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Utility of organic carbon isotope data from the Salina Group halite (Michigan Basin): A new tool for stratigraphic correlation and paleoclimate proxy resource

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ABSTRACT

Long-term global carbon isotope records ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$) for the Silurian have been largely derived from unrestricted open-marine carbonates and shales. Here, we demonstrate how organic carbon harvested from halite-dominated evaporite deposits in a restricted intracratonic basin can be used to produce a carbon isotope record. Inorganic and organic carbon isotope data were generated and compared from four subsurface cores from the Silurian Michigan Basin, representing unrestricted carbonate and restricted evaporite/carbonate deposition. The $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records exhibit a number of long-term trends and major carbon isotope excursions (CIE) that are correlated with the globally identified Ireviken, Mulde, and Linde events. These data provide temporal and stratigraphic constraints in rocks where paleontological data are sparse or absent. They also potentially highlight the effect of enhanced local evaporation on isotope fractionation. This new technique for generating a long-term organic carbon isotope profile from Silurian halite sequences, which can be correlated to the global curve, is of broad interest to the geoscience and paleoclimate science communities. These data not only provide a valuable tool for understanding the chronostratigraphic framework within an evaporative interior basin, but they also provide a rare temporal link between periods of prolonged evaporite deposition and events of known paleoclimate change.

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INTRODUCTION

Evaporative basins are an integral part of science and society. They provide reservoir seals for over half of the world's petroleum reserves (Sarg, 2001, and references therein), and they are commonly mined for a variety of manufacturing and industrial applications (Warren, 2016). In an academic sense, large halite-dominated evaporative basins are especially important because they provide a potential rare link among the ancient atmosphere, hydrosphere, and lithosphere during long-term paleoclimate change (e.g., Fanlo and Ayora, 1998; Warren, 2016). However, in order to assess the potential effects of prolonged evaporation on the local paleoenvironment, it is necessary to first constrain the depositional timing of large-scale evaporation events.

One of the biggest obstacles in halite-prone sequences is obtaining reliable age constraint, because nearly all biostratigraphically important marine organisms are typically absent. In highly evaporative settings, it is also not possible to rely on inorganic sources, such as $\delta^{13}C_{carb}$, to compare with long-term global trends, because most halites contain very little associated carbonate (Warren, 2016). As such, $\delta^{13}C_{carb}$ can, at best, provide an incomplete isotope record. Without temporal constraint in evaporite sequences, it is difficult (1) to establish stratigraphic correlations within and outside the basin, and (2) to discern the effects of changing global versus local climate conditions. These challenges become surmountable if temporally constrained and uniquely global chemostratigraphic signatures can be identified within the basin, thereby establishing a means of comparison with the global record.

In this study, we used a multiproxy data set approach. Local $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records derived from normal marine carbonate and halite-prone deposits in the Silurian Michigan Basin (Fig. 1) were compared to an established global inorganic carbon isotope curve in order to establish depositional age constraints for the onset of halite deposition. During deposition, organic matter was trapped and preserved as inclusions within the halite (Fig. 1D). By collecting this organic material at regular intervals, it should be possible to produce a long-term geochemical record for the basin. The Salina Group halite of the Michigan Basin is an ideal candidate with which to test this approach, because it is thought to be structurally intact and it does not display large-scale doming, or postdepositional salt migration (Mesolella et al., 1974; Cercone, 1984).

SILURIAN PALEOCLIMATE

The Silurian was a period of intense climatic instability dominated by highly variable ocean temperatures, strong swings in eustasy, and frequent biotic turnover (Jeppsson, 1990; Samtleben et al., 1996; Azmy et al., 1998; Munnecke et al., 2003; Kaljo et al., 2003; Lehnert et al., 2010; Noble et al., 2012; McAdams et al., 2017; and others), as evidenced by eight biostratigraphically constrained carbon isotope excursions (CIEs; Cramer et al., 2011, 2015, and references therein). From oldest to youngest, these include the early Aeronian, late Aeronian, Valgu, Ireviken, Mulde, Linde, Lau, and Klonk events. Most CIEs range 2‰ to 4‰ $\delta^{13}C_{carb}$ relative to background values, with the Lau event ranging 7‰ to 12‰. Comparisons of these CIEs with small-scale extinction and recovery events exhibit variable degrees of correlation,

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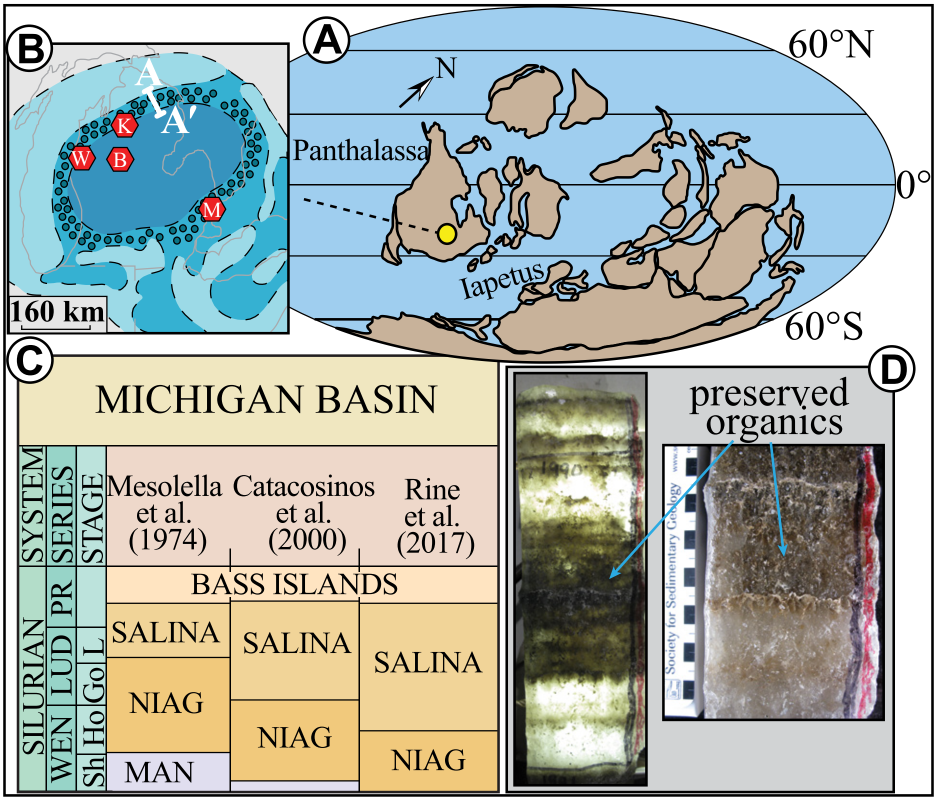

Figure 1. (A, B) Silurian paleogeography and schematic map of the Michigan Basin with location of cores at: K (State Kalkaska #2–15); B (Bruske #1–26); W (Weinert #2–6); and M (DC-Mead #1). Dark-blue circles—locations of pinnacle reefs (from Briggs et al., 1980). (C) Silurian chronostratigraphies for the Michigan Basin showing discrepancy in depositional timing for Niagara and Salina Groups. PR—Pridoli, LUD—Ludlow, WEN—Wenlock, L—Ludfordian, Go—Gorstian, Ho—Homerian, Sh—Sheinwoodian, NIAG—Niagara, MAN—Manistique. (D) Precipitated organic matter in halite from the A-2 Evaporite, DC-Mead #1 core at ~190.0 ft (58 m). Scale for D is in cm.

suggesting that no single repetitive set of paleoclimatic circumstances and/or controlling mechanism can explain these events (Munnecke et al., 2010; Noble et al., 2012; Cooper et al., 2014; Jarochowska and Munnecke, 2015; Trotter et al., 2016).

Until now, carbon isotope data ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$) for the Silurian have been derived primarily from marine carbonates (Cramer et al., 2011, and references therein) and, to a lesser extent, shales (Porębska et al., 2004; Noble et al., 2005, 2012; Lenz et al., 2006; Frýda and Štorch, 2014). We are unaware of any published study where such data were extracted from Silurian halite-dominated evaporite deposits to assess long-term trends in the organic carbon isotope record. Procurement of coeval carbon isotope data derived from both inorganic carbonate and organic matter offers an opportunity to compare the overall expression and timing of these events using a proxy that is influenced by highly variable causes of isotopic fractionation, and it also offers the potential to assess variation in atmospheric pCO_2 (i.e., changes in $\Delta^{13}C$; e.g., Kump and Arthur, 1999). In a study focusing on the timing of the "two-prong" Mulde event in Arctic Canada, Noble et al. (2005, 2012) showed variability in CIE magnitude not only between adjacent stratigraphic sections, but also between the organic and inorganic carbon isotope records. This type of interrecord variability highlights the need to evaluate long-term trends and variations in pCO_2 in these two systems in a variety of geographic locations and paleoenvironments.

GEOLOGICAL SETTING

The Michigan Basin is a tectonically stable bowl-shaped intracratonic depression in North America (Fig. 1A) that contains ~5 km (16,000 ft) of Cambrian- to Pennsylvanian-age sedimentary strata (Howell and van der Pluijm, 1999; Catacosinos et al., 2000). Throughout the Silurian, the Michigan Basin was located at low-lying (i.e., tropical) latitudes in the central part of the Laurentian Continental Seaway, which was connected to the Iapetus Ocean to the south and the Panthalassan Ocean to the west and covered much of present-day North America (Fig. 1A). During Wenlock (early Sheinwoodian–Homerian) time, elaborate barrier and pinnacle reef complexes developed along the margin and almost completely rimmed the basin (Fig. 1B). This barrier and pinnacle reef system comprises the upper part of the Niagara Group (Guelph Formation), which altogether ranges in thickness from 39 m (130 ft) to 213 m (700 ft) on the basin margin.

The Niagara barrier and pinnacle reef system is capped by up to 762 m (2500 ft) of interbedded anhydrite, halite (Fig. 1D), and organic-rich carbonate mudstone of the Salina Group, representing a major change in paleoenvironment and local sea level (Mesolella et al., 1974; Sullivan et al., 2016). The Salina Group is divided into repeating sequences of evaporites, carbonates, and shales identified as Salina units A-0 to G (Mesolella et al., 1974). Within this group, non-evaporite carbonate and shale units (e.g., A-0, A-1C, A-2C, C, E, and G) are known to have greater lateral continuity than evaporite-dominant units (Mesolella et al., 1974; Harrison and Voice, 2017).

Because the primary focus of this study centers on the subject of a new global correlation proxy, it is important to briefly discuss some confusing terminology in the local (i.e., subsurface Michigan Basin) versus regional (i.e., eastern United States) stratigraphic assignment of Silurian units. Originally, the term Lockport was designated as a group-level term in the state of New York (Brett et al., 1995; fig. 1 *in* Cramer et al., 2011), whereas in the Michigan Basin, it is used at the formation level (e.g., formally as the Lockport Dolomite Formation *in* Catacosinos et al., 2000, 2001; or informally as the Lockport Formation). Similarly, the term Niagaran is a regional time designation in North America, temporally equivalent to the combined Llandovery and Wenlock Epochs (fig. 1 *in* Cramer et al., 2011). In the Michigan Basin, the term Niagara is used as a group-level designation that is only partially temporally equivalent to the Niagaran Series (see Catacosinos et al., 2000, 2001). The term Niagara has also been used as an informal designation for stratigraphic units within the Niagara Group (e.g., informally designated as "Gray" or "Brown" Niagara to correspond to the Lockport Formation and Guelph Formation, respectively, *in* Catacosinos et al., 2000, 2001). Until this confusing terminology is clarified, it is important to use the official stratigraphic terminology of Michigan, established by Catacosinos et al. (2000, 2001).

Biostratigraphic Constraint

The base of the Salina Group was originally defined in New York State as the contact between the Vernon Shale and the underlying Guelph Dolomite, occurring at the Niagara-Cayugan boundary (fig. 4 *in* Brett et al., 1995). On the southern and western margins of the Michigan Basin, this lithological transition appears older, constrained to the upper Homerian (Wenlock) by the conodonts *Ozarkokina bohemica longa* and *Pseudooneotodus linguicornis* (NE Indiana and Ohio; Kleffner and Rexroad, 1999; Cramer, 2009; Swift, 2011; Kleffner et al., 2012) and by the onset of the Mulde event CIE (NE Indiana, Ohio, and Wisconsin; Cramer, 2009; Swift, 2011; Kleffner et al., 2012; Sullivan et al., 2016). However, this apparent difference in stratigraphic position for the base of the Salina Group between the eastern United States and the Michigan Basin area is not an implied diachroneity, rather, it is an indication that this lithological transition is complex and is less precisely known in the New York area.

In the Michigan Basin center, the base of the Salina Group is marked by the sudden change from thriving reef complexes of the Niagara Group to immense halite-dominant evaporite deposition of the Salina Group (Mesolella et al., 1974; Catacosinos et al., 2000; Rine et al., 2017). Although the depositional timing of this lithologic transition between the Michigan Basin center and its margin is inferred through stratigraphic correlation, to date there have been no high-resolution geochemical studies and very few diagnostic fossils recovered from this uppermost Niagara and Salina Group transition in the Michigan Basin. Thus making direct age correlation difficult (Fig. 1C).

A conodont analysis of rocks lower in the Niagara Group by Kuglitsch (2013) identified *Kockelella walliseri* stratigraphically above co-occurring elements of *Kockelella ranuliformis* and *Ozarkodina sagitta rhenana* from the lower Lockport Formation. This suggests that platform carbonates (predating reef deposition) were deposited during the *O. s. rhenana* and lower *K. walliseri* zones of the middle Sheinwoodian (Wenlock). Mesolella et al. (1974) also identified Wenlock brachiopods *Plicocyrtia* cf. *arkansana* and *Pentamerus* sp. from the basal Salina Group. Although brachiopods are typically known to have longer stratigraphic ranges than conodonts, and they are therefore less valuable for age correlation, the presence of both fossil groups indicates a Wenlock age for the pre–Salina Group sediments. These observations suggest that the transition to evaporite deposition potentially occurred within the Wenlock, after the lower *K. walliseri* zone, which generally coincides with the known timing on the basin margin.

SILURIAN $\delta^{13}C_{ORG}$ DATA FROM THE MICHIGAN BASIN

Methodology

In total, 433 samples were collected and analyzed for $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ from the Miller Brothers-Weinert #2–6 (Permit #37731), Northern Michigan Exploration Corp–State Kalkaska #2–15 (Permit #29218), Roadrunner-Bruske #1–26A (Permit #59271), and Diamond Crystal Salt Co.–Saint Clair River Associates, a.k.a. DC-Mead #1 (Permit #28135), cores, representing the greater Niagara–middle Salina Group stratigraphy in the Michigan Basin (Figs. 2–5). In the Weinert #2–6 and State Kalkaska #2–15 cores, inorganic and organic carbon was analyzed from the Lockport and Guelph Formations of the Niagara Group, and in the State Kalkaska #2–15 core, only organic carbon was analyzed from the A-0C to A-1C units of the Salina Group. In the Bruske #1–26A core, inorganic and organic carbon was analyzed from the uppermost A-1E to A-1C units of the Salina Group (only organic carbon was analyzed from the uppermost A-1E unit). In the DC-Mead #1 core, only organic carbon was analyzed from the A-1C to C units of the Salina Group.

All organic carbon isotope samples were analyzed at the stable isotope biogeochemistry laboratory at Durham University, Durham, UK, and samples for inorganic carbon isotopes were analyzed at either the stable isotope laboratory at the University of Michigan (Weinert #2–6 and Bruske #1–26A well cores) or at the laboratory at Durham University (State Kalkaska #2–15 well core).

Stable Isotope Laboratory, University of Michigan

Samples weighing a minimum of 10 µg were placed in stainless-steel boats. Samples were then transferred to individual borosilicate reaction vessels and reacted at 77 °C ± 1 °C with 4 drops of anhydrous phosphoric acid in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 triple collector–isotope ratio mass spectrometer (IRMS). Limestones, dolomites, apatite, and siderite were reacted for 8, 12, 17, and 22 min, respectively. O^{17} data were corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by two standards (NBS 18 and NBS 19). All stable isotope data are reported in standard delta (δ) notation in per mil (‰) relative to the Vienna Peedee belemnite (VPDB) scale. Precision and accuracy were monitored through daily analysis of a variety of powdered carbonate standards, with at least four standards reacted and analyzed daily. Measured precision was maintained at better than 0.1‰ for both carbon and oxygen.

Stable Isotope Biogeochemistry Laboratory, Durham University

Inorganic and organic $\delta^{13}C$ data were obtained following the methods of Skrzypek and Debajyoti (2006) and Gröcke et al. (2009), respectively. Acquisition of $\delta^{13}C_{org}$ data from halite included an additional desalinization step. Approximately 200 mg aliquots of sediment were dissolved in deionized water for 1 h and centrifuged, and the supernatant was discarded. Wet samples were decalcified using 3 *M* HCl, left overnight at room temperature. Samples were then neutralized using deionized water and dried in an oven at 55 °C. Sample sets from the Bruske #1–26A and DC-Mead #1 cores were treated with hot HCl and then reanalyzed for $\delta^{13}C_{org}$, in an effort to assess secondary effects of dolomitization (red text in supplemental data file[1]). The $\delta^{13}C_{org}$ data were acquired using a Costech Elemental Analyzer (ECS 4010) coupled to a Thermo Finnigan Delta V Advantage IRMS. Carbon isotope ratios were corrected for ^{17}O contribution and reported in standard delta (δ) notation in per mil (‰) relative to the VPDB scale. Data accuracy was monitored through routine analyses of in-house standards, which were calibrated against international standards (USGS 40, USGS 24, IAEA 600, IAEA CH6): This provided a linear range in $\delta^{13}C$ between +2‰ and –47‰. Analytical uncertainty for δ^{13}Corg was typically ±0.1‰ for replicate analyses of the international standards and typically <0.2‰ on replicate sample analysis.

RESULTS

Numerous time-correlative excursions are recorded within the inorganic and organic carbon isotope data. These excursions exhibit the same direction of offset, and they appear in multiple wells. In the Weinert #2–6 core, a positive CIE of 2‰ ($\delta^{13}C_{org}$) and 2.5‰ ($\delta^{13}C_{carb}$) occurs from 4590 ft to 4540 ft (1399 m to 1384 m) (Fig. 2). Above the CIE, from 4540 ft to 4465 ft (1384 m to 1361 m) in the core, $\delta^{13}C_{carb}$ values are consistent at approximately +1‰, and $\delta^{13}C_{org}$ values show several smaller 1‰–1.5‰ positive CIEs in the upper part of the Lockport Formation

[1]GSA Data Repository item 2018153, organic carbon isotope data from the Salina Group halite (MI Basin) USA, is available at http://www.geosociety.org/datarepository/2018 or by request to editing@geosociety.org.

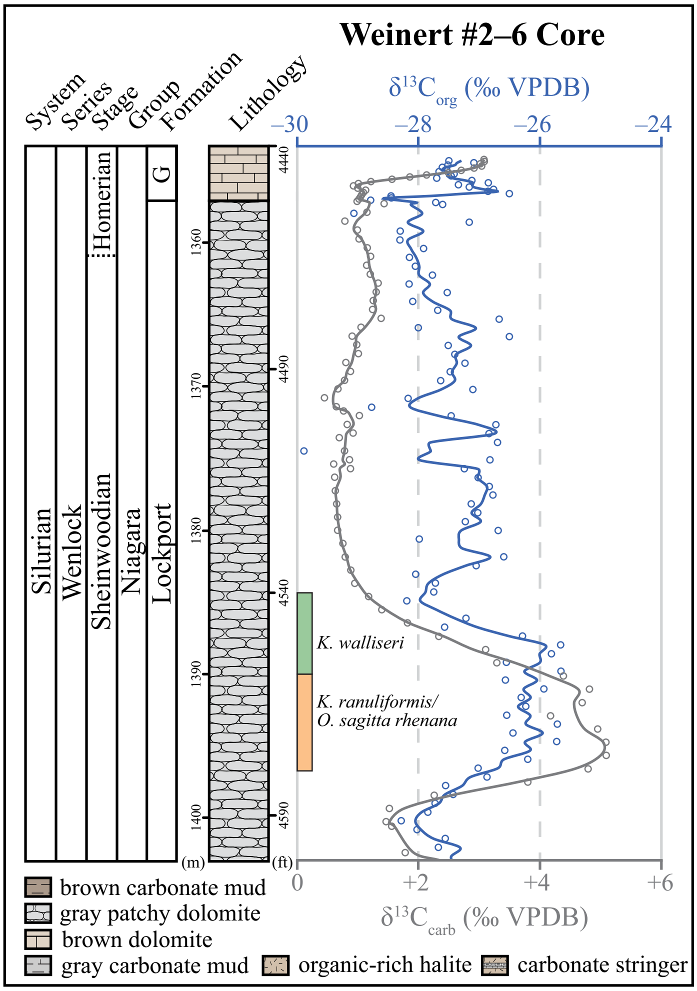

Figure 2. Niagara Group (Lockport and lower Guelph Formations) $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ data from the Weinert #2–6 core, Michigan Basin, presented as a three-point moving average (solid line). Open circles represent actual data points. G—Guelph; VPDB—Vienna Peedee belemnite standard; *K.—Kockelella*; *O.—Ozarkodina*.

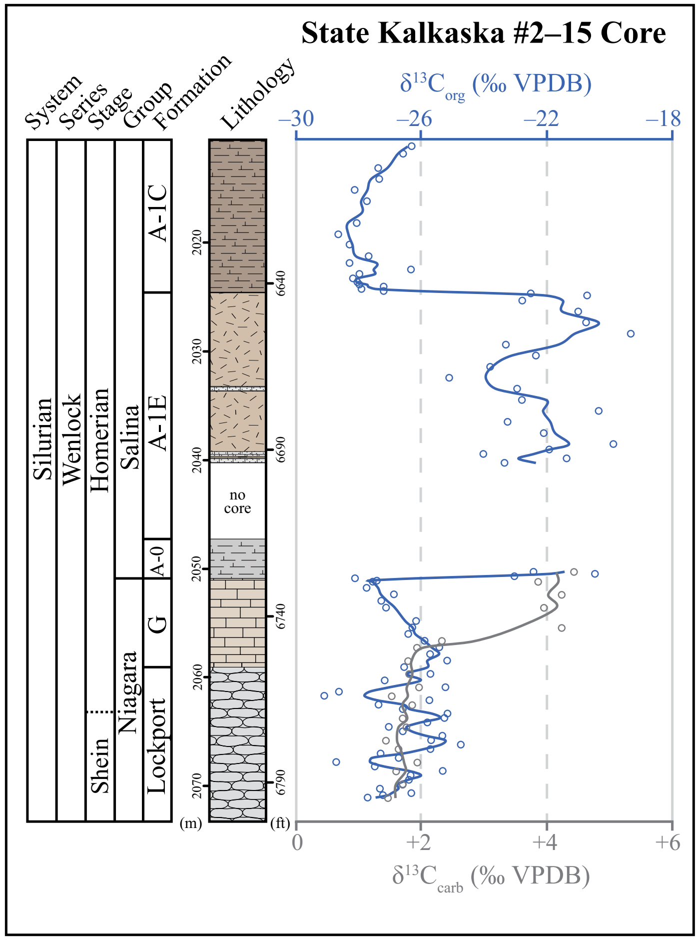

Figure 3. Niagara (Lockport and Guelph Formation) and Salina (A-0C, A-1E, and A-1C units) Group $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ data from the State Kalkaska #2–15 core, Michigan Basin, presented as a three-point moving average (solid line). Open circles represent actual data points. See Figure 2 for lithology key. G—Guelph; VPDB—Vienna Peedee belemnite standard.

that range between –28‰ and –27‰. From 4465 ft to 4440 ft (1361 m to 1353 m), there is an abrupt and slightly offset +2‰ CIE in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values that occurs near the base of the Guelph; the CIE in $\delta^{13}C_{carb}$ occurs slightly above the CIE in $\delta^{13}C_{org}$.

In the State Kalkaska #2–15 core, several 3‰–3.5‰ CIEs in $\delta^{13}C_{org}$ occur from 6792 ft to 6740 ft (2070 m to 2054 m), spanning the upper Lockport and lowermost Guelph Formations (Fig. 3). There is a +2‰ CIE in $\delta^{13}C_{carb}$ that occurs in the lowermost Guelph Formation at 6752 ft (2058 m) and extends to the boundary between the Niagara and Salina units. From 6732 ft to 6640 ft (2052 m to 2024 m), there is a large, abrupt, +8‰ CIE in $\delta^{13}C_{org}$ that begins in the lowermost Salina Group (A-0 unit), extends throughout the overlying A-1E unit, and terminates in the lowermost A-1C unit. Within this large positive CIE, $\delta^{13}C_{org}$ values show a high degree of variability, fluctuating 2‰–3‰, with maximum values reaching –20‰. Above this large positive CIE, from 6640 ft (2024 m) to the top of the core, $\delta^{13}C_{org}$ values show a broad positive trend from –28‰ to –26‰ throughout the A-1C unit. Samples treated with hot HCl showed no change in $\delta^{13}C_{org}$ values.

In the Bruske #1–26A core, $\delta^{13}C_{org}$ values show a returning limb of a large positive CIE (–21‰ to –27‰) at 7272 ft (2217 m) that crosses the A-1E and A-1C unit boundary (Fig. 4). Above this returning limb, $\delta^{13}C_{org}$ values record a steady, slightly negative, trend that spans the A-1C unit to 7218 ft (2200 m), with values that reach –29‰. From 7264 ft to 7218 ft (2214 m to 2200 m), $\delta^{13}C_{carb}$ values are steady at +1‰, with a small 0.5‰ to +1‰ negative CIE at 7232 ft (2204 m) of the A-1C unit, correlative with the appearance of anhydrite.

In the DC-Mead #1 core, there is a large, abrupt, positive 10‰ CIE in $\delta^{13}C_{org}$ from 2349 ft to 2212 ft (716 m to 674 m), where values reach –20‰ in the lowermost A-2E unit and then show a steady return to consistent values of approximately –30‰ in the lower A-2C unit (Fig. 5). In the upper A-2C unit, there is a broad positive 6‰ CIE in $\delta^{13}C_{org}$ that begins at 2135 ft (651 m) and spans the Salina B unit to 1784 ft (544 m), terminating very close to the contact with the overlying C unit. Organic carbon isotope values show a high degree of variation throughout the B unit, frequently fluctuating between approximately –27‰ and –25‰ $\delta^{13}C_{org}$.

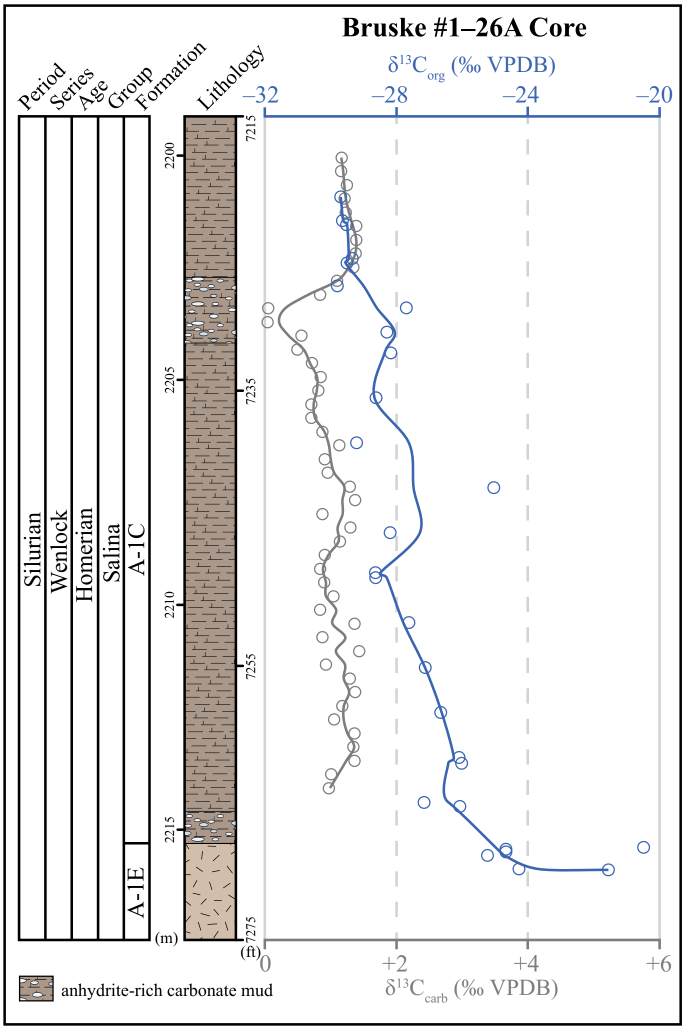

Figure 4. Salina Group (A-1E and A-1C unit) $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ data from the Bruske #1–26A core, Michigan Basin, presented as a three-point moving average (solid line). Open circles represent actual data points. See Figure 2 for lithology key. VPDB—Vienna Peedee belemnite standard.

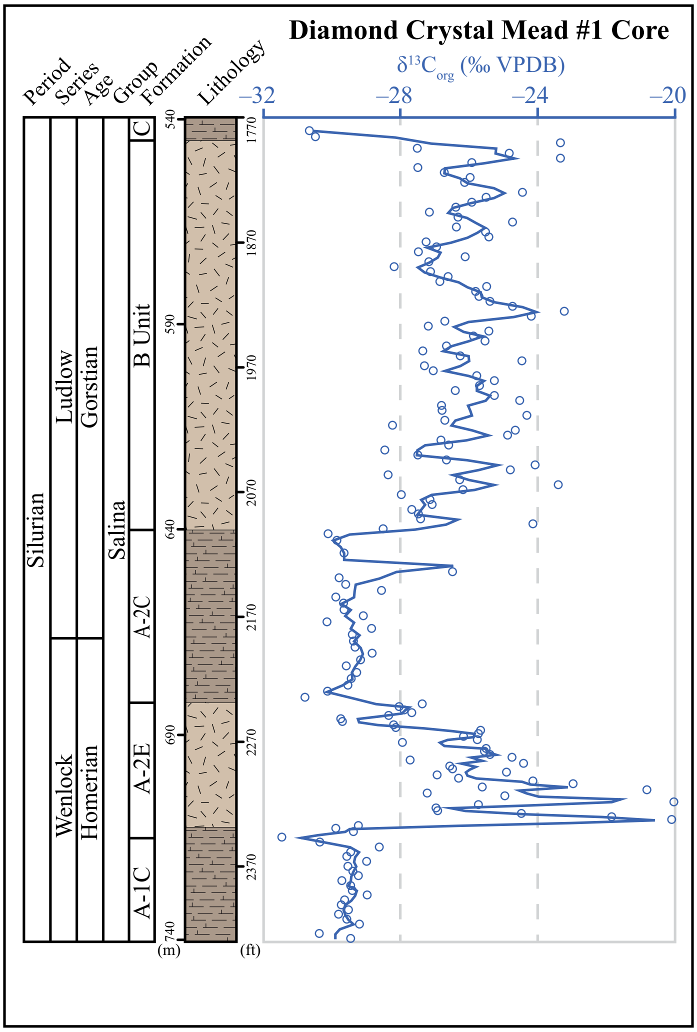

Figure 5. Salina Group (A-1C, A-2E, A-2C, B, and C unit) $\delta^{13}C_{org}$ data from the DC-Mead #1 core, Michigan Basin, presented as a three-point moving average (solid line). Open circles represent actual data points. See Figure 2 for lithology key. C—C unit; VPDB—Vienna Peedee belemnite standard.

DISCUSSION

Carbon isotope data from the Michigan Basin show four large positive CIEs in the $\delta^{13}C_{org}$ records from the Weinert #2–6, State Kalkaska #2–15, Bruske #1–26A, and DC-Mead #1 cores. Two of these CIEs are also identified in $\delta^{13}C_{carb}$ records from the Weinert #2–6 and State Kalkaska #2–15 cores. Figure 6 presents data from the four wells in a single composite isotope curve. The four large positive CIEs include: coeval ~3‰–5‰ ($\delta^{13}C_{carb}$) and ~3‰–4‰ ($\delta^{13}C_{org}$) CIEs in the lower Lockport Formation; two successive ~8‰–10‰ ($\delta^{13}C_{org}$) CIEs that span the upper Niagara Guelph Formation to lower Salina A-2 Evaporite (onset of the lower CIE in the Guelph Formation is also evident as a 2‰ perturbation in $\delta^{13}C_{carb}$); and one broad 4‰–5‰ ($\delta^{13}C_{org}$) positive excursion spanning the uppermost Salina A-2 Carbonate Unit to uppermost Salina B unit (Fig. 6). In order to evaluate the geological significance and potential global correlation of these CIEs, it is important to first assess the potential impact of any local secondary processes that may have altered or affected the primary isotope signal.

Secondary Effects on $\delta^{13}C$ Fractionation

Did diagenetic processes such as dolomitization and/or thermal maturation of buried of organic carbon control the primary signal (or magnitude) of these CIEs? This is one of the most important questions to address because secondary effects could result in diagenetic overprinting that could potentially impact the carbon isotope record and impede reliable correlation with global events. In order to answer this question, it is vital to first understand the physical characteristics of these CIEs (e.g., associated lithologies and magnitude of isotope perturbation).

Three observations suggest that the carbon isotope record in the Michigan Basin is a primary signal. First, carbon isotope data presented in Figures 3–5 show that the recorded CIEs spanned multiple lithologies and were not restricted to a particular interval (e.g., CIEs are not restricted to specific zones of halite or dolomite), as would be expected if secondary fractionation of carbon isotopes during diagenesis was the principal cause of the observed CIEs. Dolomitization, for instance, is quite common throughout the Silurian strata of the Michigan Basin and occurs throughout the Niagara and

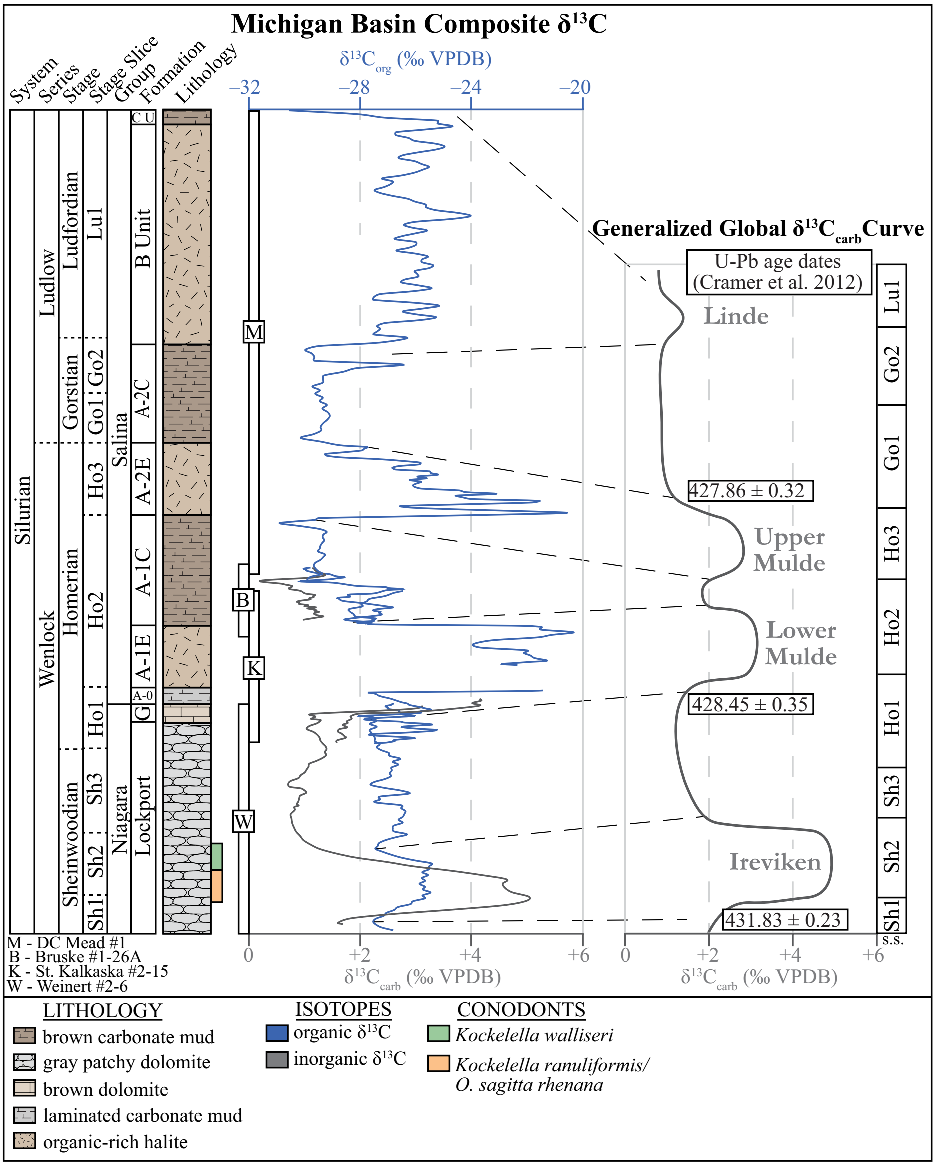

Figure 6. Composite Niagara–Salina Group $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ data from the Michigan Basin, presented as a three-point moving average, showing correlation with the global Ireviken and Mulde carbon isotope excursions (CIEs). Cores: K (State Kalkaska #2–15); B (Bruske #1–26); W (Weinert #2–6); and M (DC-Mead #1). Generalized global $\delta^{13}C_{carb}$ curve and biostratigraphy are modified after Cramer et al. (2011, 2012) and Melchin et al. (2012). Sh—Sheinwoodian, Ho—Homerian, Go—Gorstian, Lu—Ludfordian, G—Guelph, E—Evaporite, C—Carbonate, C U—C Unit, *O.*—*Ozarkodina*, VPDB—Vienna Peedee belemnite standard.

Salina Group carbonates (Catacosinos et al., 2001). If dolomitization caused the observed CIEs, isotopic changes should be restricted to the dolomitized intervals of the A-0C and A-1C units. There would be no major fluxes in carbon isotope values (or CIEs) that extend into the A-1E or A-2E units. In order to evaluate this possibility, however, samples from the Bruske #1–26A and DC-Mead #1 cores were reprocessed using hot HCl (red text in supplemental data [see footnote 1]). Hot HCl is commonly known to more fully dissolve dolomite crystals, thereby eliminating the mineralogical fractionation effect of dolomitization. The $\delta^{13}C_{org}$ values showed no change from their original values, which reinforces the interpretation that the isotopes reflect a primary depositional signal.

Second, it has long been known that secondary salt crystal growth occurs throughout the Salina Group carbonate units (Catacosinos et al., 2001). It could be the case that during thermal maturation, migrating fluids containing salt and hydrocarbons with isotopically light organics could have infiltrated sediment at various stratigraphic intervals, thus altering the original long-term carbon isotope record (Lewan, 1983). If this were the case, carbon isotope values would be expected to be lighter (more positive) wherever secondary reprecipitated salt crystal growth is present. However, our data show that organic carbon isotopes in the A-1C and A-2C units maintain more negative values (–29‰) than either the pre-excursion levels of –27‰ or the CIE levels of approximately –22‰ to –20‰ ($\delta^{13}C_{org}$), despite the presence of minor post-depositional secondary halite crystal growths (Fig. 6).

Third, the uppermost (youngest) CIE in our composite curve has different physical characteristics in comparison to the preceding large positive CIEs. This could suggest a controlling mechanism that is independent. If a secondary process was affecting these data equally, then the CIEs would be expected to have a similar magnitude and character. As shown in Figure 6, the ascending limb of this uppermost CIE is broad, and isotope values reach a lower-magnitude value, –25‰, in comparison to the two older Salina Group CIEs, which reach values of –21‰ and –20‰, respectively. The lack of apparent continuity between isotopic perturbations reinforces the claim that diagenesis or salt inclusions are unlikely to have caused these observed excursions.

Last, enhanced evaporation during Salina Group deposition could have had profound effects on the local inorganic and organic $\delta^{13}C$ values in the Michigan Basin. The composite isotope curve (Fig. 6) shows that organic carbon values reached a maximum of –20‰ during deposition of two thick halite Salina Group units (A-1E and A-2E units). Stiller et al. (1985), Schmid (2017), and others have contended that the process of evaporation leads to a loss of $[CO_2]$ within evaporative brines, which in turn is reflected in the inorganic carbon isotope record as highly enriched $\delta^{13}C_{carb}$ values in the associated carbonates. Documented Paleoproterozoic evaporite-related carbonates contain $\delta^{13}C_{carb}$ values up to +17.2‰ (Melezhik et al., 1999), whereas Permian and Triassic evaporite sequences have values up to +7‰ $\delta^{13}C_{carb}$ (Schmid et al., 2006).

Interestingly, a similar positive shift is observed in $\delta^{13}C_{org}$ values in organic biomarkers deposited during periods of enhanced evaporation. In a study of Miocene–Pliocene halite deposits in the Dead Sea, Grice et al. (1998; their fig. 2) showed large variation in $\delta^{13}C_{org}$ values of various organic biomarkers, suggesting $\delta^{13}C_{org}$ values of n-alkanes range from –25‰ to –33‰, hopanes range from –24‰ to –25‰, diaromatic steroids range from –22‰ to –24‰, and isoprenoids range from –16‰ to –15‰. In a study of Ordovician carbonates from Iowa, Pancost et al. (2013) showed two correlative positive CIEs of 2‰–3‰ ($\delta^{13}C_{carb}$) and 4‰–10‰ ($\delta^{13}C_{org}$), demonstrating that variability in the magnitude of this CIE in organic carbon can reflect different chemical compounds within the bulk organic matter. These studies show that our observed local changes in organic carbon values may have had a significant impact on the observed fractionation within the organic carbon isotope record, perhaps as a function of changing primary productivity brought on by changing paleoenvironment and pCO_2.

Correlation with the Global Carbon Isotope Curve

A fundamental argument for the global correlation of carbon isotope excursions is underpinned by identifying similar chemostratigraphic patterns recorded in variable facies that are geographically far removed from one another (Shields et al., 2002; Oehlert et al., 2012; Saltzman and Thomas, 2012). This is observed in the new halite-derived carbon isotope data set from the Michigan Basin. The composite curve in Figure 6 is in general agreement with the global curves of Cramer et al. (2011, 2015) and Sullivan et al. (2016). As mentioned, Kuglitsch (2013) identified *Kockelella walliseri* slightly above co-occurring elements of *Kockelella ranuliformis* and *Ozarkodina sagitta rhenana* from the lower Lockport Formation, at 4540 ft–4580 ft in the Weinert #2–6 core, correlative with the lowest positive CIE (orange and green bars in Figs. 2 and 6). These conodonts are indicative of the lower *K. walliseri* and underlying *O. s. rhenana* zones of the Silurian (Jeppsson et al. 2006) and suggest an early Wenlock (middle Sheinwoodian) age that is consistent with the Ireviken CIE of Cramer et al. (2011) and Noble et al. (2012).

In regards to the three overlying large positive CIEs (Fig. 6), temporal constraint is hampered by a lack of viable conodont data from the Niagara-Salina Group boundary in the Michigan Basin center (Klug, 1977; Kuglitsch, 2000; Sullivan et al., 2016), and a lack of age data from the Salina Group. However, as mentioned earlier, studies on the southern and eastern basin margin show that the Niagara-Salina transition occurred during upper Wenlock (Homerian) time (Cramer, 2009; Swift, 2011; Kleffner et al., 2012; McLaughlin et al., 2013; Sullivan et al., 2016). In a study from the western margin (modern-day Wisconsin), Sullivan et al. (2016; their fig. 5) successfully constrained the Mulde event CIE from the correlative Niagara-Salina Group boundary by demonstrating Homerian $^{87}Sr/^{86}Sr$ ratios in conodont elements recovered from the acme of the positive CIE, thus constraining this event. Therefore, if the lithologic transition from carbonates to evaporites is generally coeval across the Michigan Basin, a similar large positive CIE at approximately the same stratigraphic position within the basin center would be expected. The composite isotope curve (Fig. 6) shows carbon isotope perturbation beginning within the uppermost Niagara Group (Guelph Formation) in the Weinert #2–6 and State Kalkaska #2–15 cores and continuing in the lowermost Salina Group. This correlation, along with the occurrence of Wenlock brachiopods *Plicocyrtia* cf. *arkansana* and *Pentamerus* sp. in the basal Salina Group (Mesolella et al., 1974) at a level correlative with the ascending limb of the CIE, is strong evidence that the lowermost Salina group CIE is equivalent to the lower Mulde CIE.

Temporal constraint is not currently available for the two younger large CIEs because there have been no age-specific conodonts recovered from Salina Group sediments of the Michigan Basin center. Therefore, it remains possible that the overlying CIEs (spanning the Salina Group A-2E and B units) are an expression of the upper Mulde, Linde, or Lau events. Cramer et al. (2011, 2015) and Sullivan et al. (2016) showed the Mulde as a two-prong ~2.5‰ ($\delta^{13}C_{carb}$) CIE that occurs in the upper Wenlock; the Linde as a small ~1.5‰ ($\delta^{13}C_{carb}$) CIE that occurs in the upper Gorstian to lower Ludfordian (Calner et al., 2004); and the Lau as a large ~7‰–12‰ ($\delta^{13}C_{carb}$) CIE that occurs in the middle Ludfordian.

There is no reason to suggest that the Mulde event would not have the same two-prong character as recorded in the global curve of Cramer et al. (2015). If the Niagara-Salina Group boundary CIE is the lower Mulde event, then it is possible that this overlying large CIE of similar magnitude is the basinal expression of the upper Mulde event. The CIE in the A-2E unit is of similar magnitude as the lower Mulde event (within the A-1E unit), and its placement in the lower Salina Group appears too low to be consistent with the Linde or Lau event. However, no other study has documented carbon isotope values in the trough separating the two Mulde CIEs that return to a prolonged (and relatively stable) baseline that is more negative than pre-excursion levels. This might reflect local conditions within the Michigan Basin center. If this interpretation is correct, then it implies that the overlying broad positive CIE spanning the Salina B unit represents the smaller-magnitude Linde CIE (Fig. 6).

An alternative interpretation is that the large CIE spanning the Salina Group A-2E unit is an exceptionally large-magnitude example of the Linde event, or possibly even the Lau event. However, based on the location of the CIE within the general Salina Group stratigraphy in comparison to the timing and magnitude of perturbation expressed in the global curve, this interpretation seems less likely. Therefore, the interpretation that the lower Salina Group CIEs are examples of both Mulde excursions is most consistent with the available observations.

CONCLUSIONS

Inorganic and organic carbon isotope data extracted from carbonate- and halite-dominated sequences in the Silurian Niagara and Salina Groups of the Michigan Basin record three large excursions in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ that can be correlated with the global records of the Ireviken, Mulde, and Linde events. Organic carbon isotope values reach a maximum of –20‰ during deposition of two thick halite Salina Group units (A-1E and A-2E units), suggesting that local changes in organic carbon source material during periods of enhanced evaporation might have affected local fractionation, thereby influencing the observed values. The ability to establish a long-term carbon isotope record in halite sequences provides a new and important approach for investigating ancient evaporative depositional settings. This is of broad interest to the geoscience community because it delivers a new tool for chronostratigraphic correlation that is valuable for temporally linking periods of prolonged evaporite deposition to events of known paleoclimate change.

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REFERENCES CITED

Azmy, K., Veizer, J., Bassett, M.G., and Copper, P., 1998, Oxygen and carbon isotopic composition of Silurian brachiopods: Implications for coeval seawater and glaciations: Geological Society of America Bulletin, v. 110, p. 1499–1512, https://doi.org/10.1130/0016-7606(1998)110<1499:OACICO>2.3.CO;2.

Brett, C.E., Tepper, D.H., Goodman, W.M., LoDuca, S.T., and Eckert, B.-Y., 1995, Revised Stratigraphy and Correlations of the Niagaran Provincial Series (Medina, Clinton, and Lockport Groups) in the Type Area of Western New York: U.S. Geological Survey Bulletin 2086, 66 p.

Briggs, L.I., Gill, D., Briggs, D.Z., and Elmore, R.D., 1980, Transition from open marine to evaporite deposition in the Silurian Michigan Bain, *in* Nissenbaum, A., ed., Hypersaline Brines and Evaporitic Environments: New York, Elsevier, Developments in Sedimentology 28, p. 253–270.

Calner, M., Jeppsson, L., and Munnecke, A., 2004, The Silurian of Gotland—Part I: Review of the stratigraphic framework, event stratigraphy, and stable carbon and oxygen isotope development, *in* Munnecke, A., Servais, T., and Schulbert, C., eds., Field Guide, Erlanger Geologische Abhandlungen, Sonderband 5: Nurnberg, Germany, Druck, Tischner and Hoppe, p. 113–131.

Catacosinos, P.A., Harrison, W.B., III, and Reynolds, R.F., WestJohn, D.B., and Wollensack, M.S., 2000, Stratigraphic Nomenclature for Michigan: Michigan Department of Environmental Quality, Geological Survey Division, 1 sheet, http://www.deq.state.mi.us/documents/deq-gsd-info-geology-Stratigraphic.pdf (last accessed 2000).

Catacosinos, P.A., Harrison, W.B., III, Reynolds, R.F., WestJohn, D.B., and Wollensack, M.S., 2001, Stratigraphic Lexicon for Michigan: Michigan Department of Environmental Quality, Geological Survey Division, Bulletin 8, 56 p.

Cercone, K.R., 1984, Diagenesis of Niagara (Middle Silurian) Pinnacle Reefs, Northwest Michigan [Ph.D. thesis]: Ann Arbor, Michigan, University of Michigan, 367 p.

Cooper, R.A., Sadler, P.M., Munnecke, A., and Crampton, J.S., 2014, Graptoloid evolutionary rates track Ordovician–Silurian global climate change: Geological Magazine, v. 151, p. 349–364, https://doi.org/10.1017/S0016756813000198.

Cramer, B.D., 2009, Application of Integrated High-Resolution Biochemostratigraphy to Paleozoic Chronostratigraphic Correlation: Recalibrating the Silurian System [Ph.D. thesis]: Columbus, Ohio, Ohio State University, 286 p.

Cramer, B.D., Brett, C.E., Melchin, M.J., Männik, P., Kleffner, M.A., McLaughlin, P.I., Loydell, D.K., Munnecke, A., Jeppsson, L., Corradini, C., Brunton, F.R., and Saltzman, M.R., 2011, Revised correlation of Silurian Provincial Series of North America with global and regional chronostratigraphic units and $\delta^{13}C_{carb}$ chemostratigraphy: Lethaia, v. 44, p. 185–202, https://doi.org/10.1111/j.1502-3931.2010.00234.x.

Cramer, B.D., Condon, D.J., Soderlund, U., Marshall, C., Worton, G.J., Thomas, A.T., Calner, M., Ray, D.C., Perrier, V., Boomer, I., Patchett, P.J., and Jeppsson, L., 2012, U-Pb (zircon) age constraints on the timing and duration of Wenlock (Silurian) paleocommunity collapse and recovery during the 'Big Crisis': Geological Society of America Bulletin, v. 124, p. 1841–1857, https://doi.org/10.1130/B30642.1.

Cramer, B.D., Schmitz, M.D., Huff, W.D., and Bergström, S.M., 2015, High-precision U-Pb zircon age constraints on the duration of rapid biogeochemical events during the Ludlow Epoch (Silurian Period): Journal of the Geological Society [London], v. 172, p. 157–160, https://doi.org/10.1144/jgs2014-094.

Fanlo, I., and Ayora, C., 1998, The evolution of the Lorraine evaporite basin: Implications for the chemical and isotope composition of the Triassic ocean: Chemical Geology, v. 146, p. 135–154, https://doi.org/10.1016/S0009-2541(98)00007-2.

Frýda, J., and Štorch, P., 2014, Carbon isotope chemostratigraphy of the Llandovery in northern peri-Gondwana: New data from the Barrandian area, Czech Republic: Estonian Journal of Earth Sciences, v. 63, p. 220–226, https://doi.org/10.3176/earth.2014.22.

Grice, K., Schouten, S., Nissenbaum, A., Charrach, J., and Sinninghe Damsté, J.S., 1998, Isotopically heavy carbon in the C_{21} to C_{25} regular isoprenoids in halite-rich deposits from the Sdom Formation, Dead Sea Basin, Israel: Organic Geochemistry, v. 28, no. 6, p. 349–359, https://doi.org/10.1016/S0146-6380(98)00006-0.

Gröcke, D.R., Rimmer, S.M., Yoksoulian, L.E., Cairncross, B., Tsikos, H., and van Hunen, J., 2009, No evidence for thermogenic methane release in coal from the Karoo–Ferrar large igneous province: Earth and Planetary Science Letters, v. 277, p. 204–212, https://doi.org/10.1016/j.epsl.2008.10.022.

Harrison, W.B., III, and Voice, P.J., 2017, Evaporite facies of the Michigan Basin, *in* Grammer, G.M., Harrison, W.B., III, and Barnes, D.A., eds., Paleozoic Stratigraphy and Resources of the Michigan Basin: Geological Society of America Special Paper 531 (in press), https://doi.org/10.1130/2017.2531(10).

Howell, P.D., and van der Pluijm, B.A., 1999, Structural sequences and styles of subsidence in the Michigan Basin: Geological Society of America Bulletin, v. 111, p. 974–991, https://doi.org/10.1130/0016-7606(1999)111<0974:SSASOS>2.3.CO;2.

Jarochowska, E., and Munnecke, A., 2015, Late Wenlock carbon isotope excursions and associated conodont fauna in the Podlasie Depression, eastern Poland: A not-so-big crisis?: Geological Journal, v. 51, p. 683–703, https://doi.org/10.1002/gj.2674.

Jeppsson, L., 1990, An oceanic model for lithological and faunal changes tested on the Silurian record: Journal of the Geological Society [London], v. 147, p. 663–674, https://doi.org/10.1144/gsjgs.147.4.0663.

Jeppsson, L., Eriksson, M.E., and Calner, M., 2006, A latest Llandovery to latest Ludlow high-resolution biostratigraphy based on the Silurian of Gotland—A summary: GFF, v. 128, p. 109–114, https://doi.org/10.1080/11035890601282109.

Kaljo, D., Martma, T., Männik, P., and Viira, V., 2003, Implications of Gondwana glaciations in the Baltic Late Ordovician and Silurian and a carbon isotopic test of environmental cyclicity: Bulletin de la Société Géologique de France, v. 174, no. 1, p. 59–66, https://doi.org/10.2113/174.1.59.

Kleffner, M.A., and Rexroad, C.B., 1999, Preliminary conodont biostratigraphy of the Salina Group (Silurian) of northern Indiana and recognition of the Wenlock, *in* Eastern Section American Association of Petroleum Geologists 28th Annual Meeting, Program with Abstracts: Tulsa, Oklahoma, American Association of Petroleum Geologists, p. 33–34.

Kleffner, M.A., Swift, R.J.A., Barrick, J.E., and Karlsson, H.R., 2012, Conodont biostratigraphy and ^{13}C chemostratigraphy of the Salina Group in North American Midwestern basins and arches region (western Ohio and eastern Indiana): Geological Society of America Abstracts with Programs, v. 44, no. 5, p. 2.

Klug, C.R., 1977, Upper Silurian of Wisconsin, *in* Nelson, K.G., ed., Geology of Southeastern Wisconsin: 41st Annual Tri-State Field Conference Guidebook: Milwaukee, Wisconsin, University of Wisconsin, p. A35–A39.

Kuglitsch, J.J., 2000, Correlation of the Silurian Rocks of Southeastern and Northeastern Wisconsin Using Conodonts and Conodont Strontium Isotope Ratios and Proposed Conodont and Ostracode Biofacies Models for the Environs of the Middle Aeronian Michigan Basin [Ph.D. thesis]: Madison, Wisconsin, University of Wisconsin, 349 p.

Kuglitsch, J.J., 2013, Preliminary report of a Sheinwoodian conodont fauna from the northwestern margin of the Michigan Basin subsurface: Geological Society of America Abstracts with Programs, v. 45, no. 7, p. 836.

Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon-isotope excursions: carbonates and organic matter: Chemical Geology, v. 161, p. 181–198.

Lehnert, O., Männik, P., Joachimski, M.M., Calner, M., and Frýda, J., 2010, Palaeoclimate perturbations before the Sheinwoodian glaciation: A trigger for extinctions during the 'Ireviken event': Palaeogeography, Palaeoclimatology, Palaeoecology, v. 296, p. 320–331, https://doi.org/10.1016/j.palaeo.2010.01.009.

Lenz, A.C., Noble, P.J, Masiak, M., Poulson, S.R., and Kozłowska, A., 2006, The lundgreni Extinction Event: Integration of paleontological and geochemical data from Arctic Canada: GFF, v. 128:2, p. 153–158, https://doi.org/10.1080/11035890601282153.

Lewan, M.D., 1983, Effects of thermal maturation on stable organic carbon isotopes as determined by hydrous pyrolysis of Woodford Shale: Geochimica et Cosmochimica Acta, v. 47, p. 1471–1479, https://doi.org/10.1016/0016-7037(83)90306-X.

McAdams, N.E.B., Bancroft, A.M., Cramer, B.D., and Witzke, B.J., 2017, Integrated carbon isotope and conodont biochemostratigraphy of the Silurian (Aeronian–Telychian) of the East-Central Iowa Basin, Iowa, USA: Newsletters on Stratigraphy, v. 50, no. 4, p. 391–416, https://doi.org/10.1127/nos/2017/0375.

McLaughlin, P.I., Mikulic, D.G., and Kluessendorf, J., 2013, Age and correlation of Silurian rocks in Sheboygan, Wisconsin, using integrated stable carbon isotope stratigraphy and facies analysis: Wisconsin Geoscience, v. 21, p. 15–38.

Melchin, M.J., Sadler, P.M., and Cramer, B.D., 2012, The Silurian Period, *in* Gradstein, F.M., Ogg, J.G., Schmitz, M., and Ogg, G., eds., The Geologic Time Scale 2012: Amsterdam, Netherlands, Elsevier, p. 525–558, https://doi.org/10.1016/B978-0-444-59425-9.00021-4.

Melezhik, V.A., Fallick, A.E., Medvedev, P.V., and Makarikhin, V.V., 1999, Extreme $\delta^{13}C_{carb}$ enrichment in ca. 2.0 Ga magnesite-stromatolite-dolomite-'red beds' association in a global context: A case for the world-wide signal enhanced by a local environment: Earth-Science Reviews, v. 48, p. 71–120, https://doi.org/10.1016/S0012-8252(99)00044-6.

Mesolella, K.J., Robinson, J.D., McCormick, L.M., and Ormiston, A.R., 1974, Cyclic deposition of Silurian carbonates and evaporites in Michigan Basin: American Association of Petroleum Geologists Bulletin, v. 58, no. 1, p. 34–62.

Munnecke, A., Samtleben, C., and Bickert, T., 2003, The Ireviken event in the Lower Silurian of Gotland, Sweden—Relation to similar Palaeozoic and Proterozoic events: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 195, p. 99–124, https://doi.org/10.1016/S0031-0182(03)00304-3.

Munnecke, A., Calner, M., Harper, D.A.T., and Servais, T., 2010, Ordovician and Silurian sea-water chemistry, sea level, and climate: A synopsis: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 296, p. 389–413, https://doi.org/10.1016/j.palaeo.2010.08.001.

Noble, P.J., Zimmerman, M.K., Holmden, C., and Lenz, A.C., 2005, Early Silurian (Wenlockian) $\delta^{13}C$ profiles from the Cape Phillips Formation, Arctic Canada, and their relation to biotic events: Canadian Journal of Earth Sciences, v. 42, p. 1419–1430, https://doi.org/10.1139/e05-055.

Noble, P.J., Lenz, A.C., Holmden, C., Masiak, M., Zimmerman, M.K., Poulson, S.R., and Kozłowska, A., 2012, Isotope geochemistry and plankton response to the Ireviken (earliest Wenlock) and *Cyrtograptus lundgreni* extinction events, Cape Phillips Formation, Arctic Canada, *in* Talent, J.A., ed., Earth and Life, Part III, Global Biodiversity, Extinction Intervals and Biogeographic Perturbations Through Time: Berlin, Springer-Verlag, p. 631–652, https://doi.org/10.1007/978-90-481-3428-1_20.

Oehlert, A.M., Lamb-Wozniak, K.A., Devlin, Q.B., Mackenzie, G.J., Reijmer, J.J.G., and Swart, P.K., 2012, The stable carbon isotopic composition of organic material in platform derived sediments: Implications for reconstructing the global carbon cycle: Sedimentology, v. 59, p. 319–335, https://doi.org/10.1111/j.1365-3091.2011.01273.x.

Pancost, R.D., Freeman, K.H., Herrmann, A.D., Patzkowsky, M.E., Ainsaar, L., and Martma, T., 2013, Reconstructing Late Ordovician carbon cycle variations: Geochimica et Cosmochimica Acta, v. 105, p. 433–454, https://doi.org/10.1016/j.gca.2012.11.033.

Porębska, E., Kozłowska-Dawidziuk, A., and Masiak, M., 2004, The *lundgreni* event in the Silurian of the East European Platform, Poland: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 213, p. 271–294, https://doi.org/10.1016/j.palaeo.2004.07.013.

Rine, M., Garrett, J., and Kaczmarek, S.E., 2017, A new facies architecture model for the Silurian Niagara–Lower Salina "pinnacle" reef complexes of the Michigan Basin, *in* MacNeil, A., Lonnee, J., and Wood, R., eds., Characterization and Modeling of Carbonates—Mountjoy Symposium 1: Society for Sedimentary Geology (SEPM) Special Publication 109 (in press), https://doi.org/10.2110/sepmsp.109.02.

Saltzman, M.R., and Thomas, E., 2012, Carbon isotope stratigraphy, *in* Gradstein, F.M., Ogg, J.G., Schmitz, M., and Ogg, G., eds., The Geologic Time Scale 2012: Amsterdam, Netherlands, Elsevier, p. 207–232, https://doi.org/10.1016/B978-0-444-59425-9.00011-1.

Samtleben, C., Munnecke, A., Bickert, T., and Pätzold, J., 1996, The Silurian of Gotland (Sweden): Facies interpretation based on stable isotopes in brachiopod shells: Geologische Rundschau, v. 85, p. 278–292, https://doi.org/10.1007/BF02422234.

Sarg, J.F., 2001, The sequence stratigraphy, sedimentology, and economic importance of evaporite-carbonate transitions: A review: Sedimentary Geology, v. 140, p. 9–34.

Schmid, S., 2017, Neoproterozoic evaporites and their role in carbon isotope chemostratigraphy (Amadeus Basin, Australia): Precambrian Research, v. 290, p. 16–31, https://doi.org/10.1016/j.precamres.2016.12.004.

Schmid, S., Worden, R.H., and Fisher, Q., 2006, Carbon isotope stratigraphy using carbonate cements in the Triassic Sherwood Sandstone Group: Corrib Field, west of Ireland: Chemical Geology, v. 225, p. 137–155, https://doi.org/10.1016/j.chemgeo.2005.09.006.

Shields, G.A., Brasier, M.D., Stille, P., and Dorjnamjaa, D., 2002, Factors contributing to high $\delta^{13}C$ values in Cryogenian limestones of western Mongolia: Earth and Planetary Science Letters, v. 196, p. 99–111, https://doi.org/10.1016/S0012-821X(02)00461-2.

Skrzypek, G., and Debajyoti, P., 2006, $\delta^{13}C$ analyses of calcium carbonate: Comparison between the GasBench and elemental analyzer techniques: Rapid Communications in Mass Spectrometry, v. 20, p. 2915–2920, https://doi.org/10.1002/rcm.2688.

Stiller, M., Rounick, J.S., and Shasha, S., 1985, Extreme carbon-isotope enrichments in evaporating brines: Nature, v. 316, p. 434–435, https://doi.org/10.1038/316434a0.

Sullivan, N.B., McLaughlin, P.I., Emsbo, P., Barrick, J.E., and Premo, W.R., 2016, Identification of the late Homerian Mulde excursion at the base of the Salina Group (Michigan Basin, USA): Lethaia, v. 49, p. 591–603, https://doi.org/10.1111/let.12168.

Swift, R.J.A., 2011, Conodont Biostratigraphy and $\delta^{13}C$ Chemostratigraphy of the Salina Group (Silurian) in Western Ohio and Eastern Indiana [Ph.D. thesis]: Columbus, Ohio, Ohio State University, 91 p.

Trotter, J.A., Williams, I.S., Barnes, C.R., Männik, P., and Simpson, A., 2016, New conodont $\delta^{18}O$ records of Silurian climate change: Implications for environmental and biological events: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 443, p. 34–48, https://doi.org/10.1016/j.palaeo.2015.11.011.

Warren, J.K., 2016, Evaporites A Geological Compendium: New York, Springer, 1822 p.

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