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Expression of the Early Toarcian negative carbon-isotope excursion in separated carbonate microfractions (Jurassic, Paris Basin)

Michaël Hermoso [a,*], Laurence Le Callonnec [a], Fabrice Minoletti [a], Maurice Renard [a], Stephen P. Hesselbo [b]

[a] UPMC Univ Paris 06. JE 2477 Biominéralisations et Paléoenvironnements, Case Postale 116, 4 place Jussieu, 75252 Paris Cedex05, France
[b] University of Oxford, Department of Earth Sciences, Parks Road, Oxford OX1 3PR, United Kingdom

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ABSTRACT

The causes of the pronounced negative excursion in carbon-isotope values that was recorded during the Early Toarcian Oceanic Anoxic Event (T-OAE) are still under debate, particularly with regard to the local versus global pattern of the excursion, and the extent to which recorded signals are under a diagenetic control. In this study we employ a novel microseparation technique in order to investigate the isotopic and mineralogical characteristics of different size fractions of the carbonate content from a Toarcian section recovered from the Sancerre–Couy borehole, southern Paris Basin. Beyond the recognition of a −6‰ $\delta^{13}C$ excursion in the bulk carbonate content, our data also demonstrate that biogenic particles (such as coccoliths) and inorganic grains precipitated as early diagenetic phases (including dolomite) both record the excursion with the same magnitude. Although several black shales occur through the Paris Basin Toarcian section, it is only that associated with the onset of the OAE that coincides with a large negative carbon-isotope excursion. Taken together these observations indicate that during this event, the entire water column was characterized by homogeneous carbon-isotope values; such a pattern is incompatible with the idea that the negative excursion was generated simply through the upwelling of bottom waters enriched in re-mineralized organic carbon (cf. "the Küspert model"), since this would have required a strong vertical gradient in the water column. Additionally, the Paris Basin data show that the decrease in carbonate $\delta^{13}C$ values during the OAE occurred in several discrete steps (each of some −2‰), as has previously been found for organic carbon substrates in other European sections. The stepped nature of the isotopic profile, which is part of a stratigraphic signature previously ascribed to Milankovitch forcing, is compatible with regular pulsed input of light carbon into the whole atmosphere–ocean system from a climatically sensitive source such as gas hydrate, or from thermal methanogenesis of organic-rich sediments in the Karoo–Ferrar large igneous province. Contrasts in the amplitude of the negative carbon-isotope excursion on a regional scale remain an important unexplained aspect of the Toarcian record.

1. Introduction

Oceanic anoxic events (Schlanger and Jenkyns, 1976) correspond to periods of increased organic matter fossilization (i.e. huge ^{12}C trapping) during which the carbonate carbon isotopic ratio is relatively high (up to 2‰ as expressed in $\delta^{13}C$). However, some anoxic periods display very sharp negative shifts in the carbon isotope profiles (Scholle and Arthur, 1980; Renard, 1985; Weissert and Channell, 1989; Clarke and Jenkyns, 1999; Erba et al., 1999; Hesselbo et al., 2000; Jenkyns, 2003; Weissert and Erba, 2004; Renard et al., 2005) leading to primary $\delta^{13}C$ values less than −1‰.

During the Early Toarcian OAE, $\delta^{13}C_{carb}$ increased: the values are around −1‰ to −2‰ at the base of the middle *tenuicostatum* Zone up to +3 or +4‰ in the *falciferum* Zone (Jenkyns, 1988; Jenkyns and Clayton, 1997; Jones and Jenkyns, 2001; Röhl et al., 2001; Jenkyns et al., 2002; Duarte et al., 2003; Kemp et al., 2005; Emmanuel et al., 2006; Hesselbo et al., 2007a; Woodfine et al., 2008; Sabatino et al., in press). Disrupting this positive trend, a pronounced negative isotopic shift has been described in marine carbonates, phytoplanktonic organic matter and organic biomarkers (Schouten et al., 2000; Van Breugel et al., 2006), and also in fossil wood which monitors the atmospheric C-isotope composition (Hesselbo et al., 2000, 2007a).

These isotopic decreases, occurring during relatively brief time (about 150 ky for the Early Toarcian, according to Suan et al., 2008a), are still difficult to explain. Recycling of remineralized carbon from deepest ^{12}C-rich water of an intermittently stratified seawater as originally proposed by the "Küspert model" (Küspert, 1982; Jenkyns, 1988; Sælen et al., 1996; Schouten et al., 2000) has been thought to be

* Corresponding author. Present address: University of Oxford, Department of Earth Sciences, Parks Road, Oxford OX1 3PR, United Kingdom. Tel.: +44 1865 272010.
E-mail address: Michael.Hermoso@earth.ox.ac.uk (M. Hermoso).

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responsible for the record of such negative excursions in the sedimentary record, as such events occur in modern fjords (Van Breugel et al., 2005). Because a negative shift is recorded from limestones representing lithofacies in platform strata in westernmost Tethys, they also have been interpreted in terms of carbonate diagenesis (Jenkyns and Clayton, 1997). Rapid sea-level fluctuations in such shallow epicontinental environments have also be postulated to drive both $\delta^{13}C$ records in carbonate and phytoplanktonic organic matter (Röhl et al., 2001; Schmid-Röhl et al., 2002).

The observation of an apparently synchronous negative carbon isotope shift in Early Toarcian strata, and similarities to the well-documented Late Palaeocene event (Dickens et al., 1995), led Hesselbo et al. (2000) to consider methane hydrate dissociation as a plausible interpretation for the C-isotope negative excursion. One problem with this interpretation is the storage and causes of destabilization of methane hydrates within the European realm, because these compounds are only stable within a restricted range of temperatures and pressures that seem not compatible with warm climate of Early Jurassic times (Emmanuel et al., 2006; Beerling and Brentnall, 2007), although it is possible that methane hydrates were stored in higher latitudes.

A number of recent papers have questioned the global nature of the T-OAE and the $\delta^{13}C$ negative excursion (Van de Schootbrugge et al., 2005; Wignall et al., 2006; McArthur, 2007) based on belemnite carbon-isotope profiles, which do not clearly record the negative shift. Van de Schootbrugge et al. (2005) argue that a deep-water upwelling event is more appropriate to explain the C-isotope excursion, similarly to the Küspert model. Also on the basis of belemnite data, Jiménez et al. (1996), Rosales et al. (2001), and Bailey et al. (2003) have postulated that Toarcian bulk carbonates have not retained their pristine geochemical composition due to the burial diagenesis. Other authors have suggested that some profiles that do not show the negative carbon isotope excursion should be taken at face value and indicate that the negative excursion did not occur everywhere (e.g. McArthur, 2007). However, poor sample resolution, incomplete sedimentary record and uncertainty about the nature of carbonates in these sections may equally well explain such observations (e.g. Hesselbo et al., 2007b).

The aim of this work is to investigate the individual C-isotope characteristics of different carbonate components in a key Toarcian succession using an innovative micro-separation protocol. We have chosen to study the sedimentary and geochemical evolution of the Paris Basin because no high-resolution study has yet been published for this location in spite of an abundant literature on organic geochemistry. In the southernmost part of this basin, the Sancerre–Couy drill core (Cher, France) provides a high sedimentation rate reference section for the Toarcian strata of the Paris Basin, and allows a detailed analysis of the negative $\delta^{13}C$ excursion.

2. Geological settings of the Early Jurassic Paris Basin

During the Early Jurassic, extensional tectonics of the European realm created a seafloor morphology characterized by shoals delimiting subsiding shallow basins. The Paris Basin is one such basin in a restricted epicontinental sea (Fig. 1), and corresponds to a Boreal faunal realm where organic matter was better preserved than in more oxygenated Tethyan deposits (Bassoulet and Baudin, 1994). Palaeoclimatic reconstructions (Baudin et al., 1990; Chandler et al., 1992; Bailey et al., 2003) indicate a warm and wet climate in NW-European basins, in agreement with their subtropical 30°N palaeolatitude (Bassoulet et al., 1993).

At this time, the Toarcian biosphere underwent important changes, with extinctions affecting marine and continental life (Hallam, 1983, 1996; Bassoulet and Baudin, 1994; Harries and Little, 1999; Macchioni and Cecca, 2002), including significant overturns in the calcareous nannoflora (Mattioli et al., 2008). The causes of these crises were likely due to the conjunction of palaeoceanographic factors such as sea level rise and/or poorly oxygenated seawater (Jenkyns, 1988) and/or intense volcanic activity related to the Karoo–Ferrar large igneous province emplacement (Pálfy and Smith, 2000; Wignall, 2001; cf. Gröcke et al., accepted for publication). This peculiar framework also explains the onset of a Oceanic Anoxic Event, so-called 'Posidonienschiefer Event' (Jenkyns, 1988; Jenkyns et al., 2002), which has been linked with high volcanic emissions, enhanced continental leaching (Cohen et al., 2004), and a second-order maximum transgression corresponding to the maximum flooding onto the NW European epicontinental surface (Hallam, 2001).

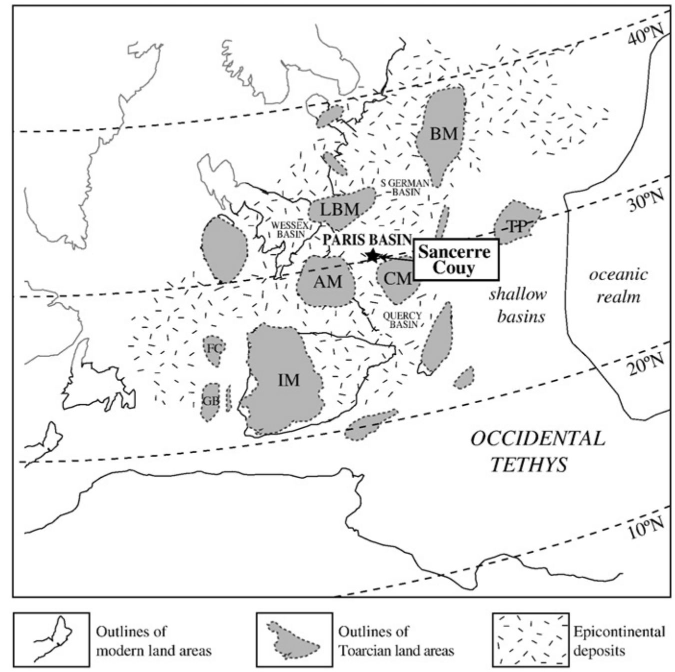

Fig. 1. Palaeogeographic map for the Toarcian in NW Europe showing the Sancerre–Couy borehole location (modified after Bassoulet et al., 1993). Emerged lands are in grey tint (BM: Bohemian Massif, LBM: London-Brabant Massif, AM: Armorican massif, CM: Central Massif, FC: Flemish Cap, GB: Galicia Bank, IM: Iberian Maseta, TP: Tisza Plate).

The Sancerre–Couy borehole is located in central France (Fig. 1), near Bourges city. It was drilled in 1986–1987 for studying the magnetic anomaly of the Paris Basin (program GPF 'Géologie Profonde de la France', Lorenz, 1987). The borehole has provided continuous recovery from Carboniferous up to the Middle Jurassic strata. The Toarcian sediments occur between 355.50 and 198.30 m depth and were fully recovered (albeit with localized drilling disturbances). The studied interval (Late Pliensbachian *spinatum* Zone to Early Toarcian *falciferum* Zone) is 20 m thick.

The biostratigraphic framework (Fig. 2) is described by Gély et al. (1996). The Pliensbachian–Toarcian boundary is placed at 355.50 m with confidence. However, the transition between *tenuicostatum* and *falciferum* Zones is imprecisely defined due to a scarcity of index fossils. Nevertheless, the biostratigraphic boundary is approximately placed at 344.50 m. The sediments are mainly composed of detrital minerals (illite, chlorite and quartz) mixed with various calcareous particles. Black shales occur between 348 and 307 m at this location (Lorenz et al., 1991). In the studied section, three distinct black shale intervals are observed, they are disrupted by bioturbated marls with low organic content (Fig. 2).

3. Material and methods

As the bulk carbonate content is the mixture of various calcareous particles (coccoliths, calcareous dinoflagellates, inorganic