**Paired carbon isotopic analysis of Ordovician bulk carbonate ($\delta^{13}\text{C}_{\text{carb}}$) and organic
matter ($\delta^{13}\text{C}_{\text{org}}$) spanning the Great Ordovician Biodiversification Event**

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Abstract

Paired measurements of bulk carbonate ($\delta^{13}\text{C}_{\text{carb}}$), organic matter ($\delta^{13}\text{C}_{\text{org}}$), and their difference ($\Delta^{13}\text{C}$) can be used to estimate changes in isotopic fractionation through time as a function of O_2/CO_2 in the atmosphere. However, because local scale processes can also affect $\Delta^{13}\text{C}$, it is essential to compare sections from widely separated water masses. Here we present new $\delta^{13}\text{C}_{\text{org}}$ data from Ordovician carbonate rocks from the Great Basin, Oklahoma, and Appalachian Basin and compare with published $\delta^{13}\text{C}_{\text{carb}}$ records from these sections and paired $\delta^{13}\text{C}$ values from other carbonate successions around North America. These new data complement previous studies that focused on Upper Ordovician $\delta^{13}\text{C}_{\text{carb}}$ excursions and now provide a composite Ordovician $\delta^{13}\text{C}_{\text{org}}$ record. New Lower Ordovician (Tremadocian Stage) $\delta^{13}\text{C}_{\text{org}}$ data range from ca. -26 to -28‰ , decreasing throughout the Lower–Middle Ordovician (Floian–Dapingian Stages) to ca. -29 to -31‰ . $\delta^{13}\text{C}_{\text{org}}$ values remain at their lowest throughout the Sandbian and are similar to other published Upper Ordovician (Sandbian–Katian) $\delta^{13}\text{C}_{\text{org}}$ data from North America. $\Delta^{13}\text{C}$ values from well-preserved intervals generally vary between $+26$ to $+28\text{‰}$ throughout the Lower to Middle Ordovician (Tremadocian to early Darriwilian), but increase to $+31\text{‰}$ during the mid–late Darriwilian and mid Sandbian, similar to published data from younger Late Ordovician positive $\delta^{13}\text{C}$ excursions known as the Guttenberg (GICE) and Hirnantian (HICE) events. The overall $\Delta^{13}\text{C}$ trend shows a $\sim 3\text{‰}$ increase throughout the Early–Middle Ordovician and coincides with a previously interpreted period of ocean cooling and some of the earliest pulses of global biodiversity of marine invertebrates and planktonic organisms. Modeling studies predict that $p\text{CO}_2$ decreased during this time, suggesting that the effect of $p\text{CO}_2$ on $\Delta^{13}\text{C}$ may have been

overwhelmed by other controls, such as an increase in pO_2 or a higher O_2/CO_2 ratio during this biodiversification event.

1. Introduction

The Ordovician represents a period in Earth history of major changes to the biosphere (Sepkoski, 1981), including a long period of biodiversification followed by a short-lived mass extinction event, which have both been linked to global cooling of shallow seas (e.g., Trotter et al., 2008). The three-fold increase in family level diversity of most faunal groups throughout the Ordovician, known as the Great Ordovician Biodiversification Event (GOBE; Webby et al., 2004), has been the focus of numerous paleontological and paleoenvironmental investigations and a picture is emerging of a complex series of diversity pulses that spanned tens of millions of years (e.g. Webby et al., 2004; Harper, 2006; Servais et al., 2010). In addition to cooling temperatures, a possible causal factor relates to the transition from intermittent ocean anoxia during the late Cambrian (Berry and Wilde, 1978; Saltzman et al., 2000; Hurtgen et al., 2009; Gill et al., 2011) to more oxygenated environments favorable for benthic marine communities and skeletal carbonate production (Pruss et al., 2010; Saltzman et al., 2011). This notion is based in part on the fact that the Cambrian contains numerous positive carbon isotope ($\delta^{13}C$) excursions linked to ocean anoxia (e.g., Saltzman et al., 2000), which diminish by the Lower Ordovician (Fig. 1) prior to the first pulses of biodiversification. Although volatility in $\delta^{13}C$ returns after the major biodiversity pulses of the GOBE in the Middle Ordovician (Patzkowsky et al., 1997; Pancost et al., 1999, 2013; Young et al., 2008, 2010; Zhang et al., 2010; Jones et al., 2011; LaPorte et al., 2011 Metzger and Fike, 2013),

the largest $\delta^{13}\text{C}$ excursion is associated with a return to icehouse conditions during the end Ordovician glaciation and mass extinction (e.g. Brenchley et al., 1994, 1995; Melchin et al., 2013).

Whereas Ordovician $\delta^{13}\text{C}$ excursions and trends in marine carbonate ($\delta^{13}\text{C}_{\text{carb}}$) have been intensely studied for chemostratigraphic correlation and the potential link between the global carbon cycle and the biosphere (Bergström et al., 2006, 2010a, b; Metzger et al., 2014), fewer studies have generated large data sets for the carbon isotope composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$). Of particular interest, paired isotopic measurements of bulk carbonate and organic matter, and the isotopic difference ($\Delta^{13}\text{C}$: $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$), have been used to make inferences into whether $\delta^{13}\text{C}$ perturbations were associated with changes in atmospheric $p\text{CO}_2$ or $p\text{O}_2$ that affected biological fractionation (Patzkowsky et al., 1997; Hayes et al., 1999; Pancost et al., 1999, 2013; Young et al., 2008; Saltzman et al., 2011). Most studies of paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ have focused on narrow time intervals (< 1–2 myr surrounding the GICE and HICE $\delta^{13}\text{C}_{\text{carb}}$ excursions; Fig. 1) rather than long-term trends throughout the Ordovician. Aside from the studies of the late Cambrian–Middle Ordovician successions in the Argentine Precordillera (Buggisch et al., 2003) and Newfoundland (Azmy and Lavoie, 2009), the only data set we are aware of covering the entire Ordovician is the study by Hayes et al. (1999), but the data are binned at 5-myr intervals and only four of those bins have data in the Ordovician.

The purpose of this paper is to combine new high-resolution paired $\delta^{13}\text{C}$ measurements from bulk carbonate and organic matter from five carbonate successions around North America (Nevada, Utah, Oklahoma, and Maryland; Fig. 2) with other

published paired $\delta^{13}\text{C}$ data to make composite $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{13}\text{C}$ curves throughout the Ordovician to complement published $\delta^{13}\text{C}_{\text{carb}}$ curves (Fig. 1; Bergström et al., 2009; Saltzman and Thomas, 2012). The advantage of using paired $\delta^{13}\text{C}$ measurements from a single section instead of combining $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ trends from separate sections around the globe is that artifacts such as errors of age assignments from correlation on $\Delta^{13}\text{C}$ are minimized. If a link between biological diversity and long-term changes in biological fractionation (ϵ_p ; $\Delta^{13}\text{C}$ roughly approximates ϵ_p) can be identified, it could potentially add new insight into causes of the GOBE, such as shifts of the dominant groups of primary producers in the planktonic realm and atmospheric O_2 levels.

2. Background

2.1 Geologic setting of Laurentia (North America)

The Ordovician depositional environments for much of the Laurentian margin were predominantly shallow carbonate ramps in passive margin settings with the cratonic interior periodically covered by an expansive and shallow epeiric sea (e.g., Ross et al., 1982; 1989). Laurentia was located in low latitudes where most of the paleocontinent was at or just south of the equator (Fig. 2). Carbonate successions that accumulated during the Early Ordovician (Tremadocian and Floian Stages) are primarily lime mudstone and wackestone lithologies with minor amounts of siliciclastic beds and occasional trilobite grainstone and flat pebble conglomerate lithologies (Hintze, 1973; Pruss et al., 2010; Miller et al., 2012; Edwards and Saltzman, 2014).

During the Middle Ordovician (Dapingian and Darriwilian Stages) relative sea level along the continental margin was at a low, which generated a continent-wide

unconformity with a complex history with respect to its age and duration. This unconformity is recognized as the Sauk-Tippecanoe Megasequence boundary in the Great Basin (Miller et al., 2012) and as the Knox-Beekmantown unconformity in the Appalachian region (Read, 1980; Mussman and Read, 1986). Sedimentation patterns shifted and became more siliciclastic dominated, particularly in the Oklahoma Aulacogen and Appalachian region with the onset of the Taconic Orogeny (e.g. Mussman and Read, 1986) during the Late Ordovician. Carbonate sedimentation shifted to the continental interior during the late Middle Ordovician (Darriwilian) and Late Ordovician (Sandbian and Katian Stages). These midcontinent carbonate successions have been the focus of studies aimed at reconstructing paleocommunities and niche development (Patzkowsky and Holland, 1993, 2007; Malizia and Stigall, 2011; Stigall, 2012), sea level change and environmental conditions (Ludvigson et al., 2004; Saltzman and Young, 2005; Brett et al., 2006; McLaughlin and Brett, 2007), and the sequence stratigraphic architecture of the midcontinent (McLaughlin et al., 2004; Holland and Patzkowsky, 2006; Patzkowsky and Holland, 2012). These Late Ordovician carbonates have also been studied for $\delta^{13}\text{C}$ stratigraphy and offer an excellent opportunity to study global trends throughout the Ordovician when combined with the new $\delta^{13}\text{C}$ data from the Early–Middle Ordovician presented here.

2.2 Literature sources of $\delta^{13}\text{C}$ data and age calibration

There is a rich literature of studies that report paired $\delta^{13}\text{C}$ from several localities and time intervals throughout the Ordovician that provide an important foundation to compare our new $\delta^{13}\text{C}$ data to in order to make a global compilation that minimizes local

effects on $\delta^{13}\text{C}$ (e.g., Patzkowsky et al., 1997; Pancost et al., 1999, 2013; Buggisch et al., 2003; Young et al., 2008, 2010; Jones et al., 2011). Literature data used here from the Lower–Middle Ordovician include Newfoundland (Azmy and Lavoie, 2009), Meiklejohn Peak, NV (Diamond, 2013), Clear Spring, MD (Leslie et al., 2011), and the Argentine Precordillera (Buggisch et al., 2003). Data from the Middle–Late Ordovician Guttenberg $\delta^{13}\text{C}_{\text{carb}}$ excursion (GICE) covers the Sandbian–Katian interval (Patzkowsky et al., 1997; Young et al., 2008; Pancost et al., 1999, 2013; Metzger and Fike, 2013). Although the late Katian and Hirnantian have also been widely studied because of the association between a large positive $\delta^{13}\text{C}_{\text{carb}}$ excursion (HICE), continental glaciation of Gondwana, and mass extinction (e.g. Brenchley et al., 1995; Bergström et al., 2006), only a few studies from North America have paired $\delta^{13}\text{C}$ values with relatively well-constrained biostratigraphic control that are used here (LaPorte et al., 2009; Young et al., 2010; Jones et al., 2011).

Age estimates of the data reported here are calibrated to the 2012 Geologic Time Scale (Cooper and Sadler, 2012) using conodont, graptolite, or chitinozoan biostratigraphic zones. Where biostratigraphic data are sparse or zonal boundaries are poorly constrained, the $\delta^{13}\text{C}_{\text{carb}}$ trend is used to estimate ages based on correlations to other sections with more precise age control. For example, the peak of the GICE is assigned an age herein of 452.4 Ma based on radiometric age dates of zircon-bearing K-bentonites (Sell et al., 2011). Sections that contain the GICE with robust $\delta^{13}\text{C}$ data but poorly constrained or conflicting biostratigraphic ages have been adjusted to more closely align with the GICE peak and rising and falling limbs (e.g., the Fittstown, OK section from Young et al., 2008).

3. Methods

Samples for $\delta^{13}\text{C}_{\text{carb}}$ analyses were micro-drilled from cut and freshly broken surfaces of micritic lithologies where available, and the micritic matrix was targeted in wackestone and packstone lithologies. Many of the same carbonate lithologies measured for $\delta^{13}\text{C}_{\text{carb}}$ were also sampled for bulk organic matter ($\delta^{13}\text{C}_{\text{org}}$). Samples were drilled using a masonry bit to produce 0.5–3 g of carbonate powder and de-carbonated with three rinses of 10 mL of 6M HCl and three rinses of 10 mL of Milli-Q water, centrifuged, and kept in an oven at 50 °C until dry.

New and previously reported $\delta^{13}\text{C}_{\text{carb}}$ analyses were analyzed at four different laboratories on Kiel and Gas Bench II devices (see Edwards and Saltzman (2014) and at the Stable Isotope Biogeochemistry lab at Washington University in St. Louis; Tables S1–S3). $\delta^{13}\text{C}_{\text{org}}$ values were measured using a Costech ECS4010 Elemental Analyzer attached to a ThermoFinnigan Delta Plus XP mass spectrometer (Indiana University), ThermoFinnigan Delta V Plus (Washington University), and a ThermoFinnigan MAT 253 mass spectrometer (Kansas University). An average of 2–5 mg (up to 30 mg for organic-poor samples) of de-carbonated residues were added to tin capsules and combusted at 1800 °C under a continuous flow of a helium carrier gas. Isotope ratios are reported in delta notation (‰) relative to the Vienna Pee Dee Belemnite (V-PDB) standard (Craig, 1957). Precision and calibration of data were monitored through routine analysis of a soil and leaf standard (NIST Ref. Mat. 2711 and 1547, respectively), acetanilide, and internal laboratory standards. Standard deviations for all $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ are less than 0.12‰ and 0.20‰, respectively, and $\delta^{13}\text{C}_{\text{org}}$ are less than 0.22‰.

4. Results

New isotope data reported here include $\delta^{13}\text{C}_{\text{carb}}$ from Oklahoma (Bally Mountain and I-35 sections; Fig. 3) and Meiklejohn Peak, NV (Fig. S1), and $\delta^{13}\text{C}_{\text{org}}$ from the Oklahoma (Fig. 3), Shingle Pass (Fig. 4), Ibex area (Fig. 5), Clear Spring (Fig. 6), and Meiklejohn Peak (Fig. S1) sections (Tables S1–S3). In general, both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ values from Oklahoma are several per mil lighter compared to age-equivalent sections from North America and Argentina (Fig. 7) yet $\Delta^{13}\text{C}$ values are within the range of values measured from all other sections.

4.1 Oklahoma $\delta^{13}\text{C}_{\text{carb}}$

New $\delta^{13}\text{C}_{\text{carb}}$ data from the Oklahoma sections are more variable and isotopically lighter compared to age-equivalent Lower-Middle Ordovician sections (Fig. 7) but consistent with previous $\delta^{13}\text{C}_{\text{carb}}$ study (Gao and Land, 1991). $\delta^{13}\text{C}_{\text{carb}}$ varies by up to 1–2‰ between closely spaced samples throughout most of the Bally Mountain section (McKenzie Hill and Cool Creek formations; Loch, 1992), but only varies by ~0.5‰ within the Kindblade and lower West Spring Creek formations at I-35 (Fig. 3). $\delta^{13}\text{C}_{\text{carb}}$ decreases from ~0‰ at the base of the Bally Mountain section (lower McKenzie Hill Formation) to ~–4‰ in the middle of the same formation (*Rossodus manitouensis* Zone). The $\delta^{13}\text{C}_{\text{carb}}$ trend increases to ~–2‰ until about 40 m below the upper contact with the Cool Creek Formation just below the Low Diversity Interval Zone (Dresbach and Ethington, 1991) before decreasing again to –4‰ in the lower Cool Creek. $\delta^{13}\text{C}_{\text{carb}}$ is highly variable between –5‰ and –1‰ throughout the Cool Creek Formation up to the

contact with the Kindblade Formation, identified by a prominent silicified oolite grainstone (Loch, 1992). Throughout the Kindblade Formation at Bally Mountain $\delta^{13}\text{C}_{\text{carb}}$ remains relatively invariant where it rises from -2.5‰ to -2.0‰ at the top of the measured section (165 m measured thickness for the lower Kindblade).

The upper ~110 m of the Kindblade Formation was sampled along the I-35 roadcut, potentially leaving a gap of 150 m of unmeasured section (a total of 275 m reported here compared to the 429.9 m total thickness of the Kindblade measured by Fay (1989)). $\delta^{13}\text{C}_{\text{carb}}$ throughout the uppermost Kindblade and lower West Spring Creek formations increases from $\sim -3.5\text{‰}$ at the base of the I-35 section to a peak of -0.7‰ in the lower half of the West Spring Creek Formation. $\delta^{13}\text{C}_{\text{carb}}$ gradually decreases until just below the prominent red beds and erosional features in the upper zone (Fig. 3; Fay, 1989). Throughout the red bed interval $\delta^{13}\text{C}_{\text{carb}}$ values are highly variable and more isotopically negative with increasing $\delta^{18}\text{O}$ up to the contact with a major subaerial surface inferred from an abundance of quartz sandstone beds and surfaces with mudcracks. The upper portion of the West Spring Creek Formation shows evidence for highly energetic wave action (rippled and scoured surfaces, trough cross-bedding), subaerial exposure (mudcracks and salt molds), and has been interpreted as representing a relative sea level lowstand between the North American Ibexian and Whiterockian Series (Derby, 1973).

The overlying Joins Formation of the Simpson Group is not exposed along the I-35 section except for the uppermost several meters below the contact with the Oil Creek Formation. $\delta^{13}\text{C}_{\text{carb}}$ of the Oil Creek Formation is relatively variable ($\leq 1.5\text{‰}$) throughout the lower half of the formation, but generally increases from -3‰ to -1.6‰ at the top of

the exposure. The overlying siliciclastic-dominant facies of the McLish and Tulip Creek formations are poorly exposed along the I-35 section with preliminary unpublished $\delta^{13}\text{C}_{\text{carb}}$ (see Young et al. (this volume)), but these data have been omitted from this dataset because $\delta^{13}\text{C}_{\text{org}}$ has not yet been measured to provide $\Delta^{13}\text{C}$ values. The end of the measured I-35 section contains the Bromide Formation and lowermost 8 m of the Viola Group sampled on the north flank of the Arbuckle Anticline (Fay, 1989; Carlucci et al., 2014). $\delta^{13}\text{C}_{\text{carb}}$ gradually increases from $\sim -3\text{‰}$ to $+0.5\text{‰}$, with a slight 1.2‰ drop in the middle of the Bromide.

4.2 Meiklejohn Peak, NV $\delta^{13}\text{C}_{\text{carb}}$

New $\delta^{13}\text{C}_{\text{carb}}$ data from the Meiklejohn Peak section were measured from carbonate mudstone lithologies collected from the Ross section on the southern face of Meiklejohn Peak (Ross, 1972) and from the Harris section on the western face (Harris et al., 1979; Diamond, 2013). The composite section includes $\delta^{13}\text{C}_{\text{carb}}$ data from the uppermost Nopah Formation, Goodwin Limestone, Ninemile Shale, and Antelope Valley Limestone (see Ross (1972) and Diamond (2013) for a detailed description of the lithostratigraphy).

The $\delta^{13}\text{C}_{\text{carb}}$ trend is generally correlative with the other Great Basin sections (Fig. 7; e.g., Edwards and Saltzman, 2014) where several $\delta^{13}\text{C}_{\text{carb}}$ excursions are preserved. $\delta^{13}\text{C}_{\text{carb}}$ decreases at the base of the section (lower Goodwin Limestone) to -1.5‰ and immediately followed by a 2.5‰ positive $\delta^{13}\text{C}_{\text{carb}}$ excursion where values reach $+1\text{‰}$. $\delta^{13}\text{C}_{\text{carb}}$ returns to baseline values of ~ -0.5 to -1‰ throughout the upper Goodwin Limestone and overlying limestone beds in the Ninemile Shale. $\delta^{13}\text{C}_{\text{carb}}$ returns to

heavier $\delta^{13}\text{C}_{\text{carb}}$ values of +0.5‰ near the Ibexian-Whiterockian boundary (arrow in Fig. 7) before another decrease to a minimum of −3.1‰ in the Lower Member of the Antelope Valley Limestone. $\delta^{13}\text{C}_{\text{carb}}$ increases briefly to −0.1‰ at the base of the Middle Member (*Histiodella holodentata* Zone) and returns to −2.9‰ at the top of the Middle Member. The Upper Member contains a large and sustained positive $\delta^{13}\text{C}_{\text{carb}}$ shift where values plateau at +0.4 to +0.7‰ before falling sharply to −2.7‰ at the contact with the overlying Eureka Quartzite. This uppermost $\delta^{13}\text{C}_{\text{carb}}$ high occurs within the *Cahabagnathus sweeti* to *Baltoniodus gerdæ* Zones (Sandbian age), which are also present in the I-35 and Clear Spring sections (Saltzman et al., 2014) and have similar positive $\delta^{13}\text{C}_{\text{carb}}$ values between 0 and +1‰ (Fig. 7).

4.3 $\delta^{13}\text{C}_{\text{org}}$ trends

4.3.1 Oklahoma

The $\delta^{13}\text{C}_{\text{org}}$ trend from Oklahoma shows an overall 3‰ decrease throughout the Lower–Middle Ordovician (Fig. 3) and is similar to a 4–5‰ decrease reported from Argentina (Buggisch et al., 2003) and Newfoundland (Azmy and Lavoie, 2009). The variability of $\delta^{13}\text{C}_{\text{org}}$ is much smaller (<0.5‰) and unlike the corresponding variable $\delta^{13}\text{C}_{\text{carb}}$ values. $\delta^{13}\text{C}_{\text{org}}$ decreases from −28‰ to −31‰ throughout the Bally Mountain section (McKenzie Hill through Kindblade formations). $\delta^{13}\text{C}_{\text{org}}$ at the base of the I-35 section remains unchanged at −30‰, but increases slightly to −29‰ in the middle of the West Spring Creek Formation before becoming highly variable ($\leq 3\%$ between closely spaced samples) within the upper zone. This higher variability corresponds to highly variable $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values (Fig. 3). $\delta^{13}\text{C}_{\text{org}}$ increases from −31‰ to −28.5‰ in

the lower half of the Oil Creek Formation before decreasing to -29.5‰ at the top of the exposure. Throughout the Bromide–Viola succession $\delta^{13}\text{C}_{\text{org}}$ varies between -31‰ to -29‰ with no clear trend compared to the corresponding $\delta^{13}\text{C}_{\text{carb}}$ trend.

4.3.2 Nevada and Utah

$\delta^{13}\text{C}_{\text{org}}$ values from the Shingle Pass and Ibex sections show an overall decrease from $\sim -27\text{‰}$ to -30‰ throughout the Lower to Middle Ordovician (Figs. 4 and 5), also similar to Argentina and Newfoundland (Buggisch et al., 2003; Azmy and Lavoie, 2009). $\delta^{13}\text{C}_{\text{org}}$ values from a preliminary study of $\delta^{13}\text{C}_{\text{org}}$ at Meiklejohn Peak are more negative (-29.4 to -31.7‰), but also follow a similar decreasing trend. $\delta^{13}\text{C}_{\text{org}}$ values from Shingle Pass are more variable compared to the Ibex and Meiklejohn Peak sections where closely spaced samples less than 10 m apart stratigraphically show $\delta^{13}\text{C}_{\text{org}}$ variations up to 4‰ (Parker Spring and Shingle Limestone), whereas variability in the Ibex section is $<2\text{‰}$ in the age-equivalent Fillmore Formation. However, the $\delta^{13}\text{C}_{\text{org}}$ is more variable (up to 4‰) and slightly less negative (up to -24‰) throughout the Wah Wah to lower Kanosh Shale interval before returning to the overall decreasing trend. At the base of the Middle Member of Antelope Valley Limestone at Meiklejohn Peak (Harris section), $\delta^{13}\text{C}_{\text{org}}$ values are less negative than in the Ross section, but decrease from a high of -28.8‰ to similar ^{13}C -depleted values (-30 to -31‰) throughout the Upper Member compared to the older Ross section (Fig. S1).

4.3.3 Maryland

The $\delta^{13}\text{C}_{\text{carb}}$ data from the Clear Spring, Maryland section was first reported in Leslie et al. (2011) and Saltzman and Thomas (2012) and is used in Young et al. (this volume) to compare with corresponding $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{34}\text{S}$ trends. The $\delta^{13}\text{C}_{\text{org}}$ trend in the Middle–Upper Ordovician Clear Spring section (Fig. 6) is relatively invariant compared to the other Lower–Middle Ordovician sections (Figs. 3–5) with variability $<1\text{‰}$. Throughout the Middle Ordovician portion $\delta^{13}\text{C}_{\text{org}}$ values increases from -30‰ to $\sim -28\text{‰}$ in the *Phragmodus polonicus* Zone. $\delta^{13}\text{C}_{\text{org}}$ decreases to -29‰ in the *Cahabagnathus friendsvillensis* Zone where it remains invariable throughout the remainder of the section except for an apparent 5‰ positive excursion at the base of Chambersburg Formation. This excursion coincides with a facies change from the New Market Formation to the Chambersburg Limestone where a zone of orange-red silty matrix is weathering from the outcrop.

5. Discussion

5.1 $\Delta^{13}\text{C}$ selection and assessment of primary values

Because a primary $\Delta^{13}\text{C}$ signal is dependent on both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ preserving their original values it is necessary to assess to what extent diagenetic alteration has affected isotopic measurements. Bulk carbonate has been shown to be a suitable material to approximate seawater $\delta^{13}\text{C}$ in the absence of brachiopod calcite (e.g., Finney et al., 1999; Kump et al., 1999; Maloof et al., 2005; Kaljo et al. 2007; Ainsa et al. 2010; Munnecke et al., 2010, 2011). Cramer et al. (2010), for example, showed that the Silurian Ireviken $\delta^{13}\text{C}$ excursion measured from bulk carbonate was nearly indistinguishable from the same trend measured from brachiopod calcite, thus

demonstrating that $\delta^{13}\text{C}_{\text{carb}}$ can be a reliable technique to generate global $\delta^{13}\text{C}$ trends. One way to assess primary isotopic values in the absence of brachiopod calcite is the use of $\delta^{13}\text{C}_{\text{carb}}-\delta^{18}\text{O}_{\text{carb}}$ cross plots and global correlation (Figs. S2 and 7, respectively), although primary $\delta^{18}\text{O}_{\text{carb}}$ values are unlikely to be preserved in most geologic settings because significant $\delta^{18}\text{O}$ isotopic exchange can occur even when porewater:rock ratios are <5 (e.g., Banner and Hanson, 1990). The respective authors of literature sources have interpreted the majority of the data compiled here as recording near primary values, and correlation of $\delta^{13}\text{C}_{\text{carb}}$ trends between sections supports this interpretation (Fig. 7).

Determining whether $\delta^{13}\text{C}_{\text{org}}$ values maintain a primary signal is less straightforward compared to $\delta^{13}\text{C}_{\text{carb}}$, particularly when the two curves are largely decoupled (e.g., Korte and Kozur, 2010; Johnston et al., 2012). The measured value of $\delta^{13}\text{C}_{\text{org}}$ encompasses the cumulative effects of biological and geological processes, which can include variations in growth rate, cell shape, and $[\text{CO}_2]$ of the local environment (Popp et al., 1998), or microbial heterotrophy or thermal diagenesis of organic matter after burial (Hayes et al., 1983). Mixing of terrestrial and marine source of organic matter is also potentially a concern (e.g., Sluijs and Dickens, 2012), although much less so in the Ordovician prior to the evolution of a major terrestrial biosphere. It may be possible to explore whether the dominant biomass producers changed using biomarker studies (e.g., Pancost et al., 2013) but this approach is not taken here. With increased respiration either from biological processes, oxidizing fluids, or thermal degradation of organic matter (kerogen), preferential removal of ^{12}C is kinetically favored (Hayes et al., 1983; Schidlowski and Aharon, 1992). As such, bulk organic measurements that are isotopically heavy (^{13}C -enriched) are expected to have lower total organic carbon (TOC).

However, cross plots of $\delta^{13}\text{C}_{\text{org}}$ and $\Delta^{13}\text{C}$ vs. TOC (Fig. 8) shows no discernible trends despite the wide range of reported TOC, particularly for samples with <0.1 wt. %. There is also no discernable trend between TOC and burial temperature for sections with thermal history estimates using the conodont color alteration index (CAI), nor do low TOC values correlate to high $\delta^{13}\text{C}_{\text{org}}$ variability within a section (compare Figs. 3 and 4). Johnston et al. (2012) emphasized that the isotopic contribution to $\delta^{13}\text{C}_{\text{org}}$ trends from contaminant sources of organic carbon (i.e., erosion of organic-rich shale on land or the migration of hydrocarbons within the basin) would be most evident when TOC values are low (e.g., < 0.1 %). These authors further suggested that such contamination from secondary sources might be manifest as invariant $\delta^{13}\text{C}_{\text{org}}$ trends that do not covary with $\delta^{13}\text{C}_{\text{carb}}$.

In our stratigraphic sections, Lower–Middle Ordovician $\delta^{13}\text{C}_{\text{org}}$ trends appear to be broadly covariant (Fig. S3) with $\delta^{13}\text{C}_{\text{carb}}$ and correlative across North America suggesting that a primary value is generally preserved, despite the greater scatter of $\delta^{13}\text{C}_{\text{org}}$ compared to $\delta^{13}\text{C}_{\text{carb}}$. Although similar trends in $\delta^{13}\text{C}_{\text{org}}$ are present across several widely separated sections, $\delta^{13}\text{C}_{\text{org}}$ values are interpreted here as preliminary in the absence of more detailed study of the organic matter itself. Future study of the compound-specific composition of the organic matter (e.g., isotopic study of biomarkers; cf. Pancost et al., 2013) would be helpful to more accurately determine the primary nature of these trends. However, based on a lack of correlation between TOC and $\delta^{13}\text{C}_{\text{org}}$ (Fig. 8) and similar long-term trends in $\delta^{13}\text{C}_{\text{org}}$ across several sections, it appears as if a global signal is still preserved even if some $\delta^{13}\text{C}_{\text{org}}$ values have been affected by local effects or diagenetically altered by some unknown amount. Consideration of potential

cause(s) of the scatter and reproducibility in $\delta^{13}\text{C}_{\text{org}}$ compared to $\delta^{13}\text{C}_{\text{carb}}$ may be helpful to omit values that may be altered and could obscure long-term isotope trends.

5.2 $\delta^{13}\text{C}_{\text{org}}$ reproducibility within a section and outliers

The signal-to-noise ratio of $\delta^{13}\text{C}_{\text{carb}}$ is larger and the signal is less variable among closely spaced samples compared to $\delta^{13}\text{C}_{\text{org}}$, both within a section and between age-equivalent sections (Fig. 9; Table S4). The scatter, or average variability, of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ in Figure 9 is determined by averaging the differences between each value and the mean (the three point moving averages, see Figs. 3–6 and S1) from each section, with error bars depicting the root-mean-square error (RMSE). Average Ordovician $\delta^{13}\text{C}_{\text{carb}}$ variability is relatively consistent between 0.14 and 0.43 (avg. 0.24), whereas $\delta^{13}\text{C}_{\text{org}}$ variability is generally greater than $\delta^{13}\text{C}_{\text{carb}}$ and ranges from 0.26 to 0.95 (avg. 0.51; Table S4). If this variability is due to alteration of one or both measurements it will yield a non-primary $\Delta^{13}\text{C}$ signal. For example, the scatter among the $\delta^{13}\text{C}_{\text{org}}$ data from Bally Mountain section of Oklahoma (Fig. 3) are fairly consistent and vary by $\sim 0.5\text{‰}$ from the mean (three point moving average line) between closely-spaced samples, but the variability of $\delta^{13}\text{C}_{\text{org}}$ from Shingle Pass, NV is up to 3.7‰ from the mean (Fig. 4) and are not used in the final compilation (see below). Furthermore, some sections contain $\delta^{13}\text{C}_{\text{org}}$ trends that have a range of isotopic variability, such as the Ibex section where $\delta^{13}\text{C}_{\text{org}}$ in the lower portion (Fillmore Formation) of the section varies by $1\text{--}1.5\text{‰}$ but varies by up to 3.4‰ from the mean in the overlying Wah Wah through Kanosh formations (Fig. 5). This variability in $\delta^{13}\text{C}_{\text{org}}$ is also present in some literature sources, particularly for the

Lower–Middle Ordovician successions, where it differs from the mean by up to 2‰ in Argentina (Buggisch et al., 2003) and up to 3.7‰ in Newfoundland (Azmy and Lavoie, 2009). For comparison, the average errors of $\delta^{13}\text{C}_{\text{org}}$ reported here are similar to six Paleozoic sections with paired $\delta^{13}\text{C}$ data (Fig. 9), as well as from the Neoproterozoic (Johnston et al., 2012), Silurian (Vandenbroucke et al., 2013), Devonian (Joachimski et al., 2002), and Triassic–Jurassic (van de Schootbrugge et al., 2008; Bachan et al., 2012). Similarly, McInerney and Wing (2011) calculated that the average excursion of -4.1% in bulk marine organic matter $\delta^{13}\text{C}$ during the Paleocene-Eocene Thermal Maximum (PETM) had a standard deviation of 2.2‰ (n=11 records).

Explaining differences in the magnitude of $\delta^{13}\text{C}_{\text{org}}$ trends between sections is less straightforward and unlikely to be due to alteration affecting an entire section. A more likely explanation is that slight isotopic variations of the carbon source (dissolved inorganic carbon; DIC) for primary producers in separate basins (i.e., local effects) accounts for some of the differences in the magnitude of $\delta^{13}\text{C}_{\text{org}}$ between sections (e.g., Oklahoma). For example, the “Küspert Hypothesis” (Küspert, 1982) predicts that density stratification in the water column during warm periods in a wet greenhouse climate would slow the sinking of organic matter. This would allow for increased oxidation of organic matter in the water column and cause the near-surface layer to become isotopically lighter (cf. Meyers, 2014). This process may have periodically occurred in more restricted localities in the epicontinental seas that covered Laurentia and over time this process could create more negative $\delta^{13}\text{C}_{\text{org}}$ trends (from an isotopically lighter DIC pool) relative to sections that experienced more open marine circulation patterns. However, this hypothesis only holds true if there is a constant supply of nutrients for

biomass production via riverine input as nutrients derived from upwelling is slowed. Additionally, this hypothesis also predicts that corresponding $\delta^{13}\text{C}_{\text{carb}}$ values will also become more negative, if $\Delta^{13}\text{C}$ remains constant, so that both $\delta^{13}\text{C}$ trends will be negatively offset from the global record.

Because we can find no consistent or predictable way to identify altered $\delta^{13}\text{C}_{\text{org}}$ values (and $\delta^{13}\text{C}_{\text{carb}}$) in this study and literature sources, we have applied a simple statistical test to remove outlier data as a first approach prior to interpreting long-term isotope trends. Isotopic values that are greater than 2σ from the mean (three-point moving average) for each section are omitted from the Ordovician compilations (Fig. 10), which removes a similar amount of outliers compared to other datasets from Estonia (Young et al., 2010) and the Silurian (Cramer and Saltzman, 2007; Gouldey et al., 2010). This rejection criterion yields a total of 1833 $\delta^{13}\text{C}_{\text{carb}}$ values, 1070 $\delta^{13}\text{C}_{\text{org}}$ values, and 866 $\Delta^{13}\text{C}$ values (Tables S1–S3) (Fig. 10).

5.3 Relationship between biological fractionation (ϵ_p), $\delta^{13}\text{C}_{\text{org}}$, and $\Delta^{13}\text{C}$

Before we interpret the cause(s) of the long-term $\delta^{13}\text{C}$ trends throughout the Ordovician, we first consider important controls on the fixation and isotopic value of organic matter via primary production. The biological fractionation effect (ϵ_p) of primary producers in the past can be estimated using the equation from Hayes et al., (1999):

$$\epsilon_p = \delta^{13}\text{C}_{\text{org}} - \Delta_{\text{carb}} + \Delta_2$$

where Δ_{carb} is the isotopic effect associated with temperature and carbonate mineral formation in seawater, and Δ_2 is the sum of secondary biologic processes of the original biomass (e.g., microbial heterotrophy). The largest control on $\delta^{13}\text{C}_{\text{org}}$ (and $\Delta^{13}\text{C}$)

is associated with the biological fractionation affect during primary production and CO₂ fixation via the Rubisco enzyme, but variations in seawater temperature can also affect $\delta^{13}\text{C}_{\text{org}}$ by several per mil. For example, Trotter et al. (2008) have interpreted that a ~12 °C cooling of sea surface temperatures occurred during the Early–Middle Ordovician based on conodont $\delta^{18}\text{O}$ data that could account for a 1.4‰ change in ϵ_p (0.12‰/°C; Hayes et al., 1999).

Studies of modern primary producers have shown that factors such as growth rate, cell shape, $p\text{CO}_2$, and $p\text{O}_2$ levels can also affect ϵ_p (Bidigare et al., 1997; Popp et al., 1998; Berner et al., 2000). Chemostat experiments using modern diatoms can produce higher ϵ_p values when growth rates are low, volume/surface area ratios are small, or $p\text{CO}_2$ is high (Popp et al., 1998). Pancost et al. (2013) used a decrease in $\Delta^{13}\text{C}$ (i.e., ϵ_p) to suggest that $p\text{CO}_2$ was lower during the GICE than previously thought based on isotope mass balance models (4–8x pre-industrial levels (PIL) compared to ~15x; Berner and Kothavala, 2001). The Early–Middle Ordovician is thought to have had some of the highest $p\text{CO}_2$ values during the Phanerozoic (17–20x PIL; Berner and Kothavala, 2001), much higher than the lower threshold (~8x PIL) where ϵ_p is potentially sensitive to $p\text{CO}_2$ variations. Because the Rubisco enzyme has a dual carboxylase/oxygenase function, O₂ can compete for the same sites as CO₂ on the enzyme and give the appearance of higher $p\text{CO}_2$ with elevated ϵ_p values (Berner et al., 2000). Thus, an increase of ϵ_p either caused by an increase in $p\text{O}_2$ or higher O₂/CO₂ ratios during the Ordovician may be expressed in the rock record as an increase in $\Delta^{13}\text{C}$.

5.4 $\delta^{13}\text{C}$ correlations and long-term trends

Our new $\delta^{13}\text{C}$ data are compared to published datasets in Figure 10 with LOWESS moving averages (Cleveland, 1979) to more easily observe long-term trends. [See Figure S4 for sensitivity testing with different smoothing factors]. In general, $\delta^{13}\text{C}_{\text{carb}}$ trends show good agreement and little scatter from the LOWESS curve except during periods of transient $\delta^{13}\text{C}$ perturbations (e.g., Tremadocian, GICE, HICE) superimposed on the long-term trend. The LOWESS curve shows no major long-term trend in $\delta^{13}\text{C}_{\text{carb}}$ throughout the Lower to Middle Ordovician where it stays near -1‰ until a Upper Ordovician increase to ~ 0 to $+1\text{‰}$. In the $\delta^{13}\text{C}_{\text{org}}$ curve, values decrease from -26.5‰ in the uppermost Cambrian (490 Ma) to about -29.5‰ by the Darriwilian Stage (465 Ma) before rising again in the Upper Ordovician back to $\sim -26.5\text{‰}$. The two prominent GICE and HICE events are also present in the $\delta^{13}\text{C}_{\text{org}}$ trend.

The $\Delta^{13}\text{C}$ trend increases from $+26.5\text{‰}$ at the base of the Ordovician to a plateau at $\sim +29.5\text{‰}$ by the uppermost Darriwilian. Throughout the Upper Ordovician there are minor fluctuations in $\Delta^{13}\text{C}$ associated with the GICE (3–5‰; Pancost et al., 2013) and HICE (2–3‰; Young et al., 2010; Jones et al., 2011), but in general baseline $\Delta^{13}\text{C}$ values are around $+29.5\text{‰}$, representing a 3.0‰ increase throughout nearly 25 myr during Early–Middle Ordovician (Fig. 10). This $\Delta^{13}\text{C}$ increase also appears to be recorded in the study by Hayes et al. (1999) where values increase from 28–29‰ to 31–32‰ throughout the Ordovician (Fig. 10). A 3‰ increase is greater than the potential 1.4‰ effect based on temperature alone (see above) and suggests that other factors may have contributed to this increase, such as higher $p\text{CO}_2$, $p\text{O}_2$, or O_2/CO_2 ratios. If $p\text{CO}_2$ is the main control on $\Delta^{13}\text{C}$ as a result of the biologic fractionation effect by primary producers on geologic time scales, then the increasing $\Delta^{13}\text{C}$ trend throughout the Ordovician suggests that $p\text{CO}_2$

increased. Atmospheric model results, however, indicate that $p\text{CO}_2$ decreased during this time (Berner, and Kothavala, 2001; Goddris et al., 2014). This prediction suggests that the controls affecting the isotopic fractionation of organic carbon due to $p\text{CO}_2$ were overwhelmed by other controls, such as increases in $p\text{O}_2$. It remains unclear what the dominant driver of these isotopic trends was without more detailed information about past atmospheric compositions with age resolution higher than 10 myr time bins (Berner and Kothavala, 2001; Goddris et al., 2014).

This long-term $\Delta^{13}\text{C}$ increase throughout the Early to Middle Ordovician also appears to coincide with major oceanographic and paleoenvironmental changes that include a major drop in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Shields et al., 2003; Young et al., 2009; Saltzman et al., 2014; Edwards et al., in press), an apparent cooling of shallow seas (Trotter et al., 2008), and the earliest pulses of biodiversification that comprise the GOBE (Fig. 11; Sepkoski, 1995; Webby et al., 2004). Possible explanations for this $\Delta^{13}\text{C}$ increase include a major change in the dominant phytoplankton group that produced to the original biomass, cell growth rates, or changes in O_2/CO_2 ratios (Popp et al., 1998; Berner et al., 2000; Pancost et al., 2013). During the GICE event, Pancost et al. (2013) interpreted a decrease in $\Delta^{13}\text{C}$ to reflect a decrease in $p\text{CO}_2$ from higher organic burial rates. Although Pancost et al. (2013) also used lithofacies associations and biomarker abundances (e.g., steranes and methylhopanes) to suggest that the dominant photoautotroph physiology or community structure responded to an environmental change (ocean circulation and increased nutrient supply) during the GICE event, they rejected this as being the primary cause of the decrease in $\Delta^{13}\text{C}$. Further work is needed to study whether long-term changes in the dominant components of the biomass occurred

throughout the Ordovician that may explain changes in $\Delta^{13}\text{C}$ not related to $p\text{O}_2$ or O_2/CO_2 .

Servais et al. (2010) consider whether a ‘plankton revolution’ and diversification of phyto- and zooplankton during the Early–Middle Ordovician contributed to the biodiversification of suspension feeders. This planktonic revolution appears to coincide with the onset of the GOBE as well as the long-term increase in $\Delta^{13}\text{C}$, indicating that changes in diversity trends of primary producers may be related to the global carbon cycle and a change in the biological fractionation effect (ϵ_p). If an increase in ϵ_p can be linked to an increase in $p\text{O}_2$ or higher O_2/CO_2 ratios in addition to a possible ocean cooling (Trotter et al., 2008), then this relationship suggests that the GOBE was facilitated in part by long-term atmospheric and ocean chemistry changes. Previous studies have speculated that organic burial rates were elevated during the Early–Middle Ordovician and led to subsequent cooling and oxygenation (Trotter et al., 2008; Pruss et al., 2010; Saltzman et al., 2011; Edwards and Saltzman, 2014), but more directed study that utilizes additional proxies for oxygen levels (e.g., sulfur isotopes, I/Ca ratios, Mo/TOC) is required to test this hypothesis. Biomarker work may also help to elucidate whether structural changes in the dominant phytoplankton ecosystem (e.g., cyanobacterial mats versus calcareous algae abundances) played a role in the observed increase in $\Delta^{13}\text{C}$.

6. Conclusions

New $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ data are presented here from five Lower-Middle Ordovician sections from North America previously studied for $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy.

These new $\delta^{13}\text{C}_{\text{org}}$ data show similar time-specific patterns to other published data and are preliminarily interpreted to record a primary and global signal with minor contributions from local effects. The composite $\delta^{13}\text{C}$ curves using new and published paired $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ data shows no significant long-term change in $\delta^{13}\text{C}_{\text{carb}}$ throughout the Ordovician, but there is an overall 3‰ decrease in $\delta^{13}\text{C}_{\text{org}}$ from the Late Cambrian (−26.5‰) to the late Middle Ordovician (−29.5‰). This $\delta^{13}\text{C}_{\text{org}}$ decrease translates into a 3‰ increase in $\Delta^{13}\text{C}$ and suggests that a significant, yet gradual change to the global carbon cycle and primary production occurred during the Early–Middle Ordovician. The $\Delta^{13}\text{C}$ increase coincides with the earliest pulses of biodiversity that comprise the GOBE and the biodiversification of planktonic life. Such a relationship indicates that the conditions that control the biological fractionation effect between dissolved CO_2 in seawater and primary biomass may be linked to global changes that fostered the diversification and radiation of most animal groups throughout the Ordovician.

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1026 **Figure Captions**

1027 **Figure 1.** $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ composite curves of the Ordovician with the approximate
 1028 timing of the Great Ordovician Biodiversification Event (GOBE). $\delta^{13}\text{C}_{\text{org}}$ data are
 1029 compiled from Argentina (Buggisch et al., 2003), Clear Spring, MD (this study), Dolly
 1030 Ridge, WV (Young et al., 2008), and Anticosti Island, Québec (Young et al., 2010).
 1031 MDICE = Middle Darriwilian $\delta^{13}\text{C}$ excursion, GICE = Guttenberg $\delta^{13}\text{C}$ excursion, HICE
 1032 = Hirnantian $\delta^{13}\text{C}$ excursion, Dap. = Dapingian, Hir. = Hirnantian. Modified from
 1033 Saltzman and Thomas (2012).
 1034

1035 **Figure 2.** Reconstruction of the paleogeography of Laurentia during the Middle
 1036 Ordovician (~470 Ma). Locations of studied sections in this study are indicated by stars,
 1037 and locations of $\delta^{13}\text{C}$ data from the literature are located with circles. MP = Meiklejohn

Peak, SP = Shingle Pass, IB = Ibex area, OK = Oklahoma, CS = Clear Spring. Modified from Blakey (2011).

Figure 3. Isotope data from bulk carbonate ($\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$), organic matter ($\delta^{13}\text{C}_{\text{org}}$), and the difference ($\Delta^{13}\text{C}$) from the Bally Mountain and I-35 sections in Oklahoma. Black lines represent three-point moving averages of that and adjacent values. Sand. = Sandbian, Dap. = Dapingian, M. = Middle, U. = Upper, Ord. = Ordovician.

Figure 4. $\delta^{13}\text{C}$ data and moving average lines of the Shingle Pass (NV) section. $\delta^{13}\text{C}_{\text{carb}}$, measured section, and conodont biostratigraphy from Edwards and Saltzman (2014). FPG = Flat Pebble Conglomerate, Camb. = Cambrian, Furon. = Furongian.

Figure 5. $\delta^{13}\text{C}$ data and moving average lines of the Ibex area (UT) section. $\delta^{13}\text{C}_{\text{carb}}$, measured section, and conodont biostratigraphy from Edwards and Saltzman (2014). Camb. = Cambrian, Furon. = Furongian, Dap. = Dapingian, Ord. = Ordovician, I = *Iapetognathus*, L = *Cordylodus lindstromi*.

Figure 6. $\delta^{13}\text{C}$ data and moving average lines of the Clear Spring (MD) section. $\delta^{13}\text{C}_{\text{carb}}$ is from Leslie et al. (2011) and Saltzman and Thomas (2012), and measured section and conodont biostratigraphy from Saltzman et al. (2014). Dap. = Dapingian, Ord. = Ordovician.

Figure 7. Chemostratigraphic correlation of $\delta^{13}\text{C}_{\text{carb}}$ trends from new and published sections across North America. $\delta^{13}\text{C}$ excursions used for age calibration are shown in the numbered shaded regions using the rising limbs (light gray) and falling limbs (dark gray) of the excursions. Black arrows indicate the approximate level where the North American Ibexian-Whiterockian Series boundary (Floian-Dapingian Stages) is based on biostratigraphic data.

Figure 8. Cross plots of $\delta^{13}\text{C}_{\text{org}}$ (A) and $\Delta^{13}\text{C}$ (B) versus total organic carbon (TOC) abundance data from this study and literature sources. Kinetic factors favor TOC to be isotopically heavier (larger $\delta^{13}\text{C}_{\text{org}}$ and smaller $\Delta^{13}\text{C}$) with low TOC, due to either increased microbial or thermal degradation (Hayes et al., 1983). Samples with very low TOC (<0.1 wt. %) show no correlation with large $\delta^{13}\text{C}_{\text{org}}$ or small $\Delta^{13}\text{C}$ values. **C)** Cross plot of $\delta^{13}\text{C}_{\text{org}}$ and TOC (wt. %) with conodont alteration index (CAI) value estimates that shows no correlation between samples with higher CAI values (3 or higher; triangles and circles) and less negative $\delta^{13}\text{C}_{\text{org}}$. **D)** Same plot as in **C** (gray shaded region) but showing samples with low TOC (<0.5 wt. %) with no correlation between high CAI values being isotopically heavier than low CAI values.

Figure 9. Average variability (scatter) of bulk carbonate and organic matter from individual measured sections. Variability was determined by taking the difference between a measured value and the mean (three point moving average). Error bars represent the variability of the average differences from the mean measured by the root-mean-square error (RMSE; Table S4).

1084

1085 **Figure 10.** Composite plots of all new and literature $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$, and $\Delta^{13}\text{C}$ data less
1086 than 2σ from the mean with LOWESS trends (black lines) using a 200-point smoothing
1087 factor. The LOWESS trend for $\delta^{13}\text{C}_{\text{carb}}$ shows no significant secular variation throughout
1088 the Early–Middle Ordovician, but the $\delta^{13}\text{C}_{\text{org}}$ trend shows a 3.0‰ decrease from –26.5‰
1089 to –29.5‰, resulting in a 3.0‰ increase in $\Delta^{13}\text{C}$. Yellow circles and error bars showing
1090 mean values from Hayes et al. (1999) converted to the 2012 Geologic Time Scale.

1091

1092 **Figure 11.** Summary plot of long-term Ordovician changes in $\delta^{13}\text{C}_{\text{carb}}$ (from Saltzman
1093 and Thomas, 2012), $\Delta^{13}\text{C}$ (trend from Fig. 10), the global biodiversity trend of total
1094 Genera with the relative proportions of the three Evolutionary Faunas (Sepkoski, 1995)
1095 with the approximate timing of the “planktonic revolution” (Servais et al., 2008, 2010), a
1096 conodont-apatite based seawater strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) curve (Edwards et al., in press), and
1097 paleotemperature (°C) based on $\delta^{18}\text{O}$ measured from conodont apatite (Trotter et al.,
1098 2008).

1099

Edwards and Saltzman, Figure 1

Edwards and Saltzman, Figure 2

Edwards and Saltzman, Figure 3

Edwards and Saltzman, Figure 4

Edwards and Saltzman, Figure 5

West

East

Edwards and Saltzman, Figure +

Edwards and Saltzman, Figure 8

**Average variability
(Difference from $\delta^{13}\text{C}$ mean)**

Edwards and Saltzman, Figure 9

Edwards and Saltzman, Figure 10

Edwards and Saltzman, Figure 11