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An alternative model for positive shifts in shallow-marine carbonate δ^{13}C and δ^{18}O

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ABSTRACT

Positive shifts in global seawater $\delta^{13}C_{DIC}$ are related to changes in the ratio of organic relative to inorganic carbon burial in oceanic basins, whereas factors such as climatic cooling and the accumulation of polar ice are known to cause positive shifts in δ^{18}O. Here, an alternative model is proposed for the formation of local positive isotope shifts in shallow-marine settings. The model involves geochemically altered platform-top water masses and the effects of early meteoric diagenesis on carbonate isotopic composition. Both mechanisms are active on modern (sub)tropical carbonate platforms and result in low carbonate δ^{13}C and δ^{18}O relative to typical oceanic values. During high-amplitude transgressive events, the impact of isotopically light meteoric fluids on the carbonate geochemistry is much reduced, and ^{13}C-depleted platform-top water mixes with open oceanic water masses having higher isotope values. Both factors are recorded as a transient increase in carbonate ^{13}C and ^{18}O relative to low background values. These processes must be taken into consideration when interpreting the geochemical record of ancient epeiric seas.

Keywords Carbonates, Carboniferous, diagenesis, epeiric seas, isotopes, palaeoceanography.

INTRODUCTION

Positive shifts in the carbon isotope record are known throughout much of Earth's history (e.g. Magaritz, 1983; Weissert *et al.*, 1985; Marshall & Middleton, 1990; Glumac & Walker, 1998; Saltzman, 2002). On scales of 10^5 years (and longer), most authors relate positive shifts of dissolved inorganic carbon (DIC) δ^{13}C in sea water to enhanced burial of sedimentary organic relative to inorganic carbon, mainly in deep-marine basins (e.g. Jenkyns, 1980; Weissert *et al.*, 1985; Erbacher *et al.*, 1996). In contrast, positive shifts in the δ^{18}O composition of sea water are mainly ascribed to changes in Earth's climate system, such as global ice volume and/or climatic change, that are active in a wide time domain ranging from 10^3 to 10^7 years (e.g. Shackleton, 1987; Schrag *et al.*, 1996 and references therein).

Here, a local Late Carboniferous (middle Atokan; Kashirian; Lower Moscovian; ≈309 Ma, Fig. 1) positive shift in δ^{13}C and δ^{18}O with a duration of at least ≈200–300 kyr is documented and discussed. This isotope shift is recorded in lithified shallow-marine carbonates in the Cantabrian Mountains of northern Spain (Fig. 1), i.e. it reflects a superposition of environmental and diagenetic effects. The purpose of this paper is to evaluate the hypothesis that the expansion and contraction of geochemically distinct coastal water masses (Holmden *et al.*, 1998) combined with early meteoric diagenesis (Allan & Matthews, 1982) can account for this local middle Atokan (and other) positive isotope shift(s) in shoalwater carbonates that is (are) otherwise difficult to explain.

The processes discussed here are well known to oceanographers dealing with modern oceans, but have yet to gain more attention among those concerned with the geochemical record of ancient epeiric seas. Features, such as the one described in this paper, are often neglected, as they are not well

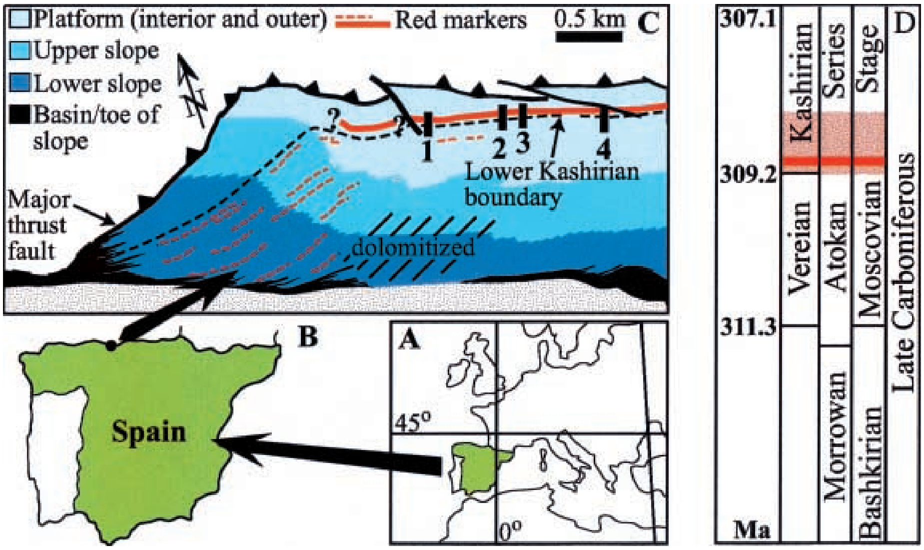

Fig. 1. (A and B) Study area in northern Spain. (C) Map view of vertically rotated thrust imbricate comprising intact Bashkirian–Moscovian platform. Physiographic zones and locations of sections 1–4 are indicated. The red marker discussed here is indicated as a thick red line. Other, laterally less extensive red markers are shown as stippled red lines. (D) Fusulinid chronostratigraphy (determination by E. Villa, Oviedo; see Della Porta *et al.*, 2002 for more detail) of local Atokan isotope shift is shown in light red. Inferred age of red marker is shown as a red line. Time scale after Harland *et al.* (1990).

understood, or discarded as local or diagenetic artifacts. Nevertheless, in epeiric seas, local effects are the rule rather than the exception (Patterson & Walter, 1994; Holmden *et al.*, 1998; Immenhauser *et al.*, 2002). Compilations of sea-water data from ancient oceans, seeking global trends, often heavily rely on information from such shoalwater settings (Holmden *et al.*, 1998). These data sets thus reflect a superposition of local, regional and global trends. The implication of this is that a more detailed understanding (and then separation) of local features (from basinwide features) is an important prerequisite for the reconstruction of changes in palaeoceanographic parameters.

GEOTECTONIC SETTING

The platform studied builds the Sierra de Cuera in Asturias, northern Spain (Fig. 1; Kenter *et al.*, 2003). The platform succession comprises the Valdeteja (Bashkirian) and Picos de Europa (Moscovian) Formations and conformably overlies the Serpukhovian Barcaliente Formation. The exposures belong to the Cantabrian Zone in the NE of the Iberian Massif, i.e. the SW part of the European Hercynian Orogen. These units consist of a thick succession of Palaeozoic strata that were deformed into a set of thrust imbricates by thin-skinned tectonism during the Late Carboniferous. The dip of the bedding planes within the carbonate platform varies between 70° and 90° but commonly approaches vertical. Five general physiographic zones are observed: platform interior, outer platform, upper slope, lower slope and toe of slope to basin (Fig. 1; Kenter *et al.*, 2003). The sections sampled for isotopic analysis are from the platform interior (Figs 1 and 2).

MATERIALS AND METHODS

Carbonate δ^{13}C and δ^{18}O values were determined on fine-grained, texturally uniform matrix micrite from platform-top carbonates. Samples were drilled from freshly cut rock slabs avoiding sparry cement, skeletal components and vein material. The sample powder was analysed on a Thermofinnigan MAT 252 ratio mass spectrometer at Amsterdam for carbon and oxygen isotope ratios (reproducibility $<0{\cdot}1‰$ for δ^{18}O and $<0{\cdot}05‰$ for δ^{13}C). Thin sections from 81 of these samples, distributed across all sections, were investigated for evidence of diagenetic alteration under a cold-stage cathode luminescence microscope operating at 10–14 kV accelerating voltage, 200–300 μA beam current and a beam diameter of 4 mm. Isotope data from meteoric and burial cements as well as from slope matrix micrites are from Immenhauser *et al.* (2002).

ISOTOPE DATA, SEDIMENTOLOGY AND BATHYMETRY

Matrix micrite isotope data are from normal marine inter- to subtidal limestones alternating with restricted lagoonal facies (Fig. 2; see Della Porta *et al.*, 2002 for a detailed description of the facies types and their depositional environments). The isotope values of these platform-top micrites are uniformly low (mean $\delta^{13}C = 0{\cdot}7\permil$, standard deviation (SD) $= 0{\cdot}69\permil$; mean $\delta^{18}O = -6\permil$, SD $= 0{\cdot}46\permil$) relative to slope micrites with values near published Moscovian sea-water data ($> 5\permil$ $\delta^{13}C$; Immenhauser *et al.*, 2002; Saltzman, 2002; see *Supplementary material* for complete data set).

The local Atokan isotope shifts towards higher values represent a deviation from low platform-top towards high open-marine values (Fig. 3) and are conspicuously related to a high-amplitude deepening event. The amplitudes of the shifts gradually decrease landwards from section 1 ($\Delta\delta^{13}C \approx 3\permil$, $\Delta\delta^{18}O \approx 3{\cdot}5\permil$) to section 4 ($\Delta\delta^{13}C \approx 2\permil$, $\Delta\delta^{18}O \approx 2{\cdot}2\permil$). A simple extrapolation of the time–thickness ratio of the Vereian/Kashirian platform interval (time scale of Harland *et al.*, 1990) suggests a duration of about ≈ 200–300 kyr for the stratigraphic interval that contains the isotope shift (≈ 27 m in section 1, Fig. 2). This is clearly a minimum value as portions of this interval are formed by a condensed facies.

The carbonate facies related to the isotope shift requires discussion. The deepening facies itself consists of condensed bioturbated skeletal packstone in a red-stained mud matrix (here referred to as 'red marker'; Figs 1 and 2; see Della Porta *et al.*, 2002 for a detailed description of the facies and sequence stratigraphic interpretation). In terms of sequence stratigraphy, the red marker represents a maximum flooding interval. The red marker is underlain by a transgressive interval characterized by increasingly higher isotope values, and overlain by a regressive interval with gradually lower isotope values (Fig. 2). The (chrono-)stratigraphic interval beneath the red marker, i.e. the Vereian–Kashirian boundary

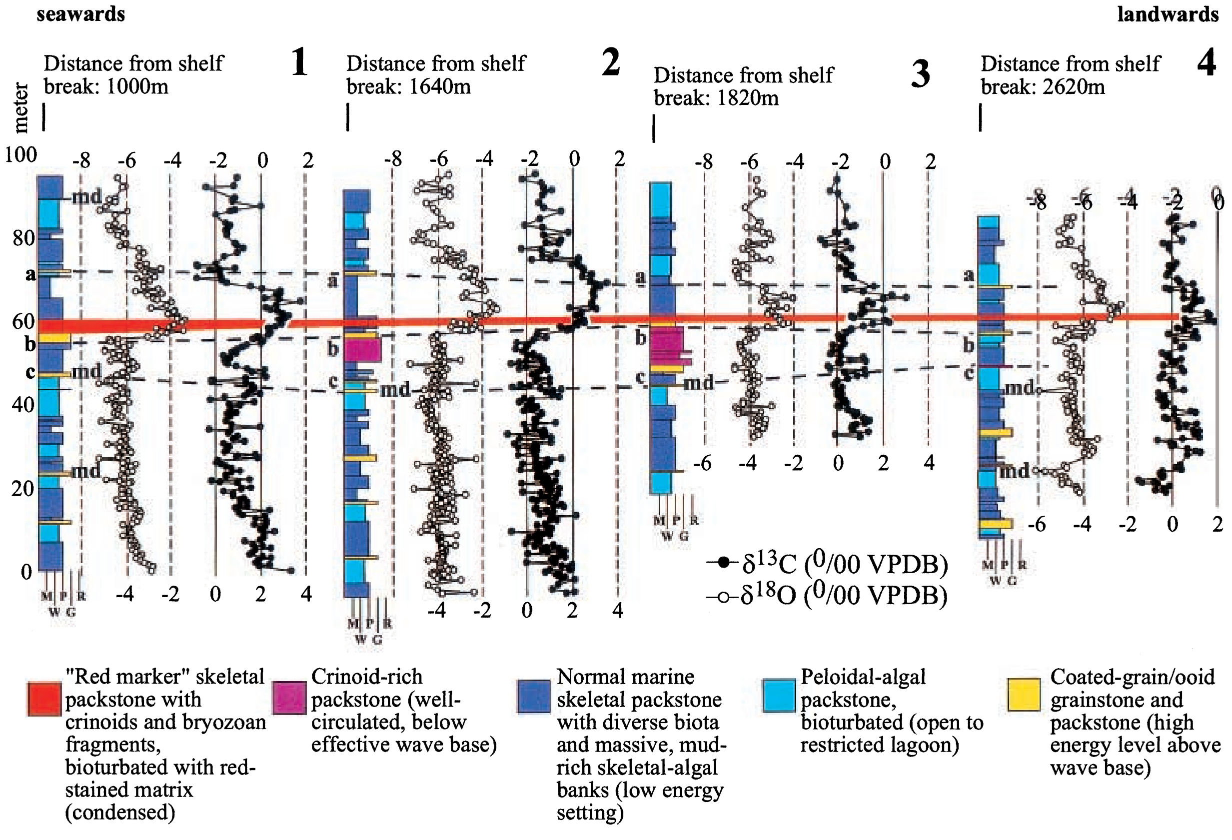

Fig. 2. Atokan sections showing isotope shift between 50 and 75 m. Subhorizontal dashed lines (a, b, c) represent stratigraphic levels walked out in the field. M, mudstone; W, wackestone; P, packstone; R, rudstone; G, grainstone. Levels with evidence of meteoric diagenesis are labelled 'md'.

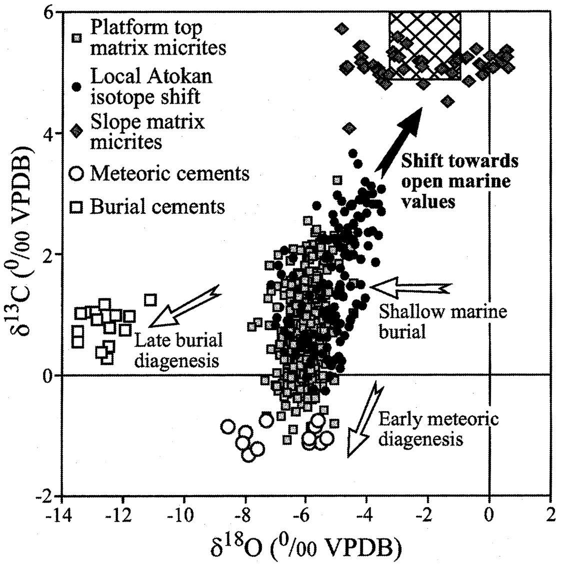

Fig. 3. Diagram of $\delta^{13}C$ vs. $\delta^{18}O$ from platform-top micrites (sections 1–4), slope micrites and from meteoric and burial cement phases. Cross-hatched region indicates Moscovian brachiopod data (Mii *et al.*, 1999). The Atokan isotope shift reflects a trend from low platform-top towards higher marine values, as opposed to meteoric and burial trends.

(Fig. 1D), is generally characterized by low sea level in NW Europe and the Moscow basin, followed by a pronounced deepening in the basal Kashirian (Ross & Ross, 1988). Considering limitations in time resolution and spasmodic tectonic basement subsidence (see Discussion in Della Porta *et al.*, 2002), it seems possible that the condensed open-marine facies of the red marker in Asturias is (at least in part) related to the lower Kashirian eustatic sea-level rise as shown in Ross & Ross (1988).

Besides intraclasts, the facies contains the following biota: echinoid spines, fusulinid and staffellid foraminifera, algae, rare brachiopods, bivalves, gastropods, fenestellid bryozoans and ostracods. The presence of echinoderms, brachiopods and bryozoans suggests open-marine, well-oxygenated water with normal salinity (Wilson, 1975). The red pigmentation is probably the result of microbial precipitation of iron in a suboxic microenvironment a few decimetres to metres below the sediment surface (Preat *et al.*, 1999). A facies control of isotope values can be ruled out as the shift extends across different facies types.

The Atokan red marker is unique on the platform top, but some minor reddish layers, wedging out within a few tens of metres, occur at the outer platform margin (Fig. 1C). Several of these minor red markers are characterized by shifts in $\delta^{13}C$ and $\delta^{18}O$ ($\Delta \approx 2‰$). In the slope setting, however, the red facies is rather common (Fig. 1C). Each of the red slope markers reflects a deepening pulse as indicated by its condensed facies and deep-water biota (Kenter *et al.*, 2003). Across red slope markers, $\delta^{18}O$ is enriched by up to 2·5‰, but $\delta^{13}C$ remains invariant (Immenhauser *et al.*, 2002). It appears that the Atokan red marker represents a time interval when the platform top shifted to a bathymetric domain usually typical of the slope setting.

DISCUSSION

The C and O isotope values of platform-top and slope micrites along with early meteoric and burial cement phases are plotted in Fig. 3. The data that represent the Atokan isotope shift trend towards the higher, open-marine values of slope sediments and away from early meteoric and burial values. It is therefore argued that, although some late diagenetic (burial) resetting of the primary micrite $\delta^{13}C$ and, particularly, the $\delta^{18}O$ values is likely, broad trends in marine environmental and early meteoric signatures are preserved (Fig. 3). The weakly to non-luminescent appearance of the carbonates in the sampled intervals indeed points to a relatively minor burial overprint (see Discussion in Immenhauser *et al.*, 2002).

A detailed model is outlined below to explain the observed C and O isotope shift (Fig. 4). Immenhauser *et al.* (2002) proposed that the low values of the platform-top carbonates (Figs 2 and 3) are mainly related to two factors: first, the influence of ^{18}O-depleted early meteoric fluids and ^{13}C-depleted soil-zone CO_2 (Allan & Matthews, 1982) that affected the bulk isotopic composition of platform-top limestone during Moscovian subaerial exposure events. However, Moscovian exposure surfaces with deep-cutting karst features are absent in these sections (Della Porta *et al.*, 2002). Well-developed pendant calcite cements at several stratigraphic levels contrast with this observation. In addition, sawtooth-shaped shifts to lower isotope values (Fig. 2) point to meteoric diagenesis of marine carbonates above the water table, meteoric influx and soil-zone CO_2 (Allan & Matthews, 1982). The apparent lack of well-developed exposure surfaces is perhaps explained by the erosive nature of many sequence boundaries that are often overlain by a lag deposit of reworked carbonate clasts including shoalwater facies

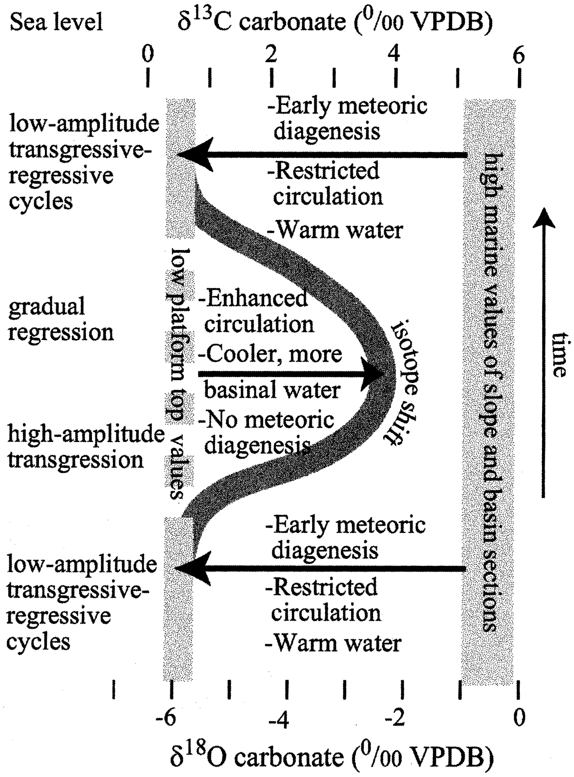

Fig. 4. An alternative model for positive shifts in shoalwater δ^{13}C and δ^{18}O. During high-amplitude transgressive events, the circulation of platform-top water masses is enhanced, and the effects of meteoric diagenesis on platform-top carbonates much reduced. Both factors lead to a transient isotope shift towards higher, more marine values.

(Della Porta *et al.*, 2002). Furthermore, many of the shoaling cycles are truncated, i.e. they lack a wave-agitated interval, and resemble the facies-incomplete cycles of Soreghan & Dickinson (1994) pointing to rapid sea-level fall. Another observation that might point to pervasive meteoric overprint of marine values is the variant δ^{13}C combined with the relatively invariant δ^{18}O signature in sections 1–4 (Fig. 2; see Discussion in Lohman, 1988). Similar effects on the bulk geochemistry of platform-top carbonates were documented from the late Pleistocene of the Great Bahama Bank (Kievman, 1998). In conclusion, the lack of well-developed exposure surfaces in the study area is probably the result of erosion during marine flooding (Wright, 1996) rather than of unusually fast basement subsidence, leading to permanently submerged sections or, even more unlikely, the absence of high-amplitude sea-level fluctuations in the Moscovian ice-house world (see Discussion in Della Porta *et al.*, 2002).

Secondly, the shallow, poorly circulated water masses atop the Atokan platform might have seen the effects of ‘sea-water ageing’ (Holmden *et al.*, 1998). This process involves the progressive oxidation of organic matter to CO_2, which then forms dominantly bicarbonate in the sea water. The uptake of this bicarbonate in organic skeletons or its inorganic precipitation results in carbonate materials with depleted δ^{13}C values (Fig. 4). The ageing effect is greatest during long residence time of water masses in shallow, poorly circulated settings such as in the present-day Florida Bay where sea-water ^{13}C is depleted by up to 4‰ (Patterson & Walter, 1994). This depletion is reflected by low δ^{13}C values of calcitic bivalves (Lloyd, 1964), whereas aragonitic muds exhibit higher δ^{13}C values (≈ 4‰) as a result of enrichment of aragonite in ^{13}C relative to calcite (Romanek *et al.*, 1992).

Maynard & Leeder (1992) proposed that Moscovian glacio-eustasy reached amplitudes of 40 m. An Atokan relative sea-level rise of this amplitude would probably not cause near drowning of the platform. This is because the growth potential of carbonate platforms is usually sufficient to match a sea-level rise of this amplitude (Schlager, 1999). Several red slope markers that grade upslope into open lagoonal sediments exemplify this conclusion (Fig. 1C; Kenter *et al.*, 2003). The middle Atokan event might thus reflect environmental factors combined with rapid deepening. As a consequence, circulation atop the deepened platform was enhanced, and aged platform water mixed with open-marine water masses (Fig. 4). With specific reference to δ^{18}O, a change of ≈ 3·5‰ might point to the combined effects of flooding of the platform top with cooler water and a relative increase in carbonate ^{18}O as a result of the shutdown of early meteoric diagenesis (Fig. 4). A change in sea-water temperature alone is perhaps unlikely in this shallow setting. This is because a δ^{18}O shift of ≈ 3·5‰ would require platform flooding with basinal sea water that was, depending on the temperature equation used, ≈ 14–15 °C cooler than the average Atokan epeiric sea water at this site. Similarly, an ≈ 3·5‰ change in the δ^{18}O of sea water as the result of an increase in ice volume alone seems unlikely, as the magnitude of the change is greater than that associated with the Pleistocene glaciation (Schrag *et al.*, 1996). Furthermore, a glaciation would cause a sea-level fall and not the inferred deepening.

The carbon isotope shift is, perhaps, even more significant in terms of palaeoceanography.

Berger & Vincent (1986) pointed out that the excess removal of 1% of the oceanic reservoir of organic carbon results in a positive shift of 0·2‰. Assuming that this value is applicable to Carboniferous oceans, the amplitude of about 3‰, observed in section 1, thus indicates a considerable change in carbon fluxes. It is assumed that a palaeoceanographic event of this magnitude should be recognized elsewhere, but a middle Atokan shift in $\delta^{13}C$ is not obvious in other coeval sections in western Europe (Bruckschen *et al.*, 1999) or Russia (Grossmann *et al.*, 2002). The Eurasian isotope curves, however, are not at a comparable resolution. Therefore, the observed shift in Asturias is possibly not resolved. In terms of resolution, the only comparable data set is from the Arrow Canyon Range, Nevada, showing a lower Atokan carbon isotope shift from about 2‰ to 4‰ (Fig. 3 in Saltzman, 2003). The biostratigraphic correlation between Eurasian and North American stages is, however, not straightforward. To date, the Eurasian Vereian/Kashirian boundary cannot be reliably correlated with any of the Atokan zones in North America. For instance, *Profusulinella*, an important marker in the Arrow Canyon Range section, occurs in North America in strata that are younger than those in Eurasia. Considering all biostratigraphic data, however, it seems that the lower Atokan isotope shift as documented in Saltzman (2003) is about 1 myr older than the middle Atokan shift in Asturias. As far as is known, there is thus no published coeval middle Atokan positive shift in carbonate $\delta^{13}C$ and $\delta^{18}O$. This implies that a global origin of the Asturian isotope shift cannot be documented. To date, the local factors discussed here thus seem the more likely interpretation.

The local Atokan isotope shift in Spain cannot be traced downslope, i.e. below the range of sea-level fluctuations and early meteoric diagenesis, as the red marker is tectonically truncated seawards of section 1 (Fig. 1C). The isotopic composition of its slope and basin facies analogues therefore remains unknown. Nevertheless, none of the Bashkirian–Moscovian red markers in the slope deposits show a shift in $\delta^{13}C$ (Immenhauser *et al.*, 2002), whereas other, stratigraphically thin, red markers in the outer platform (Fig. 1C) show positive excursions of $< 2‰$. This suggests a relation between deepening pulses and isotopic composition that is restricted to shoalwater settings. In this respect, the Atokan shift differs from, for example, the Kinderhookian–lower Osagean (Saltzman, 2002) or the Early Cretaceous excursions (Weissert *et al.*, 1998). This is because these later events are recognized on a much wider scale and occur over a much wider bathymetric range.

CONCLUSIONS

Some high-amplitude deepening pulses recorded in platform-top settings are accompanied by local positive shifts in carbonate $\delta^{13}C$ and $\delta^{18}O$. The underlying mechanisms appear to involve expansion and contraction of chemically evolved platform-top water and varying degrees of early meteoric diagenesis. Both these factors can be observed in modern shoalwater settings and are equally applicable to their fossil counterparts. The isotope shifts documented here are robust and show an onshore–offshore trend similar to that known from modern epeiric seas. The superposition of basinwide change in palaeoceanographic parameters, such as sea-water geochemistry or temperature, with local epeiric effects might thus lead to ambiguous interpretations of the geochemical record of ancient shallow-marine seas. We do not doubt the relevance of palaeoceanographic trends related to carbon burial and climatic change, but propose that the model presented here merits consideration as an alternative explanation for local isotopic change.

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SUPPLEMENTARY MATERIAL

The following material is available at http://www.blackwellpublishing.com/products/journals/suppmat/sed/sed590/sed590sm.htm

Table S1. Data repository. An alternative model for carbon and oxygen isotope shifts.

REFERENCES

Allan, J.R. and **Matthews, R.K.** (1982) Isotope signatures associated with early meteoric diagenesis. *Sedimentology*, **29,** 797–817.

Berger, W.H. and **Vincent, E.** (1986) Deep-sea carbonates: reading the carbon isotope signature. *Geol. Rundsch.*, **75,** 249–269.

Bruckschen, P., Oesmann, S. and **Veizer, J.** (1999) Isotope stratigraphy of the European Carboniferous: proxy signals for ocean chemistry, climate and tectonics. *Chem. Geol.*, **161,** 127–163.

Della Porta, G., Kenter, J.A.M., Immenhauser, A. and **Bahamonde, J.R.** (2002) Lithofacies character and architecture across a Pennsylvanian inner-platform transect (Sierra de Cuera, Asturias, Spain). *J. Sed. Res.*, **72,** 898–916.

Erbacher, J., Thurow, J. and **Littke, R.** (1996) Evolution patterns of radiolaria and organic matter variations: a new approach to identify sea-level changes in mid-Cretaceous pelagic environments. *Geology*, **24,** 499–502.

Glumac, B. and **Walker, K.R.** (1998) A Late Cambrian positive carbon-isotope excursion in the southern Appalachians: Relation to biostratigraphy, sequence stratigraphy, environments of deposition, and diagenesis. *J. Sed. Res.*, **68,** 1212–1222.

Grossmann, E.L., Bruckschen, P., Mii, H.-S., Chuvashov, B.I., Yancey, T.E. and **Veizer, J.** (2002) Carboniferous paleoclimate and global change: Isotopic evidence from the Russian Platform. In: *Carboniferous Stratigraphy and Paleogeography in Eurasia*, pp. 61–71. Institute of Geology and Geochemistry, Russian Academy of Sciences, Urals Branch, Ekaterinburg.

Harland, W.B., Armstrong, R.L., Cox, A.V., Craig, L.E., Smith, A.G. and **Smith, D.G.** (1990) *A Geologic Time Scale*. Cambridge University Press, New York, 265 pp.

Holmden, C., Creaser, R.A., Muehlenbachs, K., Leslie, S.A. and **Bergström, S.M.** (1998) Isotopic evidence for geochemical decoupling between ancient epeiric seas and bordering oceans: Implications for secular curves. *Geology*, **26,** 567–570.

Immenhauser, A., Kenter, J.A.M., Ganssen, G., Bahamonde, J.R., van Vliet, A. and **Saher, M.H.** (2002) Origin and significance of isotope shifts in Pennsylvanian carbonates (Asturias, NW Spain). *J. Sed. Res.*, **72,** 82–94.

Jenkyns, H.C. (1980) Cretaceous anoxic events: from continents to oceans. *J. Geol. Soc. London*, **137,** 171–188.

Kenter, J.A.M., Hoeflaken, F., Bahamonde, J.R., Bracco-Gartner, G.L., Keim, L. and **Besems, R.E.** (2003) Anatomy and lithofacies of an intact and seismic-scale Carboniferous carbonate platform (Asturias, NW Spain): analogues of hydrocarbon reservoirs in the Pricaspian Basin (Kazakhstan). In: *Paleozoic Carbonates of the Commonwealth of Independent States (CIS): Subsurface Reservoirs and Outcrop Analogs* (Eds W. Zempolich and H. Cook), *SEPM Spec. Publ.*, **74,** 185–207.

Kievman, C.M. (1998) Match between late Pleistocene Great Bahamas Bank deep-sea oxygen isotope records of sea level. *Geology*, **26,** 635–638.

Lloyd, M.R. (1964) Variations in the oxygen isotope ratios of Florida Bay mollusks and their environmental significance. *J. Geol.*, **72,** 84–111.

Lohman, K.C. (1988) Geochemical patterns of meteoric diagenetic systems and their application to studies of paleokarst. In: *Paleokarst* (Eds N.P. James and P.W. Choquette), pp. 58–80. Springer, Berlin.

Magaritz, M. (1983) Carbon and oxygen isotope composition of recent and ancient coated grains. In: *Coated Grains* (Ed. T.M. Peryt), pp. 27–37. Springer, Berlin.

Marshall, J.D. and **Middleton, P.D.** (1990) Changes in marine isotopic composition and the late Ordovician glaciation. *J. Geol. Soc. London*, **147,** 1–4.

Maynard, J.R. and **Leeder, M.R.** (1992) On the periodicity and magnitude of Late Carboniferous glacio-eustatic sea-level changes. *J. Geol. Soc. London*, **149,** 303–311.

Mii, H.-S., Grossman, E.L. and **Yancey, T.E.** (1999) Carboniferous isotope stratigraphies of North America: Implications for Carboniferous paleoceanography and Mississippian glaciation. *Geol. Soc. Am. Bull.*, **111,** 960–973.

Patterson, W.P. and **Walter, L.M.** (1994) Depletion of ^{13}C in seawater ΣCO_2 on modern carbonate platforms: Significance for the carbon isotopic record of carbonates. *Geology*, **22,** 885–888.

Preat, A., Mamet, B., Bernard, A. and **Gillan, D.** (1999) Role of microbial organisms in the formation of Paleozoic red matrices, Devonian, Montagne Noire. *Rev. Micropaléontol.*, **42,** 161–182.

Romanek, C.S., Grossman, E.L. and **Morse, J.W.** (1992) Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochim. Cosmochim. Acta*, **56,** 419–430.

Ross, C.A. and **Ross, J.P.R.** (1988) Late Paleozoic transgressive-regressive deposition. In: *Sea-Level Change: an Integrated Approach* (Eds C.K. Wilgus, B.S. Hastings, C.G.StC. Kendall, H.W. Posamentier, C.A. Ross and J.C. Van Wagoner), *SEPM Spec. Publ.*, **42,** 227–247.

Saltzman, M.R. (2002) Carbon and oxygen isotope stratigraphy of the Lower Mississippian (Kinderhookian-lower Osagean), western United States: implications for seawater chemistry and glaciation. *Geol. Soc. Am. Bull.*, **98,** 475–487.

Saltzman, M.R. (2003) The Late Paleozoic ice age: oceanic gateway or pCO$_2$? *Geology*, **31,** 151–154.

Schlager, W. (1999) Scaling of sedimentation rates and drowning of reefs and carbonate platforms. *Geology*, **27,** 183–186.

Schrag, D.P., Hampt, G. and **Murray, D.W.** (1996) Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean. *Science*, **272,** 1930–1932.

Shackleton, N.J. (1987) Oxygen isotopes, ice volume and sea level. *Quatern. Sci. Rev.*, **6,** 183–190.

Soreghan, G.S. and **Dickinson, W.R.** (1994) Generic types of stratigraphic cycles controlled by eustasy. *Geology*, **22,** 759–761.

Weissert, H., Lini, A., Föllmi, K.B. and **Kuhn, O.** (1998) Correlation of Early Cretaceous carbon isotope stratigraphy and platform drowning events: a possible link? *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **137,** 189–203.

Weissert, H.J., McKenzie, J.A. and **Channel, J.E.T.** (1985) Natural Variations in the Carbon Cycle during the Early Cretaceous. In: *The Carbon Cycle and Atmospheric CO$_2$: Natural Variations Archean to Present* (Eds E.T. Sundquist and W.S. Broeker), *Am. Geophys. Union Monogr.*, **32,** 531–546.

Wilson, J.L. (1975) *Carbonate Facies in Geologic History*. Springer, Berlin, 471 pp.

Wright, V.P. (1996) Use of paleosols in sequence stratigraphy of peritidal carbonates. In: *Sequence Stratigraphy in British Geology* (Eds S.P. Hesselbo and D.N. Parkinson), *Geol. Soc. London Spec. Publ.*, **103,** 63–74.

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