

Early Mississippian ocean anoxia triggered organic carbon burial and late Paleozoic cooling: Evidence from uranium isotopes recorded in marine limestone

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ABSTRACT

The Early Mississippian (Tournaisian) positive $\delta^{13}\text{C}$ excursion (mid-Tournaisian carbon isotope excursion [TICE]) was one of the largest in the Phanerozoic, and the organic carbon (OC) burial associated with its development is hypothesized to have enhanced late Paleozoic cooling and glaciation. We tested the hypothesis that expanded ocean anoxia drove widespread OC burial using uranium isotopes ($\delta^{238}\text{U}$) of Lower Mississippian marine limestone as a global seawater redox proxy. The $\delta^{238}\text{U}$ trends record a large Tournaisian negative excursion lasting ~1 m.y. The lack of covariation between $\delta^{238}\text{U}$ values and facies changes and proxies for local depositional and diagenetic influences suggests that the $\delta^{238}\text{U}$ trends represent a global seawater redox signal. The negative $\delta^{238}\text{U}$ excursion is coincident with the first TICE positive excursion, supporting the hypothesis that an expanded ocean anoxic event controlled OC burial. These results provide the first evidence from a global seawater redox proxy that an ocean anoxic event drove Tournaisian OC burial and controlled Early Mississippian cooling and glaciation. Uranium and carbon modeling results indicate that (1) there was an ~6× increase in euxinic seafloor area, (2) OC burial was initially driven by expanded euxinia followed by expanded anoxic/suboxic conditions, and (3) OC burial mass was ~4–17× larger than that sequestered during other major ocean anoxic events.

INTRODUCTION

Large, repeated positive carbon isotope ($\delta^{13}\text{C}$) excursions are a common feature in Proterozoic–Phanerozoic marine carbonate and organic carbon isotope records (e.g., Veizer et al., 1999). Several of the “Big 5” mass extinctions were associated with large positive $\delta^{13}\text{C}$ excursions, highlighting the fact that these excursions record key processes and events in Earth history (e.g., Joachimski and Buggisch, 1993). These positive excursions are attributed to an increase in the burial fraction of organic carbon (OC) produced by oxygenic photosynthesis, resulting in the withdrawal of atmospheric CO_2 , and $p\text{O}_2$ buildup. Increased primary productivity, expanded marine anoxia, or increased sedimentation rates have all been suggested as possible drivers for enhanced OC burial during these events (Kump and Arthur, 1999). However, distinguishing among these potential drivers is not straightforward, leading to competing interpretations involving global or local processes.

Traditional tools used for deciphering the mechanism that best explains enhanced OC burial events include lithologic and paleobiologic features, elemental geochemistry, Fe speciation, and sulfur and nitrogen isotopes (e.g., Meyer and Kump, 2008); however, these tools reflect local rather than global processes.

Uranium isotope variations ($\delta^{238}\text{U}$) recorded in marine carbonates provide a novel way to distinguish between drivers for marine OC burial by providing an independent estimate of globally integrated ocean redox conditions. The $\delta^{238}\text{U}$ value of marine carbonates is a global redox proxy because U isotopes fractionate during reduction with ^{238}U , which is preferentially sequestered into marine sediments deposited under anoxic conditions, leaving seawater enriched in ^{235}U (Weyer et al., 2008). Because the residence time of U in seawater is significantly longer than ocean mixing times, the U isotope composition of open-ocean seawater is homogeneous (Tissot and Dauphas, 2015); as a result,

limestone precipitated from that seawater has the potential to record global ocean $\delta^{238}\text{U}$.

We applied the $\delta^{238}\text{U}$ redox proxy to the one of the largest positive $\delta^{13}\text{C}$ excursion in the Phanerozoic—the Early Mississippian (Tournaisian) $\delta^{13}\text{C}$ isotope excursion, or mid-Tournaisian carbon isotope excursion (TICE) (Saltzman et al., 2004). Previous TICE studies interpreted that OC burial generating the positive excursion was the result of either OC sequestration in foreland basin deposits (tectonic-sedimentation driver; Saltzman et al., 2000, 2004) or oxygen minimum zone expansion (marine anoxia driver; Saltzman, 2003; Buggisch et al., 2008; Liu et al., 2018; Maharjan et al., 2018a). To test which process was responsible for TICE OC burial, we used $\delta^{238}\text{U}$ of Tournaisian limestone in Nevada (USA) to generate a global seawater redox curve.

BACKGROUND

The Early Mississippian spans the climatic transition between the Devonian greenhouse and the late Paleozoic ice age (LPIA) (Montañez and Poulsen, 2013). The timing of initial LPIA cooling is debated as occurring by the Middle to Late Devonian (e.g., Isaacson et al., 2008), Early Mississippian (Buggisch et al., 2008), or the middle-late Mississippian (e.g., Isbell et al., 2003). North American TICE magnitudes range from ~6‰ to 7‰, and most are characterized by a double spike (Saltzman, 2002; Maharjan et al., 2018a). TICE magnitudes from Europe and Russia range from 4‰ to 6‰ (Saltzman et al., 2004). The $\delta^{18}\text{O}$ trends from Tournaisian apatite, calcite, and carbonate-associated sulfate indicate a positive ~1‰–2‰ shift concurrent with the TICE, indicating seawater cooled as OC was buried (Mii et al., 1999; Buggisch et al., 2008; Maharjan et al., 2018b). Previous studies using $\delta^{15}\text{N}$ (Yao et al., 2015; Maharjan

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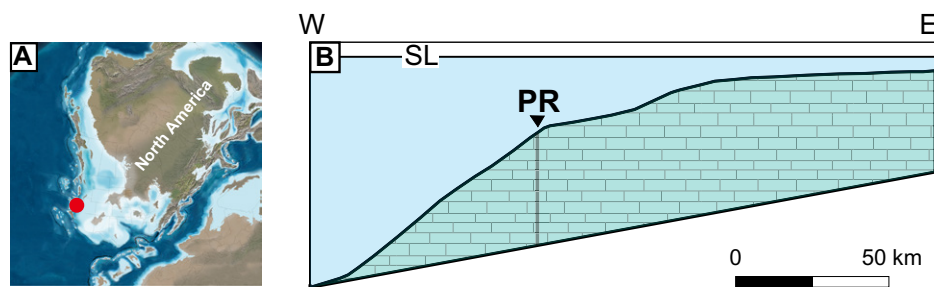


Figure 1. (A) Early Mississippian paleogeography of North America, from Blakey (2013). Red circle shows location of study area in present-day southern Nevada, USA (GPS coordinates 37°23'39.1"N, 115°15'42.1"W). (B) Schematic east-west cross section across the Mississippian carbonate ramp, showing location of study area (PR—Pahranagat Range, Nevada, USA; SL—sea level; modified from Maharjan et al., 2018a).

et al., 2018a) and $\delta^{34}\text{S}_{\text{CAS}}$ (CAS—carbonate-associated sulfate) (Gill et al., 2007; Maharjan et al., 2018b) to evaluate Tournaisian seawater redox reported mixed results between adjacent sections, leaving the question of global redox conditions unanswered.

We sampled the Lower Mississippian Joana Limestone and Limestone X in the Pahranagat Range of southeastern Nevada, USA (Fig. 1; GPS coordinates 37°23'39.1"N, 115°15'42.1"W), where previous conodont biostratigraphy and $\delta^{13}\text{C}$ studies provide a robust temporal framework and indicate that the ~250-m-thick succession spans ~4 m.y. (Saltzman, 2002; Maharjan et al., 2018a, 2018b). Detailed paleogeographic, stratigraphic, and biostratigraphic background, and our methods, are provided in the GSA Data Repository¹.

Uranium is sourced from weathered continental crust, and the main sinks are suboxic-anoxic-euxinic marine sediments, altered ocean crust, and biogenic carbonates (Tissot and Dauphas, 2015). Under anoxic conditions, U is reduced to insoluble U(IV) species and adsorbed by organic ligands or precipitated as U-rich minerals within sediments and is consequently removed from seawater (Weyer et al., 2008). During reduction, the larger ^{238}U nucleus is preferentially concentrated into the reduced U(IV) species due to the nuclear volume effect. During times of expanded ocean anoxia and anoxic seafloor area, more U is reduced, and ^{238}U is sequestered into sediments, leaving seawater enriched in ^{235}U , with carbonate minerals recording the lower $^{238}\text{U}/^{235}\text{U}$ ratios. Because the residence time of U is significantly longer (~400 k.y.; Dunk et al., 2002) than ocean mixing times, U isotopes in limestone should record global seawater redox conditions (e.g., Brenneke et al., 2011; Lau et al., 2016; Elrick

et al., 2017; Zhang et al., 2018). U-isotope compositions are reported as:

$$\delta^{238}\text{U} = \left[\frac{(^{238}\text{U}/^{235}\text{U})_{\text{sample}}}{(^{238}\text{U}/^{235}\text{U})_{\text{standard}}} - 1 \right] \times 1000\text{‰}, \quad (1)$$

where the standard is CRM-145 (Uranyl Nitrate Assay and Isotopic Solution; New Brunswick Laboratory, 2010).

RESULTS

Measured $\delta^{238}\text{U}$ values ranged from -1.02‰ to 0.02‰ (Table DR4 in the Data Repository), and stratigraphic trends are shown in Figure 2. The $\delta^{13}\text{C}_{\text{carb}}$ (carb—carbonate) values ranged from -1.1‰ to 7.0‰ . Cross-plots of $\delta^{238}\text{U}$ values against proxies of local redox conditions (U, V, Mo), detrital influx (Al/U, Th/U, Fe, wt% carbonate), nutrients (Fe, P), and diagenesis (Mn/Sr, $\delta^{18}\text{O}_{\text{carb}}$) show no covariation (Fig. 3; Fig. DR2).

DISCUSSION

Several lines of evidence argue against local depositional conditions controlling $\delta^{238}\text{U}$ trends. First, each facies deposited in poorly oxygenated to well-oxygenated settings records a wide range of $\delta^{238}\text{U}$ values; for example, lime mudstone facies deposited under moderately to poorly oxygenated conditions record the same spread of $\delta^{238}\text{U}$ values as the most oxygenated crinoid packstone facies (Fig. 3). Second, the prominent negative $\delta^{238}\text{U}$ shift occurs in a relatively uniform succession of crinoid packstone deposited in oxic waters, whereas the return positive shift occurs within facies deposited in a mix of poorly, moderately, and well-oxygenated waters. Third, the complete negative $\delta^{238}\text{U}$ excursion continues across two depositional sequence boundaries, indicating that water depths and depositional environment changes did not influence $\delta^{238}\text{U}$ trends.

We cross-plotted $\delta^{238}\text{U}$ values against Al/U, Th/U, and wt% carbonate to evaluate the influence of local detrital or riverine water input on $\delta^{238}\text{U}$ trends (Fig. 3). The lack of covariation among these proxies and the very low

concentrations of Th (<0.6 ppm) indicate that measured $\delta^{238}\text{U}$ trends were not influenced by these local processes. To evaluate potential effects of local reducing bottom water or pore waters, we compared $\delta^{238}\text{U}$ versus selected redox-sensitive metals and Mn/Sr (Fig. 3). The lack of covariation and low Mn/Sr values (<0.3) among these redox proxies indicate that the $\delta^{238}\text{U}$ trends were not controlled by local reducing conditions. All samples had Mg/Ca values <0.05 , indicating that they have not been dolomitized.

Previous studies of Bahamian carbonates indicated that early diagenesis results in an average $\sim 0.27\text{‰}$ enrichment of bulk limestone sediments (Tissot and Dauphas, 2015; Romaniello et al., 2013; Chen et al., 2018). We assume that the Lower Mississippian samples were also affected by similar levels of diagenetic U-isotopic enrichment, and we argue that the samples were enriched uniformly throughout the succession, based on the early diagenetic closure of the U isotopic system due to the low solubility of U^{4+} in anoxic pore waters and limited variation in Mn/Sr and $\delta^{18}\text{O}_{\text{carb}}$ values (Fig. 3; Fig. DR2). Given the lithologic, sedimentologic, and geochemical results, we interpret the observed $\delta^{238}\text{U}$ trends to represent original changes in global seawater redox conditions and recognize a clear negative excursion representing a major Tournaisian ocean anoxic event (OAE). Using conodont biostratigraphy and numeric age control (Buggisch et al., 2008), the duration of the OAE was ~1 m.y.

The onset and peak of the Tournaisian OAE coincide with the onset and first peak of the TICE (Fig. 2). This temporal coincidence supports the hypothesis that enhanced OC burial was driven by expanded ocean anoxia, which drove the positive $\delta^{13}\text{C}$ shift. In contrast to previous studies using local redox proxies ($\delta^{15}\text{N}$ —Yao et al., 2015; Maharjan et al., 2018a; $\delta^{34}\text{S}_{\text{CAS}}$ —Maharjan et al., 2018b), these results provide the first evidence from a globally integrated seawater redox proxy, and they provide clear evidence that Early Mississippian cooling and glaciation, as evidenced by the coeval positive $\delta^{18}\text{O}_{\text{apatite}}$ shift (Mii et al., 1999; Buggisch et al., 2008), were controlled by an anoxia-driven OC burial event.

We used a dynamic U cycle model (Lau et al., 2016) to quantitatively estimate changes in anoxic seafloor area during the Tournaisian OAE (see methods in the Data Repository) with the following simplified oxygenation terms: Euxinic refers to conditions reducing enough to significantly fractionate and reduce U, and anoxic/suboxic refers to low O_2 conditions, but with low reduction and fractionation of U (i.e., denitrification zones; Morford and Emerson, 1999). To generate the observed 0.3‰ negative shift using only anoxic/suboxic sediment sinks versus euxinic sinks, $>90\%$ of the global seafloor

¹GSA Data Repository item 2020104, geologic background, methods, stratigraphic trends, evaluation of diagenetic effects, and uranium and carbon modeling explanations, is available online at <http://www.geosociety.org/datarepository/2020/>, or on request from editing@geosociety.org.

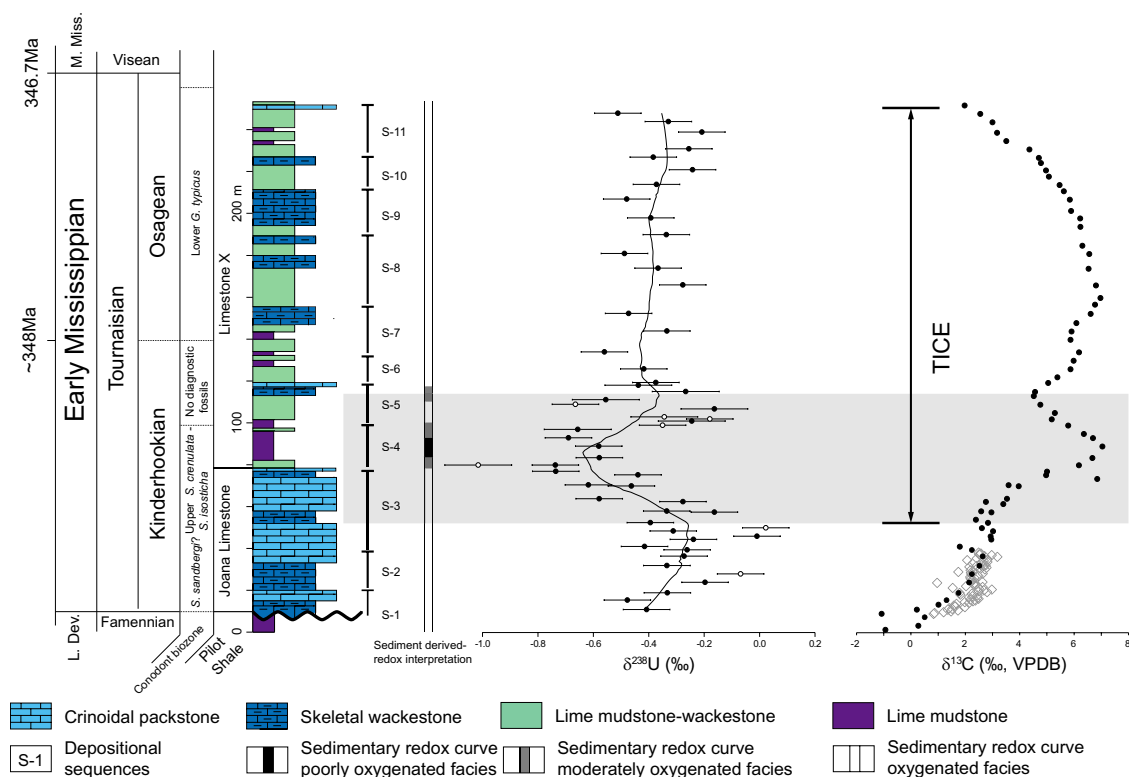


Figure 2. Stratigraphy, age, depositional sequences, redox interpretations, and LOWESS-smoothed $\delta^{238}\text{U}$ and $\delta^{13}\text{C}$ trends of the studied section PR (Pahrnagat Range, Nevada, USA). Outliers (open circles) are based on anomalous elemental concentrations. Gray band is interpreted Tournaisian ocean anoxic event (OAE) defined by ~1-m.y.-long negative $\delta^{238}\text{U}$ excursion. Black circles in $\delta^{13}\text{C}$ curve are from this study; open diamonds are from Maharjan et al. (2018a). Shaded vertical bar left of $\delta^{238}\text{U}$ curve shows oxygenation interpretations based on sedimentologic field observations discussed in the Data Repository (see footnote 1). TICE—mid-Tournaisian carbon isotope excursion; VPDB—Vienna Pee Dee belemnite standard. Conodont biozones: *S.*—*Siphonodella*, *G.*—*Gnathus*.

would have experienced anoxic/suboxic conditions. Such large-scale, low- O_2 seafloor conditions are not supported by global Lower Mississippian sedimentary and paleobiologic records (e.g., Davydov et al., 2004); consequently, we modeled the negative $\delta^{238}\text{U}$ shift using euxinic sediment sinks, which have significantly higher fractionation and U flux rates (Table DR3). Assuming euxinia, the model results suggest that there was an ~6× increase in euxinic seafloor area (5% to 30%; Fig. 4B). For comparison, the

modern ocean is characterized by <0.5% euxinic seafloor (Tissot and Dauphas, 2015).

To estimate the amount of OC buried during the Tournaisian OAE and its effects on the global climate, we used the Kump and Arthur (1999) carbon model and the observed $\delta^{13}\text{C}$ curve (see modeling methods in the Data Repository). The model curve generated two OC burial events corresponding to the TICE double spike (Fig. 4F); integrating the curve over the entire 4 m.y. TICE indicated a total OC burial

of $\sim 8.4 \times 10^{20}$ g, which is similar to estimates by Saltzman et al. (2004). For context, the amount of OC burial at the peak OAE was ~40% of the total C flux into the atmosphere-ocean reservoir (Kump and Arthur, 1999), and the total Tournaisian OC burial amount was ~12× larger than that estimated for the Cretaceous OAE-2 (Owens et al., 2018) and ~4× to 17× larger than the Late Ordovician (Hirnantian) positive $\delta^{13}\text{C}$ excursion (or HICE; see the Data Repository for HICE modeling). The modeled estimate of the

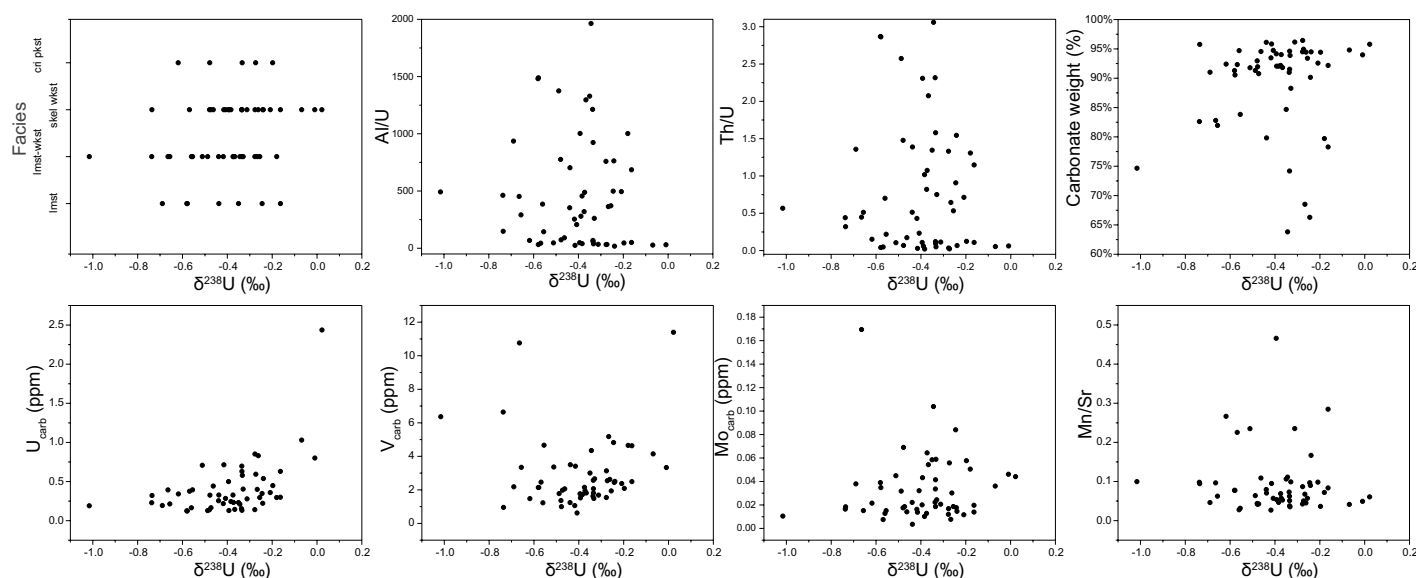


Figure 3. Cross-plots of $\delta^{238}\text{U}$ against four main Tournaisian facies, proxies for detrital sediment (A/U, Th/U, carb wt%), and redox (U, V, Mo, Mn/Sr). Lack of covariation among proxies indicates that measured $\delta^{238}\text{U}$ values were not influenced by local processes. Lmst—lime mudstone, lmst-wkst—lime mudstone-wackestone, skel wst—skeletal wackestone, cri pkst—crinoidal packstone.

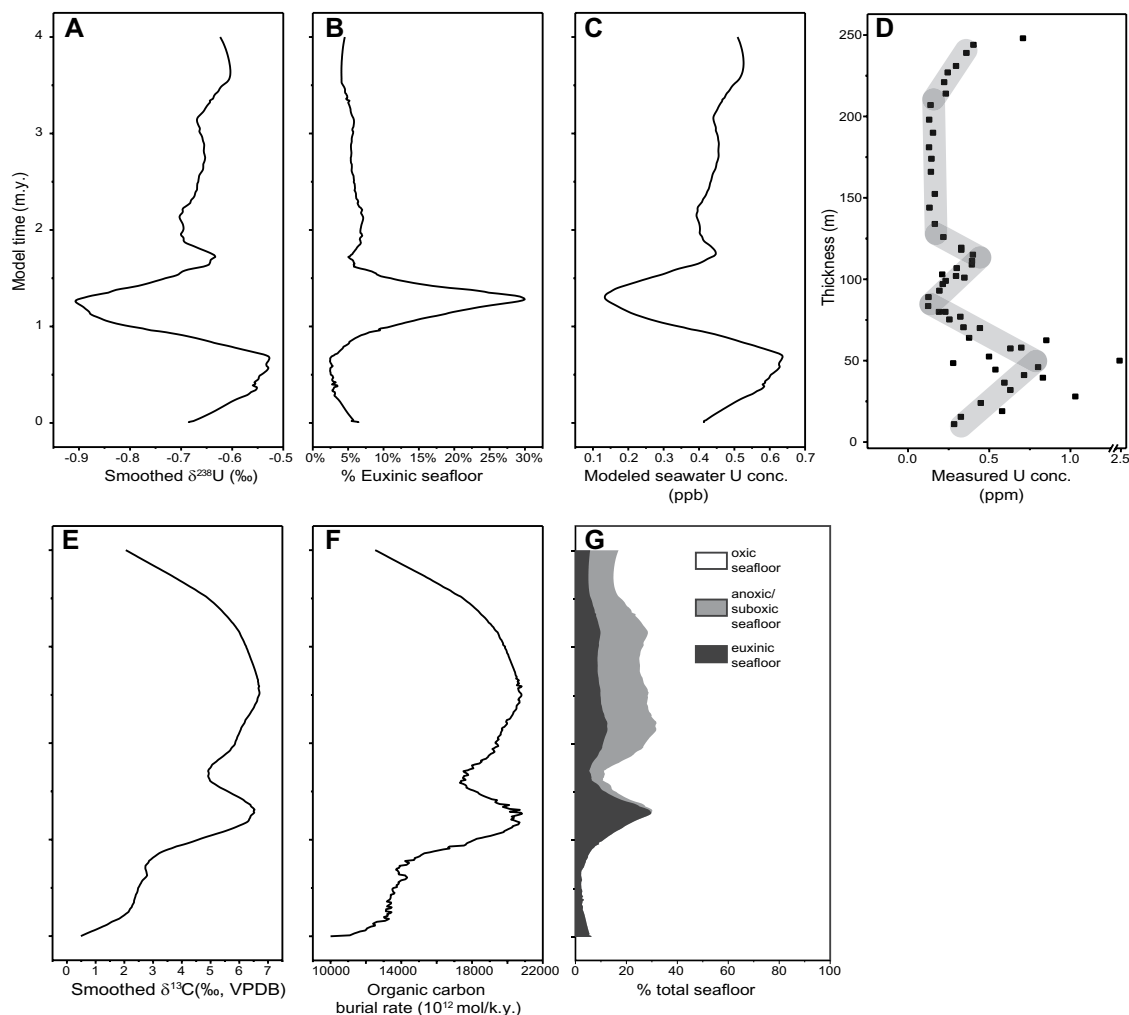


Figure 4. (A) Smoothed $\delta^{238}\text{U}$ curve. (B) Modeled percent euxinic seafloor changes. (C) Modeled seawater U concentrations (ppb). (D) Measured U_{carb} concentrations (ppm). (E) LOWESS-smoothed $\delta^{13}\text{C}$ curve. VPDB—Vienna Pee Dee belemnite standard. (F) Modeled variations in organic carbon (OC) burial rate estimated using smoothed $\delta^{13}\text{C}$ curve. (G) Percent euxinic, anoxic/suboxic, and oxic seafloor changes utilized in U model to best fit measured $\delta^{238}\text{U}$ and $\delta^{13}\text{C}$ curves; see the Data Repository for model parameters (see footnote 1). Note that this model curve is not unique.

Tournaisian OC burial flux illustrates its significance in cooling the late Paleozoic climate and further supports an Early Mississippian LPIA onset. Comparisons between the TICE and HICE are particularly pertinent to this study because extensive HICE OC burial is implicated in driving peak Hirnantian cooling/glaciation (e.g., Hammarlund et al., 2012), when peak glacier volumes are estimated to have exceeded those during the Last Glacial Maximum.

The second broad $\delta^{13}\text{C}$ TICE peak indicates continued OC burial for an additional ~2 m.y. after the OAE. This peak is best explained by OC burial occurring in anoxic/suboxic sediments, where U sequestration and fractionation are significantly lower than in euxinic sediments. We estimated the changes in euxinic, anoxic/suboxic, and oxic seafloor percentages using the observed $\delta^{238}\text{U}$ curve and U model. The best-fit, but nonunique model curve includes a gradual increase in euxinic seafloor area until the OAE peak, followed by a gradual replacement by dominantly anoxic/suboxic seafloor (Fig. 4G; see the Data Repository for U modeling method). A shift from euxinic to dominantly anoxic/suboxic conditions may have occurred when (1) atmospheric O_2 increased to sufficient levels (due to

OC burial) to reoxygenate oceans, and/or (2) marine phosphorus inventories eventually declined below the levels required to sustain expanded euxinia. The latter explanation is supported by measured phosphorus concentrations (Fig. DR2).

The Tournaisian OAE occurred during ongoing late Paleozoic cooling (starting in the Devonian), and its occurrence adds to the list of OAEs developed during cool/icehouse climates (Bartlett et al., 2018; White et al., 2018). This cooling resulted in increased latitudinal thermal gradients and intensified thermohaline circulation and meridional winds, which in turn enhanced upwelling- and wind-derived nutrient flux, increased productivity, and amplified O_2 consumption, leading to the Tournaisian OAE. This interpretation is supported by recent reports of decreased O_2 concentrations during the last two Neogene glacial stages, when high-latitude downwelling patterns reorganized, leading to decreased ventilation (e.g., Lu et al., 2016) and strengthened efficiency of the global biologic pump, enhancing OC flux to deep oceans.

CONCLUSIONS

The $\delta^{238}\text{U}$ trends across an ~4 m.y. succession of Lower Mississippian (Tournaisian) limestone

in Nevada record an ~1-m.y.-long negative $\delta^{238}\text{U}$ excursion with an ~0.3‰ magnitude. The lack of covariation between $\delta^{238}\text{U}$ values and proxies for depositional and diagenetic conditions indicates that the $\delta^{238}\text{U}$ curve represents a global seawater redox signal, and that the Tournaisian negative excursion represents an ocean anoxic event (OAE). The temporal coincidence between the $\delta^{238}\text{U}$ negative excursion and the first peak of the global positive $\delta^{13}\text{C}$ excursion (TICE) provides the first evidence from a globally integrated seawater redox proxy that enhanced Tournaisian OC burial was driven by an OAE. U modeling results suggest an ~6× increase in euxinic seafloor area during the OAE. C modeling suggests that the continued positive $\delta^{13}\text{C}$ trends after the OAE are best explained by initial euxinia replaced by more anoxic/suboxic conditions, and that the OC burial amount significantly exceeded that sequestered during other major Phanerozoic OAEs, leading to Tournaisian cooling and glaciation.

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