Sensitivity of the epeiric sea carbon isotope record to local-scale carbon cycle processes: Tales from the Mohawkian Sea

K.M. Panchuk, C. Holmden, L.R. Kump

Abstract

Ancient marine carbon isotope records derived from epeiric sea carbonates can bear a strong influence of local-scale carbon cycling processes. Across the Late Ordovician Mohawkian Sea of eastern Laurentia, the carbon isotope compositions ($\delta^{13}C$) of contemporaneous sediments range from $-2\%e$ in the interior of the sea to $+2.5\%e$ along the margin. Here we use a box model to explore the relative importance of carbon fluxes within the Mohawkian Sea from a mass balance perspective. In the model, the Mohawkian Sea carbon reservoir is coupled to but distinct from the ocean and atmosphere carbon reservoirs. At initial steady state conditions, the residence time of carbon in the Mohawkian Sea is less than 10 years. We find that to produce model $\delta^{13}C$ values representative of the range in $\delta^{13}C$ across the Mohawkian Sea we must divide the sea into an inner region and an outer region and limit dissolved inorganic carbon (DIC) exchange between the two to 15% of the initial steady state unrestricted exchange rate. It is also necessary to supply low $\delta^{13}C$ carbon ($-29\%e$) to the inner region of the sea at a rate of $17.4 \times 10^{12}$ mol C yr$^{-1}$. The required flux of low $\delta^{13}C$ carbon could not have been sustained over the long term by remineralization of organic carbon stored in sediments of the inner region of the Mohawkian Sea, and the geographic $\delta^{13}C$ pattern is unlikely to have been generated by upwelling along the Sebree Trough. Rather, the low $\delta^{13}C$ flux might have been derived from bryophyte-dominated terrestrial ecosystems, suggesting an important role for terrestrial carbon cycling prior to the advent of vascular plants. An interesting feature of the model is that the isotopic compositions of both the epeiric sea and the larger ocean-atmosphere system are sensitive to changes in exchange rates within the epeiric sea. This has important implications for interpreting global $\delta^{13}C$ records.

Keywords: Epicontinental seas; C-13; Midcontinent; Sea-level changes; Numerical models; Ordovician

1. Introduction

The marine carbon isotope record is a commonly used proxy of Earth system evolution. Its utility arises from the fact that geochemical signals of carbon
cycling can be propagated globally in a geological instant by rapid mixing of carbon within the atmosphere, within the ocean surface layer, and by exchange between these two carbon reservoirs. A change in the carbon cycle affects the carbon isotope composition ($\delta^{13}C$) of dissolved inorganic carbon (DIC) in the pelagic surface ocean, which is then recorded as a change in the $\delta^{13}C$ of carbonate sediments that originate in surface seawater. As these sediments accumulate on the ocean floor, information about the ocean-atmosphere carbon cycle is added to the stratigraphic record.

There is, however, no ocean floor sediment record of the pelagic carbon cycle preserved in rocks older than Late Jurassic (~180 million years ago). Instead, there is a marine carbonate record preserved in the sediments of broad, shallow, semi-restricted continental (epeiric) seas. The lack of ocean floor sediments poses a significant challenge for reconstructing the history of the global carbon cycle because carbon cycling within epeiric seas may have been at least as important for determining the $\delta^{13}C$ of carbonate sediments as were globally integrated rates of weathering and marine organic carbon burial.

In modern shallow-water marine environments, restricted circulation permits differences in $\delta^{13}C$ to develop across basins. In Florida Bay, for example, regions closer to the mainland receive $^{13}C$-depleted carbon from the Everglades watershed (derived from terrestrial organic matter oxidation and limestone dissolution; Patterson and Walter, 1994), and from decaying mangrove and sea grass detritus (Lloyd, 1964). Restricted circulation across Florida Bay results in the $\delta^{13}C$ of DIC and molluscan carbonate near the mainland being 4‰ lower than along the Florida Reef Tract (Lloyd, 1964; Patterson and Walter, 1994). Similarly, within ancient epeiric seas, restricted seawater circulation in combination with local environmental influences on other carbon fluxes might have resulted in geographic variations in $\delta^{13}C$. Geographic variations appear in the rock record as offsets in the baselines of correlated $\delta^{13}C$ profiles from different locations within epicontinental environments (e.g., Beauchamp et al., 1987; Ludvigson et al., 1996; Patzkowsky et al., 1997; Ainsaar et al., 1999; Saltzman, 2002; Ludvigson et al., 2004), and as differences in the magnitudes of correlated carbon isotope excursions (e.g., Immenhauser et al., 2003). Geographic variations in $\delta^{13}C$ have also been measured across a well-constrained time-slice in sediments of the Late Ordovician Mohawkian Sea of eastern Laurentia. The time-slice is marked by the Millbrig K-bentonite, a volcanic ash layer which has been correlated across eastern Laurentia (Kolata et al., 1996 and references therein). Samples consisting predominantly of micritic limestones (mudstones, wackestones, packstones) but also including grainstones, siltstones, and shales (Fig. 1b; Appendix, Panchuk et al., accepted for publication) were collected from as close as possible to the Millbrig K-bentonite. The error in the time-slice is likely less than $\pm$ 500 kyr based on sedimentation rates between the Millbrig and the slightly older Deicke K-bentonite (Leslie and Bergstrøm, 1997), and assuming that these sedimentation rates changed little immediately after deposition of the Millbrig K-bentonite. Across the time-slice, the $\delta^{13}C$ of whole rock carbonates ($\delta^{13}C_{\text{carb}}$) and amorphous kerogens ($\delta^{13}C_{\text{org}}$) vary by more than 4‰. As in Florida Bay, the lowest $\delta^{13}C$ values occurred furthest inboard, and $\delta^{13}C$ values increased toward the open ocean. (Fig. 1a; Holmden et al., 1998; Panchuk et al., accepted for publication).

The range in Mohawkian Sea $\delta^{13}C_{\text{carb}}$ may reflect spatial variability in the preservational histories of carbonates, or spatial variability in the vital effects of calcifying organisms, however it appears that, for the most part, the range in $\delta^{13}C_{\text{carb}}$ does indeed reflect variations in the $\delta^{13}C$ of ancient seawater DIC ($\delta^{13}C_{\text{DIC}}$). One indication is that $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ are positively correlated (Fig. 2). The difference between $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ ($\Delta\delta^{13}C$) is 29.2 $\pm$ 1.1‰ with the exception of two samples (Panchuk et al., accepted for publication). A small range in $\Delta\delta^{13}C$ suggests that diagenetic processes are unlikely to have been entirely responsible for the variation in $\delta^{13}C$ across the Mohawkian Sea because it is improbable that diagenetic alteration would have changed both $\delta^{13}C_{\text{carb}}$ and $\delta^{13}C_{\text{org}}$ by approximately the same amount everywhere (Knoll et al., 1986). Stratigraphic carbon isotope profiles intersecting the 454 Ma timeslice provide additional support for the idea that the 4‰ range reflects ancient seawater $\delta^{13}C$. These profiles preserve primary $\delta^{13}C_{\text{carb}}$ signals from Iowa and Pennsylvania, and reflect the $\delta^{13}C$ gradient in their baseline offsets; profiles in Iowa have baselines which...
are 2% to 3% lower than the baseline in Pennsylvania (Ludvigson et al., 1996; Patzkowsky et al., 1997; Ludvigson et al., 2004). Further, within Iowa the baselines of δ13C profiles tend to increase to the south and east (Ludvigson et al., 2004). Variations in lithological, biological, and geochemical sediment characteristics highlight differences in depositional settings which may have caused the relative importance of a given carbon flux to vary from one region of the Mohawkian Sea to the next. Aquafacies distinguish such regional differences in carbon cycling, and the Mohawkian Sea has been subdivided into four aquafacies: the Midcontinent, Southern, Taconic, and Arch Margin Aquafacies (Fig. 1b; Holmden et al., 1998; Panchuk et al., accepted for publication). Differences in carbon cycling between aquafacies in the Mohawkian Sea have been linked to water column depth and seawa-
ter circulation patterns: In the Taconic Aquafacies, a deeper, density stratified water column in the Taconic Foreland Basin (Hay and Cisne, 1988) may have facilitated biological pumping, enriching the photic zone in $^{13}$C (Holmden et al., 1998). In contrast, in the shallower water column of the low $^{13}$C Midcontinent Aquafacies, carbon from remineralized sedimentary organic matter may have been more important (Lewan, 1986; Holmden et al., 1998). The Midcontinent may also have received low $^{13}$C carbon from chemical weathering on land (Holmden et al., 1998), and from ocean oxygen minimum zone waters upwelled along the Sebree Trough (Fig. 1; Kolata et al., 2001). Seawater may have exchanged relatively freely between the Taconic Aquafacies and the Iapetus Ocean, and between the Taconic Aquafacies and the Southern and Arch Margin Aquafacies, distributing $^{13}$C-enriched DIC from the Taconic Foreland Basin photic zone. In contrast, a chain of shoals and islands along the Sebree Trough (including the Ozark, Nashville, and Jessamine Domes, Fig. 1a) may have limited circulation between the Midcontinent Aquafacies and the Taconic and Southern Aquafacies (Patzkowsky et al., 1997; Holmden et al., 1998), preserving the low $^{13}$C signals of riverine DIC and remineralized organic carbon from the sediments and from upwelling.

Changes in circulation patterns, such as those caused by sea-level change, that affected the exchange of DIC between the interior and surrounding water masses might then be expected to have shifted the relative importance of fluxes in the local carbon cycle, and show up in the rock record as carbon isotope excursions (e.g., Holmden et al., 1998; Immenhauser et al., 2003; Panchuk et al., accepted for publication). If this were the case, then interpreting epeiric sea carbon isotope excursions is a far more complex problem than if the only significant control on epeiric sea carbon isotope profiles were fluxes between the global organic and inorganic carbon reservoirs. The magnitude of carbon isotope excursions driven by sea-level change then depends on the magnitude of change in DIC fluxes between reservoirs, the $^{13}$C and DIC concentration of epeiric sea, ocean, and atmosphere carbon reservoirs, and feedbacks within the system including the effects of sea-level change on primary productivity and organic carbon burial fluxes (Panchuk et al., accepted for publication). To interpret such an excursion, we must understand the relative importance of carbon fluxes within the local carbon cycle, the relative importance of carbon fluxes within the ocean-atmosphere carbon cycle, and the degree and effect of communication between these two scales of carbon cycling.

Here we explore these questions by using a box model to test the sensitivity of the Mohawkian Sea carbon cycle to organic carbon burial, addition of riverine DIC, CO$_2$ exchange with the atmosphere, and DIC exchange with the surface ocean. We find that CO$_2$ and DIC exchange rates are important for determining the response of both the epeiric sea and the ocean-atmosphere carbon cycles to changes in epeiric sea carbon cycling, but that the range of $^{13}$C values across the Mohawkian Sea cannot be accounted for by restricted circulation alone. It is also necessary to have a flux of low $^{13}$C carbon to the interior of the Mohawkian Sea. The necessary flux is too large to be supplied by remineralization of organic carbon within the sediments of the Midcontinent Aquafacies, and upwelling of low $^{13}$C carbon from the oxygen minimum zone of the ocean is unlikely to have generated the observed pattern in $^{13}$C, leaving exported terrestrial organic carbon as the only promising source. We further conclude that changing DIC exchange rates across the epeiric sea, such as might be caused by sea-level change, can lead to counterintuitive $^{13}$C responses.

Fig. 2. Plot of $\delta^{13}$C$_{\text{carb}}$ vs. $\delta^{13}$C$_{\text{org}}$ after Panchuk et al. (accepted for publication) showing the distinction between $M_1$ $\delta^{13}$C values (circles) and $M_2$ $\delta^{13}$C values (triangles). $\Delta\delta^{13}$C = 29.2 ± 1.1‰ (dashed line) except for two samples with much higher $\delta^{13}$C$_{\text{org}}$ values. A small variation in $\Delta\delta^{13}$C suggests that both carbonate and organic carbon were derived from the same DIC reservoir.
on both epeiric sea and ocean-atmosphere scales, complicating the interpretation of global carbon isotope excursions.

2. Model approach and configuration

2.1. Approach

The geographic variability of Mohawkian Sea $\delta^{13}C_{\text{DIC}}$ can be thought of as the net result of four processes: i) DIC exchange across the Mohawkian Sea and between the Mohawkian Sea and the Iapetus Ocean via seawater circulation, ii) indirect carbon exchange between the Mohawkian Sea and the surface ocean by air-sea CO$_2$ exchange, iii) organic carbon burial, and iv) addition of low $\delta^{13}C$ carbon from land. Our approach is to use a coupled epeiric sea – ocean – atmosphere box model to determine how the carbon fluxes associated with these processes must be applied in order to generate a geographic variation in $\delta^{13}C_{\text{DIC}}$ which is representative of the $\delta^{13}C_{\text{carb}}$ variation observed across the Mohawkian Sea.

A major issue in modelling the ancient world is the large uncertainty due to a lack of constraints on model parameters. We do not attempt to quantify this uncertainty, but where possible, we do attempt to demonstrate that the parameter values we have chosen are not unreasonable.

2.2. Configuration

The marine carbon cycle can be represented as a system of carbon fluxes (arrows; Fig. 3) between well-mixed carbon reservoirs (boxes). We adapt the ocean model of Kump (1991) which consists of a surface ocean DIC reservoir ($M_s$) coupled to a deep ocean DIC reservoir ($M_d$) by transport of DIC and transport and remineralization of organic carbon from $M_s$ ($F_{sd}$, $F_{ad}$) to $M_d$, and by upwelling which returns DIC from $M_d$ to $M_s$ ($F_{ds}$). The simplest way to treat spatial variability in Mohawkian Sea $\delta^{13}C$ in the model is to consider the Mohawkian Sea as made up of two well-mixed carbon reservoirs—one with $\delta^{13}C$ representative of the low $\delta^{13}C$ Midcontinent Aquafacies ($M_1$, Fig. 1a), and one that represents the high $\delta^{13}C$ region comprising the Taconic, Southern, and Arch Margin Aquafacies ($M_2$).

We consider an end-member scenario where $M_1$ and $M_2$ are in series, so $M_1$ is coupled to $M_s$ indirectly by exchange of DIC through $M_2$ ($F_{2s}$, $F_{s2}$), $M_1$, $M_2$, and $M_s$ are also coupled to the atmosphere ($M_a$) by air–sea gas exchange ($F_{ia}$, $F_{ai}$). Carbon from chemical weathering on land is added to $M_s$ and to $M_1$ (fluxes $F_{ws}$, $F_{w1}$ respectively; note that $M_2$ does not have a coastline) and balanced by carbonate and organic carbon burial fluxes ($F_{bx}$, $F_{x2}$) from $M_1$, $M_2$, and $M_s$. The small amount of organic matter and CaCO$_3$ synthesized in the deep ocean and buried in sediments is neglected.

The carbon mass and isotope balance for the epeiric sea reservoirs, the surface and deep ocean reservoirs, and the atmosphere are shown in Eqs. (1)–(10) (see Appendix A for a summary of symbols used here). In these equations, $\Delta^a$ is the $-7\%e$ equilibrium isotopic fractionation for HCO$_3^{-}$ to CO$_2$ (Mook et al., 1974), $\Delta^o$ is the fractionation associated with photosynthesis ($-29\%e$, from the Mohawkian Sea data set), and $\delta_1$, $\delta_{w1}$, $\delta_2$, $\delta_{x1}$, $\delta_m$ are the carbon isotope compositions of $M_1$, $F_{w1}$, $M_2$, $M_s$, and $M_a$ respectively. We
neglect the small isotopic fractionation associated with carbonate precipitation.

\[
\frac{dM_1}{dt} = F_{w1} + F_{as1} + F_{21} - \left[ F_{1a} + F_{12} + F_{1x} + F_{1x}^\circ \right]
\]

\[
\frac{dM_2}{dt} = F_{a2} + F_{2a} + F_{12} - \left[ F_{2x} + F_{2a} + F_{21} + F_{2x} + F_{2x}^\circ \right]
\]

\[
\frac{dM_3}{dt} = F_{sa} + F_{as} + F_{sx} - \left[ F_{sa} + F_{s2} + F_{sx} + F_{s1} + F_{s2} + F_{s1}^\circ \right]
\]

\[
\frac{dM_4}{dt} = F_{a1} + F_{2a} + F_{sa} - \left[ F_{a1} + F_{a2} + F_{sa} \right]
\]

\[
M_1 \frac{d\delta_1}{dt} = F_{w1}(\delta_{w1} - \delta_1) + F_{a1}(\delta_a - \delta_1) + F_{21}(\delta_2 - \delta_1) - \left[ F_{1a} A^a + F_{1x} A^x + F_{1x}^\circ A^\circ \right]
\]

\[
M_2 \frac{d\delta_2}{dt} = F_{a2}(\delta_a - \delta_2) + F_{sa}(\delta_a - \delta_s) + F_{s2}(\delta_s - \delta_2) - \left[ F_{2a} A^a + F_{2x} A^x + F_{2x}^\circ A^\circ \right]
\]

\[
M_3 \frac{d\delta_s}{dt} = F_{sa}(\delta_s - \delta_s) + F_{as}(\delta_a - \delta_s) + F_{ds}(\delta_d - \delta_s) - \left[ F_{sa} A^a + F_{sx} A^x + F_{sd} A^\circ \right]
\]

\[
M_4 \frac{d\delta_a}{dt} = F_{sa}(\delta_a - \delta_a) + F_{ds}(\delta_s + \delta_d - \delta_a)
\]

\[
M_5 \frac{d\delta_s}{dt} = F_{sa}(\delta_s + \delta_a - \delta_s) + F_{sa}(\delta_s + \delta_a - \delta_s)
\]

at steady state at the pre-industrial atmospheric level (1 × PAL) of 280 ppm. Although the net exchange of CO₂ is zero at steady state, there are two balancing exchanges of 17.4 mol C m⁻² yr⁻¹. Both air–sea CO₂ exchange and DIC exchange via seawater vary linearly according to the mass of C in the reservoir of origin.

Initial rates of carbonate and organic carbon burial are calculated using estimates from Opdyke and Wilkinson (1988) of the area of global deep vs. shallow water carbonate deposition in the Cretaceous, a time more typical than today of the continental submergence of the Orдовician. The total burial flux (carbonate plus organic) is set to the modern day riverine input of DIC (F_w) and distributed between M1 and M2 in proportion to the ratio of the surface area of each reservoir (A_1 = 0.95 × 10¹² m² and A_2 = 1.31 × 10¹² m², respectively) to the total area of Cretaceous shallow water carbonate deposition (A = 27 × 10¹²; Eqs. (11), (12)). The remaining burial flux is allocated to M₅ (Eq. (13)).

\[
F_{1x} + F_{1x}^\circ = \frac{A_1}{A_k} F_w
\]

\[
F_{2x} + F_{2x}^\circ = \frac{A_2}{A_k} F_w
\]

\[
F_{sx} + F_{sx}^\circ = \frac{A_k - (A_1 + A_2)}{A_k} F_w
\]

Burial fluxes are partitioned into Corg and C_carb fractions according to a ratio Corg:C_carb of 1:3.15. This ratio is arrived at by tuning the model to achieve δ values of +2‰. The initial surface ocean composition is chosen to reflect high δ¹³C values near the Iapetus Ocean.

DIC exchange rates between the epeiric sea and surface ocean reservoirs are derived from steady state water and salt balances (Fig. 4; see Appendix B for equations). Carbon reservoirs M₁, M₂, and M₅ have corresponding water volumes and salinities V₁ and S₁, and fluxes of water are denoted Q₁. The modern-day flux of continental runoff (Q_w = 37.4 × 10¹² m³ yr⁻¹; Berner and Berner, 1996) is distributed between V₁ and Vₛ as fluxes Qw₁ and Qwₛ, respectively, by allocating runoff to Qw₁ in proportion to the ratio of total Mohawkian Sea surface area to the total area of...
have salinity $S_1$, evaporation from $V_1$, net evaporation ($e$), and exchange between reservoirs. The Mohawkian Sea is thought to have been salinity stratified, based on inferred paleocirculation patterns (Witzke, 1987) and differences in surface vs. benthic $\delta^{13}$C excursions (Ludvigson et al., 1996). Salinity stratification would have allowed for a fresher water layer at the surface, and a more saline bottom layer populated by brachiopods. The seawater exchange fluxes calculated using these salinities appear to be reasonable, in so far as they are comparable to modern environments. For $V_1$, seawater flows out at a rate of $24 \times 10^{12}$ m$^3$ yr$^{-1}$ and flows in at $21 \times 10^{12}$ m$^3$ yr$^{-1}$. In the Java Sea, which is approximately half the volume of $V_1$, total exchange fluxes are approximately half as large. Java Sea outflow rates vary between $\sim$8 and $12 \times 10^{12}$ m$^3$ yr$^{-1}$, and inflow rates vary from $\sim$8 to $11 \times 10^{12}$ m$^3$ yr$^{-1}$ (Edinger et al., 2002).

To change model DIC exchange rates between $M_1$, $M_2$, and $M_s$, we impose a sill between the $M_1$ and $M_2$ water masses. The physical analogue to the model sill is the bathymetric high along the trend of the Ozark, Nashville, and Jessamine Domes (Fig. 1a). The initial steady state rate of DIC exchange between $M_1$ and $M_2$ is decreased in proportion to the height of the exchange window above the sill (Fig. 5); the higher the sill, the more DIC exchange between $M_1$ and $M_2$ is restricted. Changes in the exchange window above the sill can be thought of in terms of variations in sea–level.

When the ratio of organic to carbonate burial is tuned to $\delta_s = +2\%$, initial steady state values for $\delta_1$ and $\delta_2$ are $+1.9\%$ and $+2.1\%$, respectively. However, the average observed $\delta^{13}$C values of the $M_1$ and $M_2$ regions are $-0.7\%$ and $+1.2\%$, respectively. Consequently, our methodology is to find out how the initial steady state parameters must be adjusted for $\delta_1$ and $\delta_2$ to match the observed averages. The model was run for exchange window depths of 100 m (initial steady state depth), 75 m, 50 m, 25 m, and 5 m at atmospheric CO$_2$ levels of 1 × PAL and then at 16 × PAL to account for higher rates of air–sea CO$_2$ exchange under elevated Ordovician atmospheric CO$_2$ levels (Yapp and Poths, 1992). DIC reservoirs were scaled as the square root of the change in atmospheric CO$_2$ levels, after Kump and
Arthur (1999). The residence times of carbon in the epeiric sea as a whole ($M_1 + M_2$) for the $1/C_2$ PAL and $16/C_2$ PAL initial steady state cases are 5 and 2 years, respectively, much shorter than the 100 kyr carbon residence time that is generally assumed to characterize both the ancient epeiric seas and the ocean.

For each exchange window depth at $1/C_2$ PAL and $16/C_2$ PAL, the rate of organic carbon burial from $M_1$ ($F_{sx}$) was varied by factors ranging from 0.5 to –100, where negative factors indicate net remineralization. Changes in the rate of organic carbon burial in $M_1$ were balanced by making the opposite adjustment to burial from the surface ocean ($F_{sx}$), representing organic carbon burial in coastal zones and deltas not covered by epeiric seas. The $\delta^{13}C$ of the riverine DIC flux into $M_1$ ($d_{w1}$) was decreased for each exchange window depth at $1/C_2$ PAL and $16/C_2$ PAL. The $\delta^{13}C$ of this flux depends on the amount of carbon that is derived from chemical weathering of carbonate vs. clastic terrains because carbonate weathering contributes DIC with an average $\delta^{13}C$ of ~0%, whereas the weathering of shales contributes DIC derived from chemical weathering of silicate minerals.

### Table 1

<table>
<thead>
<tr>
<th>Carbon Reservoir (mol C)</th>
<th>C isotopes (%)</th>
<th>Carbon fluxes ($\times 10^{12}$ mol C yr$^{-1}$)</th>
<th>DIC &amp; organic carbon exchange</th>
<th>Carbon burial</th>
<th>Weather carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1$</td>
<td>$\delta_w, \delta_{1}, \delta_{2}$</td>
<td>+2.0</td>
<td>$F_{12}$</td>
<td>44.4</td>
<td>$F_{sx}$</td>
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<tr>
<td>$M_2$</td>
<td>$\delta_d$</td>
<td>-0.2</td>
<td>$F_{21}$</td>
<td>42.8</td>
<td>$F_{2x}$</td>
</tr>
<tr>
<td>$M_3$</td>
<td>$\delta_a$</td>
<td>-5.0</td>
<td>$F_{3x}$</td>
<td>28.5</td>
<td>$F_{sx}$</td>
</tr>
<tr>
<td>$M_4$</td>
<td>$\Delta^o$</td>
<td>-7.0</td>
<td>$F_{4x}$</td>
<td>2430</td>
<td>$F_{o}$</td>
</tr>
<tr>
<td>$M_5$</td>
<td>$\Delta^o$</td>
<td>-29.0</td>
<td>$F_{5x}$</td>
<td>2640</td>
<td>$F_{sx}$</td>
</tr>
</tbody>
</table>

| Air–sea CO$_2$ exchange (mol C m$^{-2}$ yr$^{-1}$) | $F_{ai}$ | 210 | $F_{2x}$ | 0.3 |

<table>
<thead>
<tr>
<th>Water &amp; salt</th>
<th>Reservoir (m$^3$ water)</th>
<th>Salinity</th>
<th>Water fluxes ($\times 10^{12}$ m$^3$ yr$^{-1}$)</th>
<th>Net evaporation (cm yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_1$</td>
<td>95 $\times 10^{12}$</td>
<td>$S_1$</td>
<td>26</td>
<td>$Q_{12}$</td>
</tr>
<tr>
<td>$V_2$</td>
<td>131 $\times 10^{12}$</td>
<td>$S_2$</td>
<td>29</td>
<td>$Q_{21}$</td>
</tr>
<tr>
<td>$V_3$</td>
<td>70 $\times 10^{15}$</td>
<td>$S_3$</td>
<td>35</td>
<td>$Q_{3x}, Q_{4x}$</td>
</tr>
</tbody>
</table>
organic matter, with $\delta^{13}C$ of $\sim 25\%$ (e.g., Kump and Arthur, 1999). The $\delta^{13}C$ of modern riverine DIC is also influenced by CO$_2$ evolved during respiration and decomposition in soils, but we consider this additional source of low $\delta^{13}C$ carbon later in Section 4. Initial $\delta_{w1}$ is $-5\%$, representing an average distribution of 80% carbonate weathering and 20% shale weathering during the Phanerozoic (Kump and Arthur, 1999). We look at cases where $\delta_{w1}$ is $-12.5\%$, representing equal contributions from weathering of carbonates and shales, and where $\delta_{w1}$ is $-20\%$, representing 20% carbonate weathering and 80% shale weathering.

All scenarios were run for 10 Myr of model time to ensure that steady state was reached. We show scenarios here which come closest to simulating the observed geographic gradient. For reference, the average observed $\delta_1$ and $\delta_2$ values and the initial $\delta_s$ value are plotted as light dashed lines where appropriate. Initial carbon and water reservoir sizes, carbon and water flux magnitudes, and the $\delta^{13}C$ and salinity of reservoirs and fluxes at 1 $\times$ PAL are summarized in Table 1.

3. Results

3.1. DIC and CO$_2$ exchange rates

As seawater exchange is decreased, $\delta_1$ and $\delta_2$ diverge, mostly due to decreasing $\delta_1$ (Fig. 6a). As the flux of higher $\delta^{13}C$ from $M_2$ and $M_s$ is decreased, the low $\delta^{13}C$ weathering flux into $M_1$ becomes relatively more important in the carbon mass and isotope balances of $M_1$, amplifying the effect of weathered carbon on $\delta_1$. This response is damped at 16 $\times$ PAL relative to 1 $\times$ PAL. The maximum difference between $\delta_1$ and $\delta_2$ is 1.3% for the 5 m exchange window in the 1 $\times$ PAL scenario and results are more than 1% higher than the average $\delta_1$ and $\delta_2$ observed in the Mohawkian Sea. In all cases, the effect on $\delta_s$ was negligible and is not plotted.

Reduced seawater exchange also decreases $S_1$ because the volumetric rate of seawater moving between $V_1$ and $V_2$ decreases, but the influx of fresh river water to $V_1$ remains the same. $S_1$ drops from 26 at the 100 m

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**Fig. 6.** (a) $M_1$ (circles) and $M_2$ (triangles) $\delta^{13}C$ response to restricted DIC exchange across the epeiric sea at 1 $\times$ PAL (black line) and 16 $\times$ PAL (grey line). Restricted DIC exchange alone does not account for the range in Mohawkian Sea $\delta^{13}C$, and does not affect the ocean-atmosphere system. (b) Salinity response of $S_1$ (circles), $S_2$ (triangles), and $S_s$ (diamonds) to exchange window depth. Salinity decreases as seawater exchange is restricted. Note that symbols are coloured to match lines.
exchange window to ~9 for the 5 m exchange window (Fig. 6b). In contrast, $S_2$ and $S_3$ are essentially unaffected because the decrease in the salt flux from $V_1$ is small compared to the total salt reservoir of $V_s$, and mixing between $V_2$ and $V_s$ is sufficiently rapid.

3.2. Organic carbon

To approach the observed $\delta_1$ of $-0.7\%_o$, there must be net remineralization of organic carbon in $M_1$. At 1 PAL and a 100 m exchange window, net remineralization of $-5 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.9\%_o$ and $+1.6\%_o$, respectively, and net remineralization of $-10 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.1\%_o$ and $+1.2\%_o$, respectively (Fig. 7a). The difference between $\delta_1$ and $\delta_2$ is closest to that of the Mohawkian Sea at $-10 \times F_{1x}^{o}$ and ~50 m exchange window, but $\delta_1$ and $\delta_2$ are both ~$0.5\%_o$ higher than the Mohawkian Sea averages. At 16 PAL, however, the $-10 \times F_{1x}^{o}$ scenario has a negligible impact on $M_1$. At 1 PAL and a 100 m exchange window, net remineralization of $-5 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.9\%_o$ and $+1.6\%_o$, respectively, and net remineralization of $-10 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.1\%_o$ and $+1.2\%_o$, respectively (Fig. 7a). The difference between $\delta_1$ and $\delta_2$ is closest to that of the Mohawkian Sea at $-10 \times F_{1x}^{o}$ and ~50 m exchange window, but $\delta_1$ and $\delta_2$ are both ~$0.5\%_o$ higher than the Mohawkian Sea averages. At 16 PAL, however, the $-10 \times F_{1x}^{o}$ scenario has a negligible impact on $M_1$. At 1 PAL and a 100 m exchange window, net remineralization of $-5 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.9\%_o$ and $+1.6\%_o$, respectively, and net remineralization of $-10 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.1\%_o$ and $+1.2\%_o$, respectively (Fig. 7a). The difference between $\delta_1$ and $\delta_2$ is closest to that of the Mohawkian Sea at $-10 \times F_{1x}^{o}$ and ~50 m exchange window, but $\delta_1$ and $\delta_2$ are both ~$0.5\%_o$ higher than the Mohawkian Sea averages. At 16 PAL, however, the $-10 \times F_{1x}^{o}$ scenario has a negligible impact on $M_1$. At 1 PAL and a 100 m exchange window, net remineralization of $-5 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.9\%_o$ and $+1.6\%_o$, respectively, and net remineralization of $-10 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.1\%_o$ and $+1.2\%_o$, respectively (Fig. 7a). The difference between $\delta_1$ and $\delta_2$ is closest to that of the Mohawkian Sea at $-10 \times F_{1x}^{o}$ and ~50 m exchange window, but $\delta_1$ and $\delta_2$ are both ~$0.5\%_o$ higher than the Mohawkian Sea averages. At 16 PAL, however, the $-10 \times F_{1x}^{o}$ scenario has a negligible impact on $M_1$. At 1 PAL and a 100 m exchange window, net remineralization of $-5 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.9\%_o$ and $+1.6\%_o$, respectively, and net remineralization of $-10 \times F_{1x}^{o}$ decreases $\delta_1$ and $\delta_2$ to $+0.1\%_o$ and $+1.2\%_o$, respectively (Fig. 7a). The difference between $\delta_1$ and $\delta_2$ is closest to that of the Mohawkian Sea at $-10 \times F_{1x}^{o}$ and ~50 m exchange window, but $\delta_1$ and $\delta_2$ are both ~$0.5\%_o$ higher than the Mohawkian Sea averages. At 16 PAL, however, the $-10 \times F_{1x}^{o}$ scenario has a negligible impact on

![Graph showing δ13C response to net organic carbon remineralization under restricted DIC exchange across the epeiric sea.](image-url)

Fig. 7. δ13C response to net organic carbon remineralization under restricted DIC exchange across the epeiric sea. The flux of remineralized organic carbon is expressed in terms of the initial organic carbon burial flux from M1 (F1x). (a) Epeiric sea δ13C response at 1 PAL for $-5 \times F_{1x}^{o}$ (black dashed line) and $-10 \times F_{1x}^{o}$ (grey dashed line). (b) Epeiric sea δ13C response at 16 PAL to $-10 \times F_{1x}^{o}$ (grey dashed line), $-70 \times F_{1x}^{o}$ (solid grey line), and $-100 \times F_{1x}^{o}$ (solid black line). The best match for the Mohawkian Sea δ13C range is achieved at 16 PAL and $-70 \times F_{1x}^{o}$ with a 5 to 25 m exchange window. (c) Surface ocean δ13C response at 16 PAL to $-10 \times F_{1x}^{o}$ (grey dashed line), $-70 \times F_{1x}^{o}$ (solid grey line), and $-100 \times F_{1x}^{o}$ (black line). The surface ocean shows a significant decrease in δ13C at 16 PAL for $-70 \times F_{1x}^{o}$ and $-100 \times F_{1x}^{o}$ scenarios. Note that symbols are coloured to match lines.
$\delta_1$ and $\delta_2$ for the 100 m exchange window (Fig. 7b). Instead, a net remineralization flux of $-70 \times F_{1x}^o$ is required with an exchange window between 5 and 25 m.

The combination of restricted exchange and net organic carbon remineralization has a negligible effect on $\delta_s$ at 1 PAL. At 16 PAL, $\delta_s$ scarcely deviates from steady state for the $-10 \times F_{1x}^r$ case, but for the $-70 \times F_{1x}^r$ and $-100 \times F_{1x}^r$ cases $\delta_s$ decreases to $+1.4\%$ and $+0.8\%$ respectively at the 100 m exchange window, and then by an additional $\sim 0.5\%$ as the exchange window closes (Fig. 7c).

### 3.3. Weathered carbon

At 1 PAL and unrestricted circulation, setting $\delta_{w1}$ to $-12.5\%$ decreases $\delta_1$ and $\delta_2$ to $+0.8\%$ and $+1.2\%$ respectively, and setting $\delta_{w1}$ to $-20\%$ decreases $\delta_1$ and $\delta_2$ to $-0.3\%$ and $+0.4\%$ respectively (Fig. 8a). $\delta_1$ and $\delta_2$ are closest to the observed averages in the Mohawkian Sea dataset when $\delta_{w1}=-20\%$ and the exchange window is 25 m deep. At 16 PAL and unrestricted circulation, $\delta_1$ and $\delta_2$ decrease to $+1.3\%$ and $+1.4\%$ respectively with $\delta_{w1}=-12.5\%$, and to $+0.6\%$ and $+0.7\%$ respectively for $\delta_{w1}=-20\%$.

![Fig. 8. $\delta^{13}C$ response to weathered carbon $\delta^{13}C(\delta_{w1})$ of $-12.5\%$ (black line) and $-20\%$ (grey line) under restricted DIC exchange across the epeiric sea. (a) Epeiric sea $\delta^{13}C$ response at 1 PAL. (b) Epeiric sea $\delta^{13}C$ response at 16 PAL. Decreased $\delta^{13}C$ of weathered carbon under restricted DIC exchange conditions does not produce $\delta_1$ and $\delta_2$ values characteristic of the Mohawkian Sea range. (c) Surface ocean $\delta^{13}C$ response for both 1 PAL and 16 PAL. Surface ocean $\delta^{13}C$ decreases appreciably for $\delta_{w1}$ of $-12.5\%$ and $-20\%$, but is not affected by restricted DIC exchange. Note that symbols are coloured to match lines.](image-url)
both cases, $\delta_1$ and $\delta_2$ diverge by $\sim 0.5\%e$ as the exchange window closes, not enough to generate the observed $\delta_1$ and $\delta_2$ averages in the Mohawkian Sea. For both $1 \times$ PAL and $16 \times$ PAL the $\delta_{w1} = -12.5\%e$ case decreases $\delta_s$ to $+1.4\%e$ and the $\delta_{w1} = -20\%e$ case decreases $\delta_s$ to $+0.7\%e$. Changes in restriction have a negligible effect on $\delta_s$ in either case.

4. Discussion

Both the epeiric sea ($M_1$ and $M_2$) and the ocean-atmosphere systems ($M_S$, $M_d$, and $M_a$) respond to changes in carbon cycling within the epeiric sea with a sensitivity that depends on the rate of carbon exchange between these two systems. When DIC and air–sea $CO_2$ exchange rates are higher (i.e., at $16 \times$ PAL and deeper exchange windows), the epeiric sea is less sensitive to fluxes of remineralized organic carbon and riverine DIC, whereas the ocean-atmosphere system is more sensitive. To generate $\delta_1$ and $\delta_2$ values similar to the observed Mohawkian Sea averages ($-0.7\%e$ and $+1.2\%e$, respectively), the high Ordovician air–sea $CO_2$ exchange rate must be countered by a decrease in the $M_1 - M_2$ DIC exchange window from 100 m to $\sim 15$ m, and by adding remineralized organic carbon to $M_1$ at a rate 70 times greater than the initial steady state flux of organic carbon burial from $M_1$ ($-70 \times F_{1x, o}$; we will refer to this flux as $F_{70}$). These perturbations decrease $\delta_s$ from an initial steady state value of $+2\%e$ to a new steady state value of $+0.4\%e$.

At the 15 m exchange window, $S_1$ is $\sim 15$, well below the preferred salinity range of modern brachiopods, as discussed earlier. It is, however, well within the broad range of salinities found across modern semi-restricted environments. In Florida Bay, salinity ranges from 35 near the Florida Reef Tract to as low as 10 (seasonally) near the Everglades (Lloyd, 1964). Within the Baltic Sea, the average salinity is 6, but salinity increases to $>30$ through the Danish straits and toward the North Sea (Rodlie and Winsor, 2002). In the Mohawkian Sea, low salinity waters might have occurred as a plume near freshwater run-off sources. This result was observed in a three-dimensional coastal ocean model of the Cretaceous Interior Seaway (Slingerland et al., 1996).

Our results suggest that a very large flux of remineralized organic carbon would be required to achieve the observed values of epeiric sea $\delta^{13}C$. In fact, the flux $F_{70}$ is larger than the initial steady state organic carbon burial fluxes from $M_1$, $M_2$, and $M_s$ combined. The decrease in $F_{1x, o}$ is balanced in our model by increasing the flux of organic carbon burial from the surface ocean ($F_{s, o}$) by an equal amount (representing burial in coastal zones and deltas not covered by epeiric seas), but this addresses neither the source of remineralized organic carbon, nor the mechanism that brought it into the interior of the Mohawkian Sea. The low $\delta^{13}C$ values in the Mohawkian Sea have been attributed to a flux of remineralized organic carbon from sediment pore-waters within the shallow interior of the sea (Holmden et al., 1998), but this can offer only a temporary solution because organic carbon will be depleted under conditions of net remineralization. Eventually this organic carbon would be exhausted and $\delta_1$ would rise, erasing the $\delta^{13}C$ gradient. Even allowing for an unrealistically high 50 wt.% organic carbon content in $M_1$ sediments, dissolution would have to occur at a rate of $177$ m Myr$^{-1}$ in order to supply $F_{70}$, or $\sim 8$ times faster than estimated Paleozoic carbonate platform accumulation rates of $\sim 22$ m Myr$^{-1}$ (Opdyke and Wilkinson, 1988). Consequently, in Section 4.1 we consider two other potential sources of low $\delta^{13}C$ carbon: upwelling along the Sebree Trough, and non-fossil terrestrial organic carbon.

In Section 4.2, we discuss the implications of changing DIC exchange rates for interpreting the epeiric sea $\delta^{13}C$ record, including issues raised by the periodic nature of sea-level change.

4.1. Supply of low $\delta^{13}C$ carbon

4.1.1. Upwelling

Kolata et al. (2001) suggest that the Sebree Trough (Fig. 1) provided a pathway into the Mohawkian Sea for waters from the oxygen minimum zone of the Iapetus Ocean, with prevailing winds and the Coriolis effect transporting these waters northward onto the Midcontinent carbonate platform. In the context of our model, this upwelling brings carbon from $M_d$ with composition $\delta_d$ as part of the flux $F_{ds}$. At $16 \times$ PAL and $F_{70}$, $\delta_d$ is $-1.1\%e$, much higher than the $\delta^{13}C$ of organic carbon ($-29\%e$). In order to have the same effect as $F_{70}$ at $-29\%e$, the required flux of
upwelled carbon is \( 459 \times 10^{12} \text{ mol C yr}^{-1} \), equivalent to \( 58 \text{ m}^2 \text{ yr}^{-1} \) of water. This quantity is reasonable from the perspective of current velocity in modern upwelling zones (e.g., 0.02 m s\(^{-1}\) to 0.1 m s\(^{-1}\) in the Peru Margin upwelling zone; Tomczak and Godfrey, 1994), assuming a range in the width of the Sebree Trough from 25 km to 125 km (Kolata et al., 2001) and depth on the order of \( 10^2 \text{ m} \) to \( 10^3 \text{ m} \). This carbon flux is likely an underestimate of the amount of carbon required, however, because the waters that upwelled along the Sebree Trough were high in phosphate (Kolata et al., 2001), so the flux of low \( \delta^{13} \text{C} \) carbon from upwelling would have to offset the isotopic effects of enhanced productivity (Panchuk et al., accepted for publication). Another difficulty with this scenario is that low \( \delta^{13} \text{C} \) DIC from upwelling would have entered the Midcontinent from the south, then moved northward, so the lowest \( \delta^{13} \text{C} \) values would likely have occurred near the Sebree Trough, rather than along the Transcontinental Arch. Under these circumstances, upwelling is unlikely to have been the source of the large flux of low \( \delta^{13} \text{C} \) to \( M_1 \).

4.1.2. Terrestrial organic carbon

An alternative source of carbon for \( F_{70} \) is non-fossil terrestrial organic matter (i.e., derived from primary production on land, not from weathering of exposed ancient sediments) transported by rivers to the epeiric sea. This carbon could have been added to the epeiric sea in the form of reactive dissolved and particulate organic carbon (DOC and POC), and been remineralized within the Mohawkian Sea, or it could have been remineralized in transit, entering the epeiric sea as a low \( \delta^{13} \text{C} \) DIC flux in addition to the flux of DIC from chemical weathering (e.g., Longinelli and Edmond, 1983). The \( \delta^{13} \text{C} \) of biogenic CO\(_2\) derived from soils of the Transcontinental Arch suggest that this flux may have had \( \delta^{13} \text{C} \) of \( \sim -27\%_o \) (Yapp and Potts, 1993). This scenario is consistent with the \( \delta^{13} \text{C} \) distribution across the Mohawkian Sea because the lowest \( \delta^{13} \text{C} \) values occur where lithological and geochemical sediment characteristics of the Decorah Formation indicate major runoff from the Transcontinental Arch (Witzke, 1980; Ludvigson et al., 1996; Holmden et al., 1998). A similar pattern can occur in modern estuaries, where \( \delta^{13} \text{C}_{\text{DIC}} \) values increase away from the river mouth as river water mixes progressively with seawater (e.g., Chanton and Lewis, 1999).

The modern global flux of terrestrial DOC and POC to the ocean is \( \sim 32 \times 10^{12} \text{ mol C yr}^{-1} \) (Schlesinger and Melack, 1981; Smith and Hollibaugh, 1993; Ludwig and Probst, 1996). If this flux is applied to the Ordovician and distributed between \( M_1 \) and \( M_s \) according to the same scaling as \( F_{w1} \) and \( F_{ws} \), then only 8.5\%, or \( 2.7 \times 10^{12} \text{ mol C yr}^{-1} \), would go to \( M_1 \) instead of the necessary \( 17.4 \times 10^{12} \text{ mol C yr}^{-1} \). Modern-day terrestrial ecosystems are dominated by vascular plants, but in the Ordovician, before the advent of vascular plants, the land surface was colonized by bryophytes, including liverworts, hornworts, and mosses (Shear, 1991; Strother et al., 1996; Wellman and Gray, 2000). Wetlands, where these organisms are found today, have export rates per unit area which are at least an order of magnitude larger than the export rates of other terrestrial ecosystems (Lugo et al., 1989). Moreover, in the warmer, wetter, higher pCO\(_2\) Ordovician climate, export rates may have been much higher. DOC export from modern peat lands increases appreciably with increasing atmospheric CO\(_2\) levels because of higher productivity rates, especially in the production of root exudates (Freeman et al., 2004), and warming is associated with enhanced enzymatic activity that also increases the output of DOC from peat lands (Freeman et al., 2001). In a wetter climate, higher runoff rates may have flushed more organic carbon from the lowlands. Organic carbon transport in the Ordovician would not have been inhibited by the stabilizing effects of large root systems on soils, and terrestrial biomass would not have been recycled on land by herbivores. These considerations lead us to suggest that not only did Ordovician bryophyte-dominated wetlands produce and export enough organic carbon to supply \( F_{70} \), but, more generally, that terrestrial ecosystems may have played a significant role in the global carbon cycle prior to the advent of vascular plants.

4.2. Implications for interpreting epeiric sea \( \delta^{13} \text{C} \) records

The model response of epeiric sea, ocean, and atmosphere \( \delta^{13} \text{C} \) to carbon exchange rates offers a unique perspective on alternative interpretations of the epeiric sea \( \delta^{13} \text{C} \) record and on correlating and quantifying \( \delta^{13} \text{C} \) excursions. Divergence of \( \delta_1 \) and \( \delta_2 \) with decreasing exchange rates (e.g., Fig. 7a) suggests that sometimes it may be appropriate (if counter-
intuitive) to correlate $\delta^{13}$C profiles from different epeiric sea water masses by matching positive $\delta^{13}$C excursions with negative $\delta^{13}$C excursions. Where the time scale of the excursion is small compared to geological time scales, the offset in timing between positive $\delta^{13}$C excursions from different water masses may not even be detectable by correlation tools such as biostratigraphy. In this case the mismatch in the age of sediments would also be small, although for longer time scales, this error could be appreciable. The more important consequence of a mismatch is not necessarily an inaccurate timeline; rather it is that sediment characteristics such as lithology which are correlated based on the $\delta^{13}$C data may present a misleading picture of the evolution of the depositional environment.

An additional complication which the steady-state model runs do not address is periodicity. Sea-level fluctuations, and hence, fluctuations in exchange rates, can occur over a variety of time scales so that not all of the reservoirs in the system may have time to come to steady state before sea-level change switches directions again. For a single reservoir, the effect of periodic sea-level change would depend on the response time of the reservoir compared to the period of sea-level fluctuation (e.g., Richter and Turckian, 1993). For a series of coupled reservoirs, however, the effect also depends on feedbacks between reservoirs. Consider, for example, two cases where the $M_1 \rightarrow M_2$ exchange window oscillates between 100 m and 15 m; in one case the period of oscillation is 50 kyr (short relative to geological time scales) and in the other case the period is 10 Myr. In both cases the model begins with the unrestricted $F_{70}$ and $16 \times \text{PAL}$ scenario and is run until dynamic equilibrium is reached. In the first case (Fig. 9a), $\delta_1$ and $\delta_2$ fluctuate with a period if 50 kyr, but in opposite directions. As sea-level rises, $\delta_1$ increases because of an increase in the flux of higher $\delta^{13}$C DIC from $M_2$, while $\delta_2$ decreases because of an increase in the flux of lower $\delta^{13}$C DIC from $M_1$. The response of $\delta_2$ is damped relative to $\delta_1$ because of free mixing between $M_2$ and $M_3$. The responses of $\delta_3$, $\delta_4$, and $\delta_5$, on the other hand, are negligible because the response time of the ocean-atmosphere system is much longer than the period of perturbation. In the second case (Fig. 9b), the response amplitudes of $\delta_1$, $\delta_6$, $\delta_7$, and $\delta_8$ increase, so that the ocean-atmosphere system also responds visibly with oscillations with a period of 10 Myr. In this case, the flux of carbon from $M_1$ via air–sea CO$_2$ exchange is more important than DIC exchange for transmitting the forcing to $M_1$, $M_2$, and $M_3$. As the exchange window depth decreases, $M_1$ accumulates more carbon from terrestrial DOC and POC, increasing the flux of CO$_2$ from $M_1$ to $M_4$, and decreasing $\delta_1$. The signal is transmitted from $M_4$ to $M_5$, and from $M_5$ to $M_6$. In contrast, the effect of the perturbation on $\delta_2$ is very small because $M_2$ is receiving signals which cancel each other out. A decrease in the exchange window decreases the low $\delta^{13}$C DIC flux from $M_1$ to $M_2$, which results in an increase in $\delta_2$ in the 50 kyr case, but at the same time, it decreases $\delta_4$ and $\delta_8$ which act to decrease $\delta_2$.

An extension of the results in Fig. 9b is that for periodic fluctuations driven from within the epeiric sea and occurring on time scales long enough to be detected by the ocean-atmosphere system, the ocean-atmosphere $\delta^{13}$C signal could transmit the $\delta^{13}$C signal originating in one sea to other epeiric seas. The $\delta^{13}$C response of the other epeiric seas would reflect a combination of the $\delta^{13}$C signal due to their own local carbon cycles and the $\delta^{13}$C signal transmitted by the ocean-atmosphere system. The relative timing of such globally distributed excursions would depend on how rapidly different components of the system responded to the signal. Kump and Arthur (1999)
demonstrated that feedbacks between atmospheric pCO$_2$ levels and photosynthetic fractionation associated with increase in organic carbon burial could result in the peak organic $\delta^{13}$C response occurring after the peak carbonate $\delta^{13}$C response. Similarly, the feedbacks in a system including the ocean, the atmosphere, and multiple epeiric sea carbon reservoirs might in fact have introduced a non-trivial time lag between the initiation of the excursion in one carbon reservoir and the response in another reservoir.

5. Conclusion

The epeiric sea carbon isotope record is the only available record of marine carbon cycling prior to the Late Jurassic. A 4% range in $\delta^{13}$C values across a single time-slice of Ordovician Mohawkian Sea sediments suggests that this epeiric sea record may have been influenced as much by carbon cycling within the epeiric sea as by carbon cycling in the ocean-atmosphere system. We find that within our simple coupled epeiric sea – ocean – atmosphere carbon cycle model, the only way to produce $\delta^{13}$C values consistent with the Mohawkian Sea dataset and at Ordovician atmospheric pCO$_2$ levels is to restrict the exchange of DIC across the epeiric sea and add a large flux of remineralized organic carbon to the interior water mass of the epeiric sea. The required flux of remineralized organic carbon was probably not supplied by remineralization of organic carbon stored within the sediments of the Mohawkian Sea, by upwelling of low $\delta^{13}$C DIC from the deep ocean, or by export of terrestrial DOC and POC at modern rates. However, modern day analogues of the Ordovician bryophyte-dominated terrestrial plant communities export enough organic carbon to suggest that Ordovician wetlands may have been able to supply the large flux of low $\delta^{13}$C carbon required by the model. The potential for high rates of organic carbon export from land in the Ordovician suggests that terrestrial ecosystems may have played an important role in the global carbon cycle prior to the advent of vascular plants.

Our model results suggest that both epeiric sea and ocean-atmosphere $\delta^{13}$C were sensitive to variations in carbon exchange rates within the epeiric sea and between the epeiric sea and the ocean-atmosphere system. We conclude that changes in exchange rates, whether due to changing sea-level, or changing atmospheric pCO$_2$, are plausible drivers of epeiric sea carbon isotope excursions. By modelling periodic variations in sea-level within the epeiric sea, it becomes apparent that the epeiric sea $\delta^{13}$C record may also reflect a complex superposition of the effects of direct local carbon cycle perturbations and subsequent feedbacks from the ocean-atmosphere system. This points to complexity that is not addressed when steady state mass balance calculations are used to determine the magnitude of a change in carbon cycling as represented by locally or globally distributed $\delta^{13}$C excursions.

Both our steady state and transient model results suggest two broader implications for interpreting regionally or globally distributed $\delta^{13}$C excursions within epeiric sea sediments: First, the interactions between the epeiric sea and the ocean-atmosphere system imply that globally distributed carbon isotope excursions may have been driven not only by events acting directly on the ocean-atmosphere carbon cycle (e.g., via changes in thermohaline circulation), but also by events that initially acted on a much smaller scale within an epeiric sea. Second, the presence of similar-looking $\delta^{13}$C excursions in epeiric sea sediments of ostensibly the same age does not guarantee that the excursions are contemporaneous within a reasonable error, and consequently, could result in non-trivial errors in correlations based on carbon isotope stratigraphy.

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Appendix A. List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>1</td>
<td>Interior epeiric sea watermass</td>
</tr>
<tr>
<td>2</td>
<td>Seaward epeiric sea watermass</td>
</tr>
<tr>
<td>a</td>
<td>Atmosphere</td>
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</table>
Appendix B. Water and salt balances

\[
\frac{dV_i}{dt} = Q_{w1} + Q_{21} - [Q_{12} + Q_{1e}] \quad \text{B1}
\]

\[
\frac{dV_j}{dt} = Q_{12} + Q_{2s} - [Q_{21} + Q_{2a} + Q_{2e}] \quad \text{B2}
\]

\[
\frac{dV_s}{dt} = Q_{ws} + Q_{2s} - [Q_{2a} + Q_{se}] \quad \text{B3}
\]

\[
\frac{dS_i}{dt} = Q_{21}(S_2 - S_1) - S_1(Q_{w1} + Q_{1e}) \quad \text{B4}
\]

\[
\frac{dS_j}{dt} = Q_{12}(S_1 - S_2) + Q_{2a}(S_s - S_2) + Q_{2a}S_2 \quad \text{B5}
\]

\[
\frac{dS_s}{dt} = Q_{2a}(S_2 - S_s) - S_s(Q_{ws} + Q_{se}) \quad \text{B6}
\]

\[
\delta_i \quad \text{Carbon isotope composition of carbon reservoir } i, \text{ where } i = (1, 2, s, d, a).
\]

\[
d \quad \text{Deep ocean}
\]

\[
\Delta^a \quad \text{Carbon isotope fractionation due to air–sea CO}_2 \text{ exchange}
\]

\[
\Delta^o \quad \text{Carbon isotope fractionation due to primary productivity}
\]

\[
F_{ia}, F_{ai} \quad \text{Flux of carbon due to air–sea CO}_2 \text{ transfer from reservoir } i \text{ to the atmosphere, and from the atmosphere to reservoir } i\text{, respectively, where } i = (1, 2, s).
\]

\[
F_{ij} \quad \text{Flux of dissolved inorganic carbon from reservoir } i \text{ to reservoir } j \text{, where } i, j = (1, 2, s, d)
\]

\[
F_{sd} \quad \text{Flux of organic carbon from the surface ocean to the deep ocean}
\]

\[
F_{ix}, F_{ix}^* \quad \text{Flux of inorganic and organic carbon burial, respectively, from reservoir } i \text{, where } i = (1, 2, s).
\]

\[
Q_{ie} \quad \text{Net evaporation from reservoir } i \text{, where } i = (1, 2, s)
\]

\[
Q_{ij} \quad \text{Flux of water from reservoir } i \text{ to reservoir } j \text{, where } i, j = (1, 2, s)
\]

\[
Q_{w1}, Q_{ws} \quad \text{Flux of riverine carbon to reservoirs 1 and } s \text{, respectively.
\]

\[
S_i \quad \text{Salinity of reservoir } i \text{, where } i = (1, 2, s)
\]

\[
V_i \quad \text{Water volume of reservoir } i \text{, where } i = (1, 2, s)
\]

\[
\text{References}
\]


