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Gradients in the carbon isotopic composition of Ordovician shallow water carbonates: A potential pitfall in estimates of ancient CO_2 and O_2

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ABSTRACT

The carbon isotopic composition of the global dissolved inorganic carbon (DIC) reservoir is best estimated from open ocean pelagic carbonate sediments ($\delta^{13}C_{carb}$). However, this is not practical for most of geologic time because seafloor subduction has removed the pre-Jurassic record and these time periods may have lacked planktonic calcifying organisms, and therefore shallow water carbonate platform or periplatform sediments are utilized. Shallow water deposits are susceptible to a wide range of post-depositional alteration processes and syn-depositional controls on $\delta^{13}C_{carb}$ that include carbonate mineralogy, water mass restriction, and a host of related variables (e.g., pH, temperature, organic decomposition, evaporation and CO_2 solubility) that can produce local gradients in DIC. The degree to which shallow water $\delta^{13}C$ curves diverge from open marine deposits may be critical to understanding how well global carbon cycle isotope mass balance models can predict organic carbon burial rates, but documentation of such divergence is often hindered by factors that limit chronostratigraphic correlation in restricted water masses (e.g., endemic faunas). Here we integrate strontium isotope ($^{87}Sr/^{86}Sr$) stratigraphy and biostratigraphy to compare $\delta^{13}C$ curves in a case study along a depth transect in Middle–Late Ordovician carbonate platform settings. The restricted tidal flat and more open marine deposits are offset by a maximum of ~2‰ during sea level drop and ~0‰ during highstand flooding of the platform. Global carbon cycle models such as GEOCARBSULF use published $\delta^{13}C_{carb}$ curves to drive organic carbon burial rates under the assumption that $\delta^{13}C_{carb}$ reflects a global seawater signal. We show here the potential pitfalls of using a published $\delta^{13}C_{carb}$ curve that violates this global assumption. For the 460 million year Middle–Late Ordovician time bin in GEOCARBSULF, improper usage of our locally depleted $\delta^{13}C$ curve to drive global organic carbon burial would result in erroneous atmospheric O_2 (~10.8% O_2, equal to about a 30% reduction from what it should be at ~15.2% O_2 using global $\delta^{13}C$) 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 $\delta^{13}C$ samples that record the influences of local carbon cycling from global carbon cycle models such as GEOCARBSULF.

1. Introduction

Carbon isotope ($\delta^{13}C$) 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 ($\delta^{13}C_{carb}$) to quantify global rates of ^{13}C-depleted organic carbon burial over a range of timescales (e.g., Berner, 2006; Kump and Arthur, 1999; Goddéris and Joachimski, 2004; Bergman et al., 2004; Royer et al., 2014; Bachan and Payne, 2016). Alternatively, these $\delta^{13}C_{carb}$ 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 $\delta^{13}C_{carb}$ 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

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the assumption that the $\delta^{13}C_{carb}$ 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 $\delta^{13}C$ 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 $\delta^{13}C_{carb}$ from global $\delta^{13}C_{DIC}$ remain a potential pitfall in global carbon cycle models.

The list of processes that may potentially decouple $\delta^{13}C_{carb}$ curves from global $\delta^{13}C_{DIC}$ is long, and may include water mass restriction that generates a $\delta^{13}C_{DIC}$ 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 $\delta^{13}C$ fractionation associated with equilibrium air–sea exchange of CO_2 ($\sim+1‰$ 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 $\delta^{13}C$ 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 $\delta^{13}C_{DIC}$ that varies from at or near global surface ocean $\delta^{13}C_{DIC}$ (~2‰) 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 $\delta^{13}C_{carb}$ that is heavier than $\delta^{13}C_{DIC}$ by anywhere from $+1‰$ for calcite to about $+2.7‰$ 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 $\delta^{13}C$ depending on water–rock interactions, such as observed in the strongly negative $\delta^{13}C_{carb}$ 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 $\delta^{13}C$ 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 $\delta^{13}C_{carb}$ 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 $\delta^{13}C_{DIC}$ are clearly recorded. For example, prominent global $\delta^{13}C$ 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 Cenomanian–Turonian Oceanic Anoxic Event (OAE) (Parente et al., 2007), and the Early Jurassic Toarcian OAE (Woodfine et al., 2008). However, the magnitudes of these $\delta^{13}C$ excursions recorded in shallow water carbonates often appear to be exaggerated relative to the global signal (Immenhauser et al., 2008), which is problematic for use as a $\delta^{13}C_{DIC}$ proxy in global carbon cycle models. Sea level fall, in particular, affects $\delta^{13}C_{carb}$ in platform or periplatform settings by restricting exchange with the open ocean or even other parts of the platform (Panchuk et al., 2005), promoting shedding of aragonite-rich (high $\delta^{13}C$ relative to calcite) sediments into adjacent platform or periplatform settings (Swart, 2008), or diagenesis (Immenhauser et al., 2003). Although the lack of pelagic (open ocean) carbonate in pre-Jurassic examples precludes straightforward comparisons to global $\delta^{13}C_{DIC}$, significant spatial variation in $\delta^{13}C$ in platform settings has been documented for several time intervals in the Paleozoic (e.g., Immenhauser et al., 2008).

A significant challenge for improved characterization of gradients in $\delta^{13}C$ along depth transects in ancient platforms is precise chronostratigraphic correlation. Strontium isotope ($^{87}Sr/^{86}Sr$) stratigraphy provides a useful correlation tool that is independent of biostratigraphy and carbon isotope-based correlations. Strontium has a residence time in the ocean nearly an order of magnitude longer than carbon, which supports the assumption of global homogeneity, but also impacts the potential time resolution attainable (McArthur et al., 2012). Therefore, success in correlating $\delta^{13}C$ curves is dependent on the rate of change in the seawater $^{87}Sr/^{86}Sr$ curve (Woodfine et al., 2008; Huck et al., 2011; Di Lucia et al., 2012; Frijia et al., 2015; Navarro-Ramirez et al., 2015) as well as the uncertainty associated with measuring ancient $^{87}Sr/^{86}Sr$ in geologic samples. Here we utilize a rapid change in $^{87}Sr/^{86}Sr$ in the Middle–Late Ordovician (465 to 455 Myrs) to correlate a $\delta^{13}C$ 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 $^{87}Sr/^{86}Sr$ at $\sim 50–100 \times 10^{-6}$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ as large as ~2‰ during relative sea level fall. Ultimately, the aim of our study is not to uniquely isolate the factors responsible for the $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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