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Carbon cycle models based on extreme changes in δ^{13}C: an example from the lower Mississippian

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Abstract

The Lower Mississippian $\delta^{13}C_{carb}$ excursion is one of the largest in the Phanerozoic, reaching ≥+7‰ in parts of western North America. Two new sections analyzed in Belgium and the Ural Mountains record the event, but peak values are ≤+5.5‰. The presence of key conodont zones allows for good correlation between Europe and North America, and indicates that a major time gap cannot account for the differences in $\delta^{13}C_{carb}$. Patterns of diagenetic alteration are similar among sections and also do not appear to fully explain the lower values in European carbonate. The observed variability of several per mil, which is typical for Paleozoic excursions that are also recorded in epeiric sea carbonates, likely reflects a significant role for local carbon cycling in δ^{13}C of dissolved inorganic carbon. Enhanced regeneration of phosphate under anoxic conditions in western North American basins is interpreted to have increased biological pumping of ^{12}C and locally elevated δ^{13}C relative to mean surface ocean water. The lower δ^{13}C in the European sections is interpreted to be more representative of the global surface oceans, rather than having been influenced by influx of respired ^{12}C during increased water mass residence time on the shelf. The interpretation of the influence of local carbon cycling on $\delta^{13}C_{carb}$ has implications for calculations of global organic carbon burial rates. Model input of a shift to values of ≥+7‰ predicts steady-state increases in the fraction of carbon buried as organic matter of as much as 50–75‰, assuming no changes in the riverine input. This would require a rapid buildup of extensive global sinks for C_{org} that could accommodate ~1.5×10^{20} g of excess burial above and beyond the steady state during the ~2 Myr event. However, use of a lower value for $\delta^{13}C_{carb}$ (closer to the +5.5‰ in European sections) in global models makes it easier to account for carbon storage in basins such as the Antler and related foreland basins of the western margin of Euramerica, in addition to the unknown amounts buried in deep-sea environments during the Early Mississippian.

Keywords: Mississippian; Carbon isotope; Belgium; Urals; Nevada

1. Introduction

Secular trends in the carbon isotope compositions of marine carbonates ($\delta^{13}C_{carb}$) can provide a robust and

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virtually uninterrupted proxy indicator of global imbalances in organic carbon burial rates. The $\delta^{13}C_{carb}$ curve has thus had a long history of usage in models of atmospheric O_2 and CO_2 levels (e.g., Junge et al., 1975; Garrels and Lerman, 1984; Kump and Garrels, 1986; Shackleton, 1987; Des Marais et al., 1992; Berner, 1990, 2001, 2003; Derry and France-Lanord, 1996; Petsch and Berner, 1998; Hayes et al., 1999). While these previous efforts have been largely focused on the redox significance of long-term gradual trends ($\geq 10^7$ yr) in $\delta^{13}C_{carb}$, a more volatile record is becoming apparent that includes numerous short-term excursions lasting a few million years or less. Transient $\delta^{13}C_{carb}$ anomalies represent an emerging challenge to current models of the geochemical carbon cycle and typically coincide with abrupt environmental change (Kump and Arthur, 1999; Broecker and Peacock, 1999; Schrag et al., 2002; Berner, 2002; Rothman et al., 2003; Goddéris and Joachimski, 2004; Bartley and Kah, 2004). One of the largest such $\delta^{13}C_{carb}$ excursions in the Phanerozoic appears to have taken place in the Early Mississippian (Mii et al., 1999; Bruckschen et al., 1999), reaching a peak of $\geq$+7‰ in parts of western North America (Saltzman, 2002, 2003a). Peaks of this magnitude have been observed during the Late Ordovician (Finney et al., 1999; Kump et al., 1999) and are similar to those preceding some glaciations in the Neoproterozoic 'Snowball Earth' interval (e.g., Knoll et al., 1986; Kaufman and Knoll, 1995; Hoffman et al., 1998; Hoffman and Schrag, 2002). However, because observed $\delta^{13}C_{carb}$ peaks in ancient epeiric sea environments can vary in magnitude by several per mil due to local carbon cycling (e.g., Patzkowsky et al., 1997; Holmden et al., 1998; Immenhauser et al., 2002, 2003), there is uncertainty as to which values to use in models that calculate global changes in carbon reservoir sizes or fluxes.

Model input of a large $\delta^{13}C_{carb}$ shift to values of $\geq$+7‰, such as observed in the Lower Mississippian excursion, predicts a steady-state increase in the fraction of carbon buried as organic matter of as much as 50–75‰. This requires a relatively rapid buildup of extensive global sinks for C_{org} that could accommodate ~1.5×10^{20} g of excess burial (i.e., above and beyond the steady state) during the ~2 Myr event, using Phanerozoic average flux values in Kump and Arthur (1999). These average starting values include an organic carbon burial flux of 1×10^{19} mol C/Myr with a $\delta^{13}C$=−29‰ a carbonate carbon burial flux of 4×10^{19} mol C/Myr with $\delta^{13}C$=1‰, which change to ~1.9×10^{19} moles C/Myr and 3.2×10^{19} mol C/Myr, respectively, as dictated by the enhanced carbon burial associated with a +7‰ shift in $\delta^{13}C_{carb}$. Although a useful first approximation, this calculation assumes that the combined riverine C and metamorphic–volcanic C fluxes were constant at steady state during the Mississippian ($\delta^{13}C$=−22‰ for organic carbon weathering, −5‰ for volcanic degassing, and 0‰ for carbonate weathering), which may not be the case (e.g., Kump et al., 1999; Goddéris and Joachimski, 2004).

Based on the isotope mass balance calculations driven by observed changes in $\delta^{13}C$, it has been suggested that the Lower Mississippian episode of enhanced organic carbon burial may be linked to drawdown of atmospheric CO_2 levels and the beginnings of the Late Paleozoic ice age (Mii et al., 1999; Bruckschen et al., 1999; Saltzman et al., 2000a). The increased carbon burial should also have had a major impact on modeled atmospheric O_2 levels (Kump, 1989, 1993; Petsch and Berner, 1998; Berner, 2001), depending on compensating factors such as oxidation of sulfide in the Early Mississippian (Kampschulte et al., 2001). The true impact of these changes in carbon burial on the CO_2 and O_2 contents of the atmosphere, however, depends on the size of the modeled $\delta^{13}C_{carb}$ excursion. The purpose of this paper is to evaluate the significance of regional variation in the magnitude of the Lower Mississippian $\delta^{13}C_{carb}$ excursion by: 1) expanding the geographic data base for the event outside of North America to include sections in Belgium and the northern Ural Mountains; 2) relating the observed variations to local versus global changes in carbon and nutrient cycling; and 3) examining the sensitivity of excess organic carbon burial calculations to different $\delta^{13}C_{carb}$ peak values.

Currently, the Lower Mississippian $\delta^{13}C_{carb}$ excursion remains poorly documented outside of North America, so far based on three brachiopod samples from Belgium (Bruckschen and Veizer, 1997). The need for an expanded geographic data base is underscored by previous studies of $\delta^{13}C_{carb}$ excursions in Paleozoic epeiric seas, which indicate that local variations in peak values are typically $\geq$+2‰, and thus significantly larger than would be predicted based on the modern surface oceans (~0.5‰ separates the tropical to subtropical seas today; Gruber et al., 1999).

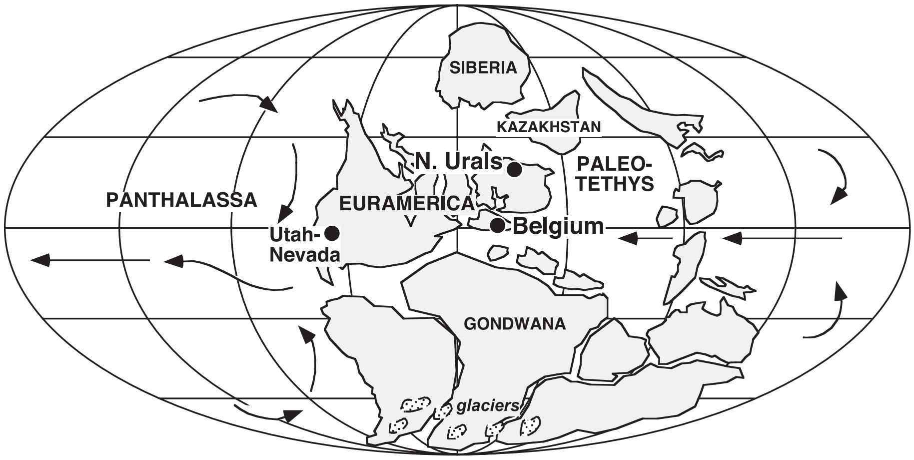

Fig. 1. Early Mississippian paleogeography after Scotese and McKerrow (1990). New $\delta^{13}C$ data from Belgium and the Northern Urals of eastern Euramerica are compared with the Nevada–Utah region of western Euramerica. Arrows indicate generalized ocean currents, and minor glaciers are shown on Gondwana (from Saltzman, 2003b).

Examples of variable $\delta^{13}C_{carb}$ peaks in the Paleozoic include the well-known Late Ordovician Hirnantian excursion, in which the positive shift from ~ +1‰ to +7‰ observed in Nevada only reaches +4‰ at Anticosti Island in eastern Canada (Brenchley et al., 1994; Finney et al., 1999); and a positive $\delta^{13}C$ excursion in the Late Silurian (Ludlow), with observed peaks of ~ +5‰ in parts of central Europe and North

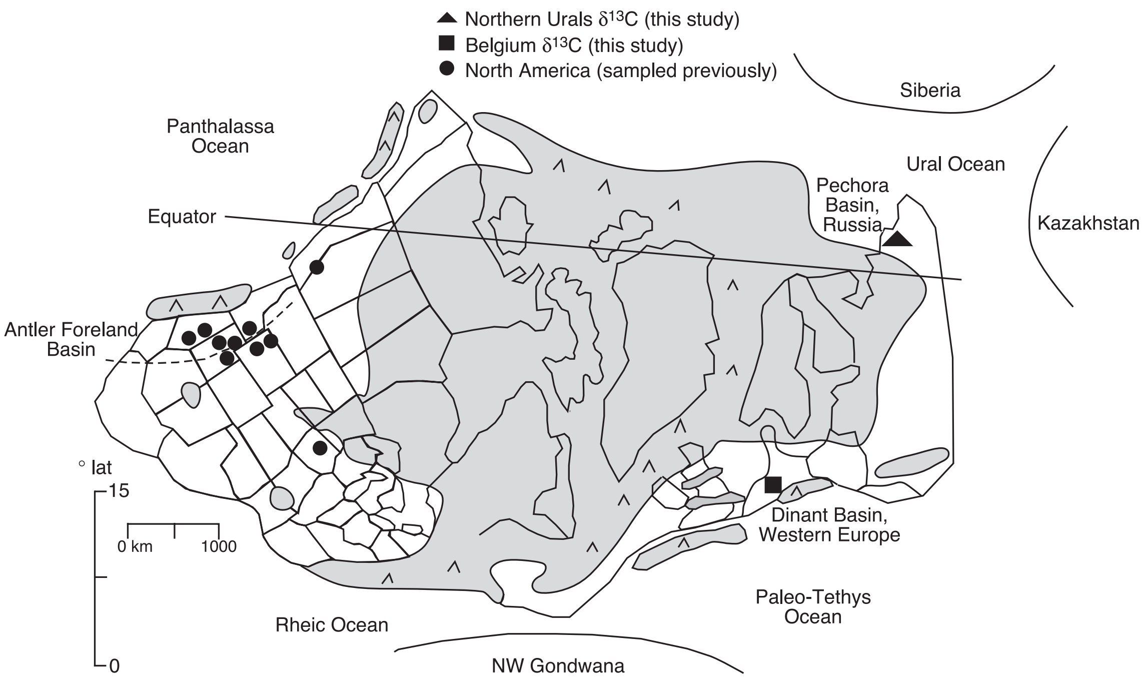

Fig. 2. Early Mississippian paleogeography of Euramerica for the Kinderhookian and early Osagean Stages (Tournaisian) after Witzke (1990). Filled circles represent 10 previously studied localities in North America that record a large positive $\delta^{13}C$ excursion (Nevada, Utah, Idaho, Wyoming, Iowa, and Alberta; Budai et al., 1987; Mii et al., 1999; Buggisch and Haas, 2000; Saltzman, 2002, 2003a). New sections in Belgium and Northern Urals are indicated. Land areas are shaded, and mountains shown by inverted V symbol.

America (Kaljo et al., 1997; Saltzman, 2001) that reach as high as +8‰ to +12‰ in Sweden and Australia (Andrew et al., 1994; Wenzel and Joachimski, 1996; Bickert et al., 1997; Azmy et al., 1998; Wigforss-Lange, 1999). Although possible causes of local variability in $\delta^{13}C_{carb}$ include depositional hiatuses (Brenchley et al., 2003) and diagenetic alteration (e.g., Immenhauser et al., 2002, 2003; Railsback et al., 2003), it is likely that local oceanographic factors also play an important role, particularly when there is good independent evidence for continuous sedimentation or similar patterns of diagenesis.

In order to address possible local variations in the absolute magnitude of the Lower Mississippian $\delta^{13}C_{carb}$ excursion, we have examined carbonates from two new sections on the eastern margins of Euramerica (Fig. 1). These successions in Belgium and the Northern Ural Mountains can be correlated with previously studied sections in western Euramerica using conodont-based and foram-based biostratigraphy. Correlations are particularly well established for the Belgium succession, which has been the subject of high-resolution stratigraphic investigations spanning more than three decades (e.g., Paproth et al., 1983; Conil et al., 1990; Hance et al., 2002) and is commonly referred to in investigations of time-correlative strata in other parts of the world (Webster and Groessens, 1990). Our results confirm both the global significance of the large positive $\delta^{13}C$ excursion in the Lower Mississippian and also the presence of variations in observed peaks, which likely reflect superimposed local effects of nutrient cycling in western Euramerican basins. Based on these results, the use of the lower European $\delta^{13}C$ values (~ +5.5‰) to calculate steady-state changes in the fraction of carbon buried as organic matter seems most reasonable.

2. Geological background

2.1. The Namur-Dinant basin of southern Belgium

The Namur-Dinant basin in southern Belgium formed the northern part of the larger Rheno-Hercynian basin (Hance et al., 2002), which bordered the Paleo-Tethys ocean (Fig. 2). The basement in this region was originally a subunit of the Avalonia Plate that collided with Baltica during Siluro-Devonian time (Ziegler, 1989). Renewed subsidence formed the Rheno-Hercynian basin in latest Devonian and early Carboniferous time as a result of the encroachment of Gondwana from the south, and an epeiric sea developed over the region extending from southern Ireland through northern Germany to southeastern Poland. Following a period of dominantly clastic deposition during a major latest Devonian regression in the basin, a carbonate ramp formed during subsequent transgression in the Tournaisian and evolved into a rimmed shelf by early Visean time (Hance et al., 2002). Several distinct depositional settings have been recognized within the Namur-Dinant Basin based on thickness and facies trends (including the presence of Waulsortian buildups), and the outcrops examined here (Fig. 3) represent the Namur, Condroz, and Dinant sedimentation areas of Hance et al. (2002).

The sampled section for $\delta^{13}C$ is a composite of five nearby segments (Fig. 3) beginning in the upper part of the Hastiere Limestone at a level that is just below the

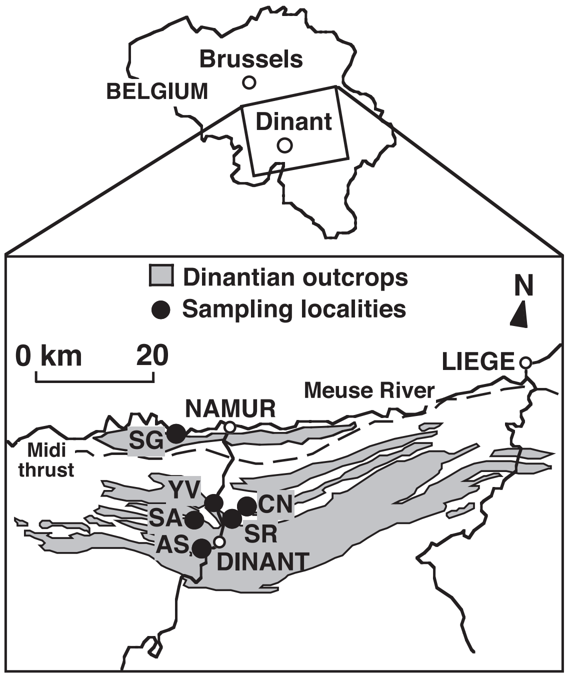

Fig. 3. Locality map of the Dinant Basin in Belgium (after Hance et al., 2002) showing the positions of the six Lower Mississippian sections that were used in the composite section sampled for carbonate $\delta^{13}C$: SG=Soignes; YV=Yvoir; CN=Carriere Nutons; SA=Salet; SR=St. Roch; AS=Anseremme. Unfilled circles are major cities.

base of sequence 2 of Hance et al. (2002). The position of maximum flooding within sequence 2 is placed within the overlying Pont d' Arcole Shale, and the thick-bedded crinoidal limestones of the overlying Landeiles Formation form a highstand systems tract (Van Steenwinkel, 1990; Hance et al., 2002). Renewed transgression at the base of sequence 3 is represented by the argillaceous limestones of the Hun Member of the du Bocq Formation, with the overlying Yvoir and Ourthe Limestones and their Waulsortian equivalents forming the progradational highstand deposits. No evidence of exposure horizons or karstic surfaces has been recognized in the region of the Namur-Dinant basin sampled (Hance et al., 2002). The conformable nature of the facies transitions between depositional sequences in the study area is consistent with the completeness of the recognized biostratigraphy in the region.

The Lower Mississippian of Belgium contains the type sections of the Dinantian subsystem, and is richly fossiliferous and well documented in terms of both foraminifera and conodont zones (Webster and Groessens, 1990). The critical zonal horizon that can be recognized globally is the last occurrence of the conodont taxon *Siphonodella*, which marks the base of the overlying *typicus* zone of the standard zonation (Sandberg et al., 1978; Lane et al., 1980), equivalent to the *Polygnathus communis carina* zone of Groessens (1971) (see also Thompson and Fellows, 1970; Lane, 1974, 1978; Carman, 1987; Chen et al., 1994). This horizon is tightly constrained to the transition zone between the Hun and Yvoir Limestone Members of the du Bocq Formation by the collections of Groessens (1971), and corresponds to the Hastarian–Ivorian stage boundary (mid-Tournaisian). This level can be confidently correlated with Kinderhookian–Osagean stage boundary in North America (Webster and Groessens, 1990). Additional collections containing *Siphonodella crenulata* and *cooperi*, as well as *Gnathodus cuneiformis* and *Scaliognathus anchoralis* also provide useful tie points with sections in North America and the Ural Mountains.

2.2. The Pechora Basin of the Northern Urals, Russia

The Pechora Basin formed on the northeastern margin of the East European Platform (Fig. 4), which underwent renewed subsidence in the Late Devonian and Early Mississippian above a westward-dipping Uralian subduction zone (Nikishin et al., 1996). A

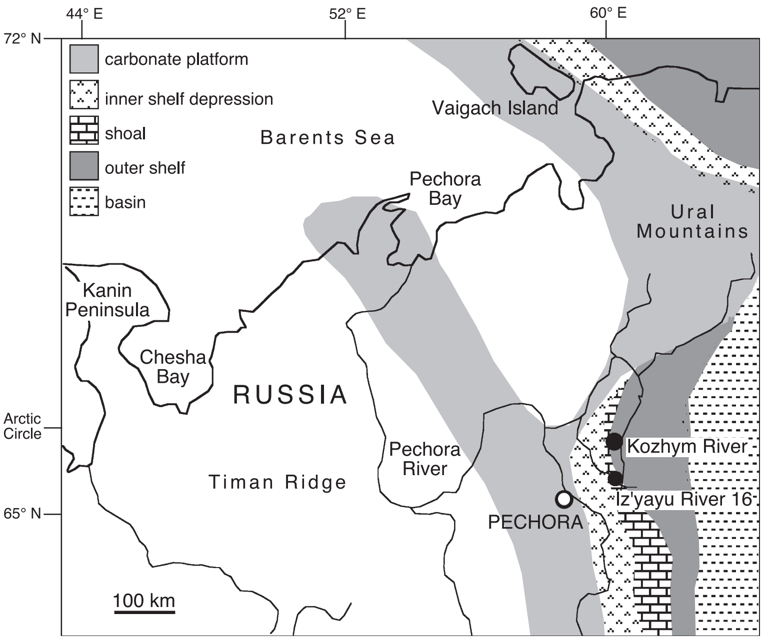

Fig. 4. Locality map and paleogeography of the Northern Urals region (Sobolev et al., 2000; Zhuravlev, 2000) showing the positions of the two Lower Mississippian sections that were used in the composite $\delta^{13}C$ section.

rimmed carbonate platform developed with widespread organic buildups (stromatoporoid–microbial) forming the outer shelf margin (Antoshkina, 1998) and a narrow transition zone into a deep basin setting. The stratigraphic sequence described by Ulmishek (1988) and Sobolev et al. (2000) indicates that the Lower Mississippian carbonates formed a progradational, basin-filling deposit during a highstand of sea level. The two segments examined here for $\delta^{13}C$ (Iz'yauy and Kozhym River sections; Fig. 4) represent outer platform facies close to the break in slope. Carbonate lithologies are predominantly skeletal (crinoid, foram, bryozoan, and coral) packstone to wackestone, with minor algal bioherms and abundant chert. A lack of exposure features and karstic surfaces indicates a relatively conformable sequence (Sobolev et al., 2000).

Biostratigraphic zonation for the Northern Urals is based primarily on conodonts at the Kozhym River section and foraminifera in the Iz'yayu section (Zhuravlev et al., 1999; Sobolev et al., 2000). The *Siphonodella isosticha* standard conodont zone of Sandberg et al. (1978) is equivalent to the *Siphonodella obseleta–S. isosticha* shallow water zone of the Northern Urals (Zhuravlev et al., 1999; Sobolev et al., 2000), which is represented by a low-diversity interval in skeletal limestones of the lower part of the Kozhym River section. Conodonts are rare in the Izyayu (Iz-16) section, but foraminifera present in the lower part of the section include *Tournayella* (Y.A. Vevel, personal communication), which represents the upper part of the *Chernyshinella glomiformis* foraminifer zone. This zone is correlated with the lowermost Ivorian Cf2 zone of the Belgium succession, which includes in its lower part the *typicus* zone of the standard conodont zonation (Webster and Groessens, 1990).

3. Methods and results

3.1. Sample selection and rationale

Brachiopod calcite is considered to be the most reliable component for stable isotope analysis in the Mississippian (Mii et al., 1999; Bruckschen et al., 1999). However, brachiopods are not continuously available for high-resolution chemostratigraphy in the studied sections. For $\delta^{13}C$ analysis, fine-grained, micritic components appear to be a reliable alternative (Joachimski and Buggisch, 1993; Kump et al., 1999; Saltzman, 2003a), although the same does not hold true for the more easily reset $\delta^{18}O$ values. Many authors have examined the reliability of fine-grained, micritic components for the Paleozoic (Gao and Land, 1991; Saltzman et al., 1998, 2004; Kump et al., 1999; Montañez et al., 2000; Joachimski et al., 2002; among others) and confidence in this methodology is based on several lines of evidence. First, comparisons of brachiopod calcite and micrite-based $\delta^{13}C$ curves for the same time periods are possible using the literature, and are both found to yield similar trends in the Mississippian (Mii et al., 1999; Saltzman, 2002, 2003b), Ordovician (e.g., Marshall et al., 1997; Finney et al., 1999), and Silurian (e.g., Azmy et al., 1998; Saltzman, 2001). Second, high-resolution micrite-based $\delta^{13}C$ curves are reproducible in cases where it is possible to confidently correlate sections between continents using biostratigraphy (e.g., Middle Ordovician in Ainsaar et al., 1999; Late Cambrian in Saltzman et al., 2000b; Late Devonian in Joachimski et al., 2002). In addition, the results of quantitative modeling studies have shown that $\delta^{13}C$ values, unlike $\delta^{18}O$, are typically rock-buffered for a wide range of diagenetic environments that are commonly observed in ancient platform carbonates (Banner and Hanson, 1990).

Even though there is good potential for reliable $\delta^{13}C$ results using micrites in Paleozoic successions, diagenetic alteration is a concern, particularly in more heterogeneous samples that average variable proportions of original lime mud and diagenetic phases. The proportion of meteoric diagenetic carbonate carrying a $\delta^{13}C$ different from seawater can be particularly high for shallowing-upward carbonate cycles capped by subaerial exposure surfaces. Exposure surfaces have been shown to be marked by abrupt, negative $\delta^{13}C$ deflections within a meter or less of the exposure horizon that result from incorporation of soil-derived CO_2 (Allan and Matthews, 1982; Goldstein, 1991; Railsback et al., 2003). For example, in thick sections characterized by relatively high-amplitude and high-frequency stratigraphic cyclicity such as the intracratonic basins of middle to late Pennsylvanian age in the southwestern U.S. (e.g., Orogrande and Pedregosa Basins), highly variable $\delta^{13}C$ trends with strongly negative excursions marking cycle tops have been observed (e.g., Algeo et al., 1992).

The $\delta^{13}C$ values in this study were derived primarily from micritic limestones drilled from fresh rock surfaces. We have attempted to avoid pitfall associated with diagenetic resetting by carefully selecting samples within our measured sections in various parts of the perserved marine sedimentary basin (see detailed section on primary versus secondary signals in $\delta^{13}C$ in the Discussion section 4.1 below). Powders were roasted under vacuum at 380 °C for 1 h to remove volatile contaminants, and isotope samples were reacted with 100% phosphoric acid at 75° C in an online carbonate preparation line connected to a Finnigan Mat 251 mass spectrometer. Analytical precision based on duplicate analyses and on multiple analyses of NBS19 was ≤0.04‰.

3.2. Carbon isotope profiles

In the Belgium succession, the lowest $\delta^{13}C$ values in the Hastiere Limestone at Anserreme are near 0‰ and rise to +2‰ in the lowermost samples taken in the Landelies Limestone, which overlies the unsampled Pont d'Arcole Shale (Fig. 5). A steady rise in $\delta^{13}C$ occurs in the Black Member of the Landelies Limestone sampled at the St. Roch quarry, reaching peak values of +5.3‰ in the overlying Hun Member of the du Bocq Formation. The $\delta^{13}C$ peak occurs at a level several meters below the last occurrence of *Siphonodella* in the Yvoir roadcut. Following a second peak in the Yvoir Limestone Member of the du Bocq Formation that is dated to the Ivorian *typicus* zone,

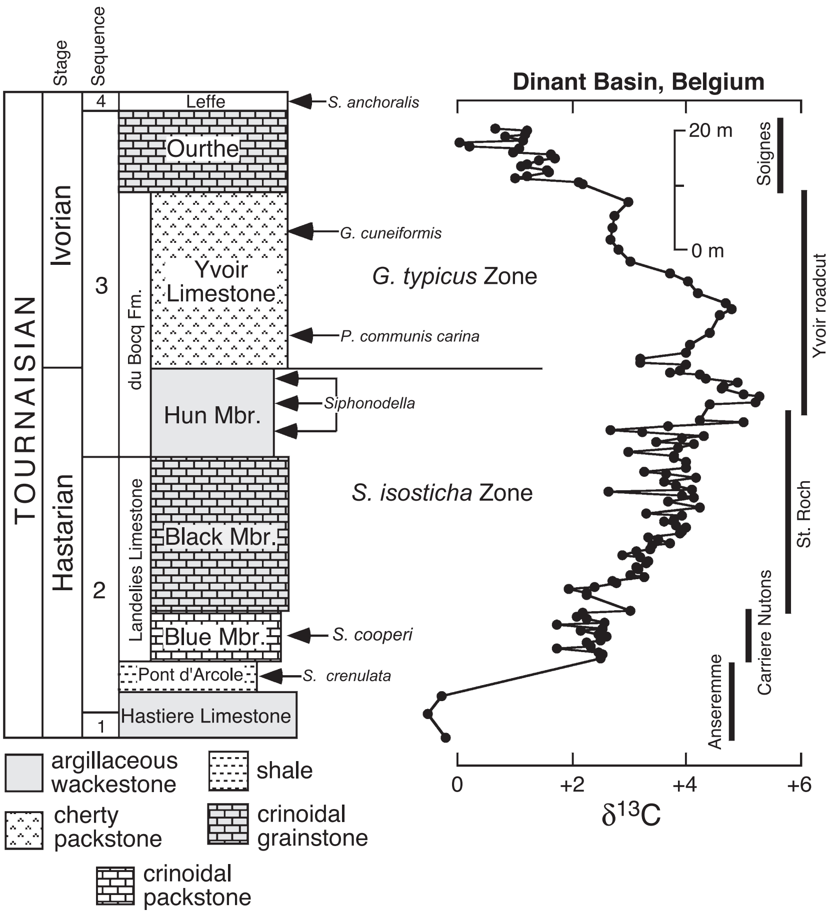

Fig. 5. Lithologic column $\delta^{13}C$ results from the Dinant Basin, Belgium (see Fig. 3). Biostratigraphic zonation and conodont horizons after Groessens (1971) and Webster and Groessens (1990). Depositional sequences after Hance et al. (2002).

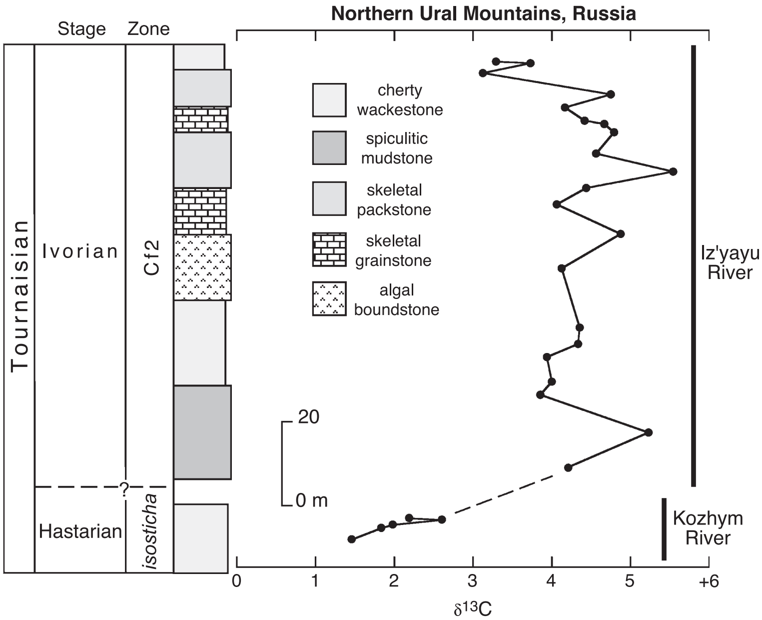

Fig. 6. Lithologic column $\delta^{13}C$ results from the Northern Urals (see Fig. 4). Biostratigraphic zonation and lithologic column after Sobolev et al. (2000) and Zhuravlev (2000).

values fall steadily to pre-excursion levels of 0‰ through the du Bayard Formation.

In the Northern Urals, samples from the lower part of the Kozhym River section that are dated to the Hastarian *isosticha* conodont zone are between +1‰ and +3‰. Samples from the basal part of the Ivorian strata in the Iz'yayu River section record values ≥+5‰ and stay between +4‰ and +5‰ for most of the section. A trend to values below +4‰ is observed in the topmost samples.

4. Discussion

The results from $\delta^{13}C$ analyses of Lower Mississippian sections in Belgium and the Ural Mountains reveal a positive excursion to peak values between +5‰ and +5.5‰. In time equivalent sections in western North America, corresponding to the *isosticha* and *typicus* conodont zones, a larger positive shift to values ≥+7‰ has been recorded (Fig. 7; Saltzman, 2003ab). Thus, although the positive $\delta^{13}C$ trends correlate well on opposite sides of the ancient Euramerican landmass and likely represent a global shift in the burial (or weathering) fraction of organic carbon, the difference in the net magnitude of the shift must relate to local factors. In the following sections, we first discuss the possible diagenetic and local paleoceanographic causes of the variable expression of the $\delta^{13}C$ excursion, and then examine the implications for estimates of organic carbon burial.

4.1. Primary versus secondary signals in $\delta^{13}C$

One possible explanation for the lower $\delta^{13}C$ values in European sections is that they have been preferentially altered by meteoric diagenesis relative to North American sections. There are numerous examples in which the $\delta^{13}C$ values of ancient limestones (Precambrian to Pleistocene) have been shifted towards lighter values beneath surfaces of subaerial exposure, reflecting the incorporation of oxidized organic carbon (pedogenic CO_2) in diagenetic phases (e.g., Allan and Matthews, 1982; Algeo et al., 1992; see summary table in Railsback et al., 2003). However, the sharp drops in $\delta^{13}C$ observed in these studies, with amplitudes commonly exceeding 4‰ in close proximity to the exposure surface (typically ~1–5 m depth; Railsback et al., 2003) have not been not observed near the peak of the

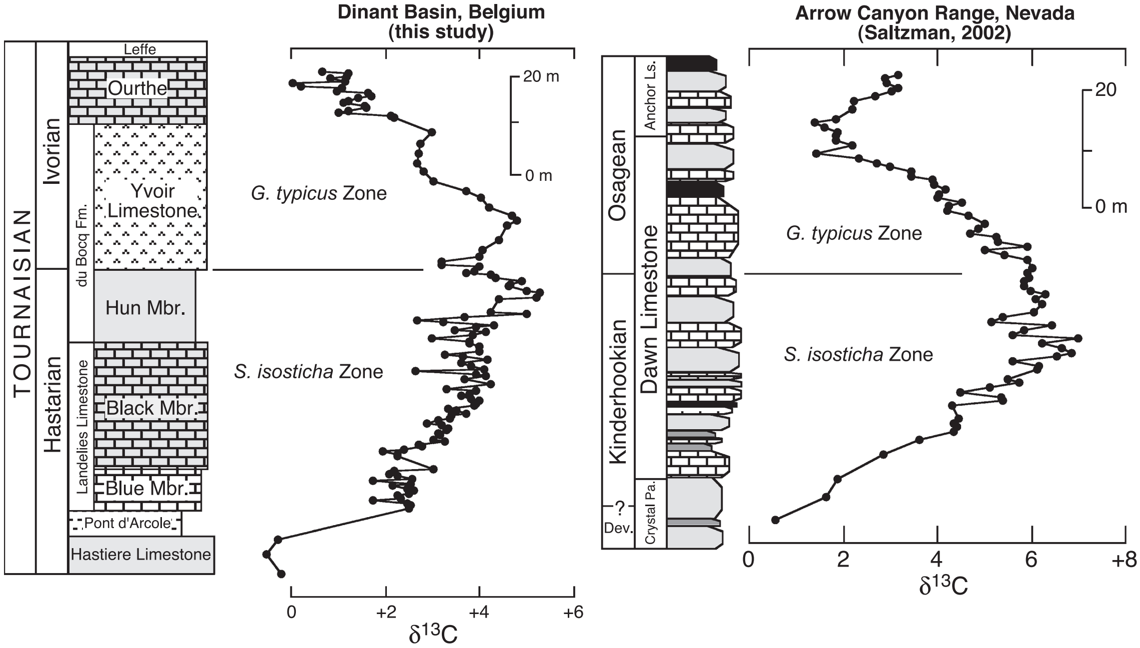

Fig. 7. Comparison of $\delta^{13}C$ results from the Dinant Basin, Belgium (Fig. 5) and Arrow Canyon, Nevada (see Saltzman, 2002). Note higher peak values in Nevada.

excursion in the intensively sampled section in the Dinant Basin (Fig. 5). Furthermore, several of the sections in western North America, which record the anomalously heavy $\delta^{13}C$ peaks, show $\delta^{18}O$ values that are as light (an indicator of meteoric diagenesis) or lighter than what is observed in these European sections (Fig. 8). Physical evidence for karstic or erosional surfaces (e.g., sandy, oxidization crusts, solution-enlarged joints and pits, fenestrae, mud-cracks, or evaporites; Goldstein, 1991; Algeo et al., 1992) is also lacking in the shallow water grainstone facies in the excursion interval in European sections. Although the evidence for exposure may have been erased during subsequent transgression, the sections do not display well-developed high-frequency, high-amplitude sea level cycles that are more characteristic of later Pennsylvanian sequences deposited under full glacial conditions (Algeo et al., 1992; Immenhauser et al., 2002, 2003). The more subdued sea level fluctuations in the Early Mississippian and the similar positions along ramp-like profiles of the sections compared would also likely reduce the potential for differential diagenesis to produce the observed variations in $\delta^{13}C$, as has been reported in more steep-sided rimmed shelf profiles of the Pennsylvanian (Immenhauser et al., 2002, 2003).

It is also possible that the lower $\delta^{13}C$ values in European sections reflect incomplete sections in which the main peak is truncated by erosion of non-deposition, which did not leave an obvious geochemical mark (as discussed above). However, in addition to the lack of physical evidence for prolonged subaerial exposure or submarine condensation, the sections appear biostratigraphically complete, particularly in Belgium where the conodont zonation spanning the *isosticha* and *typicus* conodont zones is well-documented and often used as a standard for global correlations (Webster and Groessens, 1990). The collections that define the boundary between these two successive zones (Fig. 5; *Siphonodella* and *Polygnathus communis carina*) are separated by a thin (~7 m) nondiagnostic interval that shows a conformable relationship with overlying and underlying sediments. Furthermore, the thickness of the excursion interval in the *isosticha* and *typicus* zones in Belgium indicates that sedimentation rates are at least as high as at Arrow Canyon, Nevada, which records heavier $\delta^{13}C$ values $\geq$+7‰ (Fig. 7). The similarity in

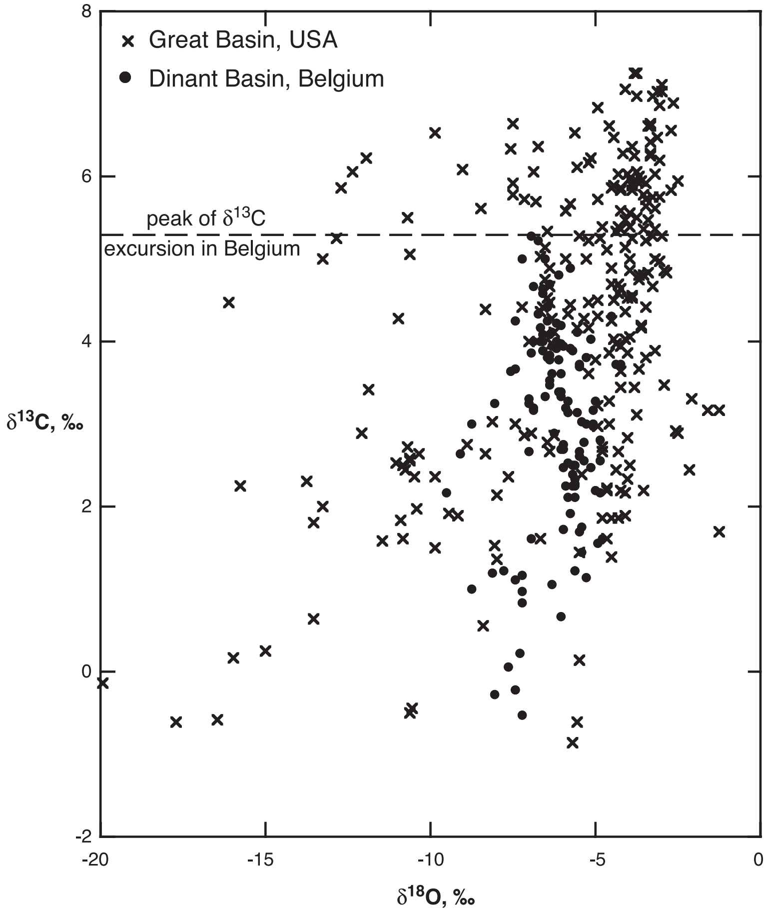

Fig. 8. Crossplot of δ^{13}C and δ^{18}O for Dinant Basin, Belgium (Fig. 5) and sections in Great Basin, USA (Arrow Canyon, Pahranagat, East Tintic, and Strawberry Creek sections from Saltzman, 2002, 2003a). Dashed line marks heaviest values recorded in Belgium, which is several per mil lower than the Great Basin.

accommodation rates also argues against the Belgium section being more prone to large-scale alteration of δ^{13}C values due to amalgamation of exposure surfaces (e.g., Railsback et al., 2003).

Additional uncertainty in the magnitude of the δ^{13}C peaks locally is also introduced by the fact that both European sections represent composite curves built from multiple segments. Because the Belgium curve is constructed using nearby, biostratigraphically well constrained, and overlapping sections that represent comparable paleogeographic settings on the carbonated platform in the Namur-Dinant basin, the full magnitude of the Lower Mississippian excursion is likely to have been adequately recorded in this region. In the Ural mountains, the curve (Fig. 6) is also constructed from two nearby sections in the Pechora Basin on the northeastern margin of the East European Platform. However, because these Ural sections represent shoal water carbonate (Iz'yayu River) and outer shelf (Kozhym River) environments, we cannot rule out the possibility that different positions within the paleo water mass (i.e., above and below the surface mixed layer) were sampled. For this reason, we consider the δ^{13}C curve in the Belgium composite section to be the most reliable record of the Lower Mississippian surface ocean environment in Europe and the discussion that follows emphasizes this record.

Although differences in diagenetic conditions or sediment accumulation may have played role in the δ^{13}C variation between regions (Fig. 7), we explore here the likelihood that the dominant control was local carbon cycling in widely separated epeiric sea water mass.

4.2. Regional variability in epeiric sea $\delta^{13}C$

The observed spatial variations in δ^{13}C between eastern and western Euramerica (≥2‰; Fig. 7) are large relative to the modern tropical to subtropical open oceans, which differ by ~0.5‰ (Gruber et al., 1999). The modern South China Sea, the largest marginal sea in the Pacific, also differs from the adjacent oceans by ≤0.5‰ (Lin et al., 1999). However, the ≥2‰ variations in Paleozoic epeiric seas are comparable to modern carbonate platforms of the Bahama Banks and Florida Bay (Lloyd, 1964; Patterson and Walter, 1994). In a rigorous study of a Middle Ordovician epeiric sea time slice constrained by regionally extensive altered volcanic ash beds, Holmden et al. (1998) delineated temperature–salinity-defined water masses ("aquafacies") that also varied in δ^{13}C by more than 2‰. Similarly, Immenhauser et al. (2002) used biostratigraphy and marker beds to document significant offsets in δ^{13}C between deep water, off-platform settings and the platform-top environment. These offsets were largest during lowstands of sea level that result in a relatively restricted platform-top water mass influenced by continual input of respired ^{12}C (Immenhauser et al., 2003). The observed spatial variability is often maintained during global δ^{13}C excursions, for example, in the Middle Ordovician (e.g., Patzkowsky et al., 1997; Ainsaar et al., 1999; Ludvigson et al., 2004). The even greater spread of values for other early Paleozoic $\delta^{13}C_{carb}$ excursions, most notably in the Late Ordovician (Brenchley et al., 1994, 2003; Kump et al., 1999; Finney et al., 1999) and Late Silurian (Andrew et al., 1994; Wenzel and Joachimski, 1996; Bickert et al., 1997; Azmy et al., 1998; Wigforss-Lange, 1999; Saltzman, 2001), further supports an important role for local carbon cycling.

Thus, although much uncertainty remains with regards to the residence time of carbon and water mass exchange rates in Paleozoic oceanic environments, sluggish or restricted circulation within epeiric seas and between epeiric seas and adjacent oceans is a likely explanation for the large observed δ^{13}C offsets compared to the modern oceans. The factors that cause the δ^{13}C of dissolved inorganic carbon ($\sum CO_2$) to vary in different parts of the modern surface ocean are temperature and nutrient contents (e.g., Kroopnick, 1985; Gruber et al., 1999). Input of nutrients and light carbon from respiration of organic matter occurs with increasing water mass residence times (or "aging") in the deep ocean (e.g., Kroopnick, 1985), which can also be observed in semirestricted water masses above modern carbonate platforms (Patterson and Walter, 1994). A temperature-dependent fractionation of about 1‰ per 10 °C cooling is associated with equilibrium air–sea exchange of CO_2, and thus cold surface waters in equilibrium with the atmosphere will generally have higher δ^{13}C values (Lynch-Stieglitz et al., 1995). This maximum fractionation is, however, nowhere fully achieved in today's oceans because surface waters are replaced too quickly. The thermodynamic fractionation can also be opposed by a bulk transfer (kinetic) effect related to invasion or evasion of atmospheric CO_2 during equilibration with the surface oceans (Lynch-Stieglitz et al., 1995).

The effect of differences in temperature and nutrient contents on δ^{13}C is perhaps best observed in the tropics, where upwelling at the equator brings isotopically light deep water to the surface. This water mass then becomes more positive in δ^{13}C by about 0.5‰, as it is carried in a southerly direction to about 15° S, at which point the thermodynamic effect begins to dominate and δ^{13}C values decrease again (Gruber et al., 1999). Because the epeiric sea carbonates examined here appear to have formed in tropical to subtropical water masses, a relatively narrow temperature range (20–30 °C) is expected and the relatively large $\delta^{13}C_{DIC}$ variations are most likely to reflect biological controls. If a negligible contribution from air–sea gas exchange is assumed, δ^{13}C values should show a good correlation with limiting nutrient levels (phosphate). This relationship can be determined for a given water mass using the following equation from Broecker and Maier-Reimer (1992):

$$\delta^{13}C - \delta^{13}C^{MO} = \Delta_{photo} \Big/ \sum CO_2{}^{MO} C \Big/ P_{org} \\ (PO_4 - PO_4{}^{MO}) \qquad (1)$$

where MO stands for mean ocean, Δ_{photo} is the photosynthetic fractionation factor, and C/P_{org} is the carbon to phosphorus ratio in marine organic matter. For the modern ocean (Δ_{photo}=−19‰, $\delta^{13}C^{MO}$=+0.5‰,

$\sum CO_2^{MO}$=2200 μmol/kg, PO_4^{MO}=2.2 μmol/kg, and C/P_{org}=128; after Broecker and Maier-Reimer, 1992), Eq. (1) becomes:

$$\delta^{13}C = 2.9 - 1.1PO_4 \quad (2)$$

From Eq. (2), the $\delta^{13}C$ of modern tropical and temperate surface waters, which averages 0.2 μmol/kg, is about 1.5‰ higher than surface waters of the Antarctic, which contains the highest PO_4 values (1.6 μmol/kg) in the surface oceans. The highest PO_4 values in the modern ocean are in the deep Pacific (up to 3 μmol/kg) and these waters have a $\delta^{13}C$ of about −0.3‰, which differs modestly from mean ocean carbon at +0.5‰ (2.2 μmol/kg; Broecker and Maier-Reimer, 1992). For the tropical to subtropical Late Paleozoic epeiric sea water masses examined here in North America (~+7‰) and Europe (~ +5 ‰) to differ in $\delta^{13}C$ by 2‰, the phosphate contents in North America should be 2 μmol/kg lower than Europe according to Eq. (2). If the North American epeiric sea is considered essentially phosphate-free (~0.2 μmol/kg in the modern ocean), then European surface waters would have phosphate contents comparable to parts of the modern deep ocean. However, this relationship may not be valid for all time periods. For example, if the value for Δ_{photo} in the Late Paleozoic was larger than the value of −19‰ used by Broecker and Maier-Reimer (1992), and closer to the maximum fractionation near −25% because of higher atmospheric pCO_2 levels or some other factor (see discussions in Popp et al., 1989, 1997; Freeman and Hayes, 1992; Bidigare et al., 1997; Hayes et al., 1999; Pancost et al., 1999; Royer et al., 2001), then Eq. (2) becomes:

$$\delta^{13}C = 3.7 - 1.5PO_4 \quad (3)$$

Eq. (3) results in a change in slope such that smaller differences in phosphate contents between water masses in Late Paleozoic epeiric seas will result in a greater separation of seawater $\delta^{13}C$ values. For example, an ~1 μmol/kg difference between water masses produces an ~1.5% spread of surface ocean $\delta^{13}C$ values in Eq. (3) compared to ~1% of separation using Eq. (2). The change in slope in Eq. (3) could similarly be accomplished by keeping Δ_{photo}=−19%, but using a higher burial ratio for C/P_{org}=168 compared to that used for the Redfield ratio by Broecker and Maier-Reimer (1992). A higher burial ratio for C/P_{org} may result from differences in oxygenation of deeper water masses (e.g., Van Cappellen and Ingall, 1994), despite a nearly constant Redfield ratio for C/P_{org}. Changes in the living C/P_{org} ratios are, however, also worth considering in light of the known changes in the dominance of various phytoplankton from the Paleozoic to the present day (Falkowski et al., 2004). A lowering of $\sum CO_2^{MO}$ to 1680 μmol/kg from the modern ocean value of 2200 μmol/kg would also produce the slope in Eq. (3), but seems unrealistic with pCO_2 levels at or near modern levels in the Late Paleozoic (Berner, 2003).

4.3. Paleogeographic controls on Early Mississippian $\delta^{13}C$ variability

An important question is what could have resulted in the seemingly higher phosphate contents (lower $\delta^{13}C$) in European epeiric seas as compared to water mass that covered western North America with its anomalously high $\delta^{13}C$ of ≥+7‰. Although plate reconstructions differ with respect to the position of equator across Euramerica (Figs. 1 and 2), coastal or equatorial upwelling in the Early Mississippian (Parrish, 1982) is a possible explanation for the lowered $\delta^{13}C$ of European carbonates. In the modern oceans, Bickert and Wefer (1999) document a lowering of the $\delta^{13}C$ of $\sum CO_2$ within the Namibia Upwelling area. A net influx of isotopically light waters from intermediate and deep ocean waters can also be achieved by “quasiestuarine flow” in epeiric sea settings, in which runoff and rainfall exceed evaporation on humid coastlines (Witzke, 1987; Bickert et al., 1997; Munnecke et al., 2003). Water mass restriction and delivery of light carbon from terrestrial environments are a third possibility (Patterson and Walter, 1994; Holmden et al., 1998; Immenhauser et al., 2002, 2003). These paleogeographic explanations would all imply that the western Euramerican (North American) values of ≥+7‰ are most representative of global mean ocean $\delta^{13}C$, and the European sections are lower due to local carbon cycling.

However, several observations do not seem to support the conclusion that European sections have undergone preferential lowering of $\delta^{13}C$ relative to mean ocean values. First, the Early Mississippian pre-excursion and postexcursion $\delta^{13}C$ ‘baseline’ appears to fall within a similar range near +1‰ in both regions of Euramerica (Fig. 7), although there is a clear need for additional data to better establish this relationship. Comparable baseline values would suggests that if equatorial or coastal upwelling related to plate tectonic setting was important, both regions were similarly affected. Second, a healthy shallow-water carbonate factory existed in both North American and European sections, including environments suitable for formation of open marine crinoidal packstones and coralline-brachiopod wackestones, which indicates comparable and generally oligotrophic, well-circulated water mass conditions during the excursion (cf. Hallock and Schlager, 1986; James, 1997). Carbonate platform drowning, which provides evidence for eutrophic or inimical conditions on the bank, occurs much later in time in both eastern and western Euramerica (in the upper part of the *typicus* conodont zone in western United States; Saltzman, 2003a; and not until the Namurian in Belgium; Hance et al., 2002).

An alternative paleoceanographic explanation must be consistent with this similarity in facies and baseline $\delta^{13}C$ values for the two opposite regions of Euramerica. We attribute the higher $\delta^{13}C$ values recorded in North American sections to enhanced phosphate regeneration and biological pumping of ^{12}C in a semirestricted foreland basin setting. Restriction of the foreland seaway from the adjacent Panthalassic ocean was accomplished by the rising Antler allochthon to the west (Jewell et al., 2000), which is well dated to the time of the isotopic excursion by conodonts (Johnson and Pendergast, 1981; Giles, 1996; Saltzman, 2002, 2003a). The deepest water mass in the axis of the foreland was dysoxic (laminated, organic-rich units; Saltzman et al., 2000a; Silberling et al., 2001) and a probable source of phosphate to the surface (cf. Van Cappellen and Ingall, 1994; Murphy et al., 2000). Because similar foreland basin settings existed farther north in Canada (Smith et al., 1993; Savoy, 1992), the water entering the narrow seaway in the Nevada–Utah area could have been depleted in ^{12}C relative to phosphate en route. However, these surface waters did not become eutrophic everywhere (≥1.0 μmol/kg phosphate; Hallock and Schlager, 1986), as indicated by the healthy carbonate factory in portions of the distal foreland above the pycnocline (Fig. 9). Ultimately, the regenerated phosphate was sequestered in phosphorites of post-excursion (Osagean) age throughout Nevada and Utah (Delle Phosphatic Member; Saltzman, 2003a). The lack of an equivalent interval of phosphatic deposition in Europe supports the notion that enhanced phosphate regeneration and biological pumping of ^{12}C may have been unique to western North America. As the ^{12}C-depleted western Euramerican (North American) water mass mixed with the adjacent oceans, global $\delta^{13}C$ values increased, but only to the extent observed in European sections examined here (~ +5.5‰).

4.4. Implications for mass balance and carbon burial

If the heaviest values obtained in European carbonate are most representative of the global surface ocean shift, a net $\delta^{13}C$ shift of about +3‰ would indicate a change in the burial fraction of organic carbon from 0.23 to 0.30. Using a 2-Myr duration for the $\delta^{13}C$ event, this translates into roughly 7.5×10^{19} g of excess carbon, revised down from the 1.5×10^{20} g calculated for a larger shift of ~ +6‰ (parameters from Kump and Arthur, 1999 are listed in the introduction). This represents a maximum value for excess carbon storage reflecting the relatively large total carbon burial flux used by Kump and Arthur (1999) as compared to others. For example, their value was four times larger than Shackleton (1987) (see also Arthur et al., 1987). It is important to also note that these calculations assume constant values for the photosynthetic discrimination factor and the $\delta^{13}C$ of the riverine input (−5‰), which Goddéris and Joachimski (2004) suggest is invalid.

Few studies have attempted to account for the excess organic carbon burial implied by positive $\delta^{13}C$ excursions. Arthur et al. (1987) estimated that the excess organic carbon burial that occurred during the +3‰ Cenomanian–Turonian excursion could be accounted for in pelagic shelf, slope, and deep-sea environments. These authors assumed that burial in deltaic-shelf environments, which represents nearly 83% of burial in the modern ocean (Berner, 1982), remained constant. Without deep-sea records, examination of those environments that were clearly important sinks for organic matter during the Cenomanian–Turonian is not possible for

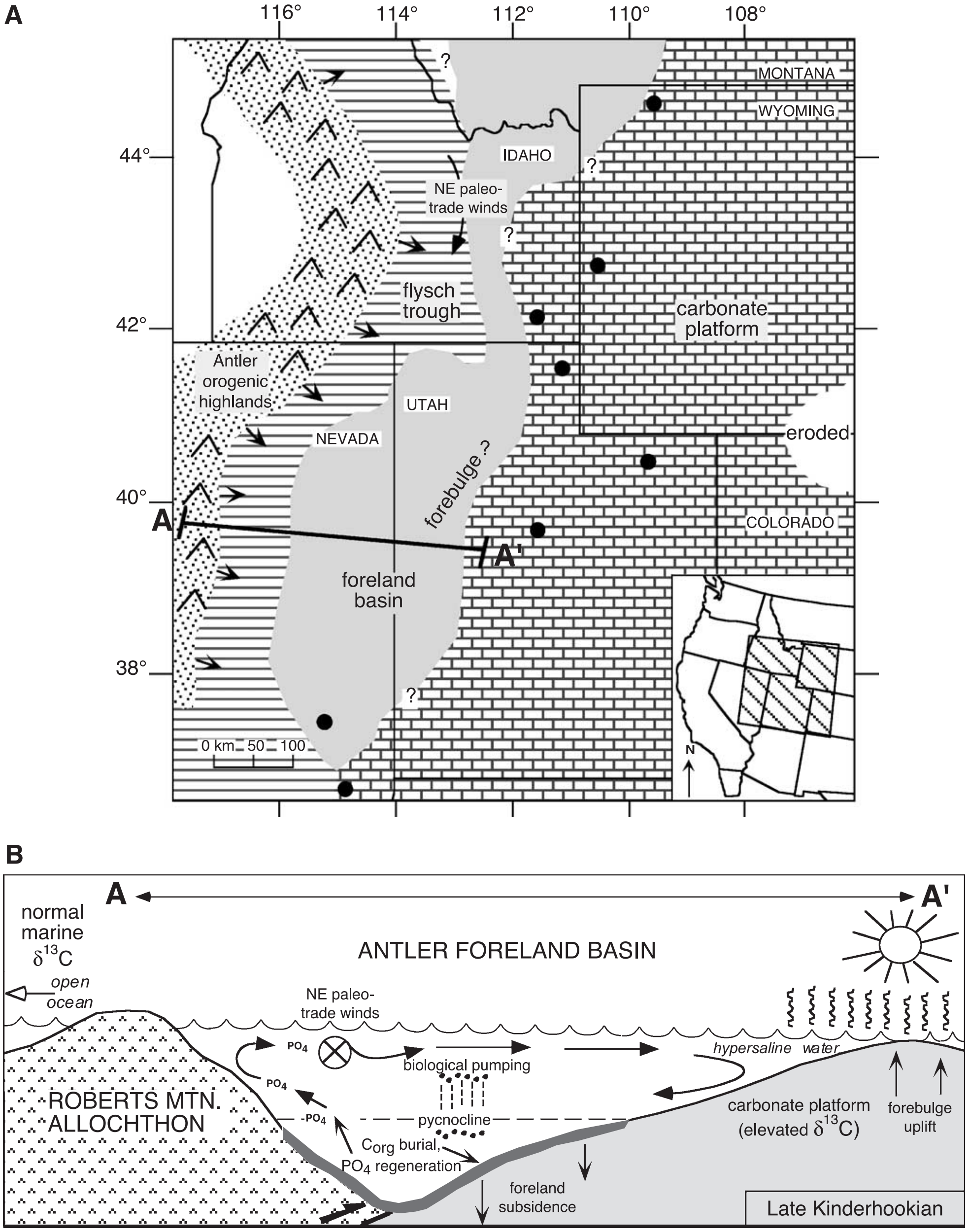

Fig. 9. (A) Paleogeographic map of the Antler foreland basin system, Great Basin, USA during the Late Kinderhookian (upper *S. isosticha* conodont zone). Filled circles represent sections that record elevated δ^{13}C values (≥+7‰) from Saltzman (2003a). (B) Paleoceanographic model for generation of δ^{13}C values that are isotopically heavier than the more open ocean values observed in European sections (≤+5.5‰). Water flowing in from the north (NE paleotrade winds) is progressively depleted in ^{12}C, while phosphate regeneration is enhanced under dysoxic conditions in the most rapidly subsiding portions of the foreland basin.

the Lower Mississippian excursion, but potential sites of significant organic carbon burial include rapidly subsiding foreland basins (e.g., Patzkowsky et al., 1997) that occur over much of the western North American Cordillera from Idaho to the Yukon (Smith et al., 1993). Calculation of burial amounts based on best estimates of the dimensions of the basin fill (1000 km×200 km) and likely TOC values (< 1%) for the ~200-m-thick excursion age sequences in Nevada and Utah come to ~1×10^{18} g C, a small percentage of the total excess estimated from isotope mass balance. Further north, additional units that may have stored organic carbon, including: 1) the Exshaw Formation in British Columbia (Savoy, 1992); 2) the Tuttle Formation, which includes thick (~900 m) siliciclastic sediments that crop out over a large area (~750 km×500 km) of northwestern Yukon, the District of Mackenzie, and east-central Alaska; and (3) the ~500-m 'black clastic' unit of the Earn Group in the southern Yukon (Gordey et al., 1987; Smith et al., 1993). The extremely thick (up to 3 km) accumulations of proximal terrigenous clastics in the Pioneer Mountains of central Idaho (Link et al., 1996) are also reasonably well dated to the excursion interval (late Kinderhookian *Siphonodella isosticha* conodont zone), and appear to be similar to what Silberling et al. (2001) describe as the potentially organic-rich Diamond Range sequence in Nevada (e.g., Dale Canyon Formation).

If the potential for carbon storage in basins globally during the late Kinderhookian and early Osagean falls short of the number required by isotopic mass balance, then alternative hypotheses for the δ^{13}C excursion must be explored. If the δ^{13}C excursion resulted in part from a positive shift in the carbon isotopic composition of the riverine flux, possibly in response to a relative increase in global carbonate weathering (e.g., Kump et al., 1999), this would lower the calculated organic carbon burial. Enhanced carbonate weathering that drove up riverine δ^{13}C worldwide is consistent with evidence for a sea level drop near the Kinderhookian–Osagean boundary in Euramerica (Saltzman, 2002). The target value of ~7.5×10^{19} g we seek to account for would also be an overestimate if the total throughput of carbon was significantly lower in the Lower Mississippian due to lower rates of volcanism and riverine carbon input (e.g., Derry et al., 1992; Schrag et al., 2002). Other factors must be considered, including the total mass of dissolved inorganic carbon in the oceans during the Lower Mississippian, which can potentially affect the magnitude of δ^{13}C excursions (Bartley and Kah, 2004).

5. Conclusions

Two new Lower Mississippian sections analyzed in Belgium and the Ural Mountains record a large $\delta^{13}C_{carb}$ excursion recognized in western North America, but peak values are almost 2‰ lower at ≤+5.5‰. Conodont-based correlations (*Siphonodella isosticha* and *G. typicus* zones) indicate that a major time gap cannot account for the differences in $\delta^{13}C_{carb}$ between Europe and North America. Patterns of diagenetic alteration based on δ^{18}O and the position of important sequence boundaries are similar among sections and also do not provide a complete explanation for the lower values in European carbonate. Variability in $\delta^{13}C_{carb}$ peaks of several per mil is well known for older Paleozoic excursions. The epeiric sea environments thus appear to record $\delta^{13}C_{carb}$ values that have been more influenced by local carbon cycling than modern surface oceans (including the marginal South China sea), but similar to that observed in smaller modern platforms such as the Bahamas. Enhanced regeneration of phosphate under anoxic conditions in western North American basins is interpreted to be the controlling influence on elevated δ^{13}C, as opposed to a local lowering of δ^{13}C in the European sections.

The debate over which values most represent mean ocean δ^{13}C is an important one because it has implications for calculations of global organic carbon burial rates. Model input of a shift to values of ≥+7‰, as recognized in North American sections, predicts steady-state increases in the fraction of carbon buried as organic matter that are too high (as much as 50–75%, if no changes in the riverine input are assumed). Use of a lower value for $\delta^{13}C_{carb}$ (closer to +5.5‰) predicts significantly lower excess organic carbon burial (7.5×10^{19} g) such that it may be possible to account for this in deep-sea, deltaic-shelf, and other depositional environments. Rapidly subsiding foreland basins such as the Antler and related basins of the western margin of Euramerica can hold a small percentage of total excess burial predicted by models.

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