



Organic geochemistry, stable isotopes, and facies analysis of the Early Aptian OAE—New records from Spain (Western Tethys)

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ABSTRACT

The Early Aptian Oceanic Anoxic Event (OAE1a) is a time interval characterized by increased organic carbon accumulation in marine sediments, notable sedimentary and biotic changes, and abrupt carbon-isotope excursions indicative of significant major palaeoenvironmental changes linked to a perturbation in the global carbon cycle. Here we present the study of four sections recording the OAE1a (Early Aptian) in Spain, which are located in two broad basins respectively located in the South and the North of Iberia: the Southern Iberian Palaeomargin (Carbonero, La Frontera and Cau sections) and the Basque–Cantabrian Basin (Puentenansa section), which represent depositional settings ranging from shallow marine (distal ramp –Cau– and drowned platform –Puentenansa–) to pelagic environments (Carbonero, La Frontera). Biomarker compositions, C-isotope profiles, biostratigraphic data and facies analysis from the four sections are correlated and integrated. The C-isotope curves all present a clear negative excursion followed by a positive shift. The integration of the C-isotope curves with the biostratigraphic data has been used to correlate the studied sections and to tentatively identify the eight segments formerly proposed from the Alpine domain, and subsequently identified in sections worldwide. Four main groups of compounds are present in all sections: *n*-alkanes, isoprenoids, hopanes and steranes. *n*-Alkanes and acyclic isoprenoids (pristane and phytane) are dominant in most samples. The hopanes are represented by a range of C₂₇ to C₃₅ components, with the specific isomers varying amongst the sections due to differences in thermal maturity. Steranes occur as a range of C₂₇, C₂₈ and C₂₉ isomers, whereas diasteranes only occur in the most thermally mature section (Carbonero). Other compounds of interest include gammacerane and dinosterane. Differences in thermal maturity appear to be the first order control on different biomarker assemblages amongst the studied sections. The Carbonero section is thermally mature, whereas the nearby La Frontera and Cau sections are immature. Puentenansa has intermediate values. Organic matter is derived from a range of terrestrial, marine and bacterial sources. The dominance of the C₂₉ sterane isomers in all sections suggests a strong contribution from higher plants. The presence of gammacerane indicates water column stratification, and high C₂₉/C₃₀ hopane ratios suggest anoxia at the water/sediment interface, respectively. Sedimentologic analysis also suggests anoxic conditions during sedimentation, but evidence for strong and persistent water column anoxia is equivocal. The correlation of the sections reveals that sedimentation of organic-rich facies started earlier in pelagic and later in the shallow marine settings, which can be related to an expansion of the favorable conditions for organic matter accumulation and preservation from deep marine waters to shallower platform environments during the development of OAE1a.

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1. Introduction

The Cretaceous was generally characterized by a greenhouse climate state (Hallam, 1985; Wilson and Norris, 2001), with a reduced latitudinal temperature gradient (Huber et al., 1995; Hay, 2008), elevated pCO₂ levels (Beerling and Royer, 2002, and references therein), and high sea level (e.g. Jenkyns, 1980; Skelton, 2003). In this context, significant short-term changes took place in the ocean-climate

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system, primarily reflected in the widespread deposition of organic carbon-rich marine sediments, whose relation to anoxic marine conditions led to the definition of Oceanic Anoxic Events (Schlanger and Jenkyns, 1976; Jenkyns, 1980). Subsequent research on OAEs have revealed that they represent notable perturbations in the global carbon cycle, which have been related to massive submarine volcanism, formation of oceanic plateaus, and increased rates of seafloor spreading (Leckie et al., 2002). These perturbations were reflected in rapid climate and environmental changes (Jenkyns, 2003; Dumitrescu et al., 2006; Hermoso et al., 2009) affecting both the marine and continental realms (e.g. Skelton, 2003).

Among the OAEs that punctuated the Cretaceous Period, the one that occurred during the Early Aptian (so called OAE1a) was one of the first identified and remains one of the most widely studied. It had a global extent (Arthur et al., 1990; Leckie et al., 2002) and a duration of 1.0 to 1.3 Myr (Li et al., 2008). Sediments recording this event have been recognized in the Tethys domain ("Selli level", Menegatti et al., 1998; Hochuli et al., 1999; Luciani et al., 2001; de Gea et al., 2003; Erba and Tremolada, 2004; Heimhofer et al., 2004; Aguado et al., 2008; de Gea et al., 2008b; Najarro and Rosales, 2008b; Rosales et al., 2009; Mehay et al., 2009; Millán et al., 2009; Najarro et al., 2011a, b; Stein et al., 2011, among others), in the Boreal domain (Gröcke et al., 1999; Föllmi et al., 2006), in the Pacific (Jenkyns, 1995; Ando et al., 2002; Price, 2003; Dumitrescu and Brassell, 2005), and Mexico (Bralower et al., 1999). Dramatic environmental changes occurred in association with OAE1a in settings ranging from continental to pelagic, and particularly in shallow marine carbonate platforms. Among the most striking time-related phenomena were the "nannoconid crisis" (Erba, 1994; Aguado et al., 1999; Erba et al., 2010), profound changes in the marine biota (e.g. Bralower et al., 1994; Erbacher et al., 2001; Leckie et al., 2002), and drastic perturbations in land vegetation and in continental weathering (Föllmi et al., 2006). Nevertheless, other studies suggest that major $p\text{CO}_2$ and vegetation changes did not occur during OAE1a (Heimhofer et al., 2004).

The impact of OAE1a on shallow carbonate platform environments has been analyzed in several studies. One major environmental perturbation is the widespread drowning event recorded at multiple sites (i.e. Weissert et al., 1998; Föllmi et al., 2006; Castro et al., 2008; Najarro et al., 2011a; Castro et al., 2012). In addition, notable faunal and facies changes in carbonate platforms have been related to the OAE1a (i.e. Huck et al., 2012), including the remarkable widespread development of *Lithocodium*–*Bacinnella* episodes in the Tethys domain (Immenhauser et al., 2005; Bover-Arnal, 2010; Rameil et al., 2010).

A pervasive feature of OAE1a stratigraphic successions is the series of pronounced isotopic excursions, first negative and then positive, that occur in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ (e.g. Menegatti et al., 1998; Leckie et al., 2002; de Gea et al., 2003; Herrle et al., 2004, among others). The widespread documentation of these features of the carbon isotope profile in numerous successions of marine carbonate and pelagic sediments from the aforementioned Tethys, Boreal and Pacific regions enables their use as a tool for stratigraphic correlation and as a record of the global perturbations of the carbon cycle. Although there is general agreement that the positive excursion in sedimentary $\delta^{13}\text{C}$ values arises from increased burial of organic matter during the OAE, multiple explanations have been proposed to explain the negative carbon isotope excursion at the onset of OAE1a and, by extension, the causal mechanism. One explanation is that emplacement of large igneous provinces (LIPs; e.g. Ontong-Java and Manihiki Plateaus; Larson, 1991; Larson and Erba, 1999; Tejada et al., 2009; Mehay et al., 2009) raised atmospheric $p\text{CO}_2$ and enhanced nutrient fluxes to the ocean. Other potential triggers include dissociation of gas hydrates releasing methane in continental margin sediments (Beerling and Royer, 2002; Jahren et al., 2005), or increased recycling rates of ^{12}C and nutrient-rich intermediate waters linked

to changes in ocean productivity (Menegatti et al., 1998; Larson and Erba, 1999; Erba and Tremolada, 2004; Weissert and Erba, 2004).

This paper presents the study of four sections recording the OAE1a in Spain, from two different basins (Southern Iberian Palaeomargin and North Cantabrian Basin, Fig. 1), and also representing different palaeogeographic settings (shallow marine and pelagic settings). The sections have been characterized using a combination of isotopic, elemental and biomarker approaches. The latter have been widely used in the investigation of OAEs, including the assessment of marine productivity, terrestrial vs. marine sources of organic matter, and the redox state of the ocean (Meyers, 1997; Pancost et al., 2004). The timing of C-rich sediment deposition is interpreted with respect to the local carbon isotope stratigraphy, with biomarker and elemental analyses being used to further constrain changes in organic carbon inputs and differences in thermal maturity among the four sections. Overall, the integration of stratigraphy and geochemistry, and the correlation with reference sections, has led to present a sedimentary model which assess mechanisms for the spread of anoxia, taking into consideration global and regional effects.

2. Geological setting

2.1. Palaeogeographic framework

During Aptian times the sedimentary basins of Iberia were strongly influenced by the relative motions of the contiguous Eurasian and African plates (Fig. 1). The initiation of the seafloor spreading in the North Atlantic, which started very early in the Cretaceous, led to a decrease in the sinistral movement between Iberia and Africa that had prevailed during part of the Jurassic (Ziegler, 1988), and to a phase of rapid anti-clockwise rotation of Iberia relative to Europe that would culminate in seafloor spreading in the Bay of Biscay from middle Aptian times onwards (Olivet, 1996; Vergès and García-Senz, 2001). In that geodynamic framework, extensional tectonics prevailed in the main sedimentary basins, including the two considered in this paper: the North Cantabrian Basin (NCB), which belonged to the northern margin of the Iberian plate, and the Southern Iberian Palaeomargin (SIPM) (Fig. 1). That extensional tectonism experienced a strong phase during the latest Jurassic to the Hauterivian, followed, during the Barremian–Aptian, by an interval of smaller tectonic movements but larger subsidence rates, that favored the development of wide and thick carbonate platforms (including the Urgonian facies) in the shallow areas of the basins (e.g., Martín-Chivelet et al., 2002; Vera, 2004).

The Lower Cretaceous sequence of the SIPM includes thick successions (> 3000 m) of carbonates and siliciclastics that were deposited in shallow platforms (mostly in the so-called Prebetic Zone, Fig. 2A) and hemipelagic/pelagic settings (dominant in the Subbetic Zone, Fig. 2A) (e.g. Ruiz-Ortiz, 1980; Martín-Chivelet et al., 2002; Vera, 2004). The configuration of the SIPM was defined by a series of basin-scale troughs and swells, bounded by large extensional faults roughly parallel to the continental margin, that were initiated in the Middle Jurassic (e.g., Azéma et al., 1979; García Hernández et al., 1980; Vera, 1988; Ruiz-Ortiz et al., 2001). This tectonic pattern controlled strong differential subsidence and deposition rates. The stratigraphic sections herein considered correspond to depocentral areas in both the Prebetic (Cau section), and the Subbetic (Carbonero and La Frontera sections) (Fig. 2A).

The North Cantabrian Basin (NCB) was a relatively small ($\approx 20 \times 80$ km), E–W elongated sub-basin, which belonged during the Mesozoic to the larger Basque–Cantabrian Basin (BCB). Located in the northwestern margin of the BCB, this sub-basin behaved independently for most of the Cretaceous, and was relatively less subsident than other areas of the BCB. It was separated from the rest of the basin to the east by a N–S complex fault structure (Río Miera Flexure; Feuillée and Rat, 1971). The NBC was generated by rifting tectonics linked to the opening of the Bay of Biscay and

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