Gradients in the carbon isotopic composition of Ordovician shallow water carbonates: A potential pitfall in estimates of ancient CO₂ and O₂

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1 **ABSTRACT**

2 The carbon isotopic composition of the global dissolved inorganic carbon (DIC)
3 reservoir is best estimated from open ocean pelagic carbonate sediments ($\delta^{13}\text{C}_{\text{carb}}$).
4 However, this is not practical for most of geologic time because seafloor subduction has
5 removed the pre-Jurassic record and these time periods may have lacked planktonic
6 calcifying organisms, and therefore shallow water carbonate platform or periplatform
7 sediments are utilized. Shallow water deposits are susceptible to a wide range of post-
8 depositional alteration processes and syn-depositional controls on $\delta^{13}\text{C}_{\text{carb}}$ that include
9 carbonate mineralogy, water mass restriction, and a host of related variables (e.g., pH,
10 temperature, organic decomposition, evaporation and CO_2 solubility) that can produce
11 local gradients in DIC. The degree to which shallow water $\delta^{13}\text{C}$ curves diverge from open
12 marine deposits may be critical to understanding how well global carbon cycle isotope
13 mass balance models can predict organic carbon burial rates, but documentation of such
14 divergence is often hindered by factors that limit chronostratigraphic correlation in
15 restricted water masses (e.g., endemic faunas). Here we integrate strontium isotope
16 ($^{87}\text{Sr}/^{86}\text{Sr}$) stratigraphy and biostratigraphy to compare $\delta^{13}\text{C}$ curves in a case study along
17 a depth transect in Middle-Late Ordovician carbonate platform settings. The restricted
18 tidal flat and more open marine deposits are offset by a maximum of $\sim 2\text{‰}$ during sea
19 level drop and $\sim 0\text{‰}$ during highstand flooding of the platform. Global carbon cycle
20 models such as GEOCARBSULF use published $\delta^{13}\text{C}_{\text{carb}}$ curves to drive organic carbon
21 burial rates under the assumption that $\delta^{13}\text{C}_{\text{carb}}$ reflects a global seawater signal. We show
22 here the potential pitfalls of using a published $\delta^{13}\text{C}_{\text{carb}}$ curve that violates this global
23 assumption. For the 460 million year Middle-Late Ordovician time bin in

GEOCARBSULF, improper usage of our locally depleted $\delta^{13}\text{C}$ curve to drive global organic carbon burial would result in erroneous atmospheric O_2 ($\sim 10.8\%$ O_2 , equal to about a 30% reduction from what it should be at $\sim 15.2\%$ O_2 using global $\delta^{13}\text{C}$) and CO_2 (~ 400 ppm too high, equal to about a 13% increase from what it should be at 2570 ppm CO_2). With detailed sedimentologic analysis, it may be possible to identify and exclude $\delta^{13}\text{C}$ samples that record the influences of local carbon cycling from global carbon cycle models such as GEOCARBSULF.

Keywords: Carbon isotope/Ordovician/Strontium isotope/global carbon cycle

1. INTRODUCTION

Carbon isotope ($\delta^{13}\text{C}$) stratigraphy has a unique role in the interpretation of Earth history as both a proxy for global carbon cycling and a correlation tool. Models of ancient atmospheric CO_2 and O_2 levels commonly utilize the carbon isotopic composition of marine carbonate ($\delta^{13}\text{C}_{\text{carb}}$) to quantify global rates of ^{13}C -depleted organic carbon burial over a range of timescales (e.g., Berner, 2006; Kump and Arthur, 1999; Goddris and Joachimski, 2004; Bergman et al., 2004; Royer et al., 2014; Bachan and Payne, 2015). Alternatively, these $\delta^{13}\text{C}_{\text{carb}}$ fluctuations may reveal global changes in the burial flux of ^{13}C -depleted carbonate that formed in sediments as a byproduct of iron or sulfate reduction (authigenic carbonate *sensu* Schrag et al., 2013, although enrichment in ^{13}C relative to seawater is also possible). Observed $\delta^{13}\text{C}_{\text{carb}}$ fluctuations may also reflect changes in the size of the global dissolved inorganic carbon (DIC) reservoir relative to total carbon throughput (e.g., Bartley and Kah, 2004; Maloof et al., 2010). The usefulness

of isotope mass balance models, however, is critically dependent on the assumption that the $\delta^{13}\text{C}_{\text{carb}}$ curves utilized record changes in the global DIC reservoir. For example, the magnitude of the well-known peak in atmospheric O_2 near the Carboniferous-Permian boundary (~ 300 million years ago) depends on whether the $\delta^{13}\text{C}$ input curve is based on rock from the ancient Tethys or from the isotopically lighter Panthalassic ocean basin (e.g., Berner, 2006; Royer et al., 2014). Thus, even after more traditional screening for post-depositional diagenesis, syn-depositional local processes that may decouple $\delta^{13}\text{C}_{\text{carb}}$ from global $\delta^{13}\text{C}_{\text{DIC}}$ remain a potential pitfall in global carbon cycle models.

The list of processes that may potentially decouple $\delta^{13}\text{C}_{\text{carb}}$ curves from global $\delta^{13}\text{C}_{\text{DIC}}$ is long, and may include water mass restriction that generates a $\delta^{13}\text{C}_{\text{DIC}}$ gradient reflecting local carbon fluxes (e.g., Patterson and Walter, 1994; Immenhauser et al., 2003, 2008; Panchuk et al., 2005; Gilleaudeau and Kah, 2013), changes in the ratio of aragonite to calcite in sampled sediment (Swart, 2008), local contributions from authigenic carbonate driven by alkalinity formed in sediments during iron or sulfate reduction (*sensu* Schrag et al., 2013), along with post-depositional burial or meteoric diagenesis (Melim et al., 2001). The pH of the system may also be important (Immenhauser et al., 2008) as well as a temperature-dependent $\delta^{13}\text{C}$ fractionation associated with equilibrium air–sea exchange of CO_2 ($\sim +1\text{‰}$ per 10°C cooling), although this maximum fractionation is nowhere fully achieved in today’s oceans because surface waters are replaced too quickly (e.g., upwelling) or the thermodynamic fractionation is opposed by a bulk transfer (kinetic) effect related to invasion or evasion of atmospheric CO_2 (Lynch-Stieglitz et al., 1995).

The influence of local carbon cycle processes can generally be minimized in studies that utilize $\delta^{13}\text{C}$ in pelagic (open ocean) carbonate, but potentially play a greater role in shallow water (neritic) platform carbonates (Panchuk et al., 2005; Immenhauser et al., 2008). Modern shallow water carbonate settings reveal $\delta^{13}\text{C}_{\text{DIC}}$ that varies from at or near global surface ocean $\delta^{13}\text{C}_{\text{DIC}}$ ($\sim 2\text{‰}$) in the isolated platform of the Great Bahama Bank (GBB) to ~ -2 to -4‰ lighter in terrestrially-influenced waters of Florida Bay (Patterson and Walter, 1994; Swart et al., 2009). Carbonate sediments that precipitate from DIC, whether in restricted or open ocean settings, also record $\delta^{13}\text{C}_{\text{carb}}$ that is heavier than $\delta^{13}\text{C}_{\text{DIC}}$ by anywhere from $+1\text{‰}$ for calcite to about $+2.7\text{‰}$ for aragonite as a result of fractionation during mineral formation (Swart, 2008, and references therein). Post-depositional carbonate diagenesis has the potential to alter primary $\delta^{13}\text{C}$ depending on water-rock interactions, such as observed in the strongly negative $\delta^{13}\text{C}_{\text{carb}}$ trend in the top ~ 100 m of GBB sediment cores linked to meteoric diagenesis during Pleistocene sea level fluctuations (Melim et al., 2001). Further complications arise where shallow platform sediments that have acquired a local $\delta^{13}\text{C}$ signal (i.e., due to diagenesis, mineralogy, or local carbon cycling) mix with pelagic carbonate in periplatform settings (Godet et al., 2006; Swart, 2008).

Despite the potential for ancient platform and periplatform $\delta^{13}\text{C}_{\text{carb}}$ to record trends unrelated to the global carbon cycle (e.g., Swart, 2008), there are many well-studied examples in which positive or negative shifts in global $\delta^{13}\text{C}_{\text{DIC}}$ are clearly recorded. For example, prominent global $\delta^{13}\text{C}$ excursions in pelagic carbonates have been traced into shallow carbonate settings for the early Cenozoic Paleocene-Eocene Thermal Maximum (PETM) (Robinson, 2011; Zamagni et al., 2012), the Late Cretaceous

92 Cenomanian-Turonian Oceanic Anoxic Event (OAE) (Parente et al., 2007), and the Early
93 Jurassic Toarcian OAE (Woodfine et al., 2008). However, the magnitudes of these $\delta^{13}\text{C}$
94 excursions recorded in shallow water carbonates often appear to be exaggerated relative
95 to the global signal (Immenhauser et al., 2008), which is problematic for use as a $\delta^{13}\text{C}_{\text{DIC}}$
96 proxy in global carbon cycle models. Sea level fall, in particular, affects $\delta^{13}\text{C}_{\text{carb}}$ in
97 platform or periplatform settings by restricting exchange with the open ocean or even
98 other parts of the platform (Panchuk et al., 2005), promoting shedding of aragonite-rich
99 (high $\delta^{13}\text{C}$ relative to calcite) sediments into adjacent platform or periplatform settings
100 (Swart, 2008), or diagenesis (Immenhauser et al., 2003). Although the lack of pelagic
101 (open ocean) carbonate in pre-Jurassic examples precludes straightforward comparisons
102 to global $\delta^{13}\text{C}_{\text{DIC}}$, significant spatial variation in $\delta^{13}\text{C}$ in platform settings has been
103 documented for several time intervals in the Paleozoic (e.g., Immenhauser et al., 2008).

104 A significant challenge for improved characterization of gradients in $\delta^{13}\text{C}$ along
105 depth transects in ancient platforms is precise chronostratigraphic correlation. Strontium
106 isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) stratigraphy provides a useful correlation tool that is independent of
107 biostratigraphy and carbon isotope-based correlations. Strontium has a residence time in
108 the ocean nearly an order of magnitude longer than carbon, which supports the
109 assumption of global homogeneity, but also impacts the potential time resolution
110 attainable (McArthur et al., 2012). Therefore, success in correlating $\delta^{13}\text{C}$ curves is
111 dependent on the rate of change in the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Woodfine et al., 2008;
112 Huck et al., 2011; Di Lucia et al., 2012; Frijia et al., 2015; Navarro-Ramirez et al., 2015)
113 as well as the uncertainty associated with measuring ancient $^{87}\text{Sr}/^{86}\text{Sr}$ in geologic
114 samples. Here we utilize a rapid change in $^{87}\text{Sr}/^{86}\text{Sr}$ in the Middle-Late Ordovician (465

to 455 Myrs) to correlate a $\delta^{13}\text{C}$ curve from a carbonate platform deposited in a restricted, tidal flat setting in the Appalachian Basin (U.S.A.) to more open marine sections from Baltoscandia (Fig. 1). The rate of change in $^{87}\text{Sr}/^{86}\text{Sr}$ at $\sim 50\text{-}100 \times 10^{-6}$ per million years during parts of the Darriwilian and Sandbian Stages is among the fastest in the entire Phanerozoic (Supplementary Information Fig. S1; McArthur et al., 2012; Saltzman et al., 2014). Although we find evidence for strong coupling between $\delta^{13}\text{C}$ trends in restricted carbonate platform and open marine deposits that is consistent with global forcing (e.g., a change in the fraction of carbon buried as organic matter, or f_{org}), we also observe potential environmental effects from offsets in $\delta^{13}\text{C}$ as large as $\sim 2\text{‰}$ during relative sea level fall. Ultimately, the aim of our study is not to uniquely isolate the factors responsible for the $\delta^{13}\text{C}$ gradient between restricted and open ocean settings, because the potential local processes involved are too numerous and require a complex and spatially variable box modeling approach (i.e., building on the efforts of Panchuk et al., 2005). Rather, our study is aimed at: 1) providing what we believe to be an excellent case study demonstrating the existence of a $\delta^{13}\text{C}$ gradient in DIC on ancient platforms, and 2) calculating the magnitude of the potential pitfall this represents for a global carbon cycle mass balance model such as GEOCARBSULF that uses $\delta^{13}\text{C}$ to drive global organic carbon burial.

2. GEOLOGIC BACKGROUND

Middle to Late Ordovician carbonates in the central Appalachian Basin (Virginia, West Virginia, Pennsylvania, and Maryland) record shallow water environments that mark the transition between the large-scale ($\geq 10^7$ yrs) Sauk and Tippecanoe stratigraphic

sequences. The end of the Sauk sequence in this region is characterized by peritidal to supratidal dolomite of the Knox or Beekmantown groups that are overlain by shallow water, limestone-dominated successions of the basal Tippecanoe sequence (Brezinski et al., 2012). Only in the region of western Maryland and adjacent parts of Pennsylvania is the Sauk-Tippecanoe transition relatively conformable between the Pinesburg Station Dolomite of the upper Beekmantown Group and the overlying Row Park and New Market formations of the St. Paul Group (Fig. 1). The St. Paul Group, which is the main focus of our study, contains shallow subtidal to supratidal facies that have been shown to be similar to those described from the modern tidal flats of Andros Island and the Great Bahama Bank (Mitchell, 1985). The fenestral, laminated and stromatolitic facies of the St. Paul Group lack a substantial macrofauna, consistent with hypersalinity and severely restricted exchange with the open ocean (Fig. 2). Although conodont microfossils are present throughout the St. Paul, the endemic and long-ranging taxa preclude detailed age control (Brezinski et al., 2012; Saltzman et al., 2014). However, the long-ranging conodonts in the St. Paul Group can be analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ and allow for correlation between the shallow water, restricted facies in Maryland (Fig. S2; Saltzman et al., 2014) and the relatively open-marine strata of Baltoscandia (Fig. 1) that contain index fossils for the standard North Atlantic conodont zones (Fig. S3; Ainsaar et al., 2010).

3. METHODS

For $\delta^{13}\text{C}$ study, fresh rock surfaces were generated by a water-based diamond-blade saw and components were drilled (~0.5 to 1.5 g of powder) from polished slabs with a preference for micritic (fine-grained) portions. Because the samples were collected

Figure 1. A. Paleogeographic map for Middle-Late Ordovician showing position of Laurentian epicontinental sea and Baltoscandian ocean-facing sections (R. Blakey, <http://cpgeosystems.com>). B. Position of Clear Spring, Maryland section (red filled circle) within Bahamian-type carbonate platform in the Appalachian Basin (blue fill pattern). Note that although general Mid-Late Ordovician isopachs extend away from this isolated platform, rocks of the middle part of the Darriwilian Stage (Middle Ordovician) are not known outside of the blue filled area because of the Knox unconformity (Brezinski et al., 2012; Saltzman et al., 2014). C, D. Baltoscandian sections and basins discussed in text, with red box in C outlining area of interest in D (modified from Ainsaar et al., 2010). In C, squares represent sections that contain the portion of the Middle-Late Ordovician $\delta^{13}\text{C}$ curve that is also represented in the Appalachian Basin (bold text used for the section plotted in Fig. 4). Dashed blue lines delineate the boundary between the relatively deep water Scandinavian and Livonian Basins from the shallower Estonian Shelf. In D, facies belts are shown (Ainsaar et al., 2010) and filled circles represent sections that contain the portion of the Middle-Late Ordovician $\delta^{13}\text{C}$ curve that is represented in the Appalachian Basin (bold text used for the sections plotted in Fig. 4). Squares in D represent outcrops and circles are drill cores.

and analyzed over a period of several years, it became necessary for $\delta^{13}\text{C}$ values to be measured in three different laboratories using: a Kiel Carbonate Device III attached to a Thermo Finnigan MAT 253 Dual Inlet System mass-spectrometer (University of Kansas), a Kiel Carbonate Device III attached to a Thermo Delta IV mass-spectrometer (Ohio State University), and a Gas Bench II attached to a Thermo Delta Plus XP mass spectrometer (Indiana University). Powders for $\delta^{13}\text{C}$ analyses were weighed and roasted in a vacuum oven at 100°C for at least 8 hours to remove water and volatile organic contaminants. Between 0.1-0.3 mg of carbonate were reacted at 72°C with 3-5 drops of anhydrous phosphoric acid for four minutes on the Kiel devices, and at least 2 hours on the Gas Bench II. Isotope ratios were corrected for acid fractionation and ^{17}O contribution and reported in per mil notation relative to the Vienna Pee Dee Belemnite (V-PDB) standard. Precision and calibration of data were monitored through routine analysis of the IAEA NBS-18 and NBS-19 standards and internal laboratory standards. Standard deviations for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are 0.05‰ and 0.10‰, respectively (one sigma). To examine potential pitfalls in use of local $\delta^{13}\text{C}$ curves in isotope mass balance modeling, we used the model GEOCARBSULF for our 460 Myr Middle-Late Ordovician time bin (Royer et al., 2014, and https://figshare.com/articles/code_to_run_GEOCARBSULF_model/902207 available for download) (see also Supplementary Figures Fig. S4, and Supplementary Tables S3-S5).

Figure 2. Clear Spring, Maryland (Appalachian Basin) $\delta^{13}\text{C}$ curve (see Table S1) with three-point moving average (black line) plotted with sedimentary features, generalized facies interpretations, and images of hand samples (A–E) and field photographs (1–5) keyed to sample horizons (red horizontal lines) along isotope profile. A) Nodular lime wacke-packstone with brachiopod and trilobite skeletal fragments, B) Laminated, crypt-algal lime mudstone of tidal flat facies of middle New Market Fm., C) Laminated lime mudstone with mudcracks (white dashed line), D) Dark laminated lime mudstone with reworked rip-up clasts and soft-sediment deformation (microfaulting), E) Spar-filled burrows in lime mudstone of lower shallow tidal flat facies, 1) Weathered red-orange contact in roadcut between tidal flat environment of the New Market Fm. (left) and open marine mixed carbonate-siliciclastic lithologies of the Chambersburg Fm. (right), 2) Stromatolite (yellow arrow) from the restricted lagoon facies of the New Market Fm., 3) Graded, tabular rip-up clasts interbedded in fine-grained laminated-to cross-bedded wackestone-packstone reflecting high-energy, storm-influenced conditions, 4) Mud-cracked, laminated lime mudstone from peritidal tidal flat of lower Row Park Fm., 5) Fenestral lime mudstone with spar-filled voids and macluritid gastropod mold (white dashed line). All scale bars (white in field photographs and black for hand samples) represent 2 cm, m = mudstone, w = wackestone, p = packstone, g = grainstone. Dap. = Dapingian Stage.

180 4. RESULTS

181 We analyzed $\delta^{13}\text{C}$ from Middle to Late Ordovician carbonate rocks at the Clear
 182 Spring, Maryland section (central Appalachian Basin) (Fig. 2; Supplementary
 183 Information Table S1). Although our dataset spans several formations from the

Dapingian through Sandbian stages, we focus attention here on the portion of the $\delta^{13}\text{C}$ curve in the restricted marine St. Paul Group (Row Park and New Market formations) and open marine Chambersburg Formation (Mitchell, 1985) (Fig. 2) because this interval can be correlated to sections in Baltoscandia by integrating $^{87}\text{Sr}/^{86}\text{Sr}$ and conodont biostratigraphy (Fig. 3; Figs. S2, S3). The age of the St. Paul Group (Row Park and New Market formations) and Chambersburg Formation at the Clear Spring (Appalachian) section is constrained by previously published measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ on conodont apatite and calibration of the resulting $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 3; Fig. S2) to the standard conodont biozonation and geologic time scale (Saltzman et al., 2014). Although conodont species were recovered from the Clear Spring section, these faunas are largely dominated by long-ranging or endemic taxa that are of limited value for global correlations. The drop in $^{87}\text{Sr}/^{86}\text{Sr}$ from ~ 0.7087 to 0.7080 (Fig. 3) at Clear Spring corresponds to a time interval from ~ 464 to 456 Ma, which allows correlation to fossiliferous, open marine sections in Baltoscandia that contain cosmopolitan conodont index fossils representative of this same time period (Supplementary Information Fig. S3, Tables S1, S2; Ainsa et al., 2010). Studies of $^{87}\text{Sr}/^{86}\text{Sr}$ of conodont apatite have not yet been published from Baltoscandia. Ultimately, although the longer residence time of strontium relative to carbon in the oceans generally hinders the use of $^{87}\text{Sr}/^{86}\text{Sr}$ to correlate short term $\delta^{13}\text{C}$ excursions, the high rate of change in our study interval ($\sim 50\text{-}100 \times 10^{-6}$ per million years during parts of the Darriwilian and Sandbian Stages; Saltzman et al., 2014) potentially provides a unique opportunity, particularly as uncertainty in measurement of geologic samples is minimized with improved techniques.

The portion of the $\delta^{13}\text{C}_{\text{carb}}$ curve at Clear Spring that we have focused on in detail cycles from $\sim +1\text{‰}$ at the base of the St. Paul Group to -3‰ and then back again to $+1\text{‰}$ near the base of the Chambersburg (Fig. 2). The lightest $\delta^{13}\text{C}$ values correspond to intervals showing the strongest sedimentological evidence of water mass restriction while a shift to relatively less restricted conditions coincides with heavier $\delta^{13}\text{C}$ (Mitchell, 1985). For example, stromatolites are documented for the middle part of the St. Paul Group when a minimum in $\delta^{13}\text{C}$ is reached, while the basal St. Paul and Chambersburg formations record higher $\delta^{13}\text{C}$ and contain a macrofauna indicative of less restricted conditions (Fig. 2). Comparison of the use of the lightest $\delta^{13}\text{C}$ values from the St. Paul Group at Clear Spring (Appalachian Basin) and coeval heavier values from Baltoscandia in the global carbon cycle model GEOCARBSULF for the 460 million year Middle-Late Ordovician time bin shows differences in atmospheric O_2 ($\sim 10.8\%$ O_2 for Clear Spring, equal to about a 30% reduction from Baltoscandia at $\sim 15.2\%$ O_2) and CO_2 (~ 400 ppm higher for Clear Spring, equal to about a 13% increase from Baltoscandia at 2570 ppm CO_2).

5. DISCUSSION

The results of our study show evidence for both: 1) strong coupling between $\delta^{13}\text{C}$ trends in restricted carbonate platform and open marine deposits that is consistent with global forcing (e.g., a change in the fraction of carbon buried as organic matter, or f_{org}); and 2) a $\delta^{13}\text{C}$ gradient as large as $\sim 2\text{‰}$ between restricted and more open ocean settings during relative sea level fall. The existence of $\delta^{13}\text{C}$ gradient as large as $\sim 2\text{‰}$ represents a pitfall in estimates of O_2 and CO_2 in the global carbon cycle model GEOCARBSULF (that

Figure 3. $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ curves for the Clear Spring, Maryland (Appalachian) section showing basis for conodont zones and age control. For example, the $\delta^{13}\text{C}$ minimum above the MDICE is dated to the *serra* conodont zone by a $^{87}\text{Sr}/^{86}\text{Sr}$ value in that same sample horizon of ~ 0.7084 (see Fig. S2). Conodont-apatite $^{87}\text{Sr}/^{86}\text{Sr}$ data and ages based on calibration to global Sr isotope curve are from Saltzman et al. (2014) (Fig. S2; Table S1). Subdivisions of $\delta^{13}\text{C}$ curve, including Middle Darriwilian Isotope Carbon Excursion (MDICE) and Kukruse Low, are based on correlation to Baltoscandia (Fig. S3; Ainsaar et al., 2010). Upper Darriwilian Isotope Shift (UDIS) is equivalent to BC 5. L.O. = Lower Ordovician, Fl. = Floian Stage, Dap. = Dapingian Stage, undef. = undefined conodont zone, *altifron.* = *altifrons*, *sinuos.* = *sinuosa*, *varia.-holo.* = *Eoplacognathus variabilis-holodentata*, *suec.* = *suecicus*, *frie.* = *friendsvillensis*, *anser.* = *anserinus*, *var.* = *Baltoniodus variabilis*, *ger.* = *gerdae*, *alob.* =

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252 *alobatus*.

253 uses $\delta^{13}\text{C}$ to drive global organic carbon burial), which we outline in the second part of

254 our Discussion. Although we also discuss here the wide range of variables that could be

255 responsible for the $\delta^{13}\text{C}$ gradient between restricted and open ocean settings, we are

256 mainly concerned with whether a post-depositional (diagenetic) origin is plausible, and

257 therefore ultimately defer drawing conclusions on the range of possible non-diagenetic

258 explanations to a future contribution that develops a complex and spatially variable box

259 modeling approach building on the efforts of Panchuk et al. (2005).

260

261 5.1 Gradient in $\delta^{13}\text{C}_{\text{DIC}}$ between restricted platform and open marine successions

262 Using our age models based on $^{87}\text{Sr}/^{86}\text{Sr}$ and conodont zonation, we show that the

263 overall trends in $\delta^{13}\text{C}$ correlate well between the Appalachian Basin (Clear Spring,

Maryland) and Baltoscandia (Fig. 4) (Supplementary Information Figs. S2, S3; Table S2). However, the negative shift in $\delta^{13}\text{C}$ in the middle part of the St. Paul Group (late Darriwilian to early Sandbian) reaches minimum values that are 2‰ lighter in the Appalachian Basin (-3‰ compared to -1‰ in Baltoscandia). Because the Baltoscandian sections contain a relatively diverse and open marine fauna in a ramp setting with continuous deposition (Ainsaar et al., 2010) (Fig. 1), we infer these to be a reasonable approximation of the global $\delta^{13}\text{C}$ signal. With all appropriate caveats in attempting to define a global seawater endmember, including recognition of the fact that there is no ancient Ordovician analog for fully open ocean pelagic environments, we continue our discussion under the assumption that we have identified a locally ^{12}C -enriched $\delta^{13}\text{C}$ signal in the Appalachian Basin. We now consider whether these lighter values $\delta^{13}\text{C}$ can be attributed to diagenesis and mineralogic changes, or water mass restriction and a range of associated local variables (e.g., pH, temperature, organic decomposition, evaporation and CO_2 solubility) that can produce local gradients in DIC (Immenhauser et al., 2008; Swart, 2008; Swart et al., 2009).

Because meteoric waters are enriched in ^{12}C from oxidized organic carbon in soil zones and also show strong enrichment in ^{16}O derived from evaporation of seawater, meteoric diagenesis in carbonates of all ages is characteristically recognized by covariant trends in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (e.g., Melim et al., 2001). $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ do not covary in the Clear Spring (Appalachian) section or in the Baltoscandian sections (Figs. 5, 6). Instead, during the interval in which $\delta^{13}\text{C}$ cycles from $\sim +1\text{‰}$ at the base of the St. Paul Group to -3‰ and then back again to $+1\text{‰}$ near the base of the Chambersburg, there is an overall rising trend in $\delta^{18}\text{O}$ at the Clear Spring section (Fig. 5). The factors responsible for

Figure 4. Clear Spring, Maryland $\delta^{13}\text{C}$ curve and four Baltoscandian sections with age models based on available biostratigraphy (Fig. S3; Table S2, Ainsaar et al., 2010) and $^{87}\text{Sr}/^{86}\text{Sr}$ stratigraphy (Figs. S1, S2; Table S1, Saltzman et al., 2014). See Fig. 1 for locations of sections. For notes on stages, conodont zones and isotope intervals see Fig. 3. The main focus in the text is comparison of the portions of the $\delta^{13}\text{C}$ curve represented by the MDICE, Kukruse Low and UDIS because earlier intervals are poorly correlated between the Appalachian and Baltoscandian regions. Note that peak values of MDICE are overlapping and nearly indistinguishable between the Appalachian and Baltoscandian regions, while the Kukruse Low is significantly exaggerated by $\sim 2\text{‰}$ (and appears to reach a minimum earlier) in the Appalachian Basin.

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311 observed $\delta^{18}\text{O}$ trends in ancient carbonates are likely complex, and in addition to
 312 diagenesis may also include primary water mass effects (i.e., temperature or evaporation)
 313 (e.g., Kah, 2000). Noise in the $\delta^{18}\text{O}$ curve in our Clear Spring section, in which some
 314 individual samples are shifted several ‰ heavier than adjacent samples, appears to
 315 correspond largely to dolomitized beds (Fig. 5). Although there is a difference in
 316 fractionation in dolomite formation that produces heavier $\delta^{18}\text{O}$ relative to calcite
 317 (Vasconcelos et al., 2005), in many ancient studies this fractionation is not observed and
 318 thus episodes of intense evaporation (e.g., Kah, 2000) may be responsible for both
 319 dolomitization and positive shifts in $\delta^{18}\text{O}$ in our Ordovician dataset.

320 Although meteoric diagenesis seems an unlikely source of the 2‰ lighter $\delta^{13}\text{C}$
 321 values in the Clear Spring (Appalachian) section relative to Baltoscandia, we must also

consider the possibility that the sampled carbonate formed locally in sediments as a byproduct of iron or sulfate reduction (authigenic carbonate *sensu* Schrag et al., 2013) , Although this process generally results in ^{13}C -depleted $\delta^{13}\text{C}$, ^{13}C -enriched DIC is also possible (e.g., Jones et al., 2016). The lightest $\delta^{13}\text{C}$ near -3‰ are associated with darker-colored, laminated lithologies (Fig. 2), but drawing conclusions about oxygenation or rates and pathways of organic matter oxidation in the sediments is not straightforward. Contrary to expectation, these darker-colored, laminated lithologies show pyrite concentrations (between 14 and 64 ppm) that are lower than in other parts of the succession (up to 500 ppm) (Young et al., 2016). The low pyrite concentrations, together with the fact that $\delta^{13}\text{C}_{\text{org}}$ tracks the $\delta^{13}\text{C}_{\text{carb}}$ minimum (Young et al., 2016), argues against a simple relationship to the local addition of carbonate produced as a byproduct of iron or sulfate reduction. Nonetheless, we would expect to revisit these possibilities as advances are made in the how to distinguish carbonate formed in this manner (‘authigenic carbonate’ *sensu* Schrag et al., 2013).

The mixing of aragonitic and calcitic components is a potentially important process affecting $\delta^{13}\text{C}_{\text{carb}}$, but this does not seem to be a likely explanation for the temporal trends or spatial gradient in $\delta^{13}\text{C}$ that we observe (Figs. 2, 4). The mineralogy of sediment producing algae (e.g., receptaculitids), and dominant reef builders (rugose and tabulate corals, stromatoporoids) in the Ordovician was most likely calcite, but the mineralogy of abiotic precipitates shows a temperature-dependence (Balthasar and Cusack, 2015). Although the Ordovician was likely characterized by low Mg:Ca ratios and calcite seas, climatic conditions would favor abiotic aragonite precipitation in shallow, warm waters of these traditional calcite seas that may have been up to 10 °C

warmer than traditional aragonite-sea intervals (Balthasar and Cusack, 2015). If indeed calcite sea intervals were characterized by the co-precipitation of aragonite and calcite in environments above 20 °C, we might expect heavier $\delta^{13}\text{C}$ values for the dominantly mud-rich facies in the Clear Spring section compared to the cooler, skeletal-rich data from Baltoscandia. However, this is opposite to what is observed and in fact Baltoscandia records heavier $\delta^{13}\text{C}$ than Clear Spring (Fig. 4). Perhaps the cooler water temperatures in the higher latitude Baltoscandian sections in part accounts for higher $\delta^{13}\text{C}$ that results from the temperature-dependent fractionation (Lynch-Stieglitz et al., 1995), but the magnitude of this fractionation is small (~ 0.1 per °C) and unlikely to account for the observed 2‰ difference with the Clear Spring (Appalachian Basin) section.

We propose that the most likely explanation for the lower $\delta^{13}\text{C}$ values in the Appalachian Basin in the middle St. Paul Group is a flux of isotopically light carbon that drove down the $\delta^{13}\text{C}$ of DIC locally. Although the source of this light carbon could relate to either oxidation of organic matter on land delivered by rivers or marine oxidation within the water mass (or at or below the sediment-water interface), Panchuk et al. (2005) concluded that the supply of low $\delta^{13}\text{C}$ carbon (-29‰) to the inner region of an Ordovician epeiric sea (at a rate of 17.4×10^{12} mol C per yr) could not have been sustained over the long term by remineralization of organic carbon stored in sediments. Instead, Panchuk et al. (2005) suggest that the low $\delta^{13}\text{C}$ flux was likely derived from bryophyte-dominated terrestrial ecosystems prior to the advent of vascular plants. Future modeling efforts are needed to examine the robustness of this conclusion for older or younger time periods, and different size epeiric seas. Changes in pH or temperature are also unlikely to account for the full magnitude of the $\delta^{13}\text{C}$ gradient we observe.

368 Sea level fall can result in basin restriction that promotes development of local
 369 gradients in $\delta^{13}\text{C}$ (Immenhauser et al., 2008), and in the Clear Spring section there is
 370 sedimentologic and faunal evidence for a cycle of relative sea level that parallels changes

Figure 5. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stratigraphy for the Clear Spring section (Appalachian Basin; see detailed stratigraphic column in Fig. 2) section (see Table S1) showing the lack of covariation in the interval from the MDICE through the UDIS, inconsistent with meteoric diagenetic control on the negative shift (Kukruse Low). Scatter in $\delta^{18}\text{O}$ and values to the right of the dashed vertical line can be in large part accounted for by changes in dolomite % that reflect either a change in fractionation relative to calcite (Vasconcelos et al., 2005) or evaporative conditions (Kah, 2000). Calcite/dolomite ratio was measured qualitatively by noting the vigor of the reaction (on a scale of 1-5) with a drop of dilute (6%) hydrochloric acid on a polished slab (such as those shown in Fig. 2).

371 in $\delta^{13}\text{C}$ (Fig. 2) (Mitchell, 1985; Brezinski et al., 2012). Basin restriction is reflected in
 372 the transition from the shallow tidal flat facies of the lower St. Paul Group containing
 373 gastropod molds and fenestral limestone (similar to those observed northwest of Andros

374 Island on the GBB; Mitchell, 1985) into the restricted lagoonal facies in the middle part
 375 of the St. Paul Group marked by a near complete lack of a macrofauna and the presence
 376 of stromatolites (Brezinski et al., 2012) near the minimum in $\delta^{13}\text{C}$ (Fig. 2). The entire St.
 377 Paul Group succession, although representative of a restricted tidal flat and lagoonal
 378 setting, is continuously marine based on identification of conodont microfossils, a fossil
 379 group not known to inhabit freshwater environments (Fig. 2). In the base of the overlying
 380 Chambersburg Formation a fully open marine fauna, including the echinoderm taxa
 381 *Echinosphaerites*, is present in association with subtidal carbonate ramp facies, and $\delta^{13}\text{C}$
 382 values return to levels similar to the basal St. Paul Group (Fig. 2).

Figure 6. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ cross plot of all Appalachian (see Table S1) and Baltoscandian data from Fig. 4 (Ainsaar et al., 2010) showing the lack of covariation on both continents, consistent with a global marine carbon cycle driver for the shift from MDICE to Kukuruse Low (Fig. 4).

398

399 5.2 Target $\delta^{13}\text{C}$ curves for use in global carbon cycle models

400 The presence of local gradients in shallow water $\delta^{13}\text{C}_{\text{DIC}}$ requires careful scrutiny
401 of composite curves used for global carbon cycle models that estimate atmospheric O_2
402 and CO_2 over geologic time (Berner, 2006; Royer et al., 2014). Although the optimal
403 carbonate component for recording global ocean $\delta^{13}\text{C}_{\text{DIC}}$ will have formed in the deep sea
404 because it contains ~ 85 and 95% of the exogenic carbon cycle by mass (Sluijs and
405 Dickens, 2012), open surface ocean $\delta^{13}\text{C}$ can still potentially be utilized. This is because
406 the magnitude of the offset between the open surface and deep oceans can be predictable
407 ($\sim 2\text{‰}$ heavier in the surface ocean due to biological pumping of ^{12}C) and vary by $\leq 1\text{‰}$
408 even in times of enhanced primary production (e.g., Vincent and Berger, 1985) or major
409 climate change (e.g., Paleocene-Eocene Thermal Maximum (PETM; McInerney and
410 Wing, 2011). In contrast to the open surface ocean, many ancient restricted carbonate
411 platform settings show $\delta^{13}\text{C}$ depletion relative to the deep sea global ocean $\delta^{13}\text{C}_{\text{DIC}}$ such
412 as is observed in modern Florida Bay (Patterson and Walter, 1994), although $\delta^{13}\text{C}$
413 enrichment is also possible (e.g., Kozłowski, 2015).

414 Immenhauser et al. (2008) estimate that restricted platform $\delta^{13}\text{C}$ was lighter by $\leq$
415 2‰ relative to more distal settings in detailed transects constructed for single time
416 horizons in the Early Cretaceous (early Aptian) and Early Pennsylvanian (Bashkirian-
417 Moscovian). Our Ordovician example also records $\sim 2\text{‰}$ lighter $\delta^{13}\text{C}$ in the most
418 restricted facies (Appalachian Basin) relative to more open ocean settings (Baltoscandia)
419 during sea level lowstand, and this offset becomes almost nonexistent ($\sim 0.5\text{‰}$) during
420 highstand when a visible macrofauna is present (Fig. 4). Similarly, shallow water
421 restricted platform deposits of the intensively studied Late Cretaceous Cenomanian-
422 Turonian boundary interval record 2‰ lighter $\delta^{13}\text{C}$ values compared to pelagic sections

during sea level lowstand, but have nearly identical $\delta^{13}\text{C}$ to pelagic sections during transgression associated with the global positive excursion (Parente et al., 2007). Other time intervals with well-studied $\delta^{13}\text{C}$ excursions during which gradients of generally $\leq 2\text{‰}$ are observed with the lightest values in restricted settings include the PETM (Zamagni et al., 2012), early Aptian (Early Cretaceous; Huck et al., 2011), early Toarcian (early Jurassic; Woodfine et al., 2008), Hettangian (early Jurassic; Bachan et al., 2012), early Mississippian (Saltzman et al., 2004), Ludfordian (late Silurian; Fryda and Manda, 2013), Hirnantian (late Ordovician; Young et al., 2010), SPICE (Saltzman and Thomas, 2012), and possibly Mesoproterozoic (Kah et al., 2012; Gilleaudeau and Kah, 2013). Some reports of gradients in Ordovician-Silurian intervals indicate relatively heavy $\delta^{13}\text{C}$ values characterize semi-restricted epeiric seas (e.g., Kozłowski, 2015; Farkas et al., 2016), emphasizing the importance of careful evaluation of a host of variables that may be related to stratigraphic completeness, diagenesis, organic matter oxidation, and mixing of water masses (Jones et al., 2016; Kah et al., 2016).

Panchuk et al. (2005) showed that the $\delta^{13}\text{C}$ gradient between the open ocean and restricted basin (initially ^{12}C -enriched) reaches a maximum when air-sea exchange is limited, input of ^{12}C from terrestrial runoff is proportionally high and removal through burial of organic matter is low within the epicontinental sea, and removal of ^{12}C in the open ocean by photosynthesis is relatively high. Although gradients of $\leq 2\text{‰}$ appear to be the maximum achieved under conditions of severe restriction, local offsets larger than 2‰ have been reported, such as in the Late Ordovician (e.g., Holmden et al., 1998; Panchuk et al., 2005; Jones et al., 2016), Neoproterozoic (Jiang et al., 2007) or Mesoproterozoic (Gilleaudeau and Kah, 2013). However, diagenetic carbonate,

446 sedimentary hiatuses (Föllmi et al., 2006) and correlation uncertainty (e.g., Cramer et al.,
 447 2015) must be ruled out in these cases before acceptance of the existence of unusually
 448 large gradients in $\delta^{13}\text{C}$ of DIC (Metzger and Fike, 2013). Furthermore, circumstances
 449 exist in which the heaviest observed $\delta^{13}\text{C}$ values for a given time period may be local
 450 artifacts (i.e., carbonate produced by early diagenetic methanogenesis) (Jones et al.,
 451 2016) and therefore not representative of gradients that are defined by differences in DIC
 452 (i.e., between open ocean and restricted water mass as opposed to sediment pore fluids).
 453 In addition, during periods in which aragonite production is expected to be important in
 454 proximal, warm water environments while calcite dominates in distal settings, the heavier
 455 $\delta^{13}\text{C}$ of aragonite ($\sim +1.7\text{‰}$ more than calcite) will complicate efforts to compare DIC
 456 signals along a depth transect (Godet et al., 2006; Swart, 2008).

457 Global carbon cycle models such as GEOCARBSULF target $\delta^{13}\text{C}_{\text{carb}}$ curves to
 458 drive organic carbon burial rates that are presumed to reflect a global seawater signal.
 459 The potential pitfalls of using a published $\delta^{13}\text{C}_{\text{carb}}$ curve that violates this global
 460 assumption can be evaluated for our 460 million year Middle-Late Ordovician time bin in
 461 GEOCARBSULF (Royer et al., 2014, and available for download at
 462 https://figshare.com/articles/code_to_run_GEOCARBSULF_model/902207). Use of a
 463 $\delta^{13}\text{C}$ curve that exaggerates net changes by 2‰ as we observe in the Middle Ordovician
 464 (Fig. 4) will have a significant effect on estimates of the fraction of the total carbon burial
 465 flux to sediments that is organic (f_{org}), which directly influences atmospheric O_2 and to a
 466 lesser extent CO_2 in models such as GEOCARBSULF and COPSE (Bergman et al.,
 467 2004; Berner, 2006; Royer et al., 2014) (compare Middle Ordovician curves in Saltzman
 468 and Thomas, 2012 and Ainsaar et al., 2010). Using GEOCARBSULF for our 460 Myr

Middle-Late Ordovician time bin, we show that use of the relatively low $\delta^{13}\text{C}$ values as observed in the restricted tidal flat setting in the Appalachian Basin would produce O_2 levels at 10.8% compared to 15.2% if we use the more open marine (represented by Baltoscandian sections) that are heavier in $\delta^{13}\text{C}$ by 2‰ (see Table 1, Supplementary Figures Fig. S4, and Supplementary Tables S3-S5).

The pitfall of using a local $\delta^{13}\text{C}$ in global carbon cycle models is less dramatic for CO_2 , which is dominated by silicate weathering rather than organic carbon burial in GEOCARBSULF. However, the erroneous input of the lowest $\delta^{13}\text{C}$ values in the restricted marine Clear Spring (Appalachian) section into the model produces levels nearly 400 ppm higher (2960 ppm) compared to more globally representative open marine sections (2570 ppm) (Table 1). The effect of erroneous use a 2‰ lighter $\delta^{13}\text{C}$ from the restricted platform also increases model failure rate in GEOCARBSULF

Table 1. Levels of atmospheric O_2 and CO_2 and model failure rate calculated from GEOCARBSULF model (Royer et al., 2014) with varying $\delta^{13}\text{C}$ for the 460 Myr Middle Ordovician time bin (See Supplementary Information Tables S3-S5 and Fig. S4).

460 Myr	-1 ‰ ^a (Baltoscandia)	-2 ‰ (intermediate)	-3‰ (Clear Spring, MD)
O_2 (%)	15.2	12.7	10.8
CO_2 (ppm)	2570	2740	2960
Model Failure Rate (%) ^b	82.5	84.9	91.5

^a $\delta^{13}\text{C}$ of -1 ‰ is closest to the global open marine seawater value, such as observed in Baltoscandia, whereas -3 ‰ is overprinted by local carbon cycling such as in the restricted tidal flat setting at Clear Spring, Maryland.

^b Model failure occurs when, for example, negative values of atmospheric O_2 and CO_2 are calculated, or when the model fails to predict modern levels of atmospheric O_2 and CO_2 at the end of the run.

by ~ 10% (from 82.5 to 91.5), which occurs when, for example, negative values of atmospheric O_2 and CO_2 are calculated, or when the model fails to predict modern levels

of atmospheric O₂ and CO₂ at the end of the run (Royer et al., 2014) (Table 1; see also Supplementary Information Fig. S4 and Tables S3-S5).

Uncertainty over the existence and origins of $\delta^{13}\text{C}$ gradients also may have implications for atmospheric O₂ and CO₂ at other times in Earth history. For example, the peak in atmospheric O₂ near ~ 30% estimated for the Carboniferous-Permian boundary 300 million years ago could change depending on $\delta^{13}\text{C}$ curve inputs from ancient Tethyan or Panthalassic carbonates that differ by ~ 2‰ (Berner, 2006; Royer et al., 2014), although controversy remains surrounding which values best represent global seawater DIC. The relationship between $\delta^{13}\text{C}$ of DIC and atmospheric O₂ is similarly critical for the Precambrian, with large excursions occurring ~ 2.3 to 2.1 billion years ago and during the Neoproterozoic (e.g., Schrag et al., 2013).

6. CONCLUSIONS

We utilized $^{87}\text{Sr}/^{86}\text{Sr}$ and biostratigraphy to compare $\delta^{13}\text{C}$ curves in Middle-Late Ordovician carbonate platform settings and document a spatial $\delta^{13}\text{C}$ gradient as large as ~ 2‰ during a sea level fall. This 2‰ gradient cannot be explained by diagenetic alteration and is more plausibly linked to syn-depositional controls on $\delta^{13}\text{C}$ of DIC. Local inputs of isotopically light carbon into the restricted platform setting can come from multiple sources, including oxidation of organic matter on land, in the water column or at the sediment-water interface. We show the potential pitfalls of mistaken usage of a local $\delta^{13}\text{C}_{\text{carb}}$ curve in a global carbon cycle model. For the 460 million year Middle-Late Ordovician time bin in GEOCARBSULF, improper usage of our locally depleted $\delta^{13}\text{C}$ curve (reflecting a restricted water mass in the region of the Appalachian Basin) to drive

global organic carbon burial would result in erroneous atmospheric O₂ (~ 10.8% O₂, equal to about a 30% reduction from what it should be at ~15.2% O₂ using global $\delta^{13}\text{C}$) and CO₂ (~ 400 ppm too high, equal to about a 13% increase from what it should be at 2570 ppm CO₂) relative to usage of the global $\delta^{13}\text{C}$ from open marine sections in Baltoscandia. With detailed sedimentologic analysis, it may be possible to identify and exclude $\delta^{13}\text{C}$ samples that record the influences of local carbon cycling from global carbon cycle models such as GEOCARBSULF.

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