Neodymium Isotope Ratios and a Positive δ13C Excursion: Connecting Oceanographic and Climate Changes Near the M4-M5 Sequence Boundary of the Late Ordovician

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NEODYMIUM ISOTOPE RATIOS AND A POSITIVE $\delta^{13}C$ EXCURSION: CONNECTING OCEANOGRAPHIC AND CLIMATE CHANGES NEAR THE M4-M5 SEQUENCE BOUNDARY OF THE LATE ORDOVICIAN

A Thesis
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in The Department of Geology and Geophysics

by
Zachary A. Wright
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Abstract

A significant positive carbon isotope excursion first described from the Guttenberg Member of the Decorah Formation in Iowa called the GICE is a defining feature of Late Ordovician chemostratigraphy. It occurs near the M4-M5 sequence boundary of the Late Ordovician and has been correlated across the globe using prominent K-bentonite ash beds and conodont biomarkers. The cause of the GICE has been debated, with some arguing that it represents the initiation of a glacial period in a greenhouse climate 10 Ma before the end Ordovician glaciation and extinction. A variety of cooling signals have been identified across the M4-M5 sequence boundary support this hypothesis, but evidence contradicting this cooling hypothesis remains.

Neodymium isotopes were collected from Rochester, MN, to determine if the movement of water masses over space and time played a role in the cooling signals witnessed across the M4-M5 and the GICE. Original δ¹³C data were collected from Dickeyville, WI, for comparison to existing carbon isotope curves showing the GICE. The GICE is well preserved at Dickeyville, WI, and plots similarly to previous studies from the area. It occurs after two significant and widespread K-bentonites (Deicke, Millbrig) and reaches excursion values characteristic of this location (±2.0‰).

εNd data from Rochester, MN, show values initially increasing, from -16.5 to -12.16 epsilon up to the Deicke K-bentonite. A shift in εNd values occurs sometime between the Millbrig and Deicke K-bentonites. After the Millbrig K-bentonite, εNd values are lower, ranging from -14.3 to -16.65. These results are indicative of high weathering rates from the nearby Precambrian shield and possibly a major regression occurring between the Millbrig and Deicke K-bentonites. However, a previously recorded δ¹⁸O decrease in the study area and
lithostratigraphic evidence for a transgression across the M4-M5 conflicts with a glacially induced regression. Local tectonic quiescence during the GICE precludes a tectonically driven regression causing a low $\varepsilon_{\text{Nd}}$ weathering flux. Therefore the decrease in $\varepsilon_{\text{Nd}}$ values between the Millbrig and Deicke K-bentonites could be indicative of a climate induced spike in weathering rates. These findings imply that previous work suggesting $\varepsilon_{\text{Nd}}$ as a direct proxy for eustatic changes is complicated during periods of changing climate and weathering flux.
1. Introduction

The end of the Ordovician (443-445 Ma) brought about a glacially induced extinction event and positive carbon isotope excursion (HICE) in the Hirnantian. Roughly 10 Ma before this extinction event a separate series of cooling signals at the M4-M5 sequence boundary, has been used to suggest that the Hirnantian glaciation actually started much earlier (Sheehan, 2001; Hammarlund et al., 2012; Holland and Patzkowsky, 1996; Patzkowsky et al., 1997; Ludvigson et al., 1996). The following are lines of evidence for cooling across the M4-M5 boundary: 1) a transition from warm-water (shallow ramp carbonate mudstones and skeletal wackestones) to cool-water carbonates (deep ramp carbonate mudstones, brymol assemblages, shales) (Brookfield and Brett, 1988; Brookfield and Elgadi, 1998; Holland and Patzkowsky, 1996; Lavoie and Asselin, 1998; Pope and Read, 1997); 2) a widely-recognized extinction event where red and green algae along with cyanobacterial mats all dramatically decrease or disappear (Patzkowsky and Holland 1993); 3) glacial sediments of the same period in Morocco (Hamoumi, 1999); 4) a 15°C temperature drop recorded in a +1‰ $\delta^{18}$O increase in the Baltic Kullsberg Limestone (Tobin et al. 2005); 5) increased phosphatic deposits in the Decorah Formation and Viola Springs Formation (Young et al., 2005; Ludvigson et al., 1996); and 6) an increase in terrigenous sediment influx (Patzkowsky and Holland, 1996).

One of the most widely identified and interpreted cooling signals is the GICE, a positive carbon isotope excursion ($\delta^{13}$C) thought to represent a perturbation in the global carbon cycle resulting from cooling (Ainsaar et al., 1999; Saltzman and Young, 2005; Young et al., 2005). The GICE is a $\delta^{13}$C excursion of over +1.0‰, first found in the Guttenberg Member of the Decorah Formation, and has since been found in the Salona Formation of Pennsylvania, the
Viola Springs Formation of Oklahoma, the Lexington Limestone of Kentucky, and in sections as far away as Baltica and China (Fig. 1) (McLaughlin et al., 2011; Ludvigson et al., 2004; Ludvigson et al., 1996; Ainsaar et al., 1999; Young et al., 2005; Young et al., 2008). Changes in $\delta^{13}$C$_{DIC}$ are thought to predominantly occur due to widespread changes in burial and production of isotopically light organic carbon over roughly $10^3$ year timescales (Mitchel et al., 1996; Kump and Arthur 1999). This timescale allows for the mixing $\delta^{13}$C$_{DIC}$ (dissolved inorganic carbon) across the globe, preserving $\delta^{13}$C excursions worldwide.

The M4-M5 sequence boundary has been placed at a number of stratigraphic locations aided by the presence of multiple K-bentonite ash beds (Fig. 2). Holland and Patzkowsky (1997) first defined this sequence stratigraphic boundary, whose location has since been reinterpreted by McLaughlin et al. (2011), Sell et al. (2015), Ludvigson et al. (2004), Kolata et al. (2001) and others. The nature of this boundary has been disputed, with some interpreting it as an erosional surface, while others claim it is a sediment starvation, or “drowning surface” caused by transgression and flooding of the Mohawkian with deep, cool, phosphate-rich water (Kolata et al., 2001; Brett et al., 2004; Ludvigson et al., 2004). The Sebree Trough, an underwater rift formed during the Taconic Orogeny, may have acted as a conduit for these cool waters to flow into the Mohawkian Sea (Fig. 3) (Kolata et al., 2001).

$\varepsilon_{Nd}$ values are preserved during weathering and erosion and imprinted onto nearby water masses for a short period due to neodymium’s low residence time (~300 years) (Piepgras and Wasserburg, 1980). Three main terrigenous sediment sources existed in the Mohawkian Sea: the Taconic Highlands, the Transcontinental arch and Precambrian shield (Hatch et al., 1987; Patzkowsky et al., 1997; Holmden et al., 1998; Scotese and Mc Kinrow, 1991).
Figure 1: A collection of $\delta^{13}C_{\text{carb}}$ curves interpreted as the GICE (in red) from around the globe—adapted from McLaughlin et al. (2011) Ainsaar et al. (1999) and Young et al. (2008). Correlation is done largely by a series of extensive K-bentonites and curves are pinned to the M4-M5 sequence boundary.
Each of these terrigenous provinces contained rocks with distinct $^{143}\text{Nd}/^{144}\text{Nd}$ values (shortened to $\varepsilon_{\text{Nd}}$) obtained during igneous crystallization and through Sm-Nd decay (DePaolo and Wasserburg, 1976). As weathering flux and eustasy change at a given location, so too will the $\varepsilon_{\text{Nd}}$ values (Holmden et al., 2013; Dopieralska et al., 2015). This technique has been successfully employed for the Millbrig-Deicke timeslice in the Mohawkian Sea (Holmden et al., 1998), the Panthalassic Ocean during the HICE (Holmden et al., 2013; Fanton and Holmden, 2007), and the Variscan Sea of the Devonian (Dopieralska et al., 2015).
Figure 3: A model showing $\varepsilon_{Nd}$ values collected by Holmden et al. (1998) for the Millbrig-Deicke timeslice. Wind and runoff patterns are noted in red and green respectively. Major circulation patterns and the Sebree Trough (grey) are also illustrated (Wilde, 1991; Kolata et al., 2001).

$\varepsilon_{Nd}$ values appear to form a distal-proximal gradient, with nearshore settings dominated by low- $\varepsilon_{Nd}$ flux from continents and offshore settings dominated by higher- $\varepsilon_{Nd}$ open ocean values (Holmden et al., 2013; Dopieralska et al., 2015). Using $\varepsilon_{Nd}$ values as a proxy can test whether eustasy and the movement of water masses through time and space impacted cooling
signals witnessed during the M4-M5 and GICE (Holmden et al., 1998; Piepgras and Wasserburg, 1980, 1987; Holmden et al., 2013).

In order to link the M4-M5, GICE, and $\varepsilon_{\text{Nd}}$, three previously hypothesized models are tested: 1) transgression and warming at the M4-M5, which flooded the Mohawkian with cooler, nutrient-rich deep ocean waters, possibly by way of an oceanic rift known as the Sebree Trough and caused a primary productivity spike and higher $\varepsilon_{\text{Nd}}$ values (Kolata et al., 2001; Young et al., 2005; Patzkowsky et al., 1997; Ludvigson et al., 2004); 2) A major regression and cooling leading to erosion-driven siliciclastic poisoning of carbonates, increased weathering and runoff from the Precambrian shield which caused increasingly negative $\varepsilon_{\text{Nd}}$ values (Kump et al., 1999; Pope and Read, 1998; and 3) overprinting and control over the M4-M5 and GICE by local factors, such as local eustasy/tectonism, influencing both the $\varepsilon_{\text{Nd}}$ and $\delta^{13}C$ record (Panchuk et al., 2006; Pancost et al., 2013; Michell et al., 2004; Bergström et al., 2010).
2. Background

2.1 Paleogeography

Paleogeographic reconstructions place Laurentia along the equator, with the continent of Baltica to the southeast and Gondwana located east of Baltica and southwest of Laurentia (Witzke, 1990; Scotese and McKitrick, 1991) (Fig. 4). Most of Laurentia during this time, including the upper Mississippi Valley, was located between 15° and 30°S (Young et al., 2005; Scotese and McKitrick, 1991).

Figure 4: A paleogeographic reconstruction of the Late Ordovician modified from (Scotese and McKitrick, 1991). Laurentia is located at tropical latitudes and shares a major boundary with the Iapetus Ocean to the south.
The upper Mississippi Valley during the Late Ordovician was dominated by a shallow epeiric sea, known today as the Mohawkian Sea, located on the continent of Laurentia. The Mohawkian Sea inundated a large portion of what would become the Midwest of North America along with parts of the American South (Scotese and McKerrow, 1991). The Mohawkian Sea was flanked by the northeast-southwest trending Taconic Highlands (the ancestral Appalachian Mountains) and the western, similarly trending, Transcontinental Arch (Scotese and McKerrow, 1990) (Fig. 4). Closing off the sea to the north was the Precambrian shield (Scotese and McKerrow, 1990). The Mohawkian shared a major boundary with the Iapetus Ocean on its southwestern edge (Scotese and McKerrow, 1991), near present-day Oklahoma, creating an area of possible mixing between the two bodies of water (Witzke, 1990; Holmden et al., 1998).

Gondwana stretched across the South Pole to the east and west across the southern hemisphere to latitudes as high as 30°N (Scotese and McKerrow, 1990). Meanwhile Baltica was on a separate continental block at tropical latitudes during the GICE and experienced relatively little tectonic activity at that time (Nielsen, 2004). Therefore δ13C data from Baltica are important for interpreting the GICE, because it was independent of the tectonic and possibly glacial factors affecting the GICE in Laurentia and Gondwana, respectively (Fig. 4).

### 2.2 Stratigraphy

The strata of the Mohawkian Series (458-453 Ma) are divided into 6 sequences, labeled as the M1-M6, and contain the boundary between the global Sandbian and Katian stages and the Turinian and Chatfieldian stages of North America (Holland and Patzkowsky, 1996). Previously mentioned cooling signals and the GICE correspond to the M4-M5 sequence boundary, by the Spechts Ferry/Guttenberg Member of the upper Mississippi Valley, the Lexington Limestone of Kentucky and the Moldå Limestone of Baltoscandia, among others.
Correlation between these locations is aided by the presence of numerous K-bentonite ash beds, erupted from volcanoes formed during the Taconic Orogeny, and from conodont and graptolite biofacies (Sell et al., 2015; Mitchell et al., 2004; Kolata et al., 1996). In Dickeyville (42.636535, -90.578873) and Rochester (43.999304, -92.287709), these K-bentonites are labeled (in ascending order) as the Deicke, Millbrig, Elkport and Dickeyville K-bentonites (Fig. 5) (Ludvigson et al., 2004). The Galena Group of the upper Mississippi Valley, contains the Decorah Formation, my main area of study, which rests between the Platteville and Moquoketa formations (Fig 7).

2.3 The Guttenberg Isotope Carbon Excursion

The positive $\delta^{13}C$ excursion witnessed after the M4-M5 boundary, was first recorded by Hatch et al. (1987) in Iowa, and has since been recorded across the globe at paleogeographically distinct locations such as China, Estonia, Sweden, Virginia, Oklahoma, Ontario, and others (Young et al., 2005; Pancost et al., 2013, Holmden et al., 1998, Young et al., 2008; Ainsaar et al., 1999). In general, the GICE occurs at the $P. undatus/P. tenuis$ zonal boundary, ends at the $Belodina confluens$ zonal boundary and has its peak above the Millbrig (N. America) or Kinnekulle (Baltoscandia) K-bentonite (Young et al., 2005; Ainsaar et al., 1999; Saltzman et al., 2003). Across the Mohawkian, regional differences in $\delta^{13}C$ have been used to constrain aquafacies boundaries (Holmden et al., 1998). Pre-excursion values for the Midcontinent aquafacies, including those in Dickeyville, WI, range from $-0.6\%o \pm 1.3\%o$. Taconic/Southern values are between $+2.2\%o \pm 0.2\%o$ (Holmden et al., 1998). The magnitude and extent of positive excursions and pre-excursion values varies between locations largely due to differences in regional biology, oceanography, diagenesis, and local inorganic carbon reservoirs (Young et al., 2005; Pancost et al., 2013; Metzger et al., 2014). As a result of these differences, gradients
of up to 4.5\% \delta^{13}C can be found in Mohawkian Sea aquafacies during the GICE, though Metzger et al. (2014) suggest that diagenetic alteration is responsible for recorded gradients and that the Mohawkian had a relatively homogenous isotopic composition (Holmden et al., 1998; Fanton and Holmden 2007) (Fig. 1).

![Figure 5: A chronostratigraphic correlation chart for the M4-M5 boundary around the globe (Holland and Patzkowsky, 1996; Ludvigson et al., 2004; Ainsaar et al., 1999; Sell et al., 2015). K-bentonites are in shown as orange lines.](image)

260km to the northwest of Dickeyville, WI, in Rochester, MN, a 15m high section from an old quarry contains substantially different stratigraphy than in Dickeyville, WI (Fig. 6). Dark grey to green shales dominate this section, which contains only thin limestone layers or lenses. The Platteville Formation and Carimona Member contain limestones with thin shale layers of roughly 5m when taken together. Above the Carimona Member, shale lithologies dominate into the Decorah Shale, a departure from the carbonate-rich Guttenberg Member of Dickeyville, WI.
2.4 Paleooceanography

Paleogeographic reconstructions place the Mohawkian Sea at latitudes between 15° and 30°S, indicating that it experienced southerly trade winds, which would have blown from the southeast to the northwest (Fig. 4) (Scotese and McKerrow, 1990, 1991). Wind-driven surface currents drove waters near the Taconic Highlands and Southern aquafacies toward the Midcontinent aquafacies, including at Dickeyville, WI (Fig. 3). Large-scale paleocurrents in the Mohawkian ran counterclockwise due to the Coriolis Effect in the southern hemisphere. Along with prevailing wind patterns, the circulation in many ancient oceans, including the Mohawkian was controlled by thermohaline processes (Witzke, 1987; Wilde, 1991). This feature was
important to the Mohawkian aquafacies, allowing for temperature and salinity defined water masses to maintain their boundaries via density gradients (Holmden et al., 1998).

Overall, the Mohawkian Sea underwent a change from a more lagoonal mode to quasi-estuarine circulation (QEC) as climate changed and an abundance of freshwater began to run-off of the Taconic Highlands, Transcontinental Arch and Precambrian shield, increasing water-column stratification (Wilde, 1991; Fanton and Holmden, 2007). This change began in the late Turinian and is recorded throughout the Decorah Formation, as evidenced by differences in $\delta^{13}$C values found in benthic brachiopods and micritic portions of limestones thought to have formed in near-surface waters (Patzkowsky et al., 1997; Wilde, 1991; Fanton and Holmden, 2007). QEC is characterized by fresh, less dense water forming a surface layer that generally flows away from shore, while denser, cool water flows toward shore below (Witzke, 1987) (Fig. 7). Ultimately, QEC forms a stratified water column that can be strengthened during transgression as a central mixing layer (pycnocline) expands (Witzke, 1987).

A variety of depositional environments existed in the Mohawkian Sea. Extensive carbonate deposition with a “layer-cake” arrangement is indicative of the shallow, warm waters normally found in an epeiric sea setting (Holland and Patzkowsky, 1996; Ludvigson et al., 2004; Choi et al., 1999; Emmerson et al., 2004). The Taconic foreland basin and Sebree Trough represent prominent bathymetric lows, while the Cincinnati Arch, located in the center of the Mohawkian, represents a geographic high (Holland and Patzkowsky, 1996; Ludvigson et al., 2004; Brett et al., 2004; Kolata et al., 2001).
Figure 7: A diagram showing quasi-estuarine circulation in the Mohawkian Sea during the Late Ordovician modified from Kolata et al. (2001) and Witze et al. (1987). Upwelling of deep Sebree Trough waters lead to an increase in primary productivity and created $\delta^{13}$C-enriched surface waters.
3. Methods

Samples of the Upper Decorah Formation (Spechts Ferry, Guttenberg and Ion members) were collected from the US Highway 151 road cut in Dickeyville, WI. Limestone samples from this section were cleaned using standard methods and digested with 10% acetic acid. Processed $\varepsilon_{\text{Nd}}$ samples from Dickeyville were lost during analysis and samples from Rochester had to be used instead. Shale-rich samples from Rochester, MN, were liberated using kerosene. Remnants of the dissolved rock were then passed through a 230$\mu$m wire mesh sieve and density separated using approximately 250mL of sodium polytungstate (SPT), diluted to a density of 2.8g/cm$^3$. Heavy residue from this phase of density separation was then washed with deionized water and dried.

Sample carbonates were collected from the same outcrop and sent to the University of Missouri for isotopic analysis. A range of carbonate lithologies were used to construct the $\delta^{13}$C curve from Dickeyville, WI, however, due to their prevalence and reliability for high resolution chemostratigraphy, micritic components of limestone layers were preferentially used in this study (Kump et al., 1999; Young et al., 2005).

For carbonate analysis 50-100 µg of powder was milled from fresh surfaces using a low speed drill, and then analyzed for bulk carbonate $\delta^{13}$C values on a Thermo Finnigan Delta Plus Dual Inlet isotope ratio mass spectrometer connected to a Kiel III Carbonate Interface at the University of Missouri. Under vacuum, samples were digested in 100% H$_3$PO$_4$ for two minutes to produce CO$_2$. CO$_2$ was then converted to a solid by transferring it to a trap at -180°C. Heating the trap to -115°C allowed CO$_2$ to become gaseous while residual water remained frozen. The CO$_2$ was then heated to 30°C and transferred to the isotope ratio mass spectrometer.
Eight analyses of sample CO$_2$ were measured against five standard CO$_2$ gas samples to generate isotopic ratios relative to standard gas. Internal precision is ±0.03‰ for $\delta^{13}$C and was monitored using NBS-19. The Vienna Peedee Belemnite scale (‰VPDB) was used to report values.

Approximately 300 µg of hand-picked conodonts were dissolved in a 50:50 mixture of HCl:HNO$_3$. Five % of the sample was removed for Sm and Nd concentration analysis on the Element 2. The remaining sample was dried down and redissolved in 100 µl HNO$_3$ in preparation for column separation in a class 1000 clean lab in the Department of Geological Sciences at the University of Florida (UF). Bulk rare earth elements (REE) were isolated using Eichrome TRU Resin with 1N HCl as an eluent. Nd was isolated by passing the REE aliquot through Eichrome Ln Resin using 0.25N a HNO$_3$ as an eluent. Procedural blanks were 14 pg of Nd.

Nd isotopes were analyzed on a Nu Plasma multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at UF. Nd fractions were redissolved in 2% optima HNO$_3$ and diluted individually to obtain a 4-6 V beam on $^{144}$Nd. Samples were then aspirated through a desolvating nebulizer and all Nd isotopes were analyzed using a time-resolved analysis (TRA) method (Kamenov et al., 2008). On-peak-zeros were measured for approximately 30 seconds prior to sample introduction. Data was then acquired in series of 0.2 seconds integrations over an average of 1-3 minute uptake time. All reported $^{143}$Nd/$^{144}$Nd ratios were corrected for mass fractionation using $^{146}$Nd/$^{144}$Nd = 0.7219. International standard JNd1-1 was analyzed between every 5-6 samples and the average value of the daily standard runs was compared to the published value of 0.512115 from Tanaka et al. (2000) to calculate a correction factor for all samples analyzed that day. The long-term 2σ external reproducibility of JNd1-1 analyses using this method is 0.000014, which is equivalent to 0.27 $\varepsilon_{Nd}$ units (where $\varepsilon_{Nd}$ represents the
deviation in parts per $10^4$ of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the samples relative to the chondritic uniform reservoir [Jacobson and Wasserburg, 1980]).

REE concentrations were analyzed on an Element 2 ICP-MS at UF. Aliquots were dried down and redissolved in 5% HNO$_3$ spiked with Re-Rh to serve as an internal standard to correct for instrument drift. A portion of the acid-sample solution was extracted and diluted with 5% HNO$_3$ to ~2000 times dilution for analysis. All REE were analyzed at medium resolution. Measured representative values of $^{147}\text{Sm}/^{144}\text{Nd}$ from each site were then used to correct the measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for ingrowth of radiogenic $^{143}\text{Nd}$ during the 453 Ma since deposition to produce $^{143}\text{Nd}/^{144}\text{Nd}(T)$ and $\varepsilon_{\text{Nd}(T)}$ values.
Figure 8: Original $\delta^{13}$C$_{micrite}$ data from Dickeyville, WI, and $\varepsilon_{Nd}$ data from Rochester, MN. GICE location is approximated in Rochester based on K-bentonites. $\varepsilon_{Nd}$ margin of error is around 0.5 epsilon
4. Results

4.1 $\delta^{13}C$ Isotope Results

Pre-GICE $\delta^{13}C$ isotope data show roughly negative values ($\sim-0.75\%o$) for the first 1.5m, from the Platteville Formation up to the middle of the Spechts Ferry (Fig. 8). Values within this portion of the curve fluctuate ±1‰. Directly after this interval, 2m from the base of the measured section, there is a positive excursion (+1.75‰) over 0.25m followed by a well-defined negative excursion (-2‰) over 0.5m. This negative excursion postdates the Millbrig K-bentonite and the position of the M4-M5 sequence boundary as it is defined in this paper. The GICE rises from -1‰ in the Spechts Ferry, increasing steadily to a peak of +2‰ near the Elkport K-bentonite, after both the $P. \textit{undatus}$ and $P. \textit{tenuis}$ conodont zonal boundary and the Spechts Ferry-Guttenberg Member contact.

After reaching peak values, $\delta^{13}C$ decreases throughout the Guttenberg Member, settling at slightly above average pre-excursion values (+1‰). There is a brief negative excursion in the Ion Member near the top of the M5 sequence.

4.2 $\varepsilon_{Nd}$ Results

$\varepsilon_{Nd}$ values taken from nearby Rochester, MN, are initially low within the Platteville Formation, hovering around -16 epsilon before increasing at around 2m upsection. $\varepsilon_{Nd}$ values increase steadily from the top of the Platteville Formation to their highest point of -12.16 directly before the Deicke K-bentonite (Fig. 9).
Figure 9: A graph showing original $\epsilon_{\text{Nd}}$ values from Rochester, MN, obtained from conodonts plotted against $\delta^{18}$O data from conodonts from Minnesota by Buggisch et al. (2010), later corrected by Herrmann et al. (2011). Decreases and increases in $\delta^{18}$O values are often attributed to warming and cooling water temperatures, respectively.
Three samples were taken around this peak from both shale and limestone units, with values ranging from -12.16 to -13. These samples were collected close to one another and show little change across their disparate lithologies. Diagenetic alteration cannot be completely ruled out, but is unlikely based on the resistant nature of biogenic apatite and evidence from the color alteration index.

Following peak $\varepsilon_{\text{Nd}}$ values near the Deicke K-bentonite, there is a 3m gap in data to directly above the Millbrig K-bentonite. Following this gap in data, $\varepsilon_{\text{Nd}}$ values above the Millbrig K-bentonite are consistently low, ranging from -16.65 to -14.36 through the proposed Elkport K-bentonite and up to the top of the section. Major trends for $\varepsilon_{\text{Nd}}$ values at Rochester, MN, can be described as low but increasing up to the Deicke K-bentonite, followed by a gap in data, shifting towards consistently very negative values post deposition of the Millbrig K-bentonite.
5. Discussion

5.1 GICE Interpretation

Constructing a δ¹³C curve from micritic limestone at Rochester, MN, is difficult due to the shale-dominated lithology there. I was able to project location of the GICE to Rochester based on the Deicke, Millbrig and Elkport K-bentonites (Fig. 8).

Based on my results from Dickeyville, WI, I can positively identify the GICE as a positive excursion of ~±4.0‰ lasting into the Guttenberg Member, with peak values of +2.0‰ around the Elkport K-bentonite. The timing of the GICE (after the Deicke and Millbrig K-bentonites) is consistent with previous work suggesting a connection with this excursion to the M4-M5 sequence boundary (Fig. 2).

5.2 εNd Interpretation

Holmden et al. (1998) discovered that εNd values are generally very low in the Mohawkian Sea ranging from -5 and -15 epsilon, compared to higher Iapetus Ocean values (-0.5 epsilon). They identified three major aquafacies in the Mohawkian Sea corresponding to terrigenous source and open ocean proximity: the Midcontinent, Taconic, and Southern (Holmden et al., 1998) (Fig. 3). εNd values found in deposits from the Taconic foreland basin, between the Millbrig and Deicke K-bentonites, show less negative values (-6 to -9) than do those found in the Midcontinent (-14 to -19) and Southern aquafacies (-3 to -12; closer to ~-5) (Holmden et al., 1998).

These results from Rochester, MN, show the lowermost εNd values nearly identical to those identified by Holmden et al. (1998) (-12 to -19) for the Midcontinent aquafacies over the
Millbrig-Deicke timeslice. Previous work on shifting $\varepsilon_{\text{Nd}}$ values has shown its use as a proxy for sea level, particularly for epeiric seas where shallower water depths preserve shifting terrigenous input over larger distances (Holmden et al., 2013; Dopieralska et al., 2015). By using K-bentonites to interpolate where the GICE would plot in Rochester, it appears that changing $\varepsilon_{\text{Nd}}$ values do not correlate with the $\delta^{13}$C curve, suggesting that any factor that affected $\varepsilon_{\text{Nd}}$ values did not affect the GICE. However, there is limited $\varepsilon_{\text{Nd}}$ data resolution over the GICE interval. Future work may confirm or disprove this lack of correlation.

If the $\varepsilon_{\text{Nd}}$ values are representative of eustatic changes the data would ostensibly indicate the following: 1) there is a positive shift in $\varepsilon_{\text{Nd}}$ values before the Deicke K-bentonite representative of a transgression; 2) there is a negative shift in $\varepsilon_{\text{Nd}}$ values between the Millbrig and Deicke K-bentonites representative of a regression; and 3) there is a sustained period of low-$\varepsilon_{\text{Nd}}$ values after the Millbrig K-bentonite representative of a prolonged lowstand. The sections below incorporate outside data into this interpretation, suggesting that a strict eustatic model for $\varepsilon_{\text{Nd}}$ values may not be appropriate for this area.

5.3 Pre-Deicke Interpretation

Prior to the Deicke K-bentonite and potentially after it, $\varepsilon_{\text{Nd}}$ values increase from $\sim$-16 to -12 epsilon, indicative of a transgression based on previous work on $\varepsilon_{\text{Nd}}$ curves (Holmden et al., 2013; Dopieralska et al., 2015). Flooding of Iapetus Ocean waters containing high $\varepsilon_{\text{Nd}}$ values (-5 to -0.6 epsilon) into the upper Mississippi Valley may partially explain this shift. Open ocean values are derived from conodonts of the $B. \text{gerdae}$ Subzone in Scotland and metalliferous crusts.
of Iapetus pillow basalts (Holmden et al., 1998; Hooker et al., 1981). A decrease in Precambrian shield weathering (~20 epsilon) caused by this transgression is another mechanism to shift $\varepsilon_{Nd}$ toward less negative values.

Lithostratigraphic evidence supports a transgression over this interval. The Grand Detour units of the Platteville Formation are capped by a hardground surface indicating sediment starvation possibly caused by a transgression (McLaughlin et al., 2011). This interpretation supports that of Ludvigson et al. (2004) who identify the hardground at the top of the Platteville Formation as a “corrosion surface,” defined by phosphatic enrichment and pyritic crusts (Templeton and William, 1963). A major marine transgression onto the Transcontinental Arch and Precambrian shield area at the Platteville-Decorah boundary is also consistent with open-marine skeletal carbonates found in much of the Galena Group and regional downlap onto the Platteville Formation by the Decorah Formation (Ludvigson et al., 2004; Kolata et al., 2001). A transgression prior to the Deicke K-bentonite is similarly interpreted for the calm, deep-water facies of the Plattin Group of Missouri by Metzeger and Fike (2013) and in eastern Laurentia by Brett et al. (2004). Paradoxically, $\delta^{18}O$ values from the upper Mississippi Valley increase prior to the Deicke, indicating cooling (Buggisch et al., 2010). However, at higher latitudes in Oklahoma, $\delta^{18}O$ values are interpreted to decrease, representing warming, over this interval (Rosenau et al., 2012). In lieu of a matching trends in $\delta^{18}O$ data, this $\delta^{18}O$ increase may be evidence of upwelling of cool, deep water in the upper Mississippi Valley, or misinterpretation based on limited data resolution (Fig. 9) (Rosenau et al., 2012; Buggisch et al., 2010).

Past studies have speculated on the role transgressions play in shaping $\delta^{13}C$ values. Fanton and Holmden (2007) argued that transgressions coincide with increased $\delta^{13}C$ values. A transgression in the Mohawkian may have flooded the Galena platform with oxygen-depleted
bottom waters from the Sebree trough, thus increasing preservation of organics and bolstering exchange between epeiric waters and $^{13}$C-enriched ocean surface waters, and decreased weathering of isotopically light carbon from the Transcontinental arch (Fanton and Holmden, 2007). However, Bergström et al., (2010) analyzed five separate positive $\delta^{13}$C excursions from the Sandbian and Katian, and concluded that positive excursions only occur in some transgressive intervals, complicating the findings of Fanton and Holmden (2007) that the two are always coeval. Furthermore, the $\delta^{13}$C values below the Deicke K-bentonite are highly variable, ranging between -1.5‰ and +1.0‰, and do not show a prolonged positive excursion. This may suggest that the variability of pre-Deicke $\delta^{13}$C values is was caused by local factors including changes in biologic productivity, not a transgression, as $\delta^{13}$C values also do not correlate strongly with $\varepsilon_{Nd}$ values over this interval. This may also indicate that changes in weathering rate and eustasy, inferred from $\varepsilon_{Nd}$ values, did not heavily influence the observed $\delta^{13}$C pre-Deicke trend.

5.4 Negative $\varepsilon_{Nd}$ Shift between the Millbrig and Deicke K-bentonites

Following the transgressive pre-Deicke interval, $\varepsilon_{Nd}$ values decrease from ~-12 to ~-16 epsilon between the deposition of the Millbrig and Deicke K-bentonites. Samples taken directly above the Millbrig K-bentonite (-16), close to the proposed M4-M5 boundary, are more negative than pre-transgression values (-12). Nearshore/distal gradients have been recorded in $\varepsilon_{Nd}$ values, with decreasing $\varepsilon_{Nd}$ values measured during regressive periods as terrestrial weathering influence moved seaward and the influence of open ocean water decreased (Holmden et al., 2013; Dopieralska et al., 2015). A lithology change over this interval likely did not alter $\varepsilon_{Nd}$ values as three shale and carbonate samples taken directly below the Deicke K-bentonite, within close
proximity of each other, show only negligible $\varepsilon_{\text{Nd}}$ offset ($\approx 1$). In light of the cooling signals recorded after deposition of the Millbrig K-bentonite, and previous models for $\varepsilon_{\text{Nd}}$ shifts, the negative shift in $\varepsilon_{\text{Nd}}$ values can be interpreted as a regression, possibly one that is glacially driven.

At Rochester, MN, this regression may coincide with a shift from carbonates to shale between the Millbrig and Deicke K-bentonites, however due to low data resolution over this interval it is unclear if these two are directly related. A shift towards increased clastics would support a regressive model as weathering rates increased. Simo et al. (2003) interpreted the thick Decorah Shales found at Rochester to be a result of high run-off from the exposed Transcontinental Arch, which lessened during a transgression, causing carbonate deposition. Similarly, Witzke and Kolata (1988) identified shale abundance increasing towards the transcontinental arch, and lessening during interpreted transgressions. Higher weathering rates would be consistent with the increase in siliciclastics recorded after the M4-M5 boundary by Holland and Patkowsky (1996).

The most obvious mechanism for eustatic change on a relatively tectonically-stable passive margin is glaciation. Evidence for the onset of glaciation coinciding with low $\varepsilon_{\text{Nd}}$ values includes: 1) glacial sediments found in Morocco; 2) regressive sequences interpreted in Baltica; 3) transition to cool-water carbonates; and 4) an extinction of brachiopod species (Hamoumi, 1999; Ainsaar et al., 1999; Saltzman and Young, 2005; Brett et al., 2004; Holland and Patzkowsky, 1996; Patzkowsky et al., 1997).

However, the evidence supporting a non-regressive, non-glacial argument for a negative $\varepsilon_{\text{Nd}}$ shift is substantial. $\delta^{18}$O values taken from both Oklahoma and the upper Mississippi Valley
contradict a purely glacial hypothesis, especially after deposition of the Millbrig K-bentonite (Buggisch et al., 2010; Rosenau et al., 2012). Unlike the pre-Deicke interval, δ¹⁸O values in each location show a pronounced, simultaneous decrease between the Millbrig and Deicke K-bentonites, indicating that local factors played less of a role in shaping values (20.5‰ to 18.5‰ in Minnesota; 19.5‰ to 18‰ in Oklahoma) (Buggisch et al., 2010; Rosenau et al., 2012). These results indicate that warming of surface temperatures of around 6°C occurred over this interval (Buggisch et al., 2010; Rosenau et al., 2012). This evidence runs counter to my recorded εNd values, which decrease between the Millbrig and Deicke K-bentonites (Fig. 9). Though εNd and δ¹⁸O appear to correlate with each other, their relationship is the inverse of what would be expected during a period of cooling and glaciation (Fig. 9). Furthermore, work done by Quinton and MacLeod (2014) on δ¹⁸O values shows no sustained long-term cooling throughout the Katian, implying a lack of glaciation.

Warming periods often coincide with transgressive intervals. M4-M5, occurring shortly after the Millbrig K-bentonite, has been hypothesized to represent a major transgression, labeled the Trenton Transgression. Evidence for a major transgression at the M4-M5 of Holland and Patzkowsky (1997) includes increased phosphatic grains and the “cool-water” nature of carbonates found in the Trenton Limestone (Holland and Patzkowsky, 1996). Kolata et al. (2001) identified the M4-M5 as a drowning surface (DS2), while Mitchell et al. (2004) correlate a disconformity at the base of the M5 coinciding with the contact between the Tyrone Limestone and Lexington Limestone (Fig 6). Joy et al. (2000) argued that eustatic changes around the Trenton Transgression may have been attributable to increased tectonism, while Brett et al. (2004) suggest that ecstasy played a larger role in changing depositional sequences in Laurentia including those caused by the Trenton Transgression.
Increased phosphate and chert deposits found in Oklahoma after the M4-M5, and a series of drowning surfaces emanating from the Sebree Trough, support a transgressive hypothesis (Kolata et al., 2001; Railsback et al., 2003; Young et al., 2005). However, a transgression extending from before the Deicke K-bentonite up to the Millbrig K-bentonite should show $\varepsilon_{\text{Nd}}$ values that steadily increase as the northward spread of Southern aquafacies and Iapetus Ocean waters ($\varepsilon_{\text{Nd}}$: -5 and -0.5 respectively), and increased inundation of the Precambrian shield, lowered the influence of very low $\varepsilon_{\text{Nd}}$ values from nearby terrestrial sources. Instead there is a trend of increasing $\varepsilon_{\text{Nd}}$ values followed by a decrease, all during the proposed transgression, suggesting that another mechanism may be at work.

Local, tectonic influences can potentially resolve the disparity between a drop in $\varepsilon_{\text{Nd}}$ values and transgressive evidence at the M4-M5 from eastern Laurentia. Increased tectonism and crustal loading caused a deepening of the Taconic foreland basin, leading to the deposition of deep-water facies previously attributed to transgression (Patzkowsky et al., 1997; Diecchio, 1991; Cisne et al., 1982; Cisne et al., 1984; Bradley and Kidd 1991; Lehmann et al., 1994; Lehmann et al., 1995). Deep water facies of the Taconic foreland basin occur around the same time as those of the Sebree Trough, suggesting that the two are connected, possibly by reactivation of basement faults caused by tectonic activity during the Taconic Orogeny (McLaughlin et al., 2004; Mitchell and Bergström, 1991; Diecchio, 1993; Bergström and Mitchell, 1992; Wickstrom et al., 1992, Kolata et al., 2001; Ettensohn et al., 2002; Brett et al., 2004). Simultaneous tectonic uplift caused by the Taconic orogeny would have led to increased weathering rates, siliciclastically poisoning the adjacent carbonate platforms and spreading turbid run-off from the Taconic Highlands across the eastern Mohawkian Sea, leading to the
increased clastics witnessed after the M4-M5 transition (Holmden et al., 1998; Holland and Patzkowsky, 1997). Moreover, tectonically stable locations in Baltica show little stratigraphic evidence for transgression at the M4-M5 (Ainsaar et al., 1999).

A local tectonically-induced weathering increase could potentially explain the low $\varepsilon_{Nd}$ values recorded at Rochester, MN, as well. However, unlike areas proximal to the Taconic Orogeny in eastern Laurentia, local tectonic controls are unlikely to have affected the upper Mississippi Valley as significantly as they did eastern Laurentia, as tectonic variables such as subsidence rates decreased away from the Taconic Orogeny (Joy et al., 2000).

5.5 Potential Causes of Negative $\varepsilon_{Nd}$ Shift

Instead, changes in climate and weathering independent of eustasy may have caused a negative shift in $\varepsilon_{Nd}$ values between deposition of the Millbrig and Deicke K-bentonites. Increased shale deposition in the upper Mississippi Valley after the Deicke K-bentonite supports this weathering increase, however, a direct correlation between shale deposition and $\varepsilon_{Nd}$ remains uncertain due to poor data resolution over this interval. Previous work in the Jurassic by Dera et al. (2014) demonstrated how climatic warming can cause a negative $\varepsilon_{Nd}$ shift. In their work, a warming climate altered paleocurrents, bringing low-$\varepsilon_{Nd}$ waters into their study area (Dera et al., 2014). As my study area already contains low $\varepsilon_{Nd}$-values, it is unlikely that a similar process is at work here. Still, their work demonstrates the ability for $\varepsilon_{Nd}$ values to shift independently from eustasy in a warm climate. Theiling et al. (2012) measured $\varepsilon_{Nd}$ values for Pennsylvanian carbonates and discovered that the lowest $\varepsilon_{Nd}$ values corresponded with interglacial highstand sequences. They speculated that warmer temperatures facilitated more precipitation and
increased chemical weathering, causing the drop in $\varepsilon_{\text{Nd}}$ values (Theiling et al., 2012). A highstand during this interval would be consistent with my transgressive interpretation of the pre-Deicke interval.

$\delta^{13}$C values over the Deicke-Millbrig interval are difficult to interpret based on low data resolution. There appears to be a negative excursion. However, it is unclear whether or not this is related to the negative movement in $\varepsilon_{\text{Nd}}$ values. This negative excursion may once again reflect changes in local biologic controls and organic matter preservation.

5.6 Interpreting the GICE in relation to $\varepsilon_{\text{Nd}}$

$\varepsilon_{\text{Nd}}$ values remain low, between -16.65 and -14.36 epsilon, until the top of the Decorah Formation, indicating that high weathering rates remained influential before, during and after the GICE, and that eustasy changed little during the GICE interval. Low $\varepsilon_{\text{Nd}}$ data resolution during the GICE makes correlating the two difficult. However, based on nearby values and trends from the Pre-Deicke interval and Millbrig-Deicke interval, I contend that the GICE shows little correlation with $\varepsilon_{\text{Nd}}$ values from Rochester, MN. This lack of correlation suggests that mechanisms other than eustasy, and changes in weathering rates, may have caused the GICE.

Recent apatite trace-element geochemistry on over 200 K-bentonites across the Mohawkian has significantly altered the position of the GICE and M4-M5 relative to each other and certain K-bentonites in some locations (Sell et al., 2015). Currently, the GICE generally post-dates the M4-M5, and Millbrig and Deicke K-bentonites, as is the case in the upper Mississippi Valley, Oklahoma, New York and Kentucky (Sell et al., 2015; Young et al., 2005; Ludvigson et al., 2004). However, in Virginia and Pennsylvania the M4-M5 occurs after the
initiation of the GICE, indicating that initiation of the GICE varies geographically (Fig. 2). In Pennsylvania the GICE appears to occur below the Deicke and Millbrig K-bentonites, a definite departure from its normal position above these two ash layers (Pancost et al., 2013; Patzkowsky et al., 1997). Similarly, in Dolly Ridge, WV, the GICE occurs below the Millbrig K-bentonite (Sell et al., 2015). If the GICE is truly indicative of a global event, then it should not be time transgressive across the Mohawkian, as shown by its position relative to well-correlated and geologically instantaneous K-bentonites. The global ubiquity of the GICE makes it difficult to argue that there is not a global component involved, however, I interpret lithostratigraphic, isotopic and timing differences between sections to suggest that local factors had the ability to overprint the GICE. Future work showing a lack of correlation between $\varepsilon_{\text{Nd}}$ values and $\delta^{13}$C values as I do here, may support the hypothesis that the GICE was as much a product of local overprinting as it was a global perturbation in the carbon cycle.

Local variability in $\delta^{13}$C curves is often attributable to biologic pumping of carbon, as isotopically light primary producers are preserved at depth in euxinic waters, enriching surface waters in $\delta^{13}$C$_{\text{DIC}}$ (Holmden et al., 1998). Timing of the GICE is variable in part from local eustasy as the geographic extent of oxygen-poor bottom waters changes carbon cycling. Settings with shallow waters and restricted circulation such as the Bahamas, show $\delta^{13}$C variation with $\delta^{13}$C-offsets of a similar magnitude to those found in Mohawkian Sea sections (Patterson and Walter, 1994). Therefore differences in water depth and circulation between the Midcontinent aquafacies and Taconic/Southern aquafacies may help explain variance in the magnitude and timing of the GICE. High rates of organic matter preservation in deep, euxinic waters of the Taconic foreland basin allowed for the generation of isotopically heavy surface waters to form (Holland and Patzkowsky, 1996). Increased upwelling of nutrient-rich waters, caused by a
changing climate, may have caused a spike in primary productivity, leading to $\delta^{13}C_{\text{DIC}}$ enriched surface waters. In each case, $\delta^{13}C$-enriched surface waters may have then been circulated across the Mohawkian Sea, causing a widespread positive excursion, i.e. the GICE (Patzkowsky et al., 1997; Young et al., 2005; Holland and Patzkowsky, 1996). Panchuk et al. (2006) argue that differences in GICE magnitude, and pre/post excursion values reflected variability in circulation between aquafacies with different $\delta^{13}C_{\text{DIC}}$. Metzger and Fike (2013) disagree with the aquafacies model, arguing that $\delta^{13}C$ variance is in fact representative of syndepositional and post-depositional alteration and that the Mohawkian Sea is as a whole isotopically homogenous. Similarly, Metzger et al. (2014) noted how local differences in $\delta^{13}C_{\text{DIC}}$ of pore fluids during the oxygenation of organic matter can impact $\delta^{13}C_{\text{carb}}$ values during diagenesis. Future work investigating signs of diagenetic alteration may shed light on the differences between the GICE in various locations.

Kump et al. (1999) suggest that weathering of carbonates, already enriched in $^{13}C$, could cause a positive carbon isotope excursion during periods of increased weathering. An increase in weathering input would have also entrained more nutrients in the water column, causing a boost in primary productivity, bolstering the GICE and forcing average post-excursion $\delta^{13}C$ values higher than pre-excursion values. A boost in biologic productivity is consistent with numerous organic-rich brown shale beds containing abundant G. prisca in Dickeyville, WI (Pancost et al., 2013). However, a $\delta^{13}C$ system dominated by weathering in the upper Mississippi Valley is unlikely, as $\delta^{13}C$ values do not show a coeval shift with $\varepsilon_{\text{Nd}}$. In other locations, the two may show a stronger correlation, leading to the GICE’s variability.
Future work on $\delta^{13}$C curves and $\varepsilon_{Nd}$ values from across the Mohawkian Sea, along with detailed thin section analysis of the upper Mississippi Valley strata at Dickeyville, WI, will aid in interpretations of the GICE and Late Ordovician climate.
6. Conclusions

Average pre-excursion $\delta^{13}$C values of around -0.5‰ occur within the upper Platteville Formation and Carimona Member. $\varepsilon_{Nd}$ values show a steady increase (-16.65 to -12.16) over this interval, which I interpret as evidence for a transgression. Previous $\delta^{18}$O data from this interval is inconsistent with warming. Cooling here could be an artifact of low data resolution or upwelling of cool waters driven by transgression.

A drop in $\varepsilon_{Nd}$ values occurring sometime between deposition of the Deicke and Millbrig K-bentonites, predating the GICE, is interpreted as a climate-induced increase in weathering from the Precambrian shield, possibly during a highstand. Warming recorded in $\delta^{18}$O data conflicts with a regressive explanation, but supports my interpretation of a changing climate. This hypothesis also contrasts with cooling signals across the M4-M5, which can be explained as tectonically induced basinal deepening.

Original $\varepsilon_{Nd}$ data from Rochester, MN, is correlated to the GICE at Dickeyville, WI, based on the presence of major K-bentonites, specifically the Deicke, Millbrig and Elkport K-bentonites. A major negative transition $\varepsilon_{Nd}$ data between the Millbrig and Deicke K-bentonites predates the GICE indicating that the two are decoupled. My $\delta^{13}$C curve, when compared to GICE curves around the globe (Fig. 1), shows similarities in timing and magnitude with most locations across the Mohawkian Sea, but differs from those in Pennsylvania and West Virginia. I agree with previous authors that the GICE is likely a global phenomenon as its ubiquity across the globe suggests, however, I assert that local factors could overprint the GICE in some instances, evidenced by timing and magnitude differences across the Mohawkian Sea.
Lack of correlation between \( \varepsilon_{\text{Nd}} \) values and the GICE indicates that weathering and eustatic changes had little impact on the GICE here.

\( \varepsilon_{\text{Nd}} \) values during the GICE are consistently low \((-16)\) and show no positive shift near the M4-M5 sequence boundary, which would be expected during a major transgression (Trenton Transgression). Therefore, lithologic evidence for a major transgression occurring at the M4-M5 from eastern Laurentia should be attributable to local changes in eustasy driven by tectonism.

My interpretation of \( \varepsilon_{\text{Nd}} \) changes through time is in partial disagreement with a purely eustatic model for \( \varepsilon_{\text{Nd}} \) changes. While I claim eustasy as the main driver for the positive shift in \( \varepsilon_{\text{Nd}} \) values prior to the Deicke K-bentonite, I assert that it is not the main mechanism behind the negative \( \varepsilon_{\text{Nd}} \) shift, which I argued to have been caused by a climate-induced increase in weathering. I cite \( \delta^{18}O \) values from Minnesota and Oklahoma as evidence for warming during a decrease in \( \varepsilon_{\text{Nd}} \) values from \(-12\) to \(-16\) between the Deicke and Millbrig K-bentonites, which contradicts a regressive explanation for a drop in \( \varepsilon_{\text{Nd}} \) values. \( \delta^{18}O \) values from Quinton and MacLeod (2014) across this interval show no evidence of cooling, suggesting that this period did not witness the onset of glaciation.

\( \varepsilon_{\text{Nd}} \) values do not appear to have a strong stratigraphic correlation with \( \delta^{13}C \) values and the GICE lags behind a major negative shift in \( \varepsilon_{\text{Nd}} \). This is evidence that the two are unrelated and that the GICE was not primarily controlled by changes in eustasy and weathering rate. Future work on \( \varepsilon_{\text{Nd}} \) values from across Mohawkian Sea exposures, along with detailed lithostratigraphic analysis, will help resolve whether or not \( \varepsilon_{\text{Nd}} \) can be used as a reliable proxy for eustatic changes in the Mohawkian Sea.
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Appendix 1: Detailed Stratigraphy

Field Measurements and Labels
From 10/17/13, Dickeyville, WI

----Elkport K-bentonite----

20a- 154mm limestone, wavy, thins and thickens
19a- 60mm shale, wavy top
18a- 190mm limestone, thins and thickens
17a- 80mm green shale and shell beds
16a- 84mm green shale, oxidation layer 24mm above the base of this unit
15a-70mm green shale bounded by brown shales
14a- 340mm fossil rich shale
13a- 63mm limestone with fossil heavy layers
12a- 30mm green shale
11a- 34mm tempestite, fossils at the base
10a- 43mm green shale
9a- 60mm fossiliferous lime
8a- 90mm green brown shale
7a- 95mm gray micritic limestone
6a- 40mm green shale with fossils
5a- 55mm limestone, pinches out, ripple marks at base
4a- 40mm shale, pinches out nearby
3a- 60mm limestone, pinches out
2a- 225mm dark shale

----Millbrig K-bentonite----
1a- 235mm limestone, wavy bottom, flat top

----Deicke K-bentonite----

-1p- 50mm shale, not present in first section
-2p- 56mm Deicke Bentonite
-3p 30mm shale
-4p- 75mm micritic limestone
-5p- 54mm shale with remineralized fossiliferous lenses
-6p- 46mm brown shale
-7p- 96mm fossil rich limestone
-8p- 38mm shale pinches out often (possibly lacking samples)
-9p- 225mm limestone
-10p- 65mm bioturbated limestone
-11p- 83mm fingering of shale and limestone
-12p- 130mm limestone
-13p- 40mm limestone
-14p- 70mm limestone
-15p- 10mm brown shale (and bentonite)

Bottom of Section

From 10/18, Rochester, MN

Each limestone sample was measured and collected and has an "L" in the label, i.e. "2-4L"

Top of section

40mm limestone, 2-1L
280mm shale
180mm shale-lime interbeds, 2-2L
80mm shale 2-0.5m
20mm lime 2-0.5m (was grouped in with above sample)
800mm shale 2-1.0m
50mm limestone 2-3L
290mm shale 2-1.5m
20mm limestone 2-4L
310mm shale 2-2.0m
100mm limestone 2-5L
180mm red clay with limestone lenses 2-5.1L
420mm gray green shale w limestone lenses at top 2-2.5m
35mm limestone 2-6L
210mm green shale 2-3.0m
33mm limestone varying in thickness laterally 2-7L
325mm shale
28mm limestone 2-8L, 2-3.5m
76mm shale
50mm limestone 2-9L
255mm shale
30mm limestone (just a small lense)
540mm green shale 2-4m
15mm bentonite, orange clay (the Elkport K-bentonite?)
660mm green shale 2-4.5m
1200mm oxidized green shale 2-5.0m, 2-5.5m
30mm limestone 2-10L
850mm shale, with limestone lenses and ammonoid horizon, 2-6.0m
700mm shale 2-6.5m, 2-7.0m
1000mm dark grey shale 2-7.5m, 2-8.25m

----Millbrig K-bentonite----

**Bottom of section**

**K-bentonites**

The position of the Elkport K-bentonite is tenuously identified at Rochester, MN, while the Dickeyville K-bentonite is not found at all. The Deicke and Millbrig K-bentonites are found in both sections and across the Mohawkian Sea, allowing for precise stratigraphic correlation. Isotopic evidence from K-bentonites in Baltoscandia, along with inferred climate patterns, indicates that they are not identical to the K-bentonites found in Laurentia during this time, (Huff, 2007; Haynes et al., 1995). Instead, conodont and graptolite biostratigraphy are used for contemporary correlations in Baltica (Bergström et al., 2010b). Recently, Sell et al. (2015) correlated over 200 K-bentonite samples during the Late Ordovician using trace element geochemistry from apatites. Their work confirms the position of the K bentonites located within our study sections (Sell et al., 2015).

**Dickeyville, WI**

The 0.6m sampled section of the Grand Detour contains dolostone intervals along with bioturbated limestones and organic-rich brown shales (McLaughlin et al., 2011). Transitioning out of the Grand Detour and into the Carimona Member of the Decorah Formation a series of thin limestone and shale units are visible. Each of these layers is less than 0.1m in section, but still contain organic-rich brown shales, discontinuous limestone lenses and micritic limestones. The regionally visible Deicke K-bentonite can be found here in the form of a bright orange clay layer.
The Spechts Ferry Member is located above the Carimona Member and is represented by 1.5-2m of green, grey and brown shales, interspersed with thin limestone units. Brachiopod rich shales and limestones (packestones) are present, along with calcareous shales (Ludvigson et al., 1996). The Millbrig K-bentonite, a bright orange clay layer, is located 0.25m above the base of the Spechts Ferry and shows the same southward condensation as the Deicke K-bentonite (Ludvigson et al., 1996).

The Guttenberg Member represents the majority of section measured for this study at Dickeyville, WI. Overlying the Spechts Ferry, the Guttenberg begins with a layer of green shales and phosphatic carbonate mudstones (Ludvigson et al., 1996; Emmerson et al., 2004). The Elkport K-bentonite is measured at 0.4m above the base of the Guttenberg, after the second of two 0.15m thick limestone beds (Ludvigson et al., 1996; McLaughlin et al., 2011; Templeton and William, 1963). The Elkport is represented in section by a 0.02m layer of orange clay. Above the basal portion of the Guttenberg, white-grey packstones-grainstones dominate (Ludvigson et al., 1996; McLaughlin et al., 2011). This portion of the section is carbonate dominated up until the Dickeyville K-bentonite, a thin white-orange clay layer, roughly 3.5m above the base of the Guttenberg (Ludvigson et al., 1996; McLaughlin et al., 2011). The remaining 1.75m of the Guttenberg consists of interbedded calcareous shales and limestones (packstones and grainstones) with some dolomitized portions (Ludvigson et al., 1996; McLaughlin et al., 2011; Templeton and William, 1963). A series of thin organic rich brown shales, abundant in *G. prisca* microfossils can be found throughout the Guttenberg Member (Pancost et al., 2013). The Ion Member has a similar lithology as the upper Guttenberg, but may be identified by a prominent hardground surface at its base and its more dolomitized lithology (McLaughlin et al., 2011).
Appendix 2: Data

δ¹³C Data (Dickeyville, WI)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Stratigraphic Level from Diecke (cm)</th>
<th>δ¹³C</th>
<th>δ¹⁸O</th>
<th>δ¹⁵N</th>
<th>Comments</th>
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<td>-5.29</td>
<td>0.03</td>
<td>Micrite</td>
</tr>
<tr>
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<td>Micrite</td>
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<tr>
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<td>-5.99</td>
<td>0.01</td>
<td>Micrite</td>
</tr>
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Assumes age = 453 Ma

147Sm/144Nd for con samples = 0.129 (measured at 0.133 and 0.126)
147Sm/144Nd for all other samples = 0.161 (measured at 0.151 and 0.172)

### Nd Data (Rochester, MN)

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<th>eNd(t) error</th>
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Sm/Nd = .121

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2-0.5 0.511600 0.000008 9.81341 0.511625 0.000016 -19.76 0.31 -17.73 0.31 -15.98 0.31 -15.42

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2-2.0 0.511695 0.000017 1.44297 0.511702 0.000034 -18.24 0.66 -16.20 0.66 -14.36 0.66 -13.90

2-6.0 rerun 0.511633 0.000012 3.13771 0.511678 0.000024 -18.73 0.47 -16.69 0.47 -14.85 0.47 -14.39

2-3.0 | 0.511566 | 0.000007 | 7.16143 | -20.52 | 0.28 | -18.49 | 0.28 | -16.65 | 0.28 | -16.19 |

1 | 0.511707 | 0.000008 | 8.79199 | -17.81 | 0.29 | -15.95 | 0.29 | -15.77 | 0.29 | -15.47 |

4 | 0.511764 | 0.000004 | 14.0135 | -16.70 | 0.17 | -14.84 | 0.17 | -14.66 | 0.17 | -14.36 |

7 | 0.511892 | 0.000006 | 16.4433 | -14.20 | 0.26 | -10.34 | 0.26 | -12.16 | 0.26 | -9.86 |

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2 | 0.511853 | 0.000008 | 6.38332 | -14.96 | 0.29 | -11.10 | 0.29 | -12.92 | 0.29 | -10.62 |

5 | 0.511794 | 0.000010 | 2.48516 | -16.11 | 0.37 | -12.25 | 0.37 | -14.08 | 0.37 | -11.77 |

5 rerun | 0.51177 | 0.000008 | 5.91742 | -16.05 | 0.29 | -12.19 | 0.29 | -14.02 | 0.29 | -11.71 |

7 | 0.511846 | 0.000004 | 17.4078 | -15.04 | 0.15 | -11.18 | 0.15 | -13.00 | 0.15 | -10.70 |

3 | 0.511708 | 0.000009 | 8.75469 | -17.79 | 0.34 | -13.93 | 0.34 | -15.76 | 0.34 | -13.45 |

WRONG CORRECT

con = .129 con = .161

10.18.13+ 161 10.18.13+ 129
Vita

Zachary Wright is a native of the Baltimore, Maryland area and first discovered his love of geology during road trips across through the Appalachians, to western Pennsylvania to visit his grandparents. This passion would remain dormant until his sophomore year at Vanderbilt University when he enrolled in Geology 101.

With encouragement from his parents Bonny and Alan, and girlfriend, Anna Arata, Zach applied to and enrolled in graduate school for LSU. The man who would be his advisor, Dr. Achim Herrmann, reached out to him about studying neodymium isotopes in carbonates. With much assistance and patience from all parties involved, Zach successfully defended this thesis on June 16th, 2015.