mineral phases correspond to quartz, plagioclase, feldspar, micas and clays such as kaolinite and illite and/or smectite. The presence of hematite is recognized in the insoluble concentrate (Fig. 3d). Cathodoluminescence microscopy (CL) was also used to verify the diagenetic zoning undergone in the inoceramid shells (Fig. 7a–d), and elemental maps (Ca, Fe, Mg) made to determine the presence of ferromagnesian clays in the intercrystalline zones.
of planktonic foraminifer chambers, using an energy-dispersive X-ray spectroscopic instrument (Fig. 8i–l).

5.c. Upper Maastrichtian sections (Sopelana beach cliff)

In Member IV, where inoceramid bivalves are extinct, three small sections were studied (Figs 4a, 5a). Section UM1, of 2.67 m thickness and comprising six marl–limestone couplets with mean values of 20.3 cm thickness for purple marl subcouplets and 17.5 cm thickness for yellowish-grey limestone subcouplets, produces an average sedimentation rate of 2.4 cm ka$^{-1}$. This UM1 section reveals a greater compositional contrast, with c. 20% CaCO$_3$ difference between the purple marl subcouplets ($n = 48$; mean value 48% CaCO$_3$) and the yellowish-grey limestone subcouplets ($n = 83$; mean value 65% CaCO$_3$). Couplets 1, 2 and 3 show greater differences whereas couplets 5 and 6 are more continuous in their composition (Fig. 4a, b; Table 1).

In the same Sopelana cliffs, section UM1 was complemented with another, smaller section, UM1*, with similar lithological characteristics (Fig. 5a). Two complete marl–limestone couplets with a total thickness of 1.39 m were chosen for analysis. These correspond to 53 cm thickness for the two purple marl subcouplets and 86 cm thickness for the two yellowish-grey limestone subcouplets. The average sedimentation rate is 3.5 cm ka$^{-1}$. The calcimetric analyses of the yellowish-grey limestones ($n = 38$) showed a mean value of 71.5% CaCO$_3$, and of the purple marls ($n = 24$) a mean value of 48.4% CaCO$_3$ (Table 1; Fig. 5a, b, a$^*$). The resulting compositional contrast (> 20%) is similar to that obtained in section UM1.

Section UM2 is 3.60 m in thickness and contains five thicker marl–limestone couplets, with an average thickness of purple marl...
subcouplets of 38.6 cm and of purple limestone subcouplets of 33.4 cm, with a general detrital contribution noteworthy for its high sedimentation rate (3.6 cm ka\(^{-1}\)). The high-resolution calcimetric analysis shows a lower average compositional contrast (c. 10%) between the purple marl subcouplets (\(n=68\); mean value 45% CaCO\(_3\)) and the purple limestone subcouplets (\(n=82\); mean value 55% CaCO\(_3\)), with a more regular curve visible at couplets 4, 5, 6 and 7. The low CaCO\(_3\) contents of the purple limestones indicate that it is more appropriate to define them as marly limestones from now on. The differences between the last values of the marl subcouplets and the first of the marly limestone subcouplets are minimal. Couplet 8 marks a change in this trend (Fig. 3a, c, d; Table 1).

The XRD analysis reveals the presence of hematite in the insoluble concentrate of both purple lithologies. The SEM analysis shows how the carbonate matrix, although cushioned by cementation and compaction, is composed of innumerable coccolith fragments grouped together with illites, such as detrital micas (Fig. 5d, e).

5.d. Danian section (Sopelana beach cliff)

The investigated section, of 3.71 m thickness and comprising 16 continuous marl–limestone couplets, highlights the extreme thinness of the pink marl subcouplets compared with the pink limestone subcouplets (Fig. 6a, b). The average thickness of the limestone subcouplets (19 cm) is much higher on average than that of the marl subcouplets (6.4 cm). The average sedimentation rate is lower (1.2 cm ka\(^{-1}\)) than the average value for the Maastrichtian sections discussed above. In the high-resolution calcimetric analysis (c. 1 cm per sample) of the marl–limestone couplets, high calcium carbonate contents are observed for the pink and some bleached limestone subcouplets (\(n=317\); mean value of 89% CaCO\(_3\)) compared with the low values in the pink marls (\(n=11\); mean value of 39% CaCO\(_3\)) (Fig. 6e; Table 1). The XRD analysis of the pink limestones and the pink marls confirms the presence of hematite in both lithologies in the insoluble concentrate (Fig. 6d). In order to obtain elemental maps (Ca, Fe, Mg) and determine the presence of ferromagnesian clays in the intercrystalline zones, an energy-dispersive X-ray spectroscopic instrument was used (Fig. 8a–h). The SEM analysis shows how the carbonate matrix, although distorted by cementation and compaction, is composed of innumerable coccolith fragments with evidence of bacterial activity (Fig. 9e–h).

6. Discussion

The International Geoscience Programmes 463, 494 and 555 (2002–2010) allowed a substantial advance in our knowledge of Oceanic red beds, Basque–Cantabrian Basin

| Oceanic red beds in the Basque–Cantabrian region | Proportion of CaCO\(_3\) (%) | Sedimentation rate (cm ka\(^{-1}\)) |
|--------------------------------------------------|-----------------------------|----------------------------------|
| Muriola beach cliff |                             |                                  |
| Lower Turonian (Fig. 2d) |                             |                                  |
| Red marls (\(n=38\)) | 36.1 ± 5.4 |                                  |
| Grey carbonate turbidites (\(n=23\)) | 74.6 ± 14.0 |                                  |
| Sopelana beach cliffs |                             |                                  |
| Lower Maastrichtian section, El Peñón |                             |                                  |
| Grey limestones (\(n=5\)) | 78.6 ± 2.6 |                                  |
| Grey marls (\(n=5\)) | 59.8 ± 2.1 |                                  |
| Greenish-yellow marls (\(n=5\)) | 61.7 ± 3.2 |                                  |
| Red marls (\(n=5\)) | 65.3 ± 1.3 |                                  |
| Red limestones (\(n=3\)) | 86.9 ± 0.6 |                                  |
| Red limestone bleaching (\(n=3\)) | 90.8 ± 2.5 |                                  |
| Upper Maastrichtian section, UM1 (Fig. 4a) | 2.4 |                                  |
| Purple marls (\(n=48\)) | 48.1 ± 9 |                                  |
| Yellowish-grey limestones (\(n=83\)) | 65.3 ± 5.6 |                                  |
| Upper Maastrichtian section, UM1* (Fig. 5a*) | 3.5 |                                  |
| Purple marls (\(n=24\)) | 48.4 ± 7.5 |                                  |
| Yellowish-grey limestones (\(n=38\)) | 71.5 ± 6.2 |                                  |
| Upper Maastrichtian section, UM2 (Fig. 4a) | 3.6 |                                  |
| Purple marls (\(n=68\)) | 44.7 ± 6.7 |                                  |
| Purple limestones (\(n=82\)) | 55.4 ± 5.2 |                                  |
| Danian section (Fig. 6b,c,e) | 1.2 |                                  |
| Pink marls (\(n=11\)) | 39.4 ± 10 |                                  |
| Pink limestones (\(n=317\)) | 89.1 ± 4.6 |                                  |
Table 2. Proportions of CaCO$_3$ (%) and isotopic values ($\delta^{13}$C ‰, $\delta^{18}$O ‰ V-PDB) of grey, green-yellowish, red (marl–limestone) couplets and bleached parts of El Peñón section, as well as the isotopic values ($\delta^{13}$C ‰, $\delta^{18}$O ‰ V-PDB) of the inoceramid prisms collected in the grey and red facies. The isotope data are expressed in the standard $\delta$-notation relative to the Vienna PDB standard (V-PDB). PG – Peñón grey; PV – Peñón greenish-yellow; PR – Peñón red; Pcc – Peñón calcite; SD – standard deviation.

| Oceanic red beds in the Basque–Cantabrian region | Limestone | Marl | CaCO$_3$ (%) | Avg | SD | $\delta^{13}$C ‰ | SD | $\delta^{18}$O ‰ | SD |
|--------------------------------------------------|-----------|------|--------------|-----|----|----------------|----|----------------|----|
| **Lower Maastrichtian El Peñón section; inverted grey section with thicker inoceramids** |           |      |              |     |    |                 |    |                 |    |
| PG-1 (older) × | 81.3 | 1.94 | 0.01 | -2.32 | 0.01 | | | | |
| PG-2 × | 79.9 | 1.91 | 0.01 | -2.40 | 0.01 | | | | |
| PG-3 × | 79.4 | 1.93 | 0.01 | -2.25 | 0.02 | | | | |
| PG-4 × | 74.5 | 1.93 | 0.02 | -2.31 | 0.02 | | | | |
| PG-5 × | 77.8 | 1.91 | 0.01 | -2.33 | 0.02 | | | | |
| **Mean value** | | | | | | | | | |
| PG-6 × | 62.9 | 1.95 | 0.01 | -1.92 | 0.01 | | | | |
| PG-7 × | 57.5 | 2.07 | 0.01 | -2.20 | 0.01 | | | | |
| PG-8 × | 60.2 | 2.09 | 0.01 | -2.39 | 0.02 | | | | |
| PG-9 × | 60.2 | 2.07 | 0.02 | -2.21 | 0.02 | | | | |
| PG-10 (younger) × | 58.1 | 2.12 | 0.01 | -2.15 | 0.02 | | | | |
| **Mean value** | | | | | | | | | |
| **Lower Maastrichtian; greenish-yellow** |           |      |              |     |    |                 |    |                 |    |
| PV-1(older) × | 65 | 2.14 | 0.02 | -1.85 | 0.02 | | | | |
| PV-2 × | 65 | 2.11 | 0.01 | -1.86 | 0.01 | | | | |
| PV-3 × | 57.8 | 2.09 | 0.02 | -1.92 | 0.02 | | | | |
| PV-4 (XRD) × | 60.4 | 2.12 | 0.01 | -2.13 | 0.01 | | | | |
| PV-5 (XRD) × | 60.2 | 2.09 | 0.02 | -1.74 | 0.02 | | | | |
| **Mean value** | | | | | | | | | |
| **Lower Maastrichtian (red)** |           |      |              |     |    |                 |    |                 |    |
| PR-1 × | 63.7 | 2.10 | 0.01 | -2.11 | 0.02 | | | | |
| PR-2 × | 64.8 | 2.09 | 0.02 | -1.82 | 0.02 | | | | |
| PR-3 × | 64.9 | 2.14 | 0.01 | -1.82 | 0.02 | | | | |
| PR-4 (XRD) × | 66.4 | 2.11 | 0.02 | -1.85 | 0.02 | | | | |
| PR-5 (XRD) (younger) × | 66.9 | 2.14 | 0.02 | -1.90 | 0.02 | | | | |
| **Mean value** | | | | | | | | | |
| **Lower Maastrichtian bleached (PRO)** |           |      |              |     |    |                 |    |                 |    |
| PRO-1 (Red) × | 87.1 | 2.05 | 0.02 | -1.61 | 0.02 | | | | |
| PRO-2 (XRD) (Red) × | 86.3 | 2.05 | 0.03 | -1.65 | 0.03 | | | | |
| PRO-3 (XRD) (Red) × | 87.4 | 2.03 | 0.02 | -1.70 | 0.03 | | | | |
| **Mean value** | | | | | | | | | |
| PRO-4 (bleached) × | 88.1 | 2.05 | 0.01 | -1.58 | 0.01 | | | | |
| PRO-5 (XRD) (bleached) × | 92.2 | 2.03 | 0.02 | -1.72 | 0.02 | | | | |
| PRO-6 (XRD) (bleached) × | 92 | 2.05 | 0.01 | -1.70 | 0.01 | | | | |
| **Mean value** | | | | | | | | | |
| **White calcite in fractures** |           |      |              |     |    |                 |    |                 |    |
| Pcc-1 | 100.4 | 2.04 | 0.01 | -4.02 | 0.01 | | | | |

(Continued)
Cretaceous ORBs, including specific studies on chronostratigraphy, sedimentology, mineralogy, elemental and isotopic geochemistry, as well as establishing possible palaeoclimatic and palaeoceanographic relationships between OAEs and Cretaceous ORBs (e.g. Hu et al. 2005; Wagreich & Krenmayr, 2005; Wang et al. 2005; Chen et al. 2007; Cai et al. 2009). These investigations were published as SEPM Special Publication no. 91 (Hu et al. 2005) and later summarized by Hu et al. (2012). Subsequently, this research was expanded upon by other works (e.g. Gambacorta et al. 2016; Ahmed et al. 2017; Song et al. 2017). In summary, the sedimentological, mineralogical and geochemical data suggest that the ORBs were deposited in oligotrophic conditions of cold, oxygenated waters with a low sedimentation rate (Wang et al. 2009). Along these same lines, the petrographic and sedimentological study of the Rosso Ammonitico Veronese (Middle–Upper Jurassic, NE Italy) is complemented using classic microscopy, cathodoluminescence and SEM techniques (Préat et al. 2006). These authors consider that the red colour is due to bacterially mediated precipitation of iron oxyhydroxides at the water–sediment interface, but under dysoxic–anoxic conditions. Subsequently, these oxyhydroxides were completely transformed into hematite during diagenesis (neomorphism and recrystallization), producing a homogeneous red matrix. Although not mentioned by the authors, it is interesting to verify that, in the few δ18O values provided (Préat et al. 2006, table 1, Voltascura and Forte Campo di Lucerna sections), it can be observed how, in spite of the subsequent diagenesis undergone, the mean values of the red materials are slightly higher (δ18O = −0.67‰; −0.82‰) than the mean values of the pink (δ18O = −1.17‰; −0.98‰) or grey carbonate matrix (δ18O = −1.88‰; −1.05‰). In our opinion, this indicates that the isotopic signal has been partially maintained and that the

### Table 2. Oceanic red beds in the Basque–Cantabrian region

| Inoceramid in grey facies (different fragments from the same shell) | Limestone | Marl | CaCO₃ (%) | Avg | SD | δ¹³C (%) | SD | δ¹⁸O (%) | SD |
|---|---|---|---|---|---|---|---|---|---|
| PE-ino1 shell powder | × | 1.84 | 0.02 | 0.54 | 0.02 |
| PE-ino2 shell powder | × | 1.86 | 0.01 | −0.45 | 0.01 |
| PE-ino3 shell powder | × | 1.90 | 0.02 | 0.02 | 0.02 |
| PE-ino4 shell powder | × | 1.84 | 0.02 | 0.52 | 0.02 |
| PE-ino5 shell powder | × | 1.90 | 0.01 | 0.33 | 0.03 |
| PE-ino6 shell powder | × | 1.93 | 0.01 | −0.62 | 0.03 |
| PE-ino1/single prism | × | 1.92 | 0.02 | 0.96 | 0.02 |
| PE-ino2/single prism | × | 1.75 | 0.01 | 0.75 | 0.01 |
| PE-ino3/single prism | × | 1.90 | 0.02 | 1.14 | 0.02 |
| PE-ino4/single prism | × | 1.76 | 0.05 | −0.04 | 0.05 |
| PE-ino5/single prism | × | 1.76 | 0.01 | 1.09 | 0.02 |
| Mean value | 1.85 | 0.39 |

| Inoceramid in red facies (different specimens) | Limestone | Marl | CaCO₃ (%) | Avg | SD | δ¹³C (%) | SD | δ¹⁸O (%) | SD |
|---|---|---|---|---|---|---|---|---|---|
| PR-INO 1/single prism | × | 1.76 | 0.01 | 0.60 | 0.01 |
| PR-INO 2/single prism | × | 1.63 | 0.02 | −0.40 | 0.02 |
| PR-INO 3/single prism | × | 1.80 | 0.01 | −0.18 | 0.01 |
| PR-Ino 3/single prism | × | 1.35 | 0.01 | 0.18 | 0.01 |
| PR-INO 3/single prism/redone | × | 1.27 | 0.01 | 0.22 | 0.01 |
| PR-Ino 4/single prism | × | 1.43 | 0.02 | 0.33 | 0.02 |
| Mean value | 1.54 | 0.12 |
red facies were generated in association with cooler temperatures, gradually becoming warmer in the grey facies.

6.1 Collected evidence

6.1.1. Lower Turonian section

This red marl event includes 11 thin grey carbonate turbidites (2–5 cm) with bleaching in the red marls both towards the top and the bottom of the calcarenite turbiditic beds (Fig. 2a–d). The preservation of the turbidite’s grey colour is accounted for by an almost instantaneous sedimentation, which prevented oxidation of its components during rapid deposition. However, the turbidites may contain enough organic matter to decompose in the oxidizing environment once deposited. The result is a limited reducing zone that solubilizes and leaches the Fe$^{3+}$ iron oxyhydroxides already present in the red marls until they are bleached, just in the area of influence of the reducing environment. The marl bleaching is more powerful in contact with the bottom than in the turbidite top. If the red colour had occurred during burial diagenesis, once sedimentation was over it would have coloured the marls the same as the carbonate turbidite beds in an ongoing homogenizing process. This bleaching effect in reddish sections due to the
presence of turbidite beds seems to be common in many European sections, and has been reported in graph form by different authors (Jansa & Hu, 2009, fig. 1D, p. 61; Wagreich et al. 2009; fig. 5C, p. 77; Skupien et al. 2009, fig. 8A, p. 108), although its significance has not been explained in depth.

6.a.2. Lower Maastricht

If we assume a constant rate of sedimentation and similar thickness for the marl–limestone couplets, the colour difference must be due to higher oxygen content in the bottom waters and, therefore, a drop in the Fe\(^{2+}/(Fe^{2+}+Fe^{3+})\) ratio. It is generally accepted that, for greenish-yellow facies, the ratio for Fe\(^{2+}/(Fe^{2+}+Fe^{3+})\) could be higher than 0.5, whereas for red facies the Fe\(^{2+}\) has almost completely altered to Fe\(^{3+}\), with a ratio of c. 0–0.3 (see Stow, 2005, p. 121).

Epibenthic fauna are affected by the oligotrophic conditions and highly oxic palaeoenvironment, suggested by the scarce presence of small, thin inoceramid shell fragments (thickness < 1 mm) compared with the large (> 20 cm) and thick (6 mm) inoceramids below in the less oxygenated grey facies (Fig. 3b, b*). This interpretation suggests that the oxidizing and cold-water conditions on the seafloor limited the development of such organisms.

On the other hand, evidence of a very early decomposition of organic matter is denoted by both mottled burrows (Fig. 3e) and Zoophycos tracings (Fig. 3f), as well as by the scant echinoid macrofossils recognized (Fig. 3g). The early decomposition causes visible bleaching in the limited red area affected. We deduce that the destruction in situ of the organic matter, from a living organism, produced a bleached spot (in the sense defined by Tyrell, 1926 and collected in the Glossary of Geology, American Geological Institute). Such a reducing microenvironment is capable of leaching ferric iron and generating hydrogen sulphide, which very occasionally produces small frambooidal pyrite crystals (FeS\(_2\)). In addition, subsequent brittle fractures in the marl–limestone couplets of the red facies are of note since reducing fluids circulate and cause bleaching unevenly within the zone of influence of the fractures (Fig. 3h); in contrast, although fracturing is present in the grey facies, it is not marked by a change in colour.

A comparison of the isotope values in the grey, greenish-yellow and red materials, as well as in the inoceramid prisms in the El Peñón section, reveal that the red and greenish-yellow materials have higher \(\delta^{18}O\) values (mean value \(\delta^{18}O = -1.90‰\)) compared with the lighter-grey materials (mean value \(\delta^{18}O = -2.25‰\)). All these values indicate that the trend of the palaeoenvironmental signal (cooler in the red facies than in the grey facies; Wang et al. 2011) continues, although modified by burial diagenesis. With respect to the values of the grey facies inoceramids, there is an opposite trend since these values are higher (mean value \(\delta^{18}O = 0.38‰\)) than those in the red facies (mean value \(\delta^{18}O = 0.12‰\)). This difference can be explained by the scant thickness (< 1 mm) of the red facies inoceramids, which have been completely affected by diagenesis; in contrast, in the grey facies inoceramids (6 mm thick), the central parts have remained less affected and the average isotope signal is therefore higher (Table 1, Fig. 7a–d).

It is worth noting that the record of the boreal inoceramid Spyridoceramus tegulatus (Hagenow, 1842), which coincides with the positive \(\delta^{18}O\) excursion, suggests the entry of deep, cold, oxygenated waters from the North Atlantic. These observations confirm the modification of the thermocline and the distribution of
oxygen content in the ocean water column and the onset of climatic cooling around the time of the early–late Maastrichtian boundary, which might have been one of the main causes of the disappearance of inoceramids in the Basque Arc Domain (Gómez-Alday et al. 2004).

6.0.3. Upper Maastrichtian

The abrupt colour change from the grey Member II to the purple Member III in the transition from the lower to the upper Maastrichtian section (Fig. 4a) is a good example of palaeoceanographic changes occurring quickly in the shift from a highstand systems tract (HST) (Member II, grey facies, biozone G. gansseri) to a lowstand systems tract (LST) (Member III, red facies, biozone A. mayaroensis) (MacLeod, 1994; Pujalte et al. 2000; Gómez-Alday et al. 2004).

Already in Member IV, on the scale of the couplet, when passing from yellowish-grey limestone to purple marl in the marl–limestone couplets, there is a clear, abrupt change (Figs 4a, b, 5a, b). The compositional similarity revealed by XRD (except for the presence of hematite) between the yellowish-grey limestone and purple marl (section UM1) and purple marly limestone and purple marl (section UM2) (Fig. 4a) suggests the same origin of the deposit and that the change in colour occurs during the sedimentation of fundamentally calcareous ooze (coccolithophorids, planktonic foraminifera and ferromagnesian clay remains such as illite and smectite) from the warm surface waters during the Cretaceous greenhouse climate. Recall that the main original components of the limestones, as observed by SEM, are coccolithophorids and detrital clays (Fig. 5d, e) and, in oxygenated and cooler waters with higher viscosity, the sedimentation rate slows down (Stokes’ Law). This is because the earth can more effectively allow the transition from Fe²⁺ to Fe³⁺. Subsequent burial diagenesis causes the coccoliths, formed of individual plates of calcium carbonate, to partially dissolve, creating micritic cement crystals that bind them together to form the mudstone–wackestones observed in the marl–limestone couplets.

In section UM2, the range of average %CaCO₃ values between the purple marl and the purple marly limestone is significantly small (10%) and sedimentation rates are high (3.6 cm ka⁻¹). These mean values do not coincide with the idea advocated for the Cretaceous ORBs as probably being characterized by a low sedimentation rate (e.g. Hu et al. 2012). These marked differences between compositional contrast and average sedimentation rate likely reflect a change from more drastic palaeoenvironmental conditions (rainy versus longer dry periods) to a predominance of wet rainy periods, with increased terrigenous material input and less seasonality (Einsle, 1982; Arthur et al. 1984; Einsle et al. 1991; MacLeod et al. 2001; Giorgioni et al. 2012; Jiménez Berrocoso et al. 2013).

The purple colour, without reaching red tones, can be well accounted for by: (1) a higher sedimentation rate that does not allow a complete oxidation to red tones during settling to the bottom, despite a high oxygen content of the water mass; or (2) on the contrary, the presence of less oxygenated and more temperate waters, unable to completely oxidize the Fe²⁺ during sedimentation, resulting in purple marl–limestone couplets with Fe²⁺/(Fe²⁺+Fe³⁺) values of 0.3–0.5 (Stow, 2005).

6.0.4. Danian section

The palaeogeographic reconstruction of the western Pyrenean area during the Maastrichtian–Paleocene and stratigraphic profiles made by certain authors (Pujalte et al. 2000; B acet a et al. 2004) confirmed substantial colour differences in materials of the same age but from different environments. During the Danian Age, the shallow limestones that formed on a carbonate platform setting (Lizarra section, Navarra) and the breccias and turbidites that formed on a carbonate slope-apron (section of Atxola, Eruma, Gipuzkoa) are therefore all greyish-white. In contrast, the limestones and hemipelagic marls corresponding to a deep-marine basin setting (Zumaya section, lateral equivalent to the Sopelana section) have the characteristic pink colours (Fig. 1c). This suggests that the triggering factor for pink colouring is likely in the palaeoenvironmental conditions that dominate the basin bottom (cold, oxygenated waters), which do not occur in shallower environments of the same age (carbonate platform and slope-apron), despite having also undergone appreciable diagenetic compaction and recrystallization.

Other evidence on the partial preservation of the palaeoenvironmental signal in the marl–limestone couplets of the Sopelana sections is confirmed by examining the isotopic oxygen values of the lower Maastrichtian and Danian couplets obtained by Jiménez Berrocoso et al. (2013). The lower Maastrichtian grey marls have a mean value of δ¹⁸O = −3.15‰ (n = 27) versus limestones δ¹⁸O = −3.46‰ (n = 42), whereas the Danian pink marls have an average value of δ¹⁸O = −1.97‰ (n = 22) and the pink limestones an average of δ¹⁸O = −2.27‰ (n = 28). These results support the authors’ suggestion that, at the level of Milankovitch precession cycles, during the deposition of marls, temperatures were lower (a rainier, colder climate), with a higher detrital contribution from the continent, and with an increase in temperature during the deposition of the calcareous ooze (warmer and drier climate). In turn, the δ¹⁸O average values of the Danian pink marls and limestones are higher (cooler) than in the lower Maastrichtian grey limestones and marls (warmer).

In the Danian section, at the subcouplet scale, it is even detectable how a white limestone bed at the base changes to pink limestone in the middle of the bed, with a clear separation parallel to planar stratification, to continue with a pink marl (Fig. 6a–c, e). Further, a yellowish-grey marl at the base becomes pink towards the top bed and continues with a pink limestone subcouplet, in the image partially covered due to humidity by current green algae (Fig. 6c, e). Strong bioturbation (Planolites) recorded in the lower Maastrichtian grey marls and the Danish pink marls also provides an insight into their different settings. In the grey marls, fossil traces remain darker than sediment (Fig. 6f), proof that the environment did not have enough oxidative capacity to break down the organic matter provided by the organism; in contrast, in the pink marls the fossil traces are bleached (Fig. 6g) by substantial organic matter oxidation.

6.0.5. Burial diagenesis and partial preservation of the palaeoenvironmental signal

In thick Cretaceous and Paleocene sedimentary series, such as those produced in the Basque–Cantabrian Basin, there is no doubt that early and burial diagenesis occurred with different degrees of intensity, according to the height of the selected column as well as its location with respect to the depocentre or the lateral zones of the basin (Arostegui et al. 1991, 2006; Ortega-Huertas et al. 1995; Sangüesa et al. 2000). Published works on the diagenetic activity in the marl–limestone grey couplets of the lower Maastrichtian section demonstrate their effects by variations in luminescence and isotopic changes that are determined both in thick-shelled epi-benthic inoceramid organisms as well as in the grey marl–limestone couplets themselves. Illite is the most abundant clay mineral (< 2 μm), reaching a mean value of about 58%, followed
The illite–smectite (I-S) mixed layers (R1, 17% illite) and δ¹⁸O (−2.89‰ PDB) also indicate diagenetic alteration (Fig.9a, b) (Gómez-Alday et al. 2008). These same trends of diagenetic alteration in inoceramids and deep-marine sediments are also detected in grey materials from the Coniacian–Santonian sections of the Basque–Cantabrian Basin.

The transformations of the clay minerals have been recognized with more diagenetically advanced illite–smectite (I-S) mixed layers (R1, 70% illite), authigenic chlorite and low δ¹⁸O (−4.05‰ PDB) in the Barrika section (deep-marine basin) versus the platform-marine (Isla de Castro, Villamartín and Olazagutía) settings (Fig.1a, c). All these transformations are good indicators of the diagenetic activity undergone by these sediments, which reached burial depths of up to 6–9 km (Jiménez Berrocoso et al. 2004, 2008).

However, despite having undergone greater or lesser degrees of diagenetic alteration, the palaeoenvironmental signal can still be detected, preserved in inoceramid shells under CL (Fig.7a–d), oxygen isotopes, mean ⁸⁷Sr/⁸⁶Sr isotope ratios (0.707819 ± 0.000003 (2σ, n = 8) and also in the sediments, although in more attenuated form, in very favourable conditions (Gómez-Alday et al. 2004, 2008). The vertical distribution and variability of the clay minerals (≤2 μm) observed is therefore not likely to be the exclusive product of their diagenetic transformation; at 25–40 m, the sediment thickness is not enough to record notable changes in diagenetic gradients between the bottom and the top of the recognized
stratigraphic sections. Instead, tectonosedimentary causes related to unsuitable conditions for clay formation and transport from the local source areas contributed to the original clay differences (Jiménez Berrocoso et al. 2008). Finally, Jiménez Berrocoso et al. (2013) considered that the fine-scale (2 cm per sample) geochemical and sedimentological (%CaCO₃, δ¹⁸O and δ¹³C) records of calcareous couplets challenge purely diagenetic explanations. The lower Maastrichtian transition to a transgressive system tract therefore favoured a greater influence of oceanic processes in the depositional setting, whereas a relatively cool, oxygen-rich water mass with high oxidation potential influenced the geochemical and depositional patterns of Danian couplets. In other words, the geochemical and sedimentological patterns of these calcareous couplets were caused by the interplay of climate, palaeogeography and oceanography as forcing mechanisms.

6.c. End-Cretaceous North Atlantic Ocean circulation

To explain the cooling detected by the oxygen isotope signal during the early Maastrichtian Age and the presence of the boreal inoceramid SpriRoiceramus tegulatus, Gómez-Alday et al. (2004) suggest that there is a change in the type of thermohaline circulation due to the entry of deep, cold waters from high latitudes that results in greater temperature stratification in the oceans. Apparently, the origin of these deep, cold waters varied throughout the Maastrichtian Age. Up to the lower–upper Maastrichtian boundary, the ocean floor was occupied by saline and warm oxygen-poor waters with an origin in the vast epicontinental seas of the globe. During this boundary period, deep, cold and dense waters formed in the polar regions and reached low latitudes to form the intermediate and deep waters of the tropics (Saltzman et al. 1982; Barron et al. 1984; MacLeod et al. 2011; Huber et al. 2018). Further, Gambacorta et al. (2016) defend the same idea: “...although the paleotemperature reconstructions are still loose, reddish lithologies corresponding to times of relatively cooler conditions might indicate a mechanism of deep water formation different from saline waters at low-latitude characteristic of warm climatic conditions. Possibly, during times of decreasing temperature after warming episodes, cooler oxygen richer bottom water masses originated at higher latitudes.”

6.d. Iron source and distribution of Fe³⁺ in the sediment

Riverine, atmospheric, iceberg, hydrothermal and diagenetic recycling are thought to be the main iron (Fe) sources in oceans (Raiswell & Canfield. 2012). Iron in the environment exists in riverine, atmospheric, iceberg, hydrothermal and diagenetic recrystallization instead of forming iron (oxyhydroxide) precipitates. Organic ligands can also stabilize Fe²⁺ through enzymatic activity, bacteria can catalyse redox reactions. In the oceans, dissolved Fe²⁺ can be released in the intercrystalline areas with a higher concentration, the elemental maps (Ca, Fe, Mg) were examined using an energy-dispersive X-ray spectroscopic instrument on three thin-sections belonging to the Danian pink and white (Dan-p; Dan-w) and Maastrichtian lower grey (Maast-g); the examination reveals that Ca is the dominant element in the foraminifer sections and in the spartic cement that fills the chambers. The other elements (Fe, Mg) are arranged in the intercrystalline areas with a higher concentration, indicative of the presence of ferromagnesian clays (illite-smectite-chlorite) in both the grey-white and pink lithologies. There are areas where Fe predominates and can be interpreted as belonging to oxyhydroxides (later hematite in Dan-p); or (later pyrite in Dan-w/Maast-g) although, because of the size of the possible crystals (< 10 nm) found by Cai et al. (2012) in Vispi Quarry limestones, the resolution of our image does not allow us to directly observe the crystals (Fig. 8).

Bacterial activity was certainly a factor in the development of the pink colour of the Danian couplets (Fig. 9e–h); however, in the absence of more precise studies, it cannot be considered the primary cause of the red colouring in the case of the Basque–Cantabrian Basin, even though other authors consider iron-oxidizing bacteria to be the main cause of such tones in their studies on other areas (Mamet et al. 1997; Della Porta et al. 2003; Mamet & Prétat, 2005, 2006; Prétat et al. 2006, 2018; Van der Kooij et al. 2007; Song et al. 2017). Nanobacteria with coalescent structure forms (< 0.1 μm) thrive in the superficial part of the coccolith plates and ferromagnesian clays, with a strong similarity to those reported by Mamet & Prétat (2006, fig. 1A), Prétat et al. (2006, fig. 8C–F).
As a result of the points discussed above, we discard the notion that reddish-pink to greenish-yellow tones are the main product of early diagenesis, as claimed by other authors (Eren & Kadir, 1999; Hu et al. 2005, 2012; Jansa & Hu, 2009) in the Cretaceous ORBs of the Tethysian and North Atlantic basins. We are in favour of a syn-sedimentary process, where the deposition of the calcareous ooze involved mainly coccolithophorids, planktonic foraminifers and ferromagnesian clays derived from the oceanic surface and continental sources, and was sedimented towards the sea bottom through cold, oxygenated waters. These waters are not only available at different heights of the water column, but can reach the sea bottom and remain for long enough for oxidation to occur (MacLeod et al. 2011). The coating of the calcareous particles by oxyhydroxides during the slow sedimentation was conditioned by a lower temperature of the oxidizing waters and the availability of Fe$^{2+}$. The different red, pink and greenish-yellow colours may be determined by the sedimentation rate and/or oxidation capacity of the water mass. The red colour in the marl–limestone couplets was already present before the organic decomposition of echinoids, and the trace markers of ichnofossils such as Planolites and Zoophycos, was able to generate a reducing zone, with centimetric extension and bleaching of both the limestones and the marls (Fig. 3e–g). Even the presence of grey carbonate turbidites included in red marls indicates that the process is of synsedimentary origin and did not occur during burial diagenesis (Fig. 2b, c).

We have attempted a simplified model with the differentiated vertical marine stages represented schematically (Fig. 10), as well as possible variations in temperature and oxidation capacity of the water mass, which allows us to distinguish at least five types of couples according to their variable colouring (Table 3).

6.e. First possibility during sedimentation (stages (a) and (b))

Particles settling until reaching the basin bottom pass through different stages. (a) This stage ranges from the marine surface, where lesser or greater organic seasonal productivity occurs, to the oxygen minimum zone (OMZ), with a part of the organic matter still preserved. A greater or lesser contribution of clastic materials determines the subsequent formation of marls or limestones controlled by processional cycles (Fig. 10). (b) In the transit through the OMZ, with sufficient thickness and an appreciable lack of oxygen and light, partial decomposition of organic matter from protozoans (foraminifers, radiolarians) and algae (coccolithophores) is triggered, and Fe$^{2+}$ is consequently liberated in this reducing zone. Settling continues until the basin bottom, where the residual organic matter is associated with calcareous ooze in a dysoxic environment, but always above the carbonate compensation depth (CCD). The presence of Fe$^{2+}$ as pyrite (FeS$_2$) precipitation and ferromagnesian clays can be recognized inside microforaminifer chambers (Figs 7e, 8).

As a result, substantial grey sediment formation is arranged in the marl–limestone couplets, governed by orbital precession variations (c. 20 ka), consisting mainly of a calcareous ooze component and a larger (marls) or smaller (marly limestone to limestones) concentration of inherited clays (illite–smectite, kaolinite) undergoing alteration with the liberation of cations. The presence of epibenthic organisms such as large inoceramids and ichnofossils such as Planolites and Zoophycos in both the limestones and marls is remarkable. Subsequently, burial diagenesis generated neomicrite (< 1 μm) that successively underwent recrystallization to larger particles such as micrite (< 4 μm) and microsparite (> 4 μm), and the neoformation of illite–smectite (I-S) mixed layers, chlorite and illite aggregates.
produced the compaction–recrystallization and consequent differentiation of the couplets according to their content in clays and carbonates (Figs 3a, 4a).

6.f. Second possibility during sedimentation (stages (a–c))

Recall that it is accepted in the literature that Cretaceous ORBs were deposited in oligotrophic conditions of cold, oxygenated waters with a low sedimentation rate (Hu et al. 2012). In accordance with the evidence presented above, it is therefore also possible that in our basin a mass of denser-than-usual cold, oxygenated waters were incorporated from the North Atlantic Sea, possibly comprising tongues advancing and retrograding on the basin bottom at temporary intervals as short-term ORBs (<1 Ma). Stages (a) and (b) have the same characteristics as those described in Section 6.e above (first possibility), but stage (b) does not reach the sediment–water interface because the transitory arrival of colder, oxygenated water would lead to important changes in the biogeochemical cycles by modifying the extent of the OMZ. (c) The slower settling of ferromagnesian particles (Fig. 9a) and their passage through the mass of cold, well-oxygenated water allows the Fe$^{3+}$ to Fe$^{2+}$ to be transformed into oxyhydroxides. These can occur on the surface and interior of particles (detrital/shells) as a fine film (Tucker, 1994), and are deposited on the sediment–water interface as pigmented calcareous ooze.

The sediment has different colours (red, pink, greenish-yellow) depending on its settling speed and the oxygen content, and therefore the Fe$^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio, of the water. It is even possible to determine the appearance of the tongues of cold, oxygenated waters during the initial formation of a white-grey limestone subcouplet that ends up as a pink limestone, with the same morphological characteristics and with a slight increase in the %CaCO$_3$ contents (Fig. 6c, e).

6.g. Soft, unconsolidated sediments (stage (d))

(d) The calcareous ooze is already pigmented at the water–sediment interface, and a significant number of epibenthic organisms are recorded, such as small, thin inoceramids, echinoids and trace fossils such as Zoophycos and Planolites. The rapid post-mortem decomposition of organic matter generated a limited reducing environment around these remains, recognizable by bleaching due to the leaching of Fe$^{3+}$ (Fig. 3e–g). It is possible to differentiate between the soft unconsolidated sediments and the next phase of still unconsolidated sediments until very early diagenesis began.

6.h. Very early diagenesis and burial diagenesis (stage (e))

(e) Partial or complete dissolution of the calcareous ooze allowed neomicroite formation (<1 μm) that successively underwent recrystallization to larger particles such as micrite (<4 μm) and microsparite (>4 μm). Under normal microscopy, it seems that ferromagnesian clays and iron oxides (hematite) are not substantially incorporated and do not form part of the neoformed matrix crystals (micrite–microsparite) and that, in the foraminifer chambers, these minerals surround the new sparite cement without incorporating it (Fig. 7g, h). The Fe$^{3+}$ now forming nanocrystals of hematite seems to have been distributed in the matrix, but it does not become part of the sparry calcite in the filling of the foraminifer chambers. This interpretation suggests that the pigmented calcareous ooze pre-dates diagenesis as a dominant depositional feature (Fig. 8). As a result, the marl–limestone coloured couplets (red, pink, greenish-yellow) form according to the Fe$^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio.

6.i. Late diagenesis

This stage is evidenced by limited and irregular fracturing of the already consolidated rock with slight displacement that allows the circulation of reducing fluids and the consequent dissolution of Fe$^{3+}$ recognized by the bleaching in the red facies (Fig. 3b). In the greenish-yellow layers, the bleaching is more muted and barely perceptible, but it also occurs in the El Peñón section. Another late-diagenesis characteristic of the Danian limestone subcouplets is the presence of numerous small, sutured and

| Case no. | Water mass conditions and causes | Marl–limestone couplet |
|---------|---------------------------------|------------------------|
| 1       | Water mass with high oxidation capacity and sufficient thickness:  
• conditioned by the settling velocity, sedimentation rate and content in ferromagnesian clay in each subcouplet;  
• the temperature of the waters is always colder than in grey facies. | Pink marls, pink limestones, red marls, red limestones |
| 2       | Water mass with sufficient oxidation capacity, but without achieving complete material oxidation:  
• high sedimentation rate; depletion capacity of water oxidation with a thickness similar to case 1;  
• smaller water mass thickness does not give time for complete oxidation due to the high sedimentation rate in marl–limestone couplets;  
• slight warming of temperature and a higher settling velocity do not allow complete oxidation in the water masses. | Purple marls, purple limestones |
| 3       | Water mass with limited oxidation capacity, without achieving complete oxidation:  
• low quantity of detritic clays bearing Fe during settling and formation of limestone subcouplet;  
• higher settling velocity of the carbonate particles of the limestone subcouplet compared with the majority clays of the marl subcouplet;  
• independent of the temperature and thickness of the water masses. | Purple marls, yellowish-grey limestones |
| 4       | Rapid change in the oxidation capacity of the water mass towards more oxidizing and cold waters:  
• the thickness of the water masses can grow and enhance the oxygenation capacity; with this trend, the settling velocity decreases and the sedimentation rate has no decisive influence. | Modification from grey couplets to greenish-yellow to red couplets |
| 5       | No oxidation capacity of the water mass:  
• settling velocity and sedimentation rate similar, with greater temperature of the water masses. | Grey marls, grey limestones |
irregular stylolites perpendicular to the stratification surface. These are caused by a pressure–dissolution effect and are recognized at first sight by the concentration of insoluble material that highlights the suture (Fig. 6h). Analysing this concentrated residue by XRD confirms the presence of ferromagnesian micas, quartz, plagioclase and small amounts of hematite.

7. Conclusions

The ORBs present in Upper Cretaceous and Danian sections in the Basque–Cantabrian Basin are exceptional due to the presence and regularity of their marl–limestone couplets, together with the macroscopic, microscopic and geochemical evidence collected. Five types of marl–limestone couplets can be differentiated according to the exposed colouring: (1) pink-red marl versus pink-red limestone; (2) purple marl versus purple limestone; (3) greyish-yellow limestone versus purple marl; (4) steps from grey to greenish-yellow to red marl–limestone couplets; and (5) grey marl versus grey limestone. The sedimentation rate is variable, but in contrast to what is published on Cretaceous ORBs, it can be high (3.6 cm ka⁻¹) in the coloured couplets. The oxygen isotopic signal in the lower–upper Maastrichtian and Danian sections and the presence of the boreal inoceramid Sprydioceras tegulatus serve to confirm the presence of deep, cold, oxygenated waters surely coming from high latitudes (North Atlantic). The variation in colours is interpreted as the possible palaeoenvironmental transit of the particles, mainly calcareous nanoplanクトon such as coccolith plates, planktonic foraminifers and detrital clays, which settle slowly in dysoxic environments forming grey marl–limestone couplets. However, as they circulate through a cooler and more oxidizing water body, they change to greenish-yellow, purple and pink until finally reaching red tones based on the Fe²⁺/(Fe²⁺+Fe³⁺) ratio. Hematite, considered the main staining agent, was detected by XRD together with the ferromagnesian clays. The colouring is considered a depositionnal factor, without discarding the possible redistribution of oxyhydroxides changing to hematite as a final product. Given the nanometric size of the hematite particles, they are difficult to detect by SEM–EDX. The shell and chamber filling of the foraminifers do not incorporate appreciable amounts of Fe and Mg during diagenesis. In the intercrystalline sparry cement, ferromagnesian clays are distributed as detected by the Ca, Fe and Mg maps. Fe in grey facies is present as Fe⁺⁺ (pyrite). Nanobacterial activity is also detected, present both in the coccolith plates and in the ferromagnesian micas, without it being possible to establish its importance in the staining process.

Acknowledgements. JE is supported by the Universidad del País Vasco/Euskal Herriko Unibertsitatea, Spain (UPV/EHU, research group GIU18/16317/05) and by the Elorza Foundation. We thank Dr Ana Pascual (UPV/EHU) for the micropalaeontological determination. We thank the anonymous referees for their comments, which have significantly enriched the contents of the manuscript. We are also grateful to Christine Laurin and Rupert Glasgow for improving the English.

References

Ahmed MJ, Tamar-Agha MY and Alwan TA (2017) Geochemistry and depositional conditions of the Cretaceous oceanic red beds (CORBs) within the Shuransish Formation in North of Iraq. Iraqui Journal of Science 58, 2139–64.
Allison LE and Moodie CD (1965) Carbonate: volumetric calciometer method. In Methods of Soil Analysis. Part 2. Chemical and Microbiological Methods (ed CA Black), pp. 1389. Madison, WI: American Society of Agronomy.
Alonso de Linaje V, Fernández-Lerín B, Apodaca J, Biain A, Jaca E, Hernández-Martín S and Elorza J (2009) Turbiditas carbonatadas en la Playa de Muriola (Barrika, Arco Vasco): edad, deformación, contenidos de CaCO₃, y presencia de barita diagenética. Geogaceta 47, 69–72.
Álvarez Llano J, Baguer A, Martínez López de Sabando M, Múgica J, Pérez-García JR, Urnauie L and Elorza J (2006) Variedades de espesor y de contenido en CaCO₃ en los pares marga-caliza del Maastrichtiense inferior en Sopelana (Arco Vasco). Geogaceta 39, 131–4.
Arenillas J, Arz JA and Molina E (1998) El límite Cretácico-Terciario en Zumaya, Osinaga y Múzquiz (Pirineos); control biostratigráfico y cuantitativo de hiatos con foraminíferos planctónicos. Revista de la Sociedad Geológica de España 11, 127–38.
Arostegui J, Ságiüesa FJ, Nieto F and Uriarte JA (2006) Thermal models and clay diagenesis in the Tertiary–Cretaceous sediments of the Alava block (Basque-Cantabrian basin, Spain). Clay Minerals 41, 791–809.
Arostegui J, Zuluaga MC, Velasco F, Ortega-Huertas M and Nieto F (1991) Diagenesis of the Central Basque–Cantabrian basin (Iberian Peninsula) based on illite-smectite distribution. Clay Mineralogy 26, 535–48.
Arthur MA, Brumsack H-J, Jenkyns HC and Schlanger SO (1990) Stratigraphy, geochemistry, and paleoceanography of organic carbon rich Cretaceous sequences. In Cretaceous Resources Events and Rhythms (eds R Ginsburg and B Beudoin), pp. 75–119. Netherlands: Kluwer Academic Press.
Arthur MA, Dean WE, Bottjer DJ and Sholle PA (1984) Rhythmic bedding in Mesozoic–Cenozoic pelagic carbonate sequences: the primary and diagenetic origin of Milankovitch-like cycles. In Milankovitch and Climate Part I (eds A Berger, J Imbrie, J Hays, G Kukla and B Saltzman), pp. 191–222. Dordrecht: Riedel.
Baceta J, Pujaltte V, Serra-Kiel J, Rogador A and Orue-Etxebarria X (2004) El Maastrichtiense final, Paleoceno e tierno inferior de la Cordillera Pirenáica. In Geología de España (ed JA Vera), pp. 308–13. Madrid: SGE-IGME.
Barron EJ, Saltzman E and Price DA (1984) Occurrence of Inoceramus in the South Atlantic and oxygen isotopic paleotemperatures in Hole 530A. In Initial Reports of the Deep Sea Drilling Project, no. 75 (eds WJ Hay and J-C Sibuet), pp. 893–904. Washington: US Government Printing Office.
Beil S, Kuhnt W, Holbourn A, Scholz F, Ozmann J, Wallmann K, Lorenzen J, Aquit M and Chellai E (2015) Cretaceous oceanic anoxic events prolonged by phosphorus cycle feedbacks. Climate of the Past, published online 8 October 2015, https://doi.org/10.5194/cp-2015-118.
Breitbarth E, Achterberger ET, Ardalan MV, Baker AR, Bucciarelli E, Chever F, Croot PL, Duggan S, Gledhill M, Hasselmov H, Hoffmann LJ, Hunter KA, Huthins DA, Ingril J, Jickells T, Lohanc MC, Nielsdottir MC, Sarthou G, Schoemann V, Trapp JM, Turner DR and Ye E (2010) Iron biogeochemistry across marine systems-progress from the past decade. Biogeosciences 7, 1073–97.
Cai Y, Hu X, Li X and Pan Y (2012) Origin of the red colour in a red limestone from the Vispi Quarry section (central Italy): a high-resolution transmission electron microscopy analysis. Cretaceous Research 38, 97–102.
Cai Y, Li X, Hu X, Chen X and Pan Y (2009) Paleoclimatic approach to the origin of the coloring of Turonian pelagic limestones from the Vispi Quarry section (Cretaceous, Italy). Cretaceous Research 30, 1205–16.
Chen X, Wang CS, Hu X, Huang Y, Wang P, Jansa L and Zeng X (2007) Global correlation of Cretaceous oceanic red beds. Acta Geologica Sinica (English Edition) 81, 1070–86.
De Baar HJW and De Jong J (2001) The biogeochemistry of iron in seawater. In Distributions, sources and sinks of iron in seawater (eds D Turner and K Hunter), pp. 123–253. Chichester, UK: John Wiley & Sons Ltd. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems no. 7.
Della Porta G, Mamet B and Préat A (1980) The biogeochemistry of iron in sea-water. In Distributions, sources and sinks of iron in seawater (eds D Turner and K Hunter), pp. 123–253. Chichester, UK: John Wiley & Sons Ltd. IUPAC Series on Analytical and Physical Chemistry of Environmental Systems no. 7.
Dickson JAD (1965) A modified staining technique for carbonates in thin section. Nature 205, 587.
Dinárez-Turrell J, Pujaltte V, Staykova K and Elorza J (2013) Detailed correlation and astronomical forcing within the Upper Maastrichtian succession in the Basque Basin. Boletín Geológico y Minero 124, 253–82.
Dominguez E, Echeverria J, Gómez-Urtausin I, Ibisate R, Martínez-García B and Elorza J (2007) Espesaros y contenido en CaCO₃ en los pares margala-caliza del Danianse (Sopelana, Arco Vasco). Geocatetita 41, 67–70.

Einsiede G (1982) Limestone-marl cycles (periodites): diagnosis, significance, causes—a review. In Cyclic and Event Stratification (eds G Einsiede and A Seilacher), pp. 8–53. New York: Springer-Verlag.

Einsiede, G. Ricken W and Seilacher A (1991) Cycles and Events in Stratigraphy. New York: Springer-Verlag, 955 p.

Elorza J and Bustillo MA (1989) Early and late diagenetic chert in carbonate turbidites of the Senonian flysch, N.E. Bilbao. Spain. In Silicicose Deposits of the Tethys and Pacific Regions (eds JR Heijn and J Obdromic), pp. 93–105. New York: Springer-Verlag.

Elorza J, Orue-Itururain X and Lamolda MA (1984) Existencia de una fracturación intensa en el área de Sopelana–Meriacaz (N.E. Bilbao). In Actas I Congreso Español de Geología, vol III; pp. 177–84. Madrid: SGE-IGME.

Eren M and Kadir S (1999) Colour origin of upper cretaceous pelagic red sediments within the Eastern Pontides, northeastern Turkey. International Journal Earth Sciences 88, 593–5.

Floquet M (2004) El Cretácico Superior de la Cuenca Vasco Cantábrica y áreas adyacentes. In Geologia de España (ed JA Vera), pp. 299–306. Madrid: SGE-IGME.

Fugger E and Kastner C (1885) Natürwissenschaftliche Studien und Beobachtungen aus und über Salzburg. Die Steirbrüche von Bergheim und Muntthgl. Salzburg: Hermann Kerber-Verlag, pp. 62–82.

Gambacorta G, Bersezio R, Weissert H and Erba E (2016) Onset and demise of Cretaceous oceanic anoxic events: the coupling of surface and bottom oceanic processes in two pelagic basins of the western Tethys. Paleoceanography 31, 732–57.

Gibbons W and Moreno MT (eds) (2002) The Geology of Spain. Geological Society of London, 649 P.

Giojorni M, Weissert W, Bernasconi SM, Hochuli PA, Cocción R and Sella E (2003) Orbital control on carbon cycle and oceanography in the mid-Cretaceous greenhouse. Paleoceanography 27, PA1204, https://doi.org/10.1029/2001PA0002163.

Gledhill M and Buck KN (2012) The organic complexion of iron in the marine environment: a review. Frontiers in Microbiology 3, 1–17.

Gómez-Alay J, López G and Elorza J (2004) Evidence of climatic cooling at the early/late Maastrichtian boundary from inoceramid distribution and isotopes: Sopelana sections, Basque Country, Spain. Cretaceous Research 25, 649–68.

Gómez-Alay J, Zuluaga MC and Elorza J (2008) ⁸⁷Sr/⁸⁶Sr ratios in inoceramids (Bivalvia) and carbonate matrix as indicators of differential diagenesis during burial. Early Maastrichtian Bay of Biscay sections (Spain and France). Potencial use for chemostatigraphy? Cretaceous Research 29, 563–76.

Heller MI, Lam PJ, Moffett JW, Till CP, Lee J-M, Toner BM and Marcus MA (2013) Proximate environ- tectono-sedimentary influences on clay mineralogy and stable iso- topes from Upper Cretaceous marine successions of the Basque-Cantabrian Basin (N Spain). Cretaceous Research 39, 386–404.

MacLeod KG (1994) Extinction of inoceramid bivalves in Maastrichtian strata of the Bay of Biscay region of France and Spain. Journal of Paleontology 68, 1048–66.

MacLeod KG, Huber BT, Pletsch T, Röhl U and Kucera M (2001) Maastrichtian foraminiferal and paleoceanography changes on Milankovitch timescales. Paleoceanography 16, 133–54.

MacLeod KG, Isaza Londoño C, Martin EE, Jiménez Berrocoso A and Basak C (2011) Changes in the North Atlantic circulation at the end of the Cretaceous greenhouse. Nature Geoscience 4, 779–82.

MacLeod KG and Ward PD (1990) Extinction pattern of Inoceramus (Bivalvia) based on shell fragment biostratigraphy. In Global Catastrophes in Earth History (eds VL Sharpton and PD Ward), pp. 509–518. Geological Society of America, Special Paper no. 247.

Mamet B and Prétat A (2005) Why is “red marble” red? Revista Española Micropaleontología 37, 13–21.

Mamet B and Prétat A (2006) Iron-bacterial mediation in Phanerozoic red lime- stones: state of the art. Sedimentary Geology 185, 147–57.

Mamet B, Prétat A and De Ridder Ch (1997) Bacterial origin of the red pig- mentation in the Devonian Silvenec Limestone, Czech Republic. Facies 36, 173–88.

Martin Chivelet J, Berástegui X, Rosales I, Vilas L, Vera JA, Casas E, Gráfe K-U, Mas R, Puig C, Segura M, Robles S, Floquet M, Quesada S, Ruiz-Ortiz PA, Fregenal-Martínez MA, Salas R, Arias C, García A, Martín Algara A, Méndez MN, Chacón B, Molina JM, Sanz JL, Castro JM, García-Hernández M, Carenas B, García-Hidalgo J, Gil J and Ortega F (2002) Cretaceous. In The Geology of Spain (eds W Gibbons and MT Moreno), pp. 255–292. Geological Society of London.

Mathey B (1882) El Cretácico Superior del Arco Vasco. In El Cretácico de España (ed A García), pp. 111–135. Madrid: Universidad Complutense de Madrid.

Mathey B (1887) Les floches Cretacé supérieur des Pyrénées Basques. Age, anat- omie, origine du matériel, milieu de dépôt et relations avec l’ouverture du Golfe Gascogne. Dijon: Université de Dijon, Mémoires Géologiques de l’Université de Dijon no. 12, 403 p.

Najarro M, Rosales I, Moreno-Bedmar JA, de Gea GA, Barrón E, Company M and Delanyo G (2011) High-resolution chemo- and biostatigraphic records of the Early Aptian oceanic anoxic event in Cantabria (N Spain):...
