Regional palaeoenvironmental influence on organic matter sequestration and characteristics of carbon isotope segment C5 in a hemipelagic sequence, Organyà Basin, northeast Spain

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Abstract
The Cretaceous marine sedimentary record is punctuated by episodes of unusually high rates of organic carbon burial termed oceanic anoxic events. The El Pujal Section archives the response to perturbations of the global carbon cycle associated with Oceanic Anoxic Event 1a in a hemipelagic setting of the Organyà Basin. Here, the aim is to understand the lithological and geochemical responses to changing palaeoenvironmental conditions associated with carbon isotope segment C5 of Oceanic Anoxic Event 1a. A multi-proxy approach is applied to characterize how regional factors influenced the accumulation of organic-rich sediments during this period of severe oceanic oxygen deficiency. Source specific biomarkers demonstrate that the bulk organic matter derives from in-situ production, with lesser inputs from allochthonous sources. High-resolution stable carbon isotope data ($\delta^{13}$C$_{org}$) were used to establish the refined details of segment C5. Pulses of fluvial fluxes associated with climate fluctuations supplied variable quantities of terrestrial organic matter with more negative isotopic values, which left their intrinsic signature superimposed on the global $\delta^{13}$C$_{org}$ signal of segment C5 as minor negative spikes. Primary production sustained by fluvial inputs of biolimiting elements provided abundant labile organic matter conducive to oxygen-deprived conditions as attested by concomitant peaks in total organic carbon, relatively lower benthic faunal counts, lower bioturbation index, higher concentration of pyrite and enrichments in redox sensitive trace elements. However, organic matter preservation was not chiefly controlled by redox conditions as physical encapsulation by clay minerals probably played a significant role. In addition, coincident inputs of terrestrial organic matter with more inert properties and prone to be bound to clay minerals supplemented the accumulation of organic matter, especially during intervals of enhanced terrigenous fluxes. The combined results underscore how despite sharing common global forcing factors, regional palaeoenvironmental conditions are more important in determining the sedimentary expression of Oceanic Anoxic Event 1a.

KEYWORDS
Cretaceous, lipid biomarkers, OAE 1a, oceanic anoxic events, Perylene
1 | INTRODUCTION

The Cretaceous marine sedimentary record is punctuated by brief episodes of severe oxygen depletion in bottom waters termed Oceanic Anoxic Events (OAEs; Schlanger and Jenkyns, 1976; Jenkyns, 1980; Leckie et al., 2002). These short-lived episodes lasting ca 1 Ma (Li et al., 2008) are characterized by sediments with an unusually high content of organic carbon and distinct positive and negative shifts in the stable carbon isotope ($\delta^{13}C$) record of marine sediments on a global scale (Scholle and Arthur, 1980; Menegatti et al., 1998; Leckie et al., 2002; Herrle et al., 2004). The effects of these perturbations on the global carbon reservoir are expressed by synchronous isotopic shifts which manifest in the stable carbon isotope ($\delta^{13}C_{org}$) of organic carbon and distinct positive and negative shifts in the stable carbon isotope ($\delta^{13}C_{org}$) of both marine (Menegatti et al., 2014; Graziano and Raspini, 2018) and organic mat environments (OM) (δ13Corg) from both marine (Menegatti et al., 1998; Dumitrescu and Brassell, 2006; Millán et al., 2009; Gaona-Narvaez et al., 2013a; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2016) and terrestrial sources (Gröcke et al., 1999; Ando et al., 2002). Thus, the consistency and reproducibility of the carbon isotope shifts in widely distributed locations during OAE 1a provide a robust chronostratigraphic tool for stratigraphic correlation (Scholle and Arthur, 1980; Weissert and Bréhéret, 1991; Menegatti et al., 1998; Herrle et al., 2004). Nonetheless, noticeable lithologic and isotopic variations develop regionally and locally as specific responses related to basin physiography, atmospheric and basinal circulation patterns, water chemistry, ecosystem structure and dynamics, as well as the amount and type of terrestrial fluxes (Moullade et al., 1998; Grötsch et al., 1998; Danelian et al., 2004; Immenhauser et al., 2005; Chaabani and Razgallah, 2006; Heldt et al., 2010; Huck et al., 2010; Sanchez-Hernandez and Maurrasse, 2016).

The Organyà Basin located in the Iberian Peninsula (Figure 1A,B) developed as a semi-enclosed basin during the Early Cretaceous, and previous studies document extensive successions of continuous hemipelagic marls and limestones (Berástegui et al., 1990; Bachmann and Willems, 1996; Bernaus et al., 2000, 2002, 2003; García-Senz, 2002; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Llaguno, 2017; Socorro and Maurrasse, 2019). This study further extends analysis of the Early Aptian related to OAE 1a at the El Pujal section (Figure 1C,D; Socorro and Maurrasse, 2019) and aims at understanding the lithological and geochemical responses to changing palaeoenvironmental conditions associated with carbon isotope segment C5. A multi-proxy methodology is applied to better characterize the local factors that resulted in the accumulation of organic-rich sediments during this period known for widespread severe oxygen deficient conditions. The results provide additional insight on the effects of regional factors during intervals of enhanced OM sequestration, and how the input of terrestrial vegetation linked with lower values of $\delta^{13}C_{org}$ may have altered the global $\delta^{13}C_{org}$ archive in the Organyà Basin. The expanded section generated a detailed $\delta^{13}C_{org}$ curve providing an amplified record suitable for more precise chronostratigraphic correlations.

2 | GEOLOGICAL FRAMEWORK

From the Late Jurassic to the Early Cretaceous the gradual opening of the North Atlantic Ocean led to the separation of the Iberian Plate from Eurasia and Africa (Srivastava et al., 1990; Olivet, 1996; Vergés et al., 2002; Sibuet et al., 2004). The Bay of Biscay opened concurrently with this rifting phase while Iberia underwent ca 35° counter-clockwise rotation relative to Eurasia (Van der Voo, 1969; Williams, 1975; Montigny et al., 1986; Choukroune, 1992; Rosenbaum et al., 2002; Gong et al., 2008; Vissers and Meijer, 2012). The syn-rotational rifting along the northern portion of the Iberian plate produced significant extensional faulting which generated a series of pull-apart depocentres, including the Central Pyrenean Basin that is associated with the Organyà deposits (Figure 1B). The basin became inverted as Africa, Iberia and Europe converged in the Late Cretaceous (Puigdefàbregas and Souquet, 1986; Berástegui et al., 1990; Vergés and Muñoz, 1990; Muñoz, 1992; Vergés and García-Senz, 2001, 2004). The palaeogeographic position of the Organyà Basin in the Early Cretaceous was on the northern margin of the Ebro block with an estimated width of at least 15 km and a length of 70 km to 100 km along its extensional axis (Dinàrès-Turell and García-Senz, 2000; Vacherat et al., 2017). It accommodated a continuous 4,000 m sequence of shallow platform carbonates, and hemipelagic to pelagic marine sediments from the upper Tithonian to the lower Turonian, after which the basin fill was inverted and thrust southward along a detachment fault in a compressional phase associated with the Pyrenean orogeny (Vergés and García-Senz, 2001; García-Senz, 2002). Sedimentary deposits of the Organyà Basin situated in the South Pyrenean Central Unit comprise a complex series of thrust sheets, for example, Bòixols and Montsec; Cotiella and Pedraforca nappes; and the Sierras Marginales (Puigdefàbregas et al., 1992; García-Senz, 2002). Remnants of the basin outcrop in the hangingwall of the Bòixols thrust system, bound to the north by the Morreres backthrust (Figure 1C; García-Senz, 2002; Gong et al., 2009). A prominent E–W trending asymmetric syncline (Santa Fé syncline) divides the northern, relatively thick limb, from a thinner southern limb (Gong et al., 2009). Structurally the outcrop is located along the northern limb of the Santa Fé syncline (42°13’06.15″N, 1°18’55.85″E), and on the south side.
of the Cabó River valley in the municipality of Organyà (Figure 1C). Previous studies of lower beds exposed on the north side of the valley reported the OAE 1a record up to carbon isotope segment C5 (Sanchez-Hernandez and Maurrasse, 2014, 2016; Sanchez-Hernandez et al., 2014), which has been correlated with the lowermost part of the El Pujal section (Socorro and Maurrasse, 2019).

Here, the investigation focuses on 70.75 m of the Cabó Marls in continuity with the previously discussed 13.77 m basal segment of the El Pujal Section (Figure 1D; Socorro and Maurrasse, 2019), which consists of a succession of limestones, argillaceous limestones and marlstones exposed as differentially weathered packets of beds (Figure 1E).
3 | MATERIALS AND METHODS

3.1 | Field sampling and microscopy

Field sampling of the present study extends from 14.29 to 85.04 m (i.e. 70.75 m thick), with a total of 109 samples collected at an average resolution of 1 sample per 65 cm. Samples were selected based on apparent bedding and the top ca 1 m surface of the weakly lithified layers was cleared away to ensure collection of unweathered rocks. Colour description of samples is based on the modified Munsell colour system as proposed by Goddard et al. (1963).

A total of 109 thin sections were analysed using an Olympus BH-2 light transmitting microscope. The microscopic analysis focused on microfacies, mineralogical composition, index fauna identification, bioturbation, presence/absence of benthic fauna and minerals indicative of redox conditions. The micropalaeontological analysis of planktonic foraminifera was accomplished primarily using the help of illustrations in the published literature (Verga and Premoli-Silva, 2002; Heldt et al., 2008; Moullade et al., 2015). Visual estimates of allochems follow Shvetsov’s proposed percentage diagrams as summarized by Terry and Chilingar (1955).

A bioturbation index (BI) was assigned to each sample following the proposed scheme in Taylor and Goldring (1993). In addition, a sample count of benthic fauna focused on benthic foraminifera. The total counts were divided by the area of each thin section and are expressed as density (ρ) or number of specimens per centimetre squared.

3.2 | Carbon analysis

All samples (n = 109) were analysed for total carbon (TC) and total inorganic carbon (TIC) at Florida International University (FIU) using a LECO CR-412 carbon analyser following the methodology used in the Carbon Analysis Laboratory (Ponton, 2005; Gaona-Narvaez et al., 2013b; Sanchez-Hernandez and Maurrasse, 2014), and modified as proposed by Socorro and Maurrasse (2019). Calibration of the instrument was performed by producing a best-fit calibration curve using pure calcite ≥99.9% (C64-500, Fisher Scientific; Sanchez-Hernandez and Maurrasse, 2014). Analytical precision was estimated at 0.03% or better, based on four replicate analyses of the same sample, and accuracy was verified to 0.1% error by analysing a reference material (Dolomitic Limestone NIST 88b). The TIC values are reported as CaCO3% and are used to assign a general lithologic nomenclature modified from Sanchez-Hernandez and Maurrasse (2014) to allow for the wider range of lithologic variation observed in the field. Hence, samples with TIC > 70% are classified as limestones, between 65% and 70% as argillaceous limestones and between 35% and 65% as marlstones. Total organic carbon (TOC) was determined by taking the difference between TC and TIC (TC-TIC) and is expressed as C wt% (detailed in Sanchez-Hernandez and Maurrasse, 2014).

For stable carbon isotope analysis on the organic fraction (δ13Corg), powdering and de-carbonation of samples (n = 109) follow the procedures outlined in Socorro and Maurrasse (2019). Sample analysis was conducted at the Rosenstiel School of Marine and Atmospheric Science (RSMAS) stable isotope laboratory using a Costech elemental combustion system interfaced with a Thermo Scientific Delta V Advantage continuous flow isotope ratio mass spectrometer. The δ13Corg results are reported in per mil (‰) relative to the Vienna PeeDee Belemnite standard.

3.3 | Major and redox sensitive trace elements analysis

Samples (n = 65) were analysed for major (Si, Al, Ti, P, Fe) and redox sensitive trace elements (RSTEs; V, Cr, Co, Ni, Cu, Mo, U) at the FIU Trace Evidence Analysis Facility (TEAF) using an ELAN DRC II (Perkin Elmer LAS) inductively coupled plasma mass spectrometer (ICP/MS). Sample introduction was achieved through laser ablation (LA) using a 266 nm Nd-YAG laser (LSX 500, CETAC) set at a spot size of 200 μm and 10 Hz. Sample preparation and calibration followed the methodology developed by Arroyo et al. (2009) and outlined in Sanchez-Hernandez and Maurrasse (2014), and Socorro and Maurrasse (2019). Results for major elements are expressed in per cent (%) and RSTEs are expressed as parts per million (ppm).

Additionally, because RSTEs show significant enrichments under reducing conditions relative to the average local background value (Wedepohl, 1971; Tribovillard et al., 2004), enrichment indices (EIs) were calculated based on the average values of the section (Bodin et al., 2007; Socorro and Maurrasse, 2019). Usually, the background level for these elements is taken from those reported for average shale values (ASV) such as the Post Archean Australian Shale of Taylor and McLennan (1985), the North American Shale Composite of Gromet et al. (1984) or the ASV of Turekian and Wedepohl (1961) and Wedepohl (1971, 1991). As discussed in Socorro and Maurrasse (2019) this method may overlook the critical effects of crustal heterogeneity, chemical fractionation during weathering and grain-size sorting that can produce sediments very specific to the region of interest (Van der Weijden, 2002; Brumsack, 2006; White, 2013). Thus, depending on the area, the detrital portion of the sediment may have a chemical composition that differs substantially from those reported for the ‘average shale’. Therefore, an assessment of the regional lithological background value (Cole et al., 2017) is required before calculating EIs. Based on uncertainties regarding the magnitude of the background
natural value of the regional detrital signal unrelated to the redox conditions at time of deposition, reliance is placed on a baseline of the Organyà Basin's Average Background Value (OBABV) unique to the region, modified from an earlier study (Socorro and Maurrasse, 2019). Hence, the EI values should be more representative of the true detrital signal of the Organyà Basin watershed. Extensive studies for the period spanning the latest Barremian to the early Aptian provided reliable data to calculate the OBABV by combining RSTEs values from four studied upper Barremian—lower Aptian hemipelagic to pelagic sections at various sites within the basin. These include: (a) the El Pui section (233.3 m) with a total of 84 samples (Sanchez-Hernandez, 2014); (b) the Eastern Prada Quarry Section (27.98 m) with 31 samples (Llaguno, 2017); (c) the Càbó Section (35.6 m) with 17 samples (Carlos Herdocia—Data S1); and (d) the basal portion of the El Pujal Section (13.77 m) with 42 samples (Socorro and Maurrasse, 2019). The OBABV presented here also includes new data using the 65 samples obtained for this study (70.75 m). The combined values thus provide OBABV averages for V (28 ppm), Cr (33 ppm), Co (4 ppm), Ni (32 ppm), Cu (6 ppm), Mo (3 ppm) and U (1 ppm). The EI for each RSTE relative to the OBABV is calculated using the following equation:

\[
EI = \frac{[\text{RSTEs}]}{[\text{RSTEs}_{\text{Regional Background}}]} 
\]

where the numerator \([\text{RSTEs}]\) represents the concentration of each sample in ppm, and the denominator \([\text{RSTEs}_{\text{Regional Background}}]\) is the average value in ppm of the corresponding RSTE from the OBABV as discussed above. Relative enrichments are thus expressed as EIs > 1, whereas depleted elements are represented by EIs < 1.

### 3.4 Clay mineral analysis (<2 µm fraction)

Clay minerals usually form in soils as a primary function of continental climate, bedrock composition, drainage configuration and time (Eslinger and Pevear, 1988; Chamley, 1989; Weaver, 1989). Indeed, the broad distribution of clay minerals in the fine fraction of modern sediments in the Global Ocean mirrors latitudinal climate zones, drainage configuration and source rock composition (Biscaye, 1965; Griffin et al., 1968). Based on the lithological characteristics of the section provided by the TIC and TOC, seven samples (n = 7) were selected for X-ray diffraction (XRD) analysis to represent the different temporal variations of terrigenous supply to the basin. The analyses were performed at the Illinois State Geological Survey, Geochemistry Section, Prairie Research Institute, University of Illinois. Samples were prepared following the methodology described by Moore and Reynolds (1989). The oriented and glycolated clay slides were analysed with a Scintag® XDS2000 diffractometer. Step-scanned data were collected from 2° to 34° 2θ with a fixed rate of 2° per min with a step size of 0.05°/20 for each sample. All resulting traces were analysed using the semi-quantitative data reduction software from Materials Data Inc. (MDI) known as Jade®.

### 3.5 Lipid analysis

A total of 64 samples were prepared and extracted following the procedures proposed by Socorro and Maurrasse (2019) and references therein. Briefly, the total lipid extract (TE) obtained was evaporated until almost dry and dissolved in hexane. Then, the TLE was mounted on a silica gel-packed glass pipette and separated into two fractions (F1 and F2). Fraction F1 containing the aliphatic components was extracted using 4 ml of hexane, and fraction F2 containing the aromatic components was extracted using 4 ml of dichloromethane (DCM).

The aliphatic fractions (F1) (n = 64) and the aromatic fractions F2 (n = 3) were analysed using an Agilent 6890/Agilent 5973 gas chromatography mass spectrometer (GC/MS) at the FIU Advanced Mass Spectrometry Facility. The GC was equipped with an HP-5MS U1 30 m, 0.25 mm, 0.25 µm, capillary column. A 5 µl volume of each sample was injected in splitless mode with the injector temperature set at 280°C. The oven temperature program was set to hold at 65°C for 2 min, then ramped to 300°C at a rate of 4°C/min and held at 300°C for 8 min. Detection was performed by using a single quadrupole operating in positive mode electron impact ionization (EI+) with a scan range from m/z 42 to m/z 500 and a solvent delay time of 4 min.

Selected samples (n = 5) were chosen for further purification of hopanes and steranes through the removal of n-alkanes. The branched and cyclic hydrocarbons were isolated from the n-alkanes via the urea adduction method on previously separated aliphatic fractions. At the end, the non-adduct fractions containing branched and cyclic hydrocarbons (including hopanes and steranes) were combined and evaporated to ca 1 ml before GC/MS analysis.

Analysis of the non-adduct fraction (n = 5) focused on hopanes and steranes and was conducted at the FIU Advanced Mass Spectrometry Facility. Separation and detection of analytes was performed in the previously described GC/MS instrument following the same oven temperature program. However, the instrument was operated in selective ion monitoring (SIM) with a dwell time of 40 ms and a solvent delay time of 4 min. Identification of analytes was achieved on the basis of comparison of published retention times and mass spectra (Watson et al., 2000; Peters et al., 2005, 2007).
The terrigenous to aquatic ratio (TAR) was determined using the equation proposed by Bourbonniere and Meyers (1996):

\[
TAR = \frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}}
\]

The relative abundance of odd to even preferences (OEPs) of long-chain length \( n \)-alkanes was determined using the carbon preference index (CPI) after Bray and Evans (1961):

\[
\text{CPI} = \frac{1}{2} \left[ \frac{nC_{23} + nC_{25} + nC_{29} + nC_{31} + nC_{11} + nC_{13}}{nC_{23} + nC_{25} + nC_{29} + nC_{31} + nC_{13}} \right]^{100\%}
\]

The OEPs of long-chain length \( n \)-alkanes were calculated by adapting the OEP equation of Scalan and Smith (1970) to OEP (2) as published in Peters et al. (2007):

\[
\text{OEP (2)} = \frac{nC_{25} + 6nC_{27} + nC_{29}}{4nC_{26} + 4nC_{28}}
\]

Various hopane and sterane parameters were calculated as follows:

\[
\frac{T_s}{T_s + T_m} = \frac{18a22,29,30 \text{trisnorhexophane}}{18a22,29,30 \text{trisnorhexophane} + 17a22,29,30 \text{trisnorhexophane}}
\]

\[
\text{Gammacerane Index} = \frac{C_{30} \text{Gammacerane}}{C_{17a,21\beta}(H) \text{homohopane} (22S)}
\]

\[
\%C_{27}aaaR = \frac{100* C_{27,5a,14a,17\alpha}(H) \text{sterane}}{C_{27} + C_{29} + C_{25}5a,14a,17\alpha(H) \text{sterane}} (20R)
\]

\[
\%C_{29}aaaR = \frac{100* C_{29,5a,14a,17\alpha}(H) \text{sterane}}{C_{27} + C_{29} + C_{25}5a,14a,17\alpha(H) \text{sterane}} (20R)
\]

\[
\%C_{29}aaaR = \frac{100* C_{29,5a,14a,17\alpha}(H) \text{sterane}}{C_{27} + C_{29} + C_{25}5a,14a,17\alpha(H) \text{sterane}} (20R)
\]

\[
C_{29} = \frac{C_{27}}{C_{29}} \frac{5a,14a,17\alpha(H) \text{sterane}}{C_{29} 5a,14a,17\alpha(H) \text{sterane}} (20R)
\]

\[
C_{29} = \frac{20S + 20R}{20S} = \frac{C_{29}5a,14a,17\alpha(H) \text{sterane}}{C_{29}5a,14a,17\alpha(H) \text{sterane} (20S)+ C_{29}5a,14a,17\alpha(H) \text{sterane} (20S)+(20R)}
\]

\[
\%C_{29}aaaR = \frac{100* C_{29,5a,14a,17\alpha}(H) \text{sterane}}{C_{27} + C_{29} + C_{25}5a,14a,17\alpha(H) \text{sterane}} (20R)
\]

Selected samples \((n = 5)\) were chosen for quantification of polycyclic aromatic hydrocarbons (PAHs). Certified deuterated surrogate PAH mixture (Z-014J-0.5x), p-Terphenyl-d14 internal standard (M-525-FS-2) and perylene standard solution (H-121S) were purchased from AccuStandard. Additional standard mixture EPA 525 PAH Mix A and PAH Mix CRM47543 were purchased from Sigma-Aldrich. Exactly 50,000 g (dry weight) of each powdered sample was weighed and transferred to a cleaned (combusted at 560°C for 2 hr) 11-dram vial. To validate the extraction method and efficiency, 100 μl of the diluted (1 ng/μl) deuterated surrogate PAH mixture (acenaphthene-d10, chrysene-d12, perylene-d12, phenan-threne-d10) was added to each vial prior to solvent extraction. Extraction and separation follow the procedures proposed by Socorro and Maurrasse (2019) and references therein. Following the separation step, fraction (F2) containing the targeted PAHs was evaporated until almost dry and re-dissolved in 100 μl of DCM containing the internal standard, p-Terphenyl-d14 (1 ng/μl). In addition, for quality control purposes, three additional samples were prepared following the previous procedure: a method blank containing only the deuterated surrogate PAH mixture (1 ng/μl), a fortified blank containing the deuterated surrogate PAH mixture (1 ng/μl) and the targeted PAH standards (1 ng/μl) and a fortified sample containing a powdered sample, the deuterated surrogate PAH mixture (1 ng/μl) and the targeted PAH standards (1 ng/μl).

The PAH analyses were conducted at the FIU Advanced Mass Spectrometry Facility. Sample injection and GC separation were performed by an Agilent 6890 gas chromatograph equipped with an autosampler and an HP-5MS UI 30 m, 0.250 mm, 0.25 μm, capillary column using Ultra-pure 6.0 helium as the carrier gas maintained at a constant flow of 1 ml/min. The sample was introduced in splitless mode with a purge time of 1 min. The oven temperature was maintained at 70°C for 2 min and then programmed to increase to 150°C at 30°C/min and then to 310°C at 4°C/min, where it was held isothermally for 10 min. Detection was performed by a single-quadrupole mass spectrometer (Agilent 5973) using EI + mode. The mass spectrometer was operated under selective ion monitoring (SIM) mode with two or three ions per target PAH or deuterated PAH. A calibration curve was prepared by serially diluting the standard solutions to prepare six calibration standards of increasing concentrations: 25, 50, 100, 500, 1,000 and 3,000 μg/L. The internal standard, p-Terphenyl-d14 was introduced by serially diluting the stock solution to yield a concentration of 1,000 μg/L. The obtained quadratic calibration equations (all \(R^2 > .99\)) were then used to quantify the unknown samples. Concentrations are reported in nanograms per gram of initial dry weight (50,000 g) powdered rock (ng/g dw).

The serially diluted EPA 525 PAH Mix A was used as an initial calibration verification standard (ICVS), allowing a percent recovery ranging from 80% to 120%. Analysis of the method blank demonstrated that the analytical system and glassware were free of contaminants (Data S2). Additionally, analysis of the fortified blank established the efficacy of the extraction and separation method with an average percent recovery of...
101% for the primarily targeted analytes (perylene, chrysene and phenanthrene; Data S2). Furthermore, analysis of the fortified sample revealed that influence from matrix-induced bias was not an issue for the targeted analytes (Data S2). Surrogate average recovery calculated from all samples for the three primary deuterated analytes (perylene-d12, chrysene-d12 and phenanthrene-d10) were 100%, 103% and 77%, respectively.

4 | RESULTS

4.1 | Field-scale/microscopic descriptions and fossil content

In the field, the El Pujal section generally occurs as a scarp slope topography, cut by obsequent streams that allow easy exposure of the rock sequence of the present study (14.29–85.04 m) (Figure 1D,E). The outcrop is composed of a repetitive series of differentially weathered packets of indurated beds that are followed by soft, more easily weathered beds. The surficial grey (N6) (colour according to Munsell colour chart) to medium dark grey (N4) colouration of the beds is unvarying throughout but vanishes with depth to the unweathered rock into a greyish black (N2) hue. The lower 25 m (14.29–39.29 m) includes a repetitive series of soft/hard beds with a flaky-fissile weathered surface yet having excellent consolidated condition once the unweathered level is reached below the surface (Figure 2). This sequence intergrades with a 21.15 m thick (39.29–60.44 m) well-indurated rock series, and the uppermost 24.7 m (60.44–85.14) of the succession shows a recurrence of a lithology similar to that seen in the lower 25 m, but with more extended levels of the softer interbeds between 72.03 and 85.04 m (Figure 2). Identifiable macrofossils are absent throughout the section, except for occasional indistinct ferruginous clumps (ca 3–4 mm) and pyritized burrow fillings.

At the microscopic scale, changes are inconspicuous revealing a predominantly monotonous matrix with subtle textural and allochem variations as summarized in photomicrographs of Figure 3. Thin section analysis reveals a kerogen-rich micritic matrix with dispersed pyrite and allochems that rarely exceed 30% as the hallmark of this interval. Pyrite is common in easily erodible beds and less frequent in beds that are more rigid. Pyrite grains appear disseminated throughout the samples with frambooids (ca < 40 μm) infilling burrows and bioclasts, especially benthic foraminifera. Typical bioclasts include benthic and planktic foraminifera,
Figure 3. (A–S) Thin section images of common microfossils and fragments, as well as the rock matrix found throughout this study, scale at 200 µm. (A–F) Images of representative Leupoldina cabri from El Pujal. (G) Image of a planktonic foraminifera with chambers partly infilled with pyrite. (H) Image of an echinoid spine cut perpendicular to axis. (I–J) Images of a large echinoid fragment and spine. (K) Image of an ostracod valve. (L) Image of a benthic foraminifera with pyritized chambers. (M) Images of roveacrinid fragments found throughout this interval. (N) Image of an Ammodiscus benthic foraminifera. (O–Q) Images of minute gastropods and bivalve generally found in marlstone layers. (R) Image of a representative limestone sample, with high bioturbation (BI = 6). (S) Image of a representative marlstone sample with low bioturbation (BI = 3) and abundant pyrite.
echinoid fragments, rare ostracods, roveacridin fragments and rare small sized (300–800 μm) bivalves and gastropods mostly occurring in the easily erodible intervals. Temporal occurrences of bioclasts vary throughout, but benthic foraminifera are least abundant within the levels corresponding to easily erodible interbeds (Figure 2). The bioturbation index (BI) varies between 3 and 6, with minimum values correlated with intervals with the lowest benthic fauna ρ (Figure 2). Examination of index taxa from thin sections revealed the presence of the taxon Leuoldina cf. cabri. While first identified in the basal portion of the El Pujal sequence (Socorro and Maurrasse, 2019) at a stratigraphic height of 13.77 m, in this interval (14.29–85.04 m) it becomes more common, occurring in at least 25 samples of the studied section (Figure 2 noted with an X).

4.2  |  TIC/TOC/ δ13Corg

Carbon geochemistry results for this 70.75 m interval of the El Pujal section are shown in Data S4 and Figure 2. The TIC concentrations yield an average of 69.9% with the lowest value of 54.9% at 75.93 m and the highest of 81.5% at 20.14 m. As previously explained (Section 3.2), three distinct lithologies are recognized based on the range of TIC values, namely limestones, argillaceous limestones and marlstones (Figure 2). The TIC values (Figure 2) starting at stratigraphic level 14.29 m up to 46.65 m, oscillate between 61.9% and 81.5%. Succeeding TIC values increase above 70% over an interval of 13.69 m ending at 60.34 m. Above this level, the values begin to fluctuate again within a 24.7 m interval where they remain primarily below 70%, except at the levels of two limestone layers at 63.67 m (72.2%) and 72.03 m (74.9%), respectively (Figure 2).

The TOC record (Figure 2) displays an inverse (r = −0.76) pattern to that recorded by the TIC curve. Values vary throughout with an average of 1.1%, reaching a minimum of 0.4% at 72.03 m and a maximum of 1.8% at 75.22 m. The lower 24.37 m interval (14.29–38.66 m) exhibits a fluctuating pattern whereby values oscillate between 0.7% and 1.7%. By contrast, the succeeding 21.68 m (38.66–60.34 m) transitions into consistently low values (X = 0.8%) that never exceed 1.1%. The overlying 11.69 m interval, between 60.34 and 72.03 m, registers low-frequency variability in TOC with alternations between 0.4% and 1.1%. The uppermost part (ca 13 m) of the studied section shows another relative increase in TOC values (X = 1.4%), reaching a peak of 1.8%. In addition, variations in TOC inversely correlate with fluctuations in benthic foraminifera ρ (r = −.56; Figure 2) whereby these benthic organisms are less frequent in intervals of argillaceous limestones and marlstones, higher in TOC values. A similar inverse relationship occurs between TOC and BI values (r = −.68), which are lower in intervals of higher organic carbon concentration.

The δ13Corg values measured on the bulk organic fraction fluctuate throughout the studied section around an average of −24‰ (Figure 2) and within a range of 1.7‰, from a minimum of −25.1‰ to a maximum value of −23.4‰. The lower part of the studied section (14.29–33.3 m) yields δ13Corg values that vary between −24.5‰ and −23.6‰ in a high-frequency oscillatory pattern. The following values starting at 33.8–51.52 m remain relatively stable with a range of 0.5‰. Immediately after, a positive shift up to −23.4‰ is recorded at 52.58 m, marking the highest carbon isotope value in the studied section. From 52.58 to 75.22 m, the δ13Corg values follow a gentle negative trend that ends at 75.22 m with the most negative value (−25.1‰) recorded in the sequence coincident with the highest TOC value. The uppermost ca 10 m of the section (75.22–85.04 m) yields a gradual positive δ13Corg shift up to −24.6‰.

4.3  |  Elemental analysis

Data S5 and Figure 4 show the stratigraphic variations of relevant major element (Si, Al, Ti) concentrations which vary in concert throughout the studied section with the highest values in marlstones. In the basal 18.44 m portion of the section (14.0–32.44 m), Si, Al and Ti show a pattern of values that oscillates nearly consistently with the lithological variations. Fluctuations of these elements reach the lowest recorded values in a limestone layer at 32.73 m and continue in a similar pattern of variation up to 47.16 m (an interval of ca 14.43 m). Upward, Si, Al and Ti values stay generally constant throughout the limestone-dominated interval until 60.34 m. Above 60.34 m where marlstone interbeds recur more prominently, Si, Al and Ti fluctuations return, simultaneously peaking at 75.22 m within the thickest marlstone interbed. Compared with the carbon geochemistry, these major elements show a negative correlation with TIC (r = Si, −0.92; Al, −0.91; Ti, −0.90), and a positive correlation with TOC (r = Si, 0.54; Al, 0.57; Ti, 0.51).

Biolimiting elements (Fe, P; Figure 4) have a stratigraphic pattern of fluctuation similar to that exhibited by Si, Al and Ti. Iron shows a positive correlation with Al (r = 0.87) with values that vary from 0.46% to 1.35% and average 0.74%. Phosphorous shows a positive correlation with Al (r = .42) and its values are lower (X = 0.02%) than those recorded for Fe, as they fluctuate between 0.01% and 0.02%. For the most part, biolimiting elements tend to peak in argillaceous limestone and marlstone layers but have lower values in limestone layers. This relationship is highlighted by the negative correlation between TIC and these biolimiting elements, Fe (r = −.87) and P (r = −.43). Conversely, intervals of higher TOC show higher concentrations of Fe (r = .71) and P (r = .48).
The values for RSTEs (V, Cr, Co, Ni, Cu, Mo and U) analysed in this study are shown in Data S5 and Figure 5. Like the previously reported major elements, the RSTEs all show comparable trends throughout the section. In the lower 33.41 m (14.29–47.7 m) values fluctuate, with generally higher concentrations in argillaceous limestone and marlstone interbeds. Above 47.7 m and up to 60.34 m (12.64 m interval) the limestone shows most RSTE variations within relatively lower values, but Cu has an anomalously high peak at 59.27 m, and Mo increases. Above 60.34 m, the overlying 24.7 m of the studied section is characterized by the highest concurrent RSTE concentrations with maximum values of V (48 ppm), Cr (46 ppm), and U (1 ppm) at 75.22 m in the uppermost marlstone layer. Similarly, Co, Ni, Cu and Mo also show significantly higher values at that same level, although their maximum values occurred in different previous
marlstone beds: 25.14 m (Co, 1 ppm; Ni, 38 ppm); 59.27 m (Cu, 8 ppm); and 65.87 m (Mo, 3 ppm).

The EIs were calculated for each RSTE in an effort to quantify their fluctuations relative to the OBABV. As shown in Figure 5, most RSTEs show peaks coinciding with argillaceous limestone and marlstone intervals, while they shift to lower values in limestone layers. Overall, RSTEs fluctuate close to the OBABV, but only a few elements show enrichments (EIs > 1) and they are mostly correlated with marlstone layers. One such element is V with consistent enrichments above the OBABV in intervals of high TOC (r = .69) especially at 75.22 m where V content is 1.75 times higher than the background value.

4.4 | Clay mineralogy

Results of the clay mineral analyses performed on the <2 µm fraction of seven selected samples representative of the different recurrent lithologies are shown in Figure 6. The clay fraction is composed of smectite, illite, kaolinite and chlorite, but is consistently dominated by illite with percentages between 5% and 70%, and an average of 63%. Chlorite is the next most abundant clay as it averages 14% and varies between 5% and 70%, and an average of 63%. Kaolinite follows (x = 12%), displaying relatively small variability (10%–14%) Smectite represents the smallest fraction (x = 11%) of the clay mineral assemblage and varies between 2% and 23%.

4.5 | Biomarkers

The TLE yielded colour variations ranging from greisy yellow (5Y 8/4), moderate yellow (5Y 7/6) and moderate olive brown (5Y 4/4; Figure 7). Regardless of extract colour intensity, all samples display a bright, light blue (5B 7/6) fluorescence under both long and shortwave UV radiation (Figure 7). Colour variations in TLE show a relationship with lithology whereby lighter, greisy yellow extracts are associated with the low TOC of the limestone intervals; moderate yellow extracts mainly coincide with argillaceous limestone intervals, and the darkest, moderate olive brown extracts correspond with high TOC, marlstone layers.

Biomarker analysis of the aliphatic portion focused on n-alkanes, hopanes (m/z 191) and steranes (m/z 217, m/z 218, m/z 259). Figure 8 shows values obtained for different biomarker parameters. In Figure 8, the aliphatic fraction of the studied samples reveals a very low unresolved complex mixture hump (UCM) and is dominated by n-alkanes and the acyclic isoprenoids pristane (Pr) and phytane (Ph). The n-alkanes display an asymmetric range between nC10 and nC37 with a general unimodal positively skewed distribution. The TAR values average 0.27 owing to the predominance of shorter chain n-alkanes (nC15, nC17, nC19) over the relatively less abundant longer chain homologs (nC27, nC29, nC31). As shown in Table 1 the longer chain (> nC31) n-alkanes show no odd-to-even predominance with an average OEP (2) of 1.01 and an average carbon preference index (CPI) of 1.05 (for a complete list of values refer to Data S3). Among the isoprenoids, pristane to phytane ratios (Pr/Ph) range from a low of 1.91 to a maximum value of 3.13 and an overall average of 2.55. Values of Pristane/n-C17 and Phytane/n-C18 are relatively low as they average 0.32 and 0.13, respectively. A plot of Pristane/n-C17 versus Phytane/n-C18 (Figure 9A) shows most samples fall within the mixed type II/III kerogen, with some plotting towards the upper boundary into the terrigenous type III kerogen area.

The hopanoids (m/z 191 chromatograms) show a similar distribution pattern, but with varying proportions depending on lithology. In general, the studied samples are dominated by C30 hopane and C29 norhopane, 18α-22,29,30-trisnorhopane (Ts), 17α-22,29,30-trisnorhopane (Tm) and the extended hopanes or homohopanes (C31-C34). The Ts/(Ts + Tm) ratio ranges from 0.64 to 0.79 and averages 0.72 (Table 1). Homohopanes show a distribution from C31 to C34, whereby C31 > C32>C33 > C34. The C31 and C32 22S/(22S + 22R) homohopane isomerization ratio yields average values of 0.57 and 0.60, respectively. Gammacerane is also present in all the samples where it is usually found eluting just after the C31 (22R) homohopane isomer. A plot of the gammacerane index (gammacerane/C31R-homohopane) is shown in Figure 8.

Regular steranes and diasteranes occur in all the studied samples ranging from C27 to C29. The samples are characterized

FIGURE 6 Temporal variation in clay mineral content (<2 µm fraction). Selected samples were taken as representative of the various lithologies.
**FIGURE 7** Colouration of total lipid extract compared with lithology and TOC. Letters A–H next to the TOC curve correspond to letters under images of total lipid extracts taken under ambient light and both short wave and long wave UV light. Notice the intensity in lipid colouration varies with lithology and TOC content, with darker yellow extracts in argillaceous limestone and marlstone/higher TOC intervals and lighter yellow extracts in limestone/lower TOC intervals. Total ion chromatograms of the aromatic fraction from representative samples of marlstone (C-16-138), limestone (C-16-120) and argillaceous limestone sample (C-16-47) showing the relative abundance of perylene.

**FIGURE 8** Comparison between lithology and various organic geochemical proxies. Representative total ion chromatograms of the aliphatic fraction from the three lithologies. The large peaks in the chromatograms are mainly a homologous series of n-alkanes. Labelled peaks refer to n-alkane's carbon chain length for reference purposes. Peaks labelled as Pr and Ph refer to pristane and phytane, respectively.
TABLE 1  List of biomarker thermal maturity parameters, their corresponding sample number and stratigraphic position

| Sample ID | Height (m) | Ts/(Ts + Tm) | C_{31} 22S/(22S + 22R) | C_{29} 20S/(20S + 20R) | C_{29} ββ/ (ββ + αα) |
|-----------|------------|--------------|------------------------|------------------------|-----------------------|
| C-16-138  | 75.22      | 0.74         | 0.56                   | 0.46                   | 0.63                  |
| C-16-135  | 72.03      | 0.79         | 0.58                   | 0.48                   | 0.67                  |
| C-16-120  | 54.7       | 0.64         | 0.58                   | 0.45                   | 0.64                  |
| C-16-65   | 25.14      | 0.72         | 0.60                   | 0.44                   | 0.62                  |
| C-16-54   | 19.66      | 0.69         | 0.54                   | 0.46                   | 0.61                  |

CPI_{avg} OEP(2)_{avg}  
1.05 1.01

FIGURE 9  (A) Cross plot of Pristane/n-C_{17} versus Phytane/n-C_{18} of selected samples. Fields after Shanmugam (1985) from concepts proposed by Lijmbach (1975). (B) Ternary diagram showing the sterane composition of selected samples and their relationship with source. Fields after Shanmugam (1985) from concepts proposed by Huang and Meinschein (1979)

by having relatively high percentages of 5α,14α,17α(H) (20R) C_{27} (\bar{x} = 34.59%) and 5α,14α,17α(H) (20R) C_{29} regular sterane (αααR) (\bar{x} = 34.02%), but more moderate values of 5α,14α,17α(H) (20R) C_{28} regular sterane (\bar{x} = 31.39%). A ternary diagram of αααR C_{27}%, αααR C_{28}%, and αααR C_{29}% shows that the samples plot in the general area of estuarine to open marine OM (Figure 9B). A plot of the ratio of 5α,14α,17α(H) (20R) C_{27} to 5α,14α,17α(H) (20R) C_{29} (C_{27}/C_{29}) reveals values as low as 0.82 for marlstone layers and much higher values, up to 1.24 in a limestone bed at 54.7 m (Figure 8). Isomerization of the C-20 stereocenter in the 5α,14α,17α(H) C_{29} regular sterane given as the 20S/(20S + 20R) ratio ranges from 0.44 to 0.48 with an average of 0.46 (Table 1). Similarly, beta-isomerization at C-14 and C-17 in the 5α,14α,17α(H) C_{29} 20S and 20R regular sterane given as the C_{29} ββ/ (ββ + αα) ratio ranges from 0.61 to 0.67 with an average of 0.64 (Table 1).

Three aromatic fractions from samples representative of the three principal lithologies were analysed because they yielded the yellow colour variations and fluorescence previously described. Analysis by full-scan GC/MS reveals that marlstone and argillaceous limestone samples contain elevated concentrations of the pentacyclic aromatic hydrocarbon, perylene (Figure 7). In contrast, a similar chromatogram from a limestone bed representative sample, displays a relatively depressed perylene peak (Figure 7). Further analysis of the aromatic fraction focused on the quantification of perylene whose results are reported in Figure 8 and Data S2.

5  |  DISCUSSION

5.1  |  Fidelity of the preserved geochemical signals: Thermal maturity assessment

Thermal maturity concerning OM-rich sedimentary rocks is a measure of the degree of heat-driven reactions generally associated with burial, which converts OM to kerogen, petroleum, gas and graphite (Curiale et al., 1989; Peters et al., 2005, 2007). Evaluating thermal maturity through biomarker analysis relies on the essential principle of structural modification of compounds from a precursor molecule with biological functions to a thermodynamically stable, molecular fossil (Curiale et al., 1989).

Arguably, perhaps the most reliable thermal maturity indicators applicable to the El Pujal rocks are those resulting
from isomerization reactions involving the hydrogen atoms at the C-22 position in the homohopane (C\textsubscript{31}-C\textsubscript{35}) homolog series (Curiale \textit{et al.}, 1989; Peters \textit{et al.}, 2007). At the C-22 chiral centre, the biological form of these homohopanes carry a 22R configuration, which during thermal alteration converts to the 22S epimer (Curiale \textit{et al.}, 1989; Peters \textit{et al.}, 2007). The ratio of 22R to 22S, often calculated as 22S/(22S + 22R), can be determined for all of the C\textsubscript{31}-C\textsubscript{35} homohopanes (Peters \textit{et al.}, 2007), but the C\textsubscript{31}-homohopane is typically the ratio used since variations in the ratio of homohopanes C\textsubscript{32}-C\textsubscript{35} could occur with higher homologs (Zumberge, 1987; K"oster \textit{et al.}, 1997; Pan \textit{et al.}, 2008).

The 22S/(22S + 22R) ratio rises from 0, ultimately reaching a value of approximately 0.6 at equilibrium (Seifert and Moldowan, 1986; Peters \textit{et al.}, 2007). In the El Pujal section, the C\textsubscript{31} homohopane 22S/(22S + 22R) ratio varies from 0.54 to 0.60 and has an average value of 0.57 (Table 1), which indicates that the samples have probably not exceeded a thermal maturity equivalent to an early stage of the oil window (ca 50°C; Peters \textit{et al.}, 2007). Similarly, isomerization of certain steranes can also be used as thermal maturity indicators. Isomerization at the C-20 position in the 5a,14a,17a(H) C\textsubscript{29} regular sterane shifts from an exclusive 20R configuration in biologically derived steroid precursors to a 20S epimer during thermal alteration (Curiale \textit{et al.}, 1989; Peters \textit{et al.}, 2007). The 20S/(20S + 20R) C\textsubscript{29} regular sterane ratio for the El Pujal section yielded values that range from 0.44 up to 0.48 with an average of 0.46 (Table 1). Since these values are below the equilibrium value of ca 0.52–0.55, they also corroborate that OM in the section reached thermal conditions nearing the early oil window (Seifert and Moldowan, 1986; Peters \textit{et al.}, 2007). In addition, the \( \beta\beta/(\beta\beta + \alpha\alpha) \) ratio of C\textsubscript{29} 20R and 20S regular steranes caused by the isomerization of asymmetric centres at the C-14 and C-17 positions is another parameter used as a maturity indicator. The C\textsubscript{29} \( \beta\beta/(\beta\beta + \alpha\alpha) \) ratio changes from 0 to an equilibrium value of ca 0.67–0.71 with increasing thermal maturity (Seifert and Moldowan, 1986; Peters \textit{et al.}, 2007). The El Pujal section has C\textsubscript{29} \( \beta\beta/(\beta\beta + \alpha\alpha) \) values of 0.61–0.67 with an average of 0.64, below the calculated equilibrium values. Once more, the values of this thermal proxy concur with the previous criteria indicating that the OM in the different lithologies reached temperatures not exceeding the early oil window (Peters \textit{et al.}, 2007). The consistency between the biomarker thermal maturity indicators (e.g. plot of C\textsubscript{29} 20S/(20S + 20R) vs. C\textsubscript{29} \( \beta\beta/(\beta\beta + \alpha\alpha) \); Figure 10) with values below equilibrium endpoints indicate that the sediments probably experienced mild temperatures of ca 50–60°C, equivalent to the onset of oil generation. The results suggest that thermal over maturity can be ruled out when interpreting the organic geochemical results of the El Pujal section; hence, as a corollary the preserved biomarker data presumably characterize the original signals with minor to no alteration.

**5.2 | Chemo/biostratigraphic correlation**

Results of numerous studies of Lower Cretaceous sequences coeval with OAE 1a have established correlation in the long-term patterns of variations in carbon isotopic values (\( \delta^{13}\text{C}_{\text{org}} \) and \( \delta^{13}\text{C}_{\text{carb}} \)) which have also been integrated in a robust stratigraphic framework (Menegatti \textit{et al.}, 1998; Moullade \textit{et al.}, 1998, 2015; Dumitrescu and Brassell, 2006). The established records of carbon isotope data can, therefore, be used not only as an effective correlation tool, but also as a proxy to recognize changes in the global carbon reservoir associated with major crises (Jarvis \textit{et al.}, 2015) that affected both marine and non-marine environments (Gröcke \textit{et al.}, 1999; Ando \textit{et al.}, 2002).

The high sediment accumulation rate in the Organyà Basin (Sanchez-Hernandez \textit{et al.}, 2014) generated an expanded archive that documents continuous changes that permit high-resolution chemostratigraphic studies of OAE 1a. Hence, the carbon isotopic data of the Organyà Basin have revealed details of OAE 1a carbon isotope segments not disclosed elsewhere (Figure 11; Sanchez-Hernandez and Maurrasse, 2014, 2016; Sanchez-Hernandez \textit{et al.}, 2014; Socorro \textit{et al.}, 2017). The present results (70.75 m portion) obtained from the El Pujal section complement two previous carbon isotopic curves obtained for segment C1 through the early part of C5 from the El Pui section (Sanchez-Hernandez and Maurrasse, 2014, 2016; Sanchez-Hernandez \textit{et al.}, 2014) and the lower 13.77 m at El Pujal (Socorro and Maurrasse, 2019). The combined \( \delta^{13}\text{C}_{\text{org}} \) data extended at El Pujal show a pattern consistent with the positive plateau attributed to segment C5 and its characteristic short-lived positive spike (Figure 11, point marked with a star; Socorro and Maurrasse, 2019). Furthermore, the high-resolution \( \delta^{13}\text{C}_{\text{org}} \) data allow a detailed record of the variations within segment C5 to be established, beginning with the positive peak recorded at 211.40 m within the El Pui section (Figure 11), which differentiates the end of segment C4. The composite curve (Figure 11) shows a greatly expanded segment C5 starting at El Pui. The

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**FIGURE 10** Plot of C\textsubscript{29} 20S/(20S+20R) versus C\textsubscript{29} \( \beta\beta/(\beta\beta + \alpha\alpha) \) thermal maturity indicator values for selected samples. Dashed lines indicate equilibrium values.
upwards extension into the El Pujal section (Figure 11) allows segment C5 to be subdivided into six subsegments. The first subsegment (C5-a) starts at El Pui with a value of −23.7‰ at 211.40 m and extends over 16.90 m revealing an overall slight negative trend ending at 228.30 m with a value of −24.6‰. Subsegment C5-b records a pronounced positive shift of 2.1‰ from 228.30 m at El Pui up to the maximum value of −22.6‰ recorded at a stratigraphic height of 0.55 m correlated in the El Pujal section (Figure 11, point marked with a star). Upward subsegment C5-c, δ13Corg values progress stepwise to a minimum of −24.5‰ at 26.81 m. Subsegment C5-d extends over 22.64 m (52.58–75.22 m) and shows a progressive decrease in values to a minimum of −23.5‰ at 52.58 m. Subsegment C5-e extends over 22.64 m (52.58–75.22 m) and shows a progressive decrease in values to a minimum of −25.1‰ at 75.22 m. The final subsegment (C5-f) spans from 75.22 to 85.04 m, but this interval may include only the initial portion of an overextended C5 because the end of that segment includes a pronounced negative inflection identifiable in sequences elsewhere that is still lacking in the El Pujal data (Figure 11). It is anticipated that work in progress will help clarify, and probably disclose the negative shift in δ13Corg in this section, for example, La Frontera (Aguado et al., 2014a, 2014b); Roter Sattel and Cismon sections (Menegatti et al., 1998; Figure 11).

Recent biostratigraphic results from lower Aptian successions are in agreement that the occurrence of the index planktonic foraminifer, L. cabri parallels the stratigraphic interval that includes OAE 1a (Magniez-Janin et al., 1997; Aguado et al., 1999; Bellanca et al., 2002; Verga and Premoli Silva, 2002; Coccioni et al., 2006; Heldt et al., 2008; Moullade et al., 2015). The presence of L. cabri throughout the El Pujal section (Socorro and Maurrasse, 2019) (Figure 2, marked with an X) further corroborates the chemostratigraphic correlation with OAE 1a (Figure 11).

5.3 Organic matter sources and palaeoenvironments of the Organyà Basin during carbon isotope segment C5

5.3.1 Organic matter sources and trends

The general distribution of n-alkanes in the El Pujal section (Figure 8) ranges from nC10 to nC17, with a positive skew and dominance of medium to short-chain (≤nC13) homologs. Hence, these n-alkanes reflect a mixed OM source, dominantly derived from microbial phytoplankton and aquatic macrophytes, with a relatively minor, but still noticeable input from terrestrial higher plants (Winters et al., 1969; Gelpi et al., 1970; Riederer and Markstäder, 1996; Ficken et al., 2000; Mead et al., 2005). The plot of the values of Pristane/n-C17 versus Phytane/n-C18 (Figure 9A) show that most samples fall within the mixed type II/III kerogen indicative of marine and terrestrial environments, thus lending further support to
the original source provided by the \( n \)-alkane chain lengths. Nonetheless, given the possible constraint associated with the use of this ratio because heterotrophic bacteria generally degrade the more labile \( n \)-alkanes before the isoprenoids, the interpretation favoured here relies on the fact that the UCM hump is almost non-existent in the chromatograms, which indicates that biodegradation is at least minimum (Wenger and Isak, 2002; Peters et al., 2005). The \( n \)-alkane data imply that the OM pattern of mixed origin recorded in the El Pujal lithologies is compatible with typical continental margin environments where sediments archive a complex OM signal influenced by distinct interconnected ecosystems that include rivers, estuaries and the ocean system itself (Ramaswamy et al., 2008; Schmidt et al., 2010; Bauer et al., 2013; Cordeiro et al., 2018). While the range of the \( n \)-alkanes distribution in the chromatograms suggests various sources of OM were supplied to the basin in the studied interval, it does not permit a clear conclusion concerning significant temporal variability with the lithologies because most chromatograms show only subtle differences (Figure 8). A more distinct delineation emerges when the TAR is used to estimate the relative input of terrestrial versus aquatic OM by comparing the relative abundances of short (\( n \)C\(_{15}\), \( n \)C\(_{17}\), \( n \)C\(_{19}\)) and long (\( n \)C\(_{27}\), \( n \)C\(_{29}\), \( n \)C\(_{31}\)) chain length \( n \)-alkanes. The TAR temporal trend shows variation with lithologies (Figure 8), with elevated values associated with argillaceous limestone and marlstone beds concurrent with peaks in TOC, whereas lower values are in limestone layers. A possible explanation for higher TAR in beds with greater TOC values may be related to the labile characteristics of the type of chain length associated with the source OM. For instance, studies of modern open ocean environments of the Pacific have shown that degradation of plankton-derived OM only allows ca 0.1%–1% of the OM produced in the epipelagic zone to reach the seafloor, and only ca 0.01% actually accumulates in the sediment (Hernes et al., 2001). In the case of the Organyà Basin, the more inert long-chain homologs were probably more readily preserved, thus an increase in terrestrially derived OM with more resistant qualities may explain their higher relative concentration in beds with greater amounts of TOC preserved (Cranwell, 1981; Kawamura et al., 1987; Meyers and Edie, 1993). In fact, higher Si, Al and Ti content (Figure 4) concurrent with stronger terrestrial biomarker signatures in the OM-rich beds supports enhanced fluvial pulses as the principal delivery system of these long chain \( n \)-alkanes to the basin (Hedges et al., 1997; Schefuß et al., 2004; Schmidt et al., 2010).

The general phylogenetic specificity of certain steranes makes them also a viable proxy for OM source identification (Huang and Meinschein, 1979; Volkman, 1986; Peters et al., 2005). In the El Pujal section, the presence of regular steranes (\( \alpha \alpha \alpha \)R) at averages of \( C_{27} \) (34.59%), \( C_{28} \) (31.39%) and \( C_{29} \) (34.02%), further suggests a mixed input of OM from various eukaryotic organisms. A ternary diagram (Figure 9B) of the relative abundances of \( C_{27} \), \( C_{28} \) and \( C_{29} \) \( \alpha \alpha \alpha \)R steranes shows that the samples plot in the general area of estuarine to open marine OM. These results lend support to the complex nature of OM preserved in the semi-restricted Organyà Basin which accumulated hemipelagic sediments typically derived from both allochthonous terrestrial sources and autochthonous marine sources, consistent with the evidence obtained from the \( n \)-alkanes distribution (Sikes et al., 2009; O’Reilly et al., 2014; Zhang et al., 2014a). A lithologic relationship also occurs similar to that discussed for the \( n \)-alkanes. A higher proportion of \( C_{29} \) \( \alpha \alpha \alpha \)R relative to \( C_{27} \) \( \alpha \alpha \alpha \)R (\( C_{29}/C_{27} \); Figure 8) is recorded in marlstone beds attesting to the heightened input of terrestrially derived plant OM during these intervals. Because these intervals also coincide with higher TAR values, together with peaks in Si, Al and Ti, the sterane record underscores the influence of increased fluvial fluxes associated with deposition of these beds. By comparison with possible modern analogs, perhaps the modern-day East China Sea (ECS) may represent a corresponding environment since it is reported that the Cháng Jiāng (Yangtze) River delivers higher amounts of \( C_{29} \) sitosterol and stigmasterols during the spring and summer wet seasons (Kim et al., 2016; Duan et al., 2017). At El Pujal, the approximate duration of the increased terrigenous influence on sedimentation in the Organyà Basin can be estimated using the average thickness of ca 3.3 m for the argillaceous limestone and marlstone beds. Assuming that the highest sedimentation rate of 7.5 cm/kyr calculated by Sanchez-Hernandez et al. (2014) for earlier deposits also applies at this younger level, these beds represent ca 44 kyr. These intervals of increased terrigenous input may therefore indicate that enhanced riverine discharge in the Organyà Basin occurred over frequencies that approach the known Milankovitch cycle (period ca 41,000 years) associated with changes in the obliquity of the earth’s axis of rotation (Hays et al., 1976). Indeed, changes in regional climate of similar duration related to insolation-driven forcing of intensified continental runoff have been demonstrated in the Mediterranean area during the latest Miocene (Mayser et al., 2017) and the Pleistocene last interglacial (Wu et al., 2018).

The presence of hopanes, the altered and saturated version of hopanoids, provide useful information on prokaryotic contribution to the preserved OM in the section (Ourisson et al., 1979; Ourisson and Rohmer, 1992; Blumenberg et al., 2006; Peters et al., 2007). The presence of hopanes in all the studied samples implies that bacteria were also an important source of OM to the sediments. In addition, all the samples show elevated levels of gammacerane. Gammacerane further our understanding of the biotic factors involved in the supply of OM into the basin because its known precursor is the triterpenoid alcohol, tetrathymanol (gammaceran-3β-ol) generated through various biochemical mechanisms originating from freshwater and marine ciliates feeding on anaerobic bacteria (Ten Haven et al., 1989; Harvey and Mcmanus,
larval production. Such a scenario is compatible with the during the wet climate conducive to unusual molluscan molluscan planktonic larvae that flourished intermittently microscopic shells may be interpreted to represent remains of recurrent intensified riverine fluxes. Hence, these micro-
comitant with increased inputs of terrestrial OM (Figure 8) con-
ments with elevated values of Si, Al and Ti (Figure 4), con-
well-stratified water column. Thus, their presence in sedi-
cromollusc shells occur exclusively in OM-rich marlstone
bivalves and gastropods (Boué and Chanton, 1962). The mi-
size and morphology to immature veliger larvae of mollusc
section (Socorro and Maurrasse, 2019). Their consistently
as well as in the older basal 13.77 m portion of the El Pujal
the Organyà Basin deposits during the studied time interval
Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro
et al., 2001; Lin et al., 2000; Mead et al., 2005)
marine deposits of similar age found approximately 30 miles
south-west of the El Pujal section in the Montsec chains,
which contain abundant Montsechia, a primitive aquatic an-
giosperm (Selden and Nudds, 2012; Gomez et al., 2015).
Accordingly, the vegetal fossil record in the adjacent area
also demonstrates that sphagnum species and aquatic angio-
sperms were common in the region in the Early Cretaceous
and may have played a major role in the supply of OM to the
Organyà Basin.

5.3.3 Clay mineralogy: palaeoclimatic signals
A relatively high percentage of illite compared with other clays (Figure 6) characterizes the El Pujal rocks. The lack of variability with depth suggests that illite concentration rep-
resents the source composition rather than diagenetic effects
(Weaver, 1958). As the condition of thermal maturity from biomarker data suggests, the sediments experienced tempera-
atures equivalent to the onset of oil generation (ca 50–60°C),
which is too low to initiate smectite illitization (Cuadros and Linares, 1996; Du et al., 2019). The high abundance of il-
lite may find its source from low grade terranes of mica-rich metamorphic rocks related to the Hercynian orogeny that are abundant in the Pyrenees (Guitard, 1970; Wickham et al.,
1987). Illite also lacks correlation with lithology, which im-
plies that its concentration represents the constant background clay mineral input from terrigenous fluxes of the adjacent eroding landmasses. In contrast, smectite increases in lime-
stones while kaolinite is prevalent in marlstones (Figure 6),
which suggests that their variation is mostly controlled by the modulating effects of weathering processes (Biscaye, 1965;
Griffin et al., 1968; Singer, 1984; Eslinger and Pevear, 1988;
Chamley, 1989; Weaver, 1989). Here, kaolinite and smectite are interpreted as products of soil weathering under pulses of contrasting climate regimes, humid versus dry, respectively
(Weaver, 1989; Wilson, 1999). Chlorite concentration also
varies with lithology as higher values occur in marlstones relative to limestones (Figure 6). Co-variation of kaolinite and chlorite seems to be inconsistent because these two clay minerals form under dissimilar conditions (Chamley, 1989).
Their simultaneous occurrences therefore suggest two dist-
tinct sources, chlorite from the mechanical weathering of low-grade metamorphic terranes in the headwater catchment

5.3.2 Palaeoenvironmental inferences from the stratigraphic distribution of micromolluscs
In addition to their distinct geochemical characteristics, the OM-rich marlstones also include unusually high concentra-
tions of microscopic bivalves (\(\bar{x} \text{ ca } 200 \mu m\)) and gastropods (\(\bar{x} \text{ ca } 300 \mu m\); Figure 3). These microscopic shells recur in the Organyà Basin deposits during the studied time interval as well as in the older basal 13.77 m portion of the El Pujal section (Socorro and Maurrasse, 2019). Their consistently small size is of interest because they appear to be similar in size and morphology to immature veliger larvae of mollusc bivalves and gastropods (Boué and Chanton, 1962). The mi-
cromollusc shells occur exclusively in OM-rich marlstone beds together with gammacarane, a proxy indicative of a well-stratified water column. Thus, their presence in sedi-
ments with elevated values of Si, Al and Ti (Figure 4), con-
comitant with increased inputs of terrestrial OM (Figure 8) and nutrients (Figure 4), establishes their relationship with recurrent intensified riverine fluxes. Hence, these micro-
scopical shells may be interpreted to represent remains of molluscan planktonic larvae that flourished intermittently during the wet climate conducive to unusual molluscan larval production. Such a scenario is compatible with the
areas, while kaolinite originated from mature soils that probably developed in the watersheds. Ultimately, the archived clay mineral assemblage agrees with the variability of Si, Al and Ti, biomarker and sedimentological data to indicate the influence of periodic intensified riverine fluxes related to a fluctuating wet–dry climate. Periods of enhanced fluvial discharge associated with a more humid climate are reflected in the deposition of argillaceous limestone and marlstone intervals with higher kaolinite and chloride content. Moreover, the seemingly inconsistent co-variation of these two clay minerals shows that climate variability was not constrained to a localized area, but had a wider regional geographic extent.

### 5.4 Regional factors involved in OM production and preservation

The conditions required for the accumulation of OM-rich sediments have been extensively debated in the literature. One of the primary factors is a supply of OM generated either in-situ by enhanced surface productivity in the photic zone or through a combination of local productivity and fluvial transportation of terrestrial OM to the marine realm (Suess, 1980; Pederssen and Calvert, 1990; Hedges et al., 1997). However, productivity alone may not be sufficient, as it has been estimated that generally under normal oceanic conditions only approximately 0.1%–1% of the OM produced in the upper water column reaches the seafloor (Hernes et al., 2001). Therefore, in order to increase OM preservation, factors such as reducing conditions with less efficient anaerobic degraders, rapid burial, grain size and types of clays also need to be considered. Given that preservation of OM is a complex, multivariable process, unique features of each basin must be taken into account when examining the predominant originating factors (Keil et al., 1994; Mayer, 1994; Hedges and Keil, 1995; Bergamaschi et al., 1997; Kennedy et al., 2014).

In the El Puajal section, a substantial amount of preserved OM (\( \bar{X} = 1.1\% \)) occurs throughout the studied interval (14.29–85.04 m) with peaks reaching up to 1.8% (Figure 2). Since the biomarkers are dominated by shorter chain n-alkanes (≤nC\(_{19}\)), they indicate that the bulk of the OM was produced in the basin (Figure 8). As the short chain n-alkanes suggest, primary productivity may have been fuelled by relatively high concentrations of biolimiting Fe (\( \bar{X} = 0.74\% \)) and P (\( \bar{X} = 0.02\% \)) (Martin and Fitzwater, 1988; Krom et al., 1991; Martin et al., 1994; Zohary and Robarts, 1998). The presence of gammacerane, which is indicative of stratification in the basin, and a lack of siliceous microfossils such as radiolaria imply that upwelling was not a controlling mechanism for the delivery of the critical biolimiting nutrients to the epipelagic zone. Since the temporal distribution of major elemental concentrations parallels that of Fe and P (Figure 4), these critical nutrients were, therefore, apparently supplied together with terrigenous materials via fluvial fluxes sourced from the weathering of crystalline terranes and apatite-bearing Variscan rocks in the watershed (Abalos et al., 2002; García-Alcada et al., 2002; Sanchez-Hernandez et al., 2014). Moreover, because the presence of perylene concurs adequately with other proxies that imply a humic-rich catchment area was associated with the Organyà Basin, Fe chelation with soil humic and fulvic acids is an alternative pathway for its delivery into the basin. In fact, these chelation complexes are water soluble and allow Fe to be transported from fluvial waters offshore where siderophore ligands released by microorganisms and photodegradation greatly enhances its bioavailability (Laglera and van den Berg, 2009; Batchelli et al., 2010; Kuhn et al., 2014; Krachler et al., 2019). Intensified biological productivity also produces largely labile OM, which may lead to enhanced bacterial degradation and to oxygen-deprived conditions. In fact, intervals of marlstones and argillaceous limestones higher in TOC reflect some level of oxygen deficiency because they yielded relatively lower benthic faunal counts, lower bioturbation index and higher concentration of pyrite (Figure 2). The RSTE values (Figure 5) compared with benthic fauna \( \rho \) (Figure 2) also show trends in agreement with fluctuating low oxygenation levels in the basin as peaks in these elements coincide with intervals depleted in benthic organisms. Similarly, BI and RSTE values exhibit a largely inverse relationship, as indicated by the correlation between V and BI (\( r = -0.57 \)). The RSTE values are characteristically lower within high TIC/low TOC (limestone layers) intervals, and more elevated within those with low TIC/high TOC (argillaceous limestones and marlstones). This relationship is further demonstrated by the negative correlation between V and TIC (\( r = -0.92 \)) and positive correlation with TOC (\( r = 0.69 \)). Overall, RSTE peaks beyond the background natural value shown in Figure 5 are synchronous with high TOC, consistent with previously discussed oxygenation proxies. Of particular interest is the constant enrichment of V and Cr above the OBABV at intervals associated with peaks in TOC, especially in the lowermost 10.85 m (14.29–25.14 m), and the uppermost part of the section. Considering that V and Cr are the most easily reduced of the RSTEs, their fluctuating enrichment only at these levels substantiate weakly oscillating reducing conditions (Calvert and Pedersen, 1993; Li et al., 2015). The absence of RSTE enrichments in the succeeding limestone interval (47.16–60.34 m), which also contains relatively low TOC (\( \bar{X} = 0.83\% \)), signifies a time of improved oxygenation, inducing a higher rate of remineralization of the marine snow, hence reducing export production. By contrast, the uppermost 24.70 m of the section (60.34–85.04 m) comprises again OM-rich argillaceous limestones and marlstones with simultaneous enrichments of most RSTEs above the OBABV yielding peaks up to 1.75 times the background natural value as recorded at 75.22 m (Figure 5). Concurrence of RSTE enrichments with these...
OM-rich intervals thus provides robust evidence that stronger reducing conditions dominated during the deposition of these beds and contributed to OM preservation. The biochemical processes controlling the amount of OM in the sediments of the Organyà Basin at that time can thus be summarized as resulting from a combination of enhanced OM production associated with terrigenous fluxes supplying biolimiting elements together with abundant land-derived OM. Preservation was influenced by decreased remineralization due to exacerbated oxygen deficiency related to poor vertical mixing of a stratified water body.

In addition to the factors discussed above, as peaks in TOC are associated with argillaceous and marlstone beds which correlate well with major elements, especially Al ($r = .57$) derived from clays, OM preservation must have also involved physicochemical processes related to the enclosing minerals. In fact, via this process, ca 90% of the total sedimentary OM from various marine settings cannot be physically separated from its mineral matrix (Hedges and Keil, 1995). The XRD analysis conducted on the clay fraction (<2-µm) reveals illite as the predominant clay mineral ($\bar{x} = 63%$; Figure 6). Since illite contains exposed Al-OH groups that act as amphoteric points (Eslinger and Pevear, 1988), it is capable of binding negatively and/or positively charged polar organic compounds, physically encapsulating the OM and preventing bacterial degradation (Chen et al., 2018). Other organic compounds without polar functional groups, such as n-alkanes, may also bond to clay minerals through Van der Waals and hydrogen bonding (Keil and Mayer, 2014). In addition to illite, the fraction consisting of smectite ($\bar{x} = 11%$), kaolinite ($\bar{x} = 12%$) and chlorite ($\bar{x} = 14%$; Figure 6) has been demonstrated to show a strong affinity with the dissolved organic matter associated with phytoplankton biomasses, thereby improving their preservation potential (Satterberg et al., 2003). Besides the physicochemical processes associated with clay minerals, a simple increase in the suspended sediment loads causing rapid burial is another preservation factor that enhances the export of OM to the sediment by decreasing its exposure to rapid remineralization.

The OM preserved in the El Pujal section may have also experienced different preservation potentials because of their various sources (Haddad et al., 1992). The biomarker data associated with the OM-rich beds yielded a higher proportion of C29-C27 regular steranes and higher TAR values implying an increase in terrestrially derived OM (Figure 8), which consists essentially of inert, nitrogen-free compounds like lignin, cutin and cellulose. These kinds of OM are stable because they have already undergone extensive biological and abiological degradation from source to sink (Cummins and Klug, 1979; De Leeuw and Largeau, 1993; Meyers, 1997). Moreover, they are often bound to clay minerals that result from soil forming processes, hence becoming inaccessible to microbes and thereby increasing their preservation potential when compared to the readily accessible OM generated in-situ (Meyers and Ishiwatari, 1993; Jaffé et al., 2001; Holtvoeth et al., 2010).

5.5 Regional influence on the distribution of $\delta^{13}$C values of TOC

The general structure of the $\delta^{13}$Corg curve at El Pujal reveals a pattern comparable to the global signature of segment C5 in other sections elsewhere (Figure 11), albeit altered by small regional modulating influences. The minor $\delta^{13}$Corg variations in the expanded succession are of particular importance with regards to fluxes of in-situ versus allochthonous OM discussed above, as distinct organisms are known to produce different $\delta^{13}$Corg values (Raven and Johnston, 1991; Ehleringer et al., 1993). It is well established that the $\delta^{13}$Corg values of terrestrial C-3 plants are more negative (typically $-26%e$ to $-28.5%e$; Bender, 1971; Boutton, 1991; Dawson et al., 2002; Fry, 2006) than OM produced in the open ocean (generally ca $-21%e$; Wainright and Fry, 1994). Based on these distinct characteristics an attempt was made to determine the extent of modulation of the $\delta^{13}$Corg values due to the effects of the OM source on the data. The $\delta^{13}$Corg values show a negative relationship with TOC ($r = -.46$), with essentially more negative values associated with argillaceous limestone and marlstone beds. Since increases in TAR and a higher proportion of C29 $\alpha\alpha\alpha$R sterane relative to C27 $\alpha\alpha\alpha$R sterane (C27/C29) (Figure 8) demonstrate the influence of elevated inputs of terrestrial OM in these intervals, then the regional modulating effect on the $\delta^{13}$Corg curve produced by variable OM sources becomes apparent.

To estimate the relative contribution of terrestrial and marine OM in the TOC, the carbon isotope data were used as the basis of a simplified two end-member mixing model (Schlunz et al., 1999; Hu et al., 2006; Ramaswamy et al., 2008; Cordeiro et al., 2018).

The equation used: $T_{\text{om}}$% = $\frac{\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{org}}}{\delta^{13}C_{\text{marine}} - \delta^{13}C_{\text{terrestrial}}} \times 100$, where $T_{\text{om}}$% is the per cent terrestrial organic carbon, $\delta^{13}C_{\text{org}}$ is the measured $\delta^{13}$Corg of an individual sample, $\delta^{13}$Cterrestrial is the $\delta^{13}$Corg value of the local terrestrial end member, and $\delta^{13}$Cmarine is the $\delta^{13}$Corg value of the marine end member. The terrestrial end member at El Pujal was taken as $-25.1%e$ from a marlstone sample at stratigraphic height 75.22 m, because it includes the lowest $\delta^{13}$Corg value recorded in this interval and simultaneously yielded the highest terrestrial OM input previously discussed with the biomarkers. The marine end member was taken as $-23.4%e$ from a limestone sample at 52.58 m, which has the most positive $\delta^{13}$Corg value recorded in this interval and coincides with one of the lowest TAR values. Concordance of these parameters should reflect
the closest value of marine OM. The results from the end-member mixing model are presented in Figure 2. Note that the results using this approach are approximate, because of the absence of authentic end member $\delta^{13}$C$_{org}$ values for terrestrial vegetation and marine OM. Nonetheless, the model indicated distinct trends in temporal OM distribution concerning the different lithologies, in accord with other proxies. For the lower ca 24 m interval (14.29–38.66 m) no clear trends are exhibited between the model and lithology. This presumably demonstrates that the chosen end-member values might not be applicable in this interval since it seems highly unlikely to have rather positive $\delta^{13}$C$_{org}$ values as for example at 17.06 m (−23.6‰) simultaneously with a relatively high TAR value (0.28), unless the vegetation community sourcing the terrestrial OM portion may have been characterized by more positively fractionated $\delta^{13}$C$_{org}$ values reflective of their growing conditions. In the ensuing limestone-dominated interval (38.66–52.58 m) evident trends are produced with a marked decrease in the percentage of terrestrial OM ($\bar{X}$ = 14%) together with lower TAR values ($\bar{X}$ = 0.24) and more positive $\delta^{13}$C$_{org}$ values ($\bar{X}$ = −23.7‰). These data thus show how a regional decline in the input of terrestrial OM can increase the average $\delta^{13}$C$_{org}$ value. The latter pattern is reversed in the uppermost ca 32 m interval (52.58–85.04 m) starting with a gradual increase in the percentage of terrestrial OM ($\bar{X}$ = 57%) that reaches its peak at 75.22 m. At the same time, the $\delta^{13}$C$_{org}$ values slowly decrease coeval with an increase in TAR values that also reach their upper limit (0.40) in an expanded marlstone bed at 74.6 m. This interval illustrates how increased influx of terrestrial OM with typically more negative $\delta^{13}$C$_{org}$ values can decrease the average $\delta^{13}$C$_{org}$ value in the absence of global forcing factors and notwithstanding diagenetic alterations. Because the carbon isotopic signal that is ultimately recorded in the sediments is an average of the $\delta^{13}$C$_{org}$ value of all the sources of OM, areas that receive inputs from variable OM sources, as in this case, will probably archive the regional isotopic signature superimposed on the global carbon reservoir signal.

5.6 | Perylene distribution: palaeo implications and its potential as a geochemical proxy

Preliminary GC/MS analysis conducted on the aromatic fractions of a representative sample from each of the three lithologies yielded a pronounced late-eluting perylene peak (Figure 7) concordant with the yellow colouration and the vivid blue fluorescence (Figure 7) characteristic of this compound (Forster et al., 2004). The variable occurrence of perylene in the sediments thus prompted an investigation of its origin and significance in the Organyà Basin.

Perylene is a five-membered ring PAH (C$_{20}$H$_{12}$) that commonly occurs in a wide range of recent environments, including marine (Orr and Grady, 1967; Wakeham et al., 1979; Hu et al., 2014); lacustrine (Soma et al., 1996; Itoh and Hanari, 2010; Fan et al., 2011), and fluvial settings (Countway et al., 2003; Yunker and Macdonald, 2003). Perylene has also been found in peat, coal (Bergmann et al., 1964; Bechtel et al., 2007), crude oils (Golovko et al., 1999; Scarlett et al., 2019), ancient sediments and rocks (Jiang et al., 2000; Forster et al., 2004; Grice et al., 2009; Zhang et al., 2014b). Perylenequinone pigments are recognized as the most probable precursor of perylene, and they are largely produced by wood-degrading fungi (Jiang et al., 2000; Bechtel et al., 2007; Grice et al., 2009; Itoh and Hanari, 2010; Suzuki et al., 2010; Itoh et al., 2012; Marynowski et al., 2013) under very humid conditions. In most cases perylene exhibits a positive relationship with terrestrial OM proxies (Aizenshtat, 1973; Countway et al., 2003; Bertrand et al., 2013; Varnosfaderany et al., 2014; Zhang et al., 2014b), or is directly found in terrestrial material such as peat bogs and fungi-degraded wood (Malawska et al., 2002; Bechtel et al., 2007; Marynowski et al., 2013). Because perylene is usually found associated with anoxic sediments and is absent, or present only in low concentrations in oxic surface sediments (Choudhary and Routh, 2010) its occurrence also indicates that reducing conditions are involved in its depositional processes, since quinone compounds are sensitive to oxidation (Orr and Grady, 1967; Aizenshtat, 1973).

The perylene concentration in each of the selected El Pujal samples (Figure 8) revealed a variable pattern linked with lithology: values are higher in argillaceous limestones (1,577 ng/g dw) and marlstones (X = 2,788 ng/g dw) than in limestones (X = 757 ng/g dw). Also, significant positive correlation exists between perylene and the major elements Al, Si and Ti (r = .87, .84, .86), which agrees with evidence from biomarker proxies (TAR, C$_{27}$/C$_{29}$) that show a strong relationship (r = .90, −.88) between periods of intensified land-derived OM influx and elevated perylene concentration. Concurrence of these data for the El Pujal section thus provides robust evidence to suggest fluvial transport of land-based OM as the main pathway supplying perylene and/or its biogenic precursors to the Organyà Basin. This assumption is in agreement with modern findings that revealed high perylene abundances in soils (Krauss et al., 2005; Gocht et al., 2007) and in suspended river particles (Luo et al., 2006; Varnosfaderany et al., 2014). The lithological and biomarker characteristics of the El Pujal succession suggest that periodic higher riverine discharges delivered increased soil and/or woody debris from forests and wetlands during inundation (Robertson et al., 1999; Hilton et al., 2012). Conditions at that time were, perhaps, analogous to the episodic flow and flood pulses (Junk et al., 1989) characteristic of large modern river systems such as the Amazon (Hedges et al., 1986;
Given that perylene precursors are essentially sourced from terrestrially derived plant OM associated with humid climates (Baldrige and Valašková, 2008; Varnosfaderany et al., 2014), its occurrence in the El Pujal sediments implies a humid climate in the Organyà Basin during OAE 1a, confirming previous studies that suggest perylene may be a dependable indicator of moist and humid continental palaeoclimates (Suzuki et al., 2010; and references herein). Additionally, because the formation of perylene may involve reducing conditions, its highest concentrations in marlstones coeval with RSTEs enrichments above the OBABV lends evidence for some degree of recurring reducing conditions related to enhanced riverine discharges.

6 | CONCLUSIONS

The El Pujal section of the Organyà Basin provided the opportunity for a high-resolution geochemical study of continuous hemipelagic facies. The results of the multiproxy study on a 70.75 m portion of the section reveal intricate details archived in the sediments as specific responses of the basin to perturbations of the global carbon cycle associated with OAE 1a. The generated δ¹³C-org curve, together with previous investigations, reveals that the δ¹³C-org values concur with the characteristic signature recorded at coeval sites for carbon isotope segment C5 within OAE 1a, yet the studied interval may comprise only part of an overextended C5 because elsewhere the end of that segment includes a pronounced negative inflection that is lacking in the El Pujal data. Nonetheless, the expanded temporal resolution provided new details on the isotopic characteristics of segment C5, suitable for precise chronostratigraphic correlations. Biomarker results reveal n-alkanes ranging from nC₁₀ to nC₃₇, regular steranes (αααααααα) at averages of C₂₇ (34.59%), C₂₈ (31.39%) and C₂₉ (34.02%) and hopanes in all the studied samples demonstrating a mixed source of OM from in-situ primary production, bacteria, aquatic macrophytes and terrestrial vegetation, typical of hemipelagic settings. However, temporal variations in the relative proportion of autochthonous to allochthonous OM sources are registered for this interval associated with variable pulses of riverine discharge as evidenced by periodic increases in micromolluscs presumably flushed offshore from adjacent swamps and estuaries, higher concentrations of terrestrially derived elements (Si, Al, Ti) as well as increased relative inputs of terrestrial OM. In consequence, these localized factors ultimately produced a regional modulating effect on the δ¹³C-org curve due to changing OM sources. Furthermore, regional variations in fluvial discharge linked with climate fluctuations sustained surficial primary production via inputs of critical bio-limiting nutrients, thus providing a source of readily mineralizable OM whose consumption led to oxygen-deprived conditions. Indeed, peaks in TOC that reach up to 1.8% correlate well with relatively lower benthic faunal counts, lower bioturbation indexes, higher concentration of pyrite and peaks in RSTEs. Concomitant spikes in gammacerane indicates a stratified water column related to pulses of freshwater outputs that may have prevented vertical mixing of oxygen depleted bottom waters with more oxygenated surface waters. Although these results suggest that stronger reducing conditions were periodically common and contributed to OM preservation, the presence of benthic fauna throughout and enrichments of some RSTEs above natural background averages suggests preservation in the absence of full anoxia. Therefore, additional preservation factors including physicochemical processes associated with clay mineral adsorption, enhanced by inert OM from terrestrial vegetation and rapid burial were other elements that enhanced the export of OM and its preservation. These data exemplify how regionally to locally unique conditions can stimulate sustained primary productivity and influence the preservation of OM. In summary, the combined results of this study capture not only the details of segment C5 during OAE 1a, but also highlight how the specific responses of a semi-restricted basin modulated the superimposed effects of global forcing factors and determined the fundamental sedimentary expression of this event in the Organyà Basin.

ACKNOWLEDGEMENTS

This study is made possible thanks to financial support from the Glenn A. Goodfriend Memorial funds. We particularly acknowledge the help and technical support of Diane Pirie with instrumentation troubleshooting and for maintaining our FIU labs stocked with supplies. We thank Peter Swart and Amel Saied at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) for the carbon isotope analyses, Cesar Ramirez and Mario Gomez at FIU’s Advanced Mass Spectrometry Facility for their help with biomarker analyses, and Sarah Jantzi at FIU’s Trace Elements Analytical Facilities (TEAF) for her help with the LA-ICP-MS. The Earth and Environment Department at FIU generously provided supplies and other laboratory materials. We gratefully acknowledge comments from the editor and an anonymous reviewer that helped to improve the quality of the manuscript. The authors have no conflict of interest to declare.

DATA AVAILABILITY STATEMENT

Additional data that support the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Socorro J, Maurrasse FJ-MR. Regional palaeoenvironmental influence on organic matter sequestration and characteristics of carbon isotope segment C5 in a hemipelagic sequence, Organya Basin, northeast Spain. Depositional Rec. 2020;6:552–580. https://doi.org/10.1002/dep2.111