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SPECIAL

First record of the Early Toarcian Oceanic Anoxic Event from the Southern Hemisphere, Neuquén Basin, Argentina

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The first record of the Early Toarcian Oceanic Anoxic Event (*c.* 183 Ma) from the Southern Hemisphere is described from the Neuquén Basin, Argentina, identified chemostratigraphically on the basis of a relative increase in marine organic carbon and a characteristic negative carbon-isotope excursion ($\delta^{13}C_{org}$) in bulk rock and fossil wood. The negative excursion of −6‰ in bulk organic carbon (falling to −31.3‰) crosses the boundary of the *tenuicostatum–hoelderi* Andean ammonite Zones, equivalent to the *tenuicostatum–falciferum/serpentinum* zones of Europe. These data indicate that the Early Toarcian Oceanic Anoxic Event was a global phenomenon.

Supplementary material: A detailed stratigraphic log, chemostratigraphic data and nannofossil data are available at http://www.geolsoc.org.uk/SUP18411.

The Toarcian Oceanic Anoxic Event (T-OAE) was initially recognized on the basis of apparently coeval globally distributed black shales deposited in oxygen-depleted marine waters (Jenkyns 1988). Excess burial of marine organic matter implies the development of a positive $\delta^{13}C$ excursion as a result of preferential sequestration of the lighter isotope, ^{12}C, from the marine inorganic carbon pool. Although many European sections indicate an overall positive excursion, a defining characteristic of the T-OAE is an interposed negative excursion, interpreted as the result of injection of isotopically light carbon into the ocean–atmosphere system during the interval of elevated organic-matter burial (Hesselbo *et al*. 2000, 2007). This negative excursion has been recorded in marine carbonate and organic matter, as well as fossil wood, indicating that the phenomenon must involve the global carbon cycle. Despite these geochemical and stratigraphical associations, a number of workers have depicted the T-OAE, and the associated negative carbon-isotope excursion, as a regional phenomenon related to particular oceanographic conditions in the Early Jurassic shelf seas of northern Europe (e.g. McArthur *et al*. 2008).

Given the presence of different ammonite bioprovinces, there have been arguments as to the time-equivalence of organic-rich strata in northern and southern Europe (Jenkyns *et al*. 2002; Mattioli *et al*. 2004; Wignall *et al*. 2005; Mailliot *et al*. 2006). This divergence in opinion relates to problems of defining rigorously an OAE, because local environmental factors such as water depth, redox conditions and sedimentation rate control the preservation of organic carbon (e.g. Demaison & Moore 1980), and marine deoxygenation probably took place before organic matter accumulated to any significant extent (Jenkyns 2010). Consequently, exact time-equivalence of the most organic-rich strata would not necessarily be expected, even if an increase in organic productivity were globally synchronous, as has been suggested (Jenkyns *et al*. 2002).

To resolve the controversy surrounding the T-OAE it is necessary to move outside the European domain. This paper reports biostratigraphic and chemostratigraphic studies of black shales from the Neuquén Basin, Argentina. The aims are to determine whether an increase in organic-matter deposition took place during the Andean equivalents of the *tenuicostatum* and *falciferum* Zones, the age of the T-OAE in NW Europe, and whether a stratigraphically associated negative carbon-isotope excursion can be detected.

The Neuquén Basin is located in west–central Argentina (Fig. 1). The basin, palaeolatitude *c.* 35–45°S, has an approximately north–south-oriented back-arc setting and contains more than 6 km of sediments of Late Triassic to Eocene age, deposited in a series of extensional troughs (Vergani *et al*. 1995; Legarreta & Uliana 1996). Sedimentation began in the Triassic with volcanic and coarse-grained continental deposits. From the Late Triassic onwards a narrow marine corridor, connected to Panthalassa, developed in the northern part of the basin. The seaway expanded southward in the late Early Pliensbachian to Toarcian (Burgess *et al*. 2000; Vicente 2005).

Biostratigraphy and sedimentology. The Arroyo Lapa section, *c.* 900 m thick, is situated on the eastern slope of Sierra Chacaico, about 100 km SW of Zapala in Neuquén Province. The lowermost part of the section comprises Late Triassic–Early Jurassic pyroclastic deposits of the Lapa Formation, whereas the upper part of the section comprises Pliensbachian–Aalenian outer shelf to basinal shales and sandstones of the Los Molles Formation (Gulisano & Gutiérrez Pleimling 1994). The stratigraphy of the Arroyo Lapa section has been previously studied on the basis of ammonites (von Hillebrandt & Schmidt-Effing 1981; von Hillebrandt 1987, 2006), palynomorphs (Volkheimer 1973), bivalves (Damborenea 1987) and palaeomagnetic data (Iglesia Llanos & Riccardi 2000). Ammonites have been referred to a biostratigraphic zonation that is considered valid for the whole Andean region of Argentina and Chile (von Hillebrandt *et al*. 1992). A multiple zonal scheme, based on ammonites, bivalves, brachiopods and calcareous microfossils, has also been proposed for the Neuquén Basin (Riccardi *et al*. 2000).

The section studied is *c.* 72 m thick and comprises laminated black shales and siltstones interbedded with sandstones, a few of which contain volcaniclastic grains. Sand beds are typically sharp-based, commonly with climbing ripple cross-lamination,

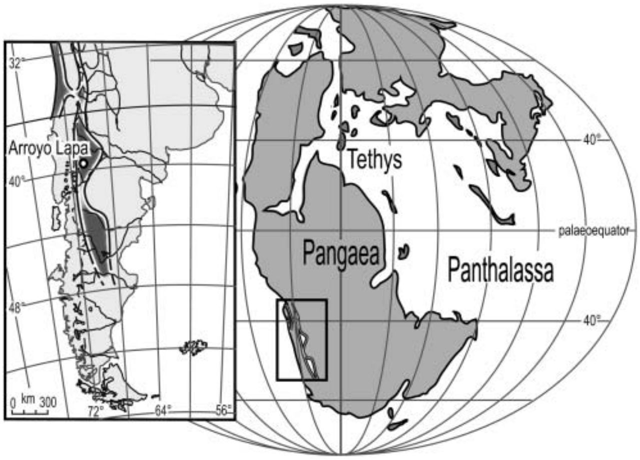

Fig. 1. Toarcian palaeogeography (after Blakey 2007) with inset showing interior seaway (after Vicente 2005) with location of Arroyo Lapa in the Neuquén Basin. Palaeogeographical map shows palaeolatitude; inset shows present-day latitude and longitude.

indicative of rapid deposition. A major erosion surface truncates the section at *c.* 66 m, marked by an abrupt change in lithology. Bivalve and ammonite fossils are abundant throughout the section and fossil wood fragments are particularly common in the sandstone beds. The sedimentary system is interpreted as deep marine (Burgess *et al.* 2000).

Ammonites and other fossils were sampled wherever found in the section. The newly determined biostratigraphy at Arroyo Lapa confirms the presence of sediments of Pliensbachian to earliest Toarcian age. In the lower part of the section (36.35–42.85 m) these ammonites include *Canavaria* (*C.*) cf. *naxensis* (Gemm.), *C.* (*C.*) cf. *finitima* (Fuc.), *Canavaria* (*C.*) cf. *pulcherrima* (Fuc.), *C.* sp., *Protogrammoceras* sp., *Lioceratoides* sp. (see von Hillebrandt 2006, pp. 34, 263), indicating the upper part of the Andean *disciforme* Zone of the Pliensbachian, approximately equivalent to the Northwest European Province *spinatum* Zone (Page 2003). The nannofossils *Biscutum finchii* (Crux), *Lotharingius hauffii* Grün and Zwili, and *Lotharingius barozii* Noël are found in the lowest samples examined (8.52–10.55 m), up to the highest (60.55–61.05 m), and some or all of these taxa may also occur below the lowest level sampled. Their presence indicates that the lowest part of the section studied is no older than latest Pliensbachian (see Mattioli & Erba 1999).

The boundary between the Pliensbachian and Toarcian stages in Arroyo Lapa (*c.* 46 m) is located at the first occurrence (FO) of ?*Dactylioceras* sp. (46.05 m), and *Dactylioceras* (*Orthodactylites*) cf. *directum* (Buck.) (see von Hillebrandt & Schmidt-Effing 1981, plate 1, figs 8–11) and *D.* (?*Eodactylites*) sp. are found at 54.55 m. Nannofossil events were identified, with the FO of *Calyculus* spp. at 43.05 m and the FO of *Lotharingius sigillatus* (Stradner) at 60.05 m: in Europe these events are characteristic of the very latest Pliensbachian and very earliest Toarcian respectively (Mattioli & Erba 1999). The upper part of the section (62.55–70.55 m) includes ammonites from the Andean *hoelderi* Zone, which is marked at Arroyo Lapa by the occurrence of *Harpoceras serpentinum* (Rein.) (see von Hillebrandt 1987, plate 5, figs 4–9; Howarth 1992, p. 109), *Hildaites* cf. *murleyi* (Moxon) (see von Hillebrandt 1987, plate 5, fig. 3; Howarth 1992, p. 168), and *Cleviceras* sp. The Andean *hoelderi* Zone is considered approximately equivalent to the *serpentinum* (= *falciferum*) ammonite Zone of northwestern Europe (von Hillebrandt & Schmidt-Effing 1981; Page 2004; Riccardi 2008).

Comparative chemostratigraphy. Bulk-rock samples were collected through the Arroyo Lapa section at *c.* 50 cm intervals. Fifteen wood fragments were collected from outcrop, with 13 additional samples recovered from bulk rock. Black shales from Arroyo Lapa may be directly compared with coeval strata from Yorkshire, England (Fig. 2). Total organic carbon (TOC) weight percentages at both locations show an upward-increasing trend with similar values in the *tenuicostatum* zones (see Hesselbo *et al.* 2000). Organic $\delta^{13}C$ values from decarbonated bulk sediment from the Arroyo Lapa section show a stepwise negative shift with a magnitude of −6‰, a feature characteristic of the T-OAE in Toarcian sections from Europe (Hesselbo *et al.* 2000, 2007; Kemp *et al.* 2005; Sabatino *et al.* 2009; Jenkyns 2010).

Bulk sediment samples from Arroyo Lapa were also analysed using Rock Eval Pyrolysis. Hydrogen Index (HI) values in the black shales range from 100 to 450 mg HC g^{-1} TOC, indicating a mixture of terrestrial and marine organic components. More specifically, samples leading up to the *tenuicostatum–hoelderi* boundary (55–65 m) have progressively increasing HI values, over the range 200–450 mg HC g^{-1} TOC, showing that the preservation of marine organic matter and/or its ratio to terrestrial organic matter increases upward over this interval (see Baudin *et al.* 1990). The overall range of HI values in the section is very similar to that recorded in coeval Early Toarcian pelagic black shales in Italy and Greece (Jenkyns & Clayton 1986; Baudin *et al.* 1990; Sabatino *et al.* 2009).

In Arroyo Lapa, bulk organic carbon $\delta^{13}C$ values fall to *c.* −31.3‰ at 64.05 m, about 1.5 m above the *tenuicostatum–hoelderi* boundary. Similar values are recorded at the *tenuicostatum–falciferum* boundary in Yorkshire (Hesselbo *et al.* 2000; Jenkyns *et al.* 2002; Kemp *et al.* 2005). Typical extreme $\delta^{13}C_{org}$ values for other locations in Europe for the T-OAE range from −30‰ to −33‰ (e.g. Jenkyns & Clayton 1986; Röhl *et al.* 2001; Sabatino *et al.* 2009; Jenkyns 2010). In Yorkshire, values mostly stay below −30‰ through the lower half of the *exaratum* Subzone, an interval probably not preserved at Arroyo Lapa because of erosional truncation. Ammonites indicate that the sediment above the erosion surface is still within the *hoelderi* Zone, and the notably heavy carbon-isotope values contained may thus represent the upper positive excursion characteristic of the T-OAE in Europe.

The $\delta^{13}C_{wood}$ record also shows the −6‰ negative shift leading up to the *tenuicostatum–hoelderi* boundary, as in Yorkshire and other European sections (Hesselbo *et al.* 2000, 2007). The fossil wood data provide a carbon-isotope record for the Southern Hemisphere that is not affected by any local oceanographic restriction of the Neuquén Basin. Biostratigraphic and chemostratigraphic data indicate that the T-OAE was recorded in the Southern Hemisphere and influenced the total ocean–atmosphere system. Although local factors, such as variable sedimentation rate and diagenesis, may have influenced values of TOC, the data are consistent with the hypothesis that the T-OAE represents an interval of globally increased organic productivity.

Conclusion. Newly determined ammonite and nannofossil biostratigraphy, total organic carbon, hydrogen indices, and $\delta^{13}C_{org}$ values in wood and bulk sediment from the Neuquén Basin, Argentina, provide the first evidence for the Early Toarcian Oceanic Anoxic Event in the Southern Hemisphere. The $\delta^{13}C$ values from bulk organic matter are comparable with carbon-isotope datasets from a coeval section of black shale in

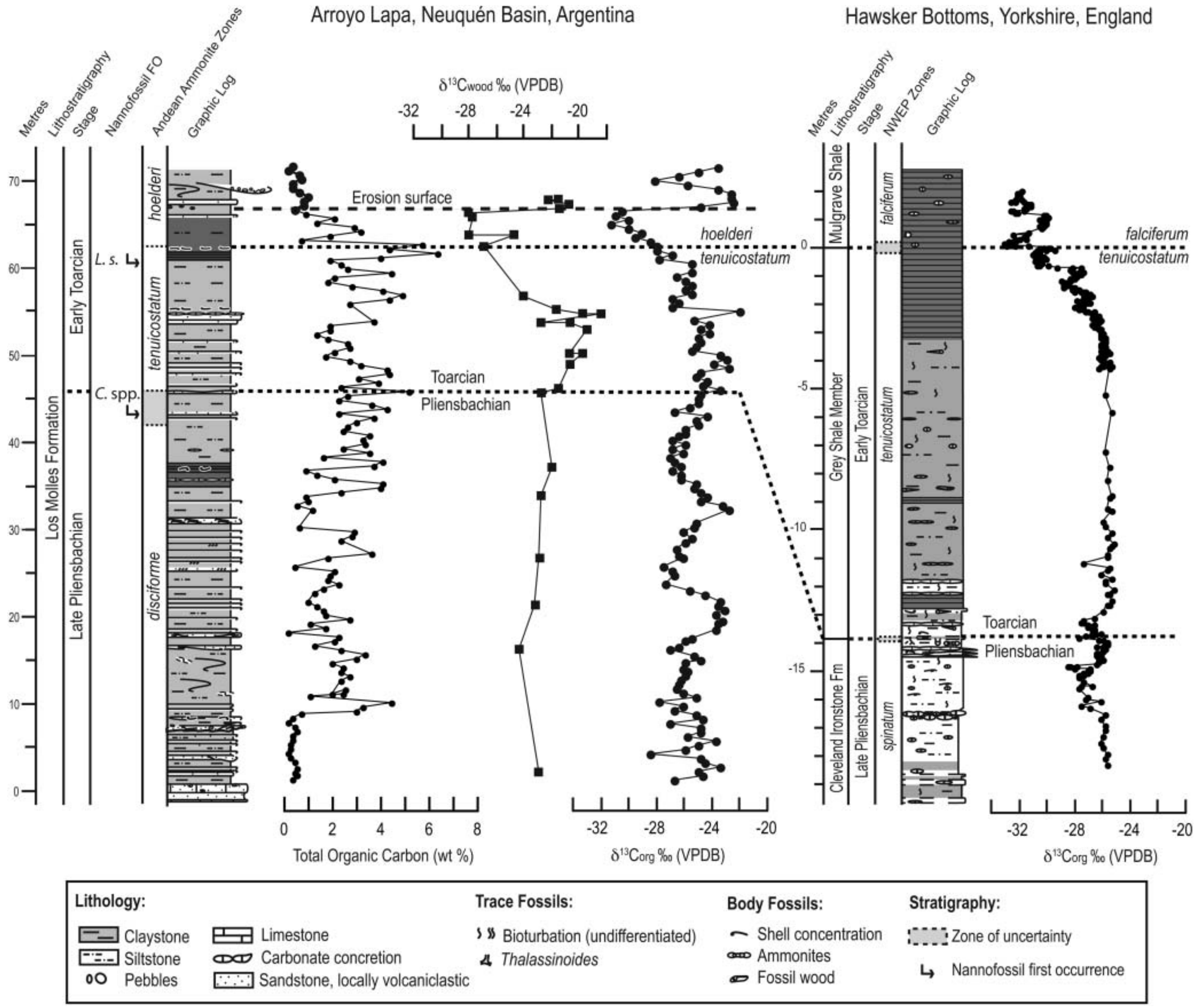

Fig. 2. Section at Arroyo Lapa, Neuquén Basin, Argentina, showing $\delta^{13}C_{org}$ values from bulk sediment and wood, and TOC profile. Section from Yorkshire, England, showing $\delta^{13}C_{org}$ values from bulk sediment, after Kemp *et al*. (2005) and Littler *et al*. (2010). Bold dotted lines indicate locations of the Toarcian–Pliensbachian boundary based on new ammonite biostratigraphy from Arroyo Lapa, as well as the zonal boundaries between the *tenuicostatum* and the overlying *falciferum* (= *serpentinum*) and *hoelderi* ammonite Zones. Nannofossil abbreviations: *C*. spp., *Calyculus* species; *L. s*., *Lotharingius sigillatus*. NWEP, Northwest European Ammonite Province (Page 2003). The increase in TOC (from 3 to 6%) leading up to the top of the *tenuicostatum* Zone in Arroyo Lapa should be noted, as well as the negative −6‰ excursion in $\delta^{13}C_{org}$ from both bulk sediment and wood, also seen in the Yorkshire section. If the stepwise carbon-isotope profile were taken as the primary stratigraphic index, the base of the *falciferum* Zone in Yorkshire might correlate with a level placed *c*. 2 m lower than the base of the *hoelderi* Zone at Arroyo Lapa. A *c*. −2‰ negative excursion in $\delta^{13}C_{org}$ at the Pliensbachian–Toarcian boundary in Arroyo Lapa might be correlative with a similar feature in Yorkshire (Littler *et al*. 2010). Biostratigraphic uncertainty because of a lack of index species is indicated by grey shading.

Yorkshire, England, in both cases showing a negative excursion of −6‰ leading up to and into the Andean *tenuicostatum–hoelderi* or its European equivalent the *tenuicostatum–serpentinum* (= *falciferum*) ammonite zonal boundary. These new data confirm the near-synchronous pattern of organic-matter burial in marine shale deposited over considerable latitudinal range, here interpreted as the result of a globally simultaneous increase in organic productivity. The new data from fossil wood provide an atmospheric record from the Southern Hemisphere and confirm that introduction of isotopically light carbon into the atmosphere during the T-OAE was a phenomenon with global expression.

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