Palaeogeography, Palaeoclimatology, Palaeoecology 399 (2014) 385–393

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Continental weathering and climatic changes inferred from clay mineralogy and paired carbon isotopes across the early to middle Toarcian in the Paris Basin

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ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form 27 December 2013
Accepted 5 February 2014
Available online 12 February 2014

Keywords:
Jurassic
Toarcian OAE
Clay mineralogy
Paired carbon isotopes
Paris Basin

ABSTRACT

Lower Toarcian strata (Lower Jurassic) have been extensively studied with a view to understanding the oceanographic, climatic and biological processes that drove the Earth's system into an Oceanic Anoxic Event (OAE). For this time period, the evolution of the European marine seaways is now relatively well constrained owing to multiple geochemical studies, but investigations regarding climatic trends in the continental realm remain sparse. In the present study, we test the clay mineralogy as a continental climate-sensitive proxy in the well-documented Sancerre core (southern Paris Basin). We compare variations in the kaolinite content with pCO_2 fluctuations (derived from paired carbon isotopes; $\Delta^{13}C = \delta^{13}C_{carb} - \delta^{13}C_{org}$), taking advantage of the detailed chemostratigraphic, palaeoenvironmental and sequence stratigraphy frameworks established for this core material. The results indicate a substantial decrease in kaolinite abundance at the end of the Pliensbachian, which is compatible with a long-term diminution in continental weathering and an inferred temperature decrease. The early Toarcian, prior to the carbon cycle perturbation and deposition of black shale facies, remained relatively cold with minima in both the proportion of kaolinite and reconstructed pCO_2. The mineralogical and geochemical responses across the prominent negative carbon isotope excursion (CIE) itself are not univocal. The first of four steps that compose the negative limb of the CIE at Sancerre is associated with decreased kaolinite and pCO_2, and increased carbonate oxygen isotope ratios. Taken together, these trends are compatible with a transient cooling phase immediately preceding the onset of black shale deposition. Conversely, the subsequent steps are marked by substantial enrichment in kaolinite that matches increased osmium isotope ratios measured in Yorkshire, providing compelling evidence for rapid increases in continental weathering and riverine runoff forced by intensification of greenhouse conditions during the CIE. Relaxation in the intensity of continental weathering, as suggested by resumed low kaolinite abundance is seen immediately after the cessation of CO_2 input (after the fourth step of the CIE). The interval spanning the upper portion of the early Toarcian and the middle Toarcian records a subsequent long-term increase in the proportion of kaolinite synchronous with significant clay enrichment of the sediment. Continued greenhouse conditions, even after the recovery from the carbon isotope perturbation and “regional” black shale deposition, are likely related to sustained CO_2 emission by Karoo–Ferrar volcanism through the considered interval.

1. Introduction

A number of periods marked by transient elevation in atmospheric CO_2 level occurred during the Mesozoic and are referred to as “hyperthermal” events (Jenkyns, 2003). These short-lived events represent sudden disruption of the carbon cycle, intensification of greenhouse conditions, and elevation in Sea Surface Temperatures (SSTs). The most severe of these events culminated into protracted episodes of oxygen depletion and widespread deposition of black shales, a phenomenon referred as to Oceanic Anoxic Events (OAEs) (see Jenkyns, 2010 for a review). The main sources forwarded to account for excess CO_2 in the atmosphere and accompanying climatic and biotic changes are thought to derive from volcanic and/or methane hydrate reservoirs (Jenkyns, 2003, 2010; references therein). Among these Mesozoic hyperthermal events, that of the early Toarcian (183 Ma) is marked by a series of perturbations in the Earth system, including a second-order biological crisis (*sensu* Raup and Sepkoski, 1984). The Pliensbachian and the Toarcian stages have experienced high background pCO_2 likely due to the activity of the Karoo–Ferrar Large Igneous Province (Duncan et al., 1997; Pálfy and Smith, 2000; Jourdan et al., 2008; Moulin et al., 2011). Substantial organic carbon enrichment is observed in lower Toarcian sediments in Europe, as represented by the Schistes carton Formation in France, the Jet Rock Formation in England, or the Posidonienschiefer

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http://dx.doi.org/10.1016/j.palaeo.2014.02.007
0031-0182/

Formation in Germany with Total Organic Carbon (TOC) concentrations yielding 15% (Fig. 1; Baudin et al., 1990).

Additionally, the most prominent negative carbon isotope excursion (CIE) of the Mesozoic recorded in the early Toarcian pinpoints possible injection of isotopically light CO_2 into the atmosphere (Hesselbo et al., 2000, 2007; Kemp et al., 2005; Hermoso et al., 2009a; Hesselbo and Pieńkowski, 2011). This sharp isotopic event (−7‰) is near coincident with the onset of black shale deposition in the European epicontinental seas at the top of the *Dactylioceras tenuicostatum* Zone suggesting a causal link (Hesselbo et al., 2000; Röhl et al., 2001; Hermoso et al., 2009a; Suan et al., 2013). Not only did the carbon cycle experience elemental and isotopic disruption, but a generalised perturbation of the chemistry of seawater, recognised in I, Li, Mg, Mn, Mo, N, Na, O, Os, Re, S, and Sr elements and/or isotopes occurred with the deposition of black shales (McArthur et al., 2000; Jenkyns et al., 2001; Jones and Jenkyns, 2001; Bailey et al., 2003; Cohen et al., 2004; Van de Schootbrugge et al., 2005; McArthur et al., 2008; Pearce et al., 2008; Hermoso et al., 2009b; Lu et al., 2010; Newton et al., 2010; Gill et al., 2011). These "spikes" testify indeed for pronounced climatic and oceanographic changes.

There have been multiple attempts to reconstruct Toarcian SSTs predominantly derived from changes in the oxygen isotopic composition of carbonate (Bailey et al., 2003; Rosales et al., 2004; Hermoso et al., 2009a; Dera et al., 2009a, 2011; Gómez and Goy, 2011). Interpreting $\delta^{18}O$ at face values may, however, give biased SST estimates due to concomitant changes in the oxygen isotope composition of seawater owing to fluctuations in fresh water (^{16}O input) supply in epicontinental seaways (Sælen et al., 1996; Dera et al., 2009a). A possible decrease in seawater $\delta^{18}O$ may be inferred in the epicontinental seaways on the basis of the osmium isotope profile that indicates acceleration of the riverine supply at the time of the negative CIE (Cohen et al., 2004). Another possible source of ^{16}O that can mimic a warming when incorporated into carbonate, may derive from Arctic waters owing to the opening of the Viking Strait during this period (Bjerrum et al., 2001; Dera et al., 2009a; Dera and Donnadieu, 2012).

Palaeo-pCO_2 estimates indicate an increase of 1200 ppm using the reduction in the stomatal index on leafs recovered from a section in Denmark (McElwain et al., 2005). The authors tentatively translated this figure into atmospheric temperatures, and suggested a 6.5 °C greenhouse warming. Despite the aforementioned reservation about the use of $\delta^{18}O$ for SST reconstruction, it is noteworthy that this temperature rise would match the −1.5‰ shift recorded in $\delta^{18}O$ of the well-preserved coccolith-bearing Sancerre core (Hermoso et al., 2009a) or in Mg/Ca ratios of belemnites recovered from Yorkshire and German sections (Bailey et al., 2003).

To date, previous works on the Sancerre core (southern Paris Basin; Fig. 1) have generated long-term $\delta^{13}C$ and $\delta^{18}O$ records, and the evolution in some trace metals for the interval spanning the *Pleuroceras spinatum*–*Harpoceras serpentinum* Zones (Hermoso et al., 2009a, 2009b). Subsequently, high-resolution estimates of pCO_2 and seawater saturation state with respect to calcium carbonate were produced for a short interval corresponding to the onset of the CIE and of black shale deposition (Hermoso et al., 2012). This latter study revealed a "precursor event" consisting of a volcanically-driven pCO_2 rise culminating in a "carbonate crash" across the first step of the negative CIE. Recently, the evolution of the redox state of the water column was attempted for this same site and compared to a sea level change framework for an extended stratigraphic interval up to the *Hildoceras bifrons* Zone in the middle Toarcian (Hermoso et al., 2013). These incremental works make the Sancerre core one of the most studied lower Toarcian sections. A recently-published ammonite and nannofossil work now allows better biostratigraphic constraints on this core material (Boulila et al., 2014). Importantly, the nannofossil biozonation now clearly establishes that the carbon isotope excursion is expressed at the base of

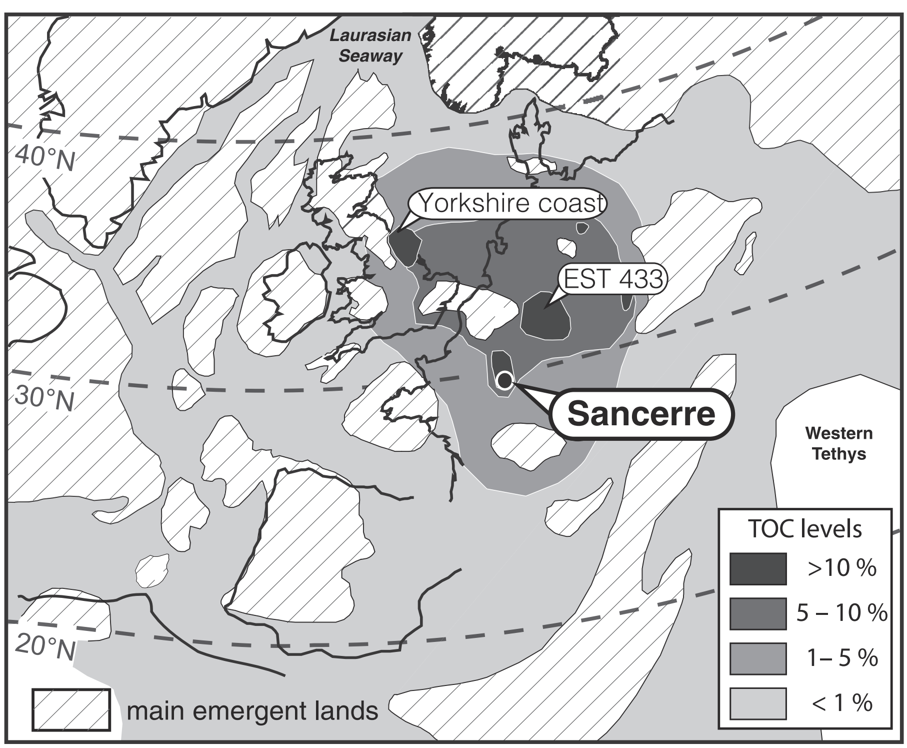

Fig. 1. Palaeogeographic map of the Early Jurassic archipelago (now positioned in NW Europe), and the geographic distribution of organic-rich rocks. Greyscale shades indicate the content range of Total Organic Carbon (TOC); key is embedded bottom right. Emergent lands delineating the basins are hatched. The map indicates the location of the Sancerre and ANDRA EST 433 boreholes in the Paris Basin and the Yorkshire sections in the Cleveland Basin. Source: Bassoulet et al. (1993), Baudin et al. (1990), Van de Schootbrugge et al. (2005), Hermoso et al. (2009b).