A Molluscan Record of Monsoonal Precipitation along the Western Shoreline of the Late Maastrichtian Western Interior Seaway

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A Molluscan Record of Monsoonal Precipitation along the Western Shoreline of the Late Maastrichtian Western Interior Seaway

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Geology
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ABSTRACT

Global warming in response to increasing levels of atmospheric CO2 concentration (pCO$_2$) has generated concern over the effects of increasing surface temperature on the hydrologic cycle. Investigating precipitation dynamics during past ‘greenhouse’ intervals provide important insights necessary to better constrain potential future climate scenarios. The Late Cretaceous greenhouse is characterized by elevated pCO$_2$ and surface temperatures, with a prolonged cooling trend which initiated in the late Campanian and an associated 4$^{th}$-order sea-level regression recorded in the Western Interior Seaway (WIS), providing an opportunity to examine the hydrologic cycle under conditions of changing temperature and sea-level. This study uses a sclerochronologic approach to examine $\delta^{18}$O and $\delta^{13}$C values in freshwater bivalves collected from two horizons separated by ~800 ka, to reconstruct the late Maastrichtian hydrology at a locality along the western shoreline of the WIS. To ensure the presence of primary calcium carbonate, valves were examined using Scanning Electron Microscopy (SEM). Bivalve $\delta^{18}$O and $\delta^{13}$C values reflecting coastal river compositions range from -10.5 to -2.8‰ and -8.2 to 5.6‰, respectively. A positive correlation between $\delta^{18}$O and $\delta^{13}$C values found in specimens lower in the section, reveals that the lowest $\delta^{18}$O values occurred during times of peak summer soil respiration, whereas the highest $\delta^{13}$C values of 5.6‰ record a marine influence, supporting rainout during a summer monsoon as the cause for the lowest $\delta^{18}$O values recorded in this group. The valves collected higher in the section have an alternating correlation between $\delta^{18}$O and $\delta^{13}$C and plot closer to high elevation precipitation values on a mixing diagram. The loss of the summer monsoon between the two unionid groups is likely
in response to decreasing surface temperatures and the retreat of the seaway, providing insight into the potential for increased intensity of modern monsoons in response to increasing surface temperatures and sea-level rise.
CHAPTER ONE:
INTRODUCTION

Global mean land surface temperatures are projected to increase by up 4°C by 2100 accompanied by an increase in mean ocean surface temperatures of up to 3°C (IPCC, 2014). Global warming has already resulted in an intensification of the hydrologic cycle throughout the 20th century (Huntington, 2006; IPCC, 2014), and this trend is projected to continue as mean land-surface temperature increases more rapidly than mean ocean-surface temperature, with the intensification of monsoons as a significant cause for alarm (IPCC, 2014). With growing concern over the effects of current global warming on the hydrologic cycle, there is increased interest in understanding precipitation dynamics during past ‘greenhouse’ intervals to better constrain future climate scenarios.

The Late Cretaceous represents the best-documented long-term interval of equable climate (Barron, 1983) and elevated atmospheric CO₂ concentration (pCO₂) in Earth history (Beerling et al., 2002; Fletcher et al., 2008; Breeker et al., 2010). Paleoenvironmental records of the Western Interior Seaway (WIS) are an excellent natural archive that can be utilized to better understand such phenomena during a well-studied greenhouse interval. The marine dynamics of the WIS have been extensively documented utilizing a variety of approaches including geochemical studies (e.g., Urey et al., 1951; Lowenstam and Epstein, 1954; Tortelot and Rye, 1969; Forester et al., 1977; Wright, 1987; Whittaker et al., 1988; Whittaker and Kyser, 1993; Fatheree et al., 1998; Fisher and Arthur, 2002; Cochran et al., 2003; He et al., 2005; Coulson et al., 2011; Dennis et al., 2013). The
nature of its freshwater input and terrestrial hydrology, however, remain poorly constrained due to the limited number of freshwater records that have been generated (e.g., Dettman and Lohmann, 2000; Fan and Dettman, 2009; Fricke et al., 2010; Dennis et al., 2013).

This study focuses on freshwater bivalves from a late Maastrichtian sequence deposited during 3rd-order sea-level regression (Haq, 2014), near the end of a 10 Ma cooling trend initiated in the late Campanian (Barerra and Savin, 1999; Li and Keller, 1999; Dennis et al., 2013). Existing late Maastrichtian studies have documented δ18O values of freshwater bivalves as low as -19 to -22‰, with intermediate values ranging from -9 to -11‰ (Dettman and Lohmann, 2000; Dennis et al., 2013). These values have been attributed to two different sources: one interpretation favors snowmelt within the catchment (Dettman and Lohmann, 2000) whereas the other supports the presence of a summer monsoon (Fricke et al., 2010). Ambient temperature estimates combined with a lapse rate for δ18O values of precipitation at an elevation of 3 km were used to support the notion of a significant snowmelt contribution into freshwater systems (Dettman and Lohmann, 2000). Conversely, these same δ18O values were attributed to the influence of a summer monsoon based on results from atmospheric general circulation modeling and the presence of both higher elevation and intermediate δ18O values, similar to those present during hypothesizes monsoonal conditions in the Campanian (Fricke et al., 2010). This study uses δ18O and δ13C values from unionids deposited in a coastal plain setting to investigate the presence of a summer monsoon during a global sea-level regression and cooling trend. Investigating changes in the summer monsoon along this gradient of changing temperature and sea-level can provide insight into potential future changes to the intensity of modern monsoons under conditions of increasing surface temperatures and sea-level rise.
CHAPTER TWO:  
GEOLOGIC SETTING

General Overview

Sediments within the Cretaceous WIS represent deposits during the Zuni cratonic sequence (Sloss, 1964), which developed through a prolonged interval of sea-level rise which peaked in the mid-Cretaceous. This transgressive phase was forced by positive dynamic topography caused by the lengthening of mid-ocean ridges associated with the breakup of Pangaea (Hardebeck and Anderson, 1996; Seton et al., 2009), seafloor-spreading pulses in the both the mid- (~120 Ma) and Late (~80) Cretaceous (Hays and Pitman, 1973; Seton et al., 2009), and ‘superplumes’ forming oceanic large igneous provinces (LIPS) in the mid-Cretaceous (Larson, 1991). This reduction in ocean basin volume was accompanied by the subduction of the Farallon plate beneath the North American plate forming an arc-trench system, which lead to Cordilleran-style tectonic compression (Cross, 1986). As the buoyant backarc region migrated eastward across the craton, a Cordilleran orogenic wedge consisting of the Luning–Fencemaker, Central Nevada (Eureka), the Sevier thrust belts and a hinterland metamorphic belt formed in the retroarc region (Cross and Pilger, 1982; Cross, 1986; DeCelles, 2004). The eastward moving thin-skinned, décollement-type tectonic compression caused flexural subsidence east of the Sevier Orogenic Belt, forming the Western Interior Foreland Basin (WIFB; Armstrong, 1968; Cross, 1986; DeCelles, 2004).
In the middle to late Albian (~105 Ma), marine waters inundated the WIFB, connecting the Arctic Ocean with the Tethys initially during the Kiowa/Skull Creek transgression, forming WIS (Blakey; DeCelles, 2004; Miall et al., 2008; Slattery et al., 2015; Yonkee and Weil, 2015). In the early to middle Campanian (~80 Ma), a change in Farallon–North American plate orientation (Cross, 1986) accompanied by an increased rate of convergence (Hays and Pitman, 1973; Cross, 1986; Seton et al., 2009) caused a shallowing of the subduction angle (Cross, 1986; Mitrovica et al., 1989; Dumitru et al., 1991; DeCelles, 2004; Painter and Carrapa, 2013; Fan and Carrapa, 2014; Yonkee and Weil, 2015). This in turn caused an eastward migration of the magmatic arc with the exception of a magmatic gap in the mid latitudes of the western United States (Cross, 1986; Mitrovica et al., 1989; Dumitru et al., 1991; DeCelles, 2004; Painter and Carrapa, 2013; Yonkee and Weil, 2015), possibly in response to the subduction of an aseismic ridge beneath the central portion of the western U.S. (Cross, 1986; Mitrovica et al., 1989; DeCelles, 2004; Liu et al., 2010; Painter and Carrapa, 2013).

Foreland basinal width also increased in response to regional dynamic subsidence as cool Farallon lithosphere displaced North American asthenosphere and increased interseismic coupling from shallow angle or possibly flat-slab subduction (Cross, 1986; Mitrovica et al., 1989; Dumitru et al., 1991; DeCelles, 2004; Liu et al., 2010; Painter and Carrapa, 2013; Yonkee and Weil, 2015). Crustal thickening from layer-parallel shortening in the various thrust belts formed the high-elevation (2-3 km above the foreland), low relief ‘Nevadaplano’ in the Sevier hinterland by the early Maastrichtian (~70 Ma) (DeCelles, 2004; DeCelles and Coogan, 2006; Yonkee and Weil, 2015). At the same time, the hingeline of the subducting Farallon plate developed beneath the eastern margin of the Colorado Plateau, activating Laramide basement-cored uplift (Cross, 1986; Painter and Carrapa, 2013; Yonkee and Weil, 2015). Combined with lowering eustatic sea level
(Haq, 2014), Laramide deformation split the WIFB into more than 20 intermontane basins before slab roll back terminated Laramide activity in the Eocene (~45-50 Ma) (Cross, 1986; DeCelles, 2004; Fan and Carrapa, 2014; Slattery et al., 2015).

Sampled Material

Fossil unionids used in this study are from 3rd-order eustatic event within the last major 2nd-order sea-level cycle recorded in the WIS: the Campanian–Maastrichtian Bearpaw Cyclothem (He et al., 2005; Miall et al., 2008; Haq, 2014; Yonkee and Weil, 2015). They were collected at the Sandstone Ranch, located ~15 km northwest of Rawlins, WY (Fig. 1) from an outcrop of the Lance Formation, a terrestrial equivalent to the marine Bearpaw Formation (Survey, 2014). The Sandstone Ranch provides access to kilometer scale outcrops of Cretaceous marine, near-shore and terrestrial deposits exposed by regional uplifting. The specimens were collected from the lower part of the fluvial Lance Formation, representing late Maastrichtian wedge-top deposits on the western margin of WIFB (McMillen and Winn, 1991; DeCelles, 2004; Pyles and Slatt, 2007).

Based on paleogeographic tectonic plate reconstructions and general circulation models, the unionids were deposited at a paleolatitude of ~45 °N (Fig.1; Pyles and Slatt, 2007). Fossil leaf physiognomy (i.e., percentage of entire margins, drip–tip apices and deciduous trees) and results from GENESIS global circulation modeling (GCM) were used to determine the paleoclimate of the study area can be classified as a subtropical broadleaved evergreen forest and woodland region and is within the estimated 20° isotherm (Wolfe, 1979, 1987; Wolfe and Upchurch, 1987; Upchurch et al., 1999; Upchurch et al., 2007). The specimens were found within a sequence of rhythmically bedded fourth-order cycles (~100 ka), with shell material found throughout very fine-
grained light yellowish brown clastic beds spanning several meters in thickness, capped by ~1 m thick, yellowish brown erosion-resistant sandstones (Figs.3 and 4; Pyles and Slatt, 2007). Four unionid valves were used in this study: two from the upper bed (C3.1 and C3.2) and two from a bed located near the bottom of the study area (B1 and B2) shown in figure (Fig. 5). The unionid groups were separated by ~230 m of sediment representing eight sedimentary cycles. These cycles likely span ~800 ka, assuming they represent the eccentricity band of Milankovitch Cyclicity.

Figure 1: Western Interior Seaway paleogeographic map of the late Maastrichtian. Red star indicates study area. Copyright 2013 Colorado Plateau Geosystems, used with permission.
Figure 2: Sampling locality in the Lance Fm, located on the Sandstone Ranch 15 km northwest of Rawlins, WY.

Figure 3: Close up photograph of specimen C3.1. The sediments have mud cracking, indicating silt or smaller grain sizes with a covering of pebble to cobble size alluvial sandstone.
Figure 4: Photograph of Specimen B1 weathering out of fine-grained clastic sediments with a covering of pebble size alluvial sandstone.
Figure 5: Map showing areas where shell material was found.
CHAPTER THREE:

METHODS

SEM

Before analyzing the specimens using scanning electron microscopy (SEM), the unionid valves were cleaned using a soft-bristled brush and deionized water to remove sediment. Samples were then prepared for SEM analysis to determine their preservation indexes (PI) according to the methods of Cochran et al. (2010). The assessment began, with the visual inspection of the aragonite on the inside of the valves. Next, razor-blade utility shears were used to cut shell samples into pieces measuring approximately 8 x 2 mm. These shell fragments were then secured to aluminum mounts using carbon adhesive tabs and sputter coated with an Au/Pd alloy for proper grounding in the Topcon Aquila Hybrid SEM located in the Electron Microscopy Core Lab, Department of Integrative Biology, University of South Florida. Samples were then photomicrographed at a magnification of 5000x to examine the nacreous structure for assigning PIs.

Milling and Stable Isotope Analysis

Samples were mounted in epoxy to prevent shell breakage during the milling process by using 3M brand epoxy and 10 ounce disposable plastic cups (Fig. 6). Upon curing for 24 hr, billets were cut using a wet saw to expose the shell profile (Figs. 7-10). Samples of ~300 μg were milled
from the thick sections at a 1 mm interval extending from the umbo to the ventral margin using a Sherline Model 5410 Milling Machine with a 0.015 4 flute square end micro carbide end mill, Kodiak Cutting Tools item number 146199. Samples were then analyzed at the University of South Florida Stable Isotope Lab (USFSIL) using phosphoric acid digestion of carbonate method as defined by McCrea (1950) and isotopic data were generated using a ThermoFisher Scientific Delta V Advantage light stable isotope ratio mass spectrometer (IRMS) equipped with a ThermoFisher Scientific GasBench II to determine δ¹⁸O and δ¹³C values of the carbonate material. δ¹⁸O and δ¹³C values were reported relative to VPDB at an analytical precision better than ±0.15‰.

Figure 6: Specimen B1 set in epoxy.  Figure 7: Profile of specimen B1.

Figure 8: Profile of specimen B2.  Figure 9: Profile of specimen C3.1.
Figure 10: Profile of specimen C3.2.
Preservation Index (PI)

All of the unionid valves used in this study have undergone varying degrees of mechanical abrasion as visible in figures 11-14. However, visual inspection reveals aragonite is still present, indicating a high degree of chemical preservation. Scanning Electron Microscopy (SEM) was used to further evaluate the preservation of the biogenic aragonite microstructure and assign a corresponding PI. According to Cochran et al. (2010), diagenesis is first visible between the nacreous tablets in the interstitial region, originally occupied by conchiolin. Photomicrographs were evaluated against examples of PI from Cochran et al (2010), ranging from excellent PI=5 to poor preservation PI=1 (Fig. 15). Samples B1, B2 and C3.2 do not appear to have any remaining conchiolin but have excellent preservation of the nacreous tablets (Figs. 16, 17 and19) and were assigned PIs of 5. The nacreous plates of specimen C3.1 were well preserved, but slightly less distinct (Fig. 18) and were assigned a PI index of 4.
Stable Isotopic Analysis

\( \delta^{18}O \) values for specimen B1 range from -9.0 to -2.9\(^\circ\) and from -9.6 to -2.8\(^\circ\) for B2 (Fig. 20). \( \delta^{18}O \) values for the C specimens range from -10.0 to -6.5\(^\circ\) and -10.5 to -5.8\(^\circ\) for C3.1 and C3.2, respectively (Fig. 20). \( \delta^{13}C \) values for specimen B1 range from -7.5 to 5.2\(^\circ\) and -6.8 to 5.6\(^\circ\) for B2 (Fig. 21). \( \delta^{13}C \) values for C3.1 range from -7 to -1.7\(^\circ\) and values for C3.2 range from -8.2 to -2.0\(^\circ\) (Fig. 21). Samples milled from B1, B2 and C1 appear to record a period of rapid growth that occurs in early stages of unionid growth, which is most visible in specimens B2 and C3.1 (Figs. 20 and 21). These points were removed to reduce bias during statistical analysis by over-representing these values. The sclerochronology of these unionids records the cycling of isotopic values for 4-7 years and exhibits a general stability of endmember values.

Histograms of \( \delta^{18}O \) and \( \delta^{13}C \) value were used to display the distribution of values and determine the suitability of the results for creating two separate groups (Figs. 22 and 23). Comparison of histograms, sample means, medians and standard deviations indicate two distinct groups are present that represent the stratigraphic differences. There is much greater similarity between values derived from co-occurring specimens than between different sampled horizons, specifically between the histograms of \( \delta^{18}O \) for specimens B1 and B2 (Fig. 22) and \( \delta^{13}C \) for specimens C3.1 and C3.2 (Fig. 23). P-values for Fligner–Killeen test for homogeneity of variance for both \( \delta^{18}O \) and \( \delta^{13}C \) are greater than 0.05 and are therefore unable to reject the null hypothesis of equal variance for the two groups: B1–B.2 and C3.1–C3.2. Mann-Whitney U test p-values are greater than 0.05 for both groups based on the \( \delta^{13}C \) data, but only support the grouping of B1-B2 based on \( \delta^{18}O \) values.
Figure 11: Photograph showing both sides of unionid specimen B1.

Figure 12: Photograph showing both sides of unionid specimen B2.

Figure 13: Photograph showing both sides of unionid specimen C3.1
Figure 14: Photograph showing both sides of unionid specimen C3.2.

Figure 15: Examples of the range of PI values from Cocharan et al. (2010): Excellent PI=5 (top), Very Good PI=4, Good PI=3, Fair PI=2, Poor PI=1.
Figure 16: SEM photomicrograph of sample B1 at 5000x.

Figure 17: SEM photomicrograph of sample B2 at 5000x.
Figure 18: SEM photomicrograph of sample C3.2 at 5000x.

Figure 19: SEM photomicrograph of sample C3.1 at 5000x.
Figure 20: Plot of $\delta^{18}$O values with rapid growth values in red. Red lines indicate peak summer values.

Figure 21: Plot of $\delta^{13}$C values with rapid growth values in red. Red lines indicate peak summer values.
Figure 22: Histogram of $\delta^{18}$O values with rapid growth samples removed.

Figure 23: Histogram of $\delta^{13}$C values with rapid growth samples removed.
CHAPTER FIVE:

DISCUSSION

$\delta^{18}O$ values of modern freshwater unionid bivalves reflect precipitation in isotopic equilibrium with ambient water (Dettman et al., 1999; Wurster and Patterson, 2001; Kaandorp et al., 2003; Goewert et al., 2007; Versteegh et al., 2010). Furthermore, $\delta^{18}O$ values of river water are typically within 1‰ of $\delta^{18}O$ values of the local precipitation (Kendall and Coplen, 2001; Dutton et al., 2005). Unionid $\delta^{18}O_{CaCO_3}$ values from this study range from -10.5‰ to -2.8‰ reflecting the profile of the catchment, distance from and $\delta^{18}O$ value of the vapor source as well as duration of precipitation events (Craig, 1961; Dansgaard, 1964; Rozanski et al., 1993; Kendall and Coplen, 2001; Dutton et al., 2005). $\delta^{13}C$ ($\delta^{13}C_{CaCO_3}$) values range from -8.2 to 5.6‰, recording the seasonal cycling of DIC values in response to changing freshwater conditions and a potential marine influence. Based on a positive correlation between $\delta^{18}O_{CaCO_3}$ and $\delta^{13}C_{CaCO_3}$ values and the influence of a potential marine influence, a monsoonal precipitation regime is hypothesized. To further investigate this hypothesis, a mixing diagram was created using estimated values for the WIS, wet-season monsoonal freshwater, dry-season groundwater dominated freshwater and the effect of snowmelt within the catchment (Fig. 24).
Raleigh processes of fractionation in the local meteoric water cycle begin with evaporation from the WIS, which requires modeling its $\delta^{18}$O value ($\delta^{18}$O$_{WIS}$). An accurate estimate for the $\delta^{18}$O$_{WIS}$ surface would require the assessment of fractionation within the local paleohydrologic cycle, seasonal and long-term freshwater reserves, and circulation and mixing patterns (Clark and Fritz, 1997; Rohling, 2013). An estimate in that detail is beyond the scope of this coastal-plain based study; but an estimate of the $\delta^{18}$O value of ice-free seas can be used as an approximation of the $\delta^{18}$O value of the vapor source ($\delta^{18}$O$_{WIS}$).

The $\delta^{18}$O value of ice-free seas was calculated using the effect of the Greenland and Antarctic ice sheets on the $\delta^{18}$O value of modern bulk ocean water ($\delta^{18}$O$_{Ocean}$) because they represent the largest reservoir of land-based ice (de Boer et al., 2012). The $\delta^{18}$O$_{Ocean}$ value of 0.03‰ was calculated from data for all of the 33 Levitus ocean climatology levels (0-5500 m) in the NetCDF version 1.1 of the database in LeGrande and Schmidt (2006). The mean salinity value of 34.66 PSU was also calculated from values for 33 climate levels using mean annual salinity values sourced in NetCDF format from the World Ocean Atlas 2009 dataset of Locarnini et al. (2010). Mean salinity and the density of water (1 g/ml) were used to determine the 1035 kg/m$^3$ density of ocean water. The mass of modern ocean water ($M_{Ocean}$) of $1.38 \times 10^{21}$ kg was determined using the density of the ocean water estimate and an ocean volume of $1.335 \times 10^9$ km$^3$ (Eakins and Sharman, 2010). The Greenland Ice Sheet (GRIS) $\delta^{18}$O value ($\delta^{18}$O$_{GRIS}$) of $-35.5$‰ is the median value in the range of $-34$ to $-37$‰ bulk value for the ice sheet (Lhomme et al.,
23

2005). A GRIS mass \( M_{\text{GRIS}} \) of \( 2.69 \times 10^{18} \) kg was determined using the density of meteoric ice of 918 kg/m\(^3\) (Le Brocq et al., 2010) and a GRIS volume of \( 2.93 \times 10^6 \) km\(^3\) (Bamber et al., 2001; de Boer et al., 2012). The bulk Antarctic Ice Sheet (AIS) \( \delta^{18}\)O value \( (\delta^{18}\text{O}_{\text{AIS}}) \) of \(-52.0\%\) represents the contribution of the Western Antarctic Ice Sheet with \( \delta^{18}\)O values ranging from \(-41.0\) to \(-42.5\%\) combined with Eastern Antarctic Ice Sheet values of \(-56\%\) as interpolated from ice cores (Lhomme et al., 2005). The \( 2.27 \times 10^{19} \) kg mass of the AIS was determined using the volume of \( 24.7 \times 10^6 \) km\(^3\) (de Boer et al., 2012) and the density of meteoric ice (Le Brocq et al., 2010). Finally, a value of \(-0.9\%\) VSMOW for \( \delta^{18}\text{O}_{\text{WIS}} \) was calculated using a mixing equation modified from (Kendall and Caldwell, 1998):

\[
\delta^{18}\text{O}_{\text{WIS}} M_{\text{WIS}} = \delta^{18}\text{O}_{\text{Ocean}} M_{\text{Ocean}} + \delta^{18}\text{O}_{\text{GRIS}} M_{\text{GRIS}} + \delta^{18}\text{O}_{\text{AIS}} M_{\text{AIS}}
\]

This value was converted to VPDB scale for reference to aragonite values using the equation:

\[
\delta^{18}\text{O}_{\text{VPDB}} = 0.97002 \times \delta^{18}\text{O}_{\text{VSMOW}} - 29.98 \text{ from Coplen et al. (1983)}, \quad 1000 \ln(\alpha) = 2.559 \times (10^6 T^{-2}) + 0.715, \text{ where } T \text{ is in Kelvin from Dettman et al. (1999) to account for aragonite fractionation at } 20^\circ\text{C, resulting in a } \delta^{18}\text{O}_{\text{WIS}} \text{ values of } -0.4 \pm 2\% \text{ per } 10 \degree\text{C.}
\]

The modern atmospheric CO\(_2\) to sea surface equilibration time is 6.8 years (Stuvier, 1980; Schlesinger, 1997). Therefore, the \( \delta^{13}\)C value for the WIS \( (\delta^{13}\text{C}_{\text{WIS}}) \) was estimated using a Late Maastrichtian \( \delta^{13}\text{C}_{\text{atm}} \) value of \(-5.9\%\) based on soil carbonate analyses (Ekart et al., 1999). Taking into account the 8.6\% fractionation between \( \delta^{13}\text{C}_{\text{atm}} \) and HCO\(_3\) \( (\delta^{13}\text{DIC}) \) at 20°C (Mook et al., 1974; Romanek et al., 1992), the \( \delta^{13}\text{C}_{\text{WIS}} \) value is estimated to be \( 2.7\% \pm 1\% \) per 10 °C change in temperature.
The $\delta^{13}C_{\text{DIC}}$ values of freshwater are strongly influenced at the soil–meteoric water interface, with $\delta^{13}C_{\text{DIC}}$ values largely regulated by rates of soil respiration (Clark and Fritz, 1997). CO$_2$ within the ‘soil atmosphere’ is primarily sourced from root respiration and the bacterial oxidation of plant detritus during warm months, where soil respiration rates are highest. During cooler months, soil respiration is decreased and the admixture of atmospheric CO$_2$ increases with respect to respired soil CO$_2$ (Cerling, 1984; Lloyd and Taylor, 1994). Because the study area is a subtropical broadleaved evergreen forest and woodland region (Wolfe, 1979, 1987; Wolfe and Upchurch, 1987; Upchurch et al., 1999; Upchurch et al., 2007), which is comprised of C3 plants (Ekblad and Högberg, 2001) and unequivocal C4 plants have not been discovered earlier than the Miocene (Osborne and Beerling, 2006), the fractionation factor for C3 plants is: $\delta^{13}C = -27.1 - 0.0125[T(\degree\text{C})]$, for 14 – 40 $^\circ$C (Troughton and Card, 1975) adjusted for the difference between the $\delta^{13}C_{\text{atm}}$ value of $-6.4\%$ from Troughton and Card (1975) to the late Maastrichtian value of $-5.9\%$ Ekart et al., 1999), was used to estimate an average $\delta^{13}C_{\text{biomass}}$ value for the study area of $-27.4\%$ at 20 $^\circ$C, with this value subject to change at a rate of -0.125\% per 10 $^\circ$C, from 14 – 40 $^\circ$C. Combining the 4.4% fractionation from the diffusion of CO$_2$ through air to $\delta^{13}C_{\text{soil}}$ (Cerling, 1984; Craig, 1954; Dörr and Münnich, 1980; Farquhar et al., 1989) with the 8.6% fractionation between CO$_2(g)$ and HCO$_3^-$ at 20 $^\circ$C (Mook et al., 1974; Romanek et al., 1992), the $\delta^{13}C$ value of wet-season freshwater is estimated to be $-14.4\% \pm 1.1\%$ per 10 $^\circ$C change in temperature.

Temperature has a positive correlation with soil respiration resulting in low $\delta^{13}C_{\text{biomass}}$ dominated wet-season values and a trend toward higher $\delta^{13}C_{\text{atm}}$ dry-season values (Cerling,
The δ\textsuperscript{13}C value for dry-season freshwater is based on equilibration with the δ\textsuperscript{13}C\textsubscript{atm} value of −5.9‰ (Ekart et al., 1999). With an 8.6‰ fractionation between δ\textsuperscript{13}C\textsubscript{atm} and HCO\textsubscript{3} (δ\textsuperscript{13}DIC) at 20 °C (Mook et al., 1974; Romanek et al., 1992), the δ\textsuperscript{13}C value of dry season freshwater is estimated to be 2.7‰ ± 1‰ per 10 °C change in temperature.

The δ\textsuperscript{18}O fractionation steps from vapor source through precipitation begin with evaporation from the WIS with an estimated value of −0.9‰. There are kinetic evaporation effects, primarily controlled by humidity (Gat, 1996; Clark and Fritz, 1997), but the closed system model of Craig and Gordon (1965) is useful when conditions are unknown and is shown to closely approximate δ\textsuperscript{18}O values of precipitation (δ\textsuperscript{18}O\textsubscript{PCPN}) collected at International Atomic Energy Agency (IAEA)/World Meteorological Organization (WMO) Global Network of Isotopes in Precipitation (GNIP) island stations (Rozanski et al., 1993; Gat, 1996; IAEA/WMO, 2016). Assuming closed system conditions for fractionation of liquid water to vapor, without additional fractionation the low-elevation coastal δ\textsuperscript{18}O\textsubscript{PCPN} values should be approximately equal to the δ\textsuperscript{18}O\textsubscript{WIS} of −0.9‰. However, wet-season δ\textsuperscript{18}O values of monsoonal precipitation are depleted with respect to vapor source values due to rainout (Rozanski et al., 1993). The wet-season monsoonal freshwater values was estimated using data collected by the GNIP (IAEA/WMO, 2016). A value of -10‰ is representative of the lowest δ\textsuperscript{18}O\textsubscript{PCPN} values for the low elevation monsoonal locations of Guam, Hong Kong and New Delhi (IAEA/WMO, 2016). This value was adjusted -0.9‰ for the difference between modern and ice-free seas to establish a monsoonal freshwater δ\textsuperscript{18}O estimate of -10.9 ± 4‰ to represent the range of values found in the GNIP dataset. This value was converted to VPDB scale for reference to aragonite values using the equation: δ\textsuperscript{18}O\textsubscript{VPDB} = 0.97002* δ\textsuperscript{18}O\textsubscript{VSMOW} - 29.98 from Coplen et al. (1983), and 1000 ln (α) = 2.559 \left(10^6T^{-2}\right) + 0.715, where T is in Kelvin from Dettman et al. (1999) to account for aragonite fractionation at 20°C, resulting in a
\( \delta^{18}O_{WIS} \) values of -10.1 ± 2‰ per 10 °C. The \( \delta^{18}O \) value for dry season freshwater was estimated using representative yearly mean \( \delta^{18}O \) values of precipitation for Guam, Hong Kong and New Delhi of -6.3 ± 1.3‰ (IAEA/WMO, 2016) adjusted -0.9‰ for the difference between modern and ice-free seas, for an estimated dry season freshwater \( \delta^{18}O \) value -7.2 ± 1.3‰. This value was converted to VPDB scale for reference to aragonite values using the equation: 

\[
\delta^{18}O_{VPDB} = 0.97002 \times \delta^{18}O_{VSMOW} - 29.98 \text{ from Coplen et al. (1983), and } 1000 \ln (\alpha) = 2.559 (10^6T^{-2}) + 0.715, \text{ where } T \text{ is in Kelvin from Dettman et al. (1999) to account for aragonite fractionation at 20°C, resulting in a } \delta^{18}O_{WIS} \text{ values of } -6.5 ± 2‰ per 10 °C.
\]

**Interpretation**

\( \delta^{13}C_{CaCO_3} \) values of 5.6‰ recorded in group B adjusted to -2.9‰ for comparison to \( \delta^{13}C_{WIS} \) by subtracting the 2.7‰ fractionation between \( \delta^{13}C_{DIC} \) and aragonite at 20°C (Romanek et al., 1992) are 0.2‰ enriched with respect to estimated \( \delta^{13}C_{WIS} \), revealing a marine influence, which indicates these unionids are derived from a low-elevation coastal plain in close proximity to the WIS. \( \delta^{18}O_{CaCO_3} \) values of -2.8‰ associated with these \( \delta^{13}C_{CaCO_3} \) values are only marginally depleted with respect to the estimated \( \delta^{18}O_{WIS} \) value of -0.4‰, further supporting the presence of a significant influence from the WIS. The lowest \( \delta^{18}O_{CaCO_3} \) values of -9.6‰ are depleted by -9.2‰ with respect to \( \delta^{18}O_{WIS} \). These low \( \delta^{18}O_{CaCO_3} \) values occur with the lowest \( \delta^{13}C_{CaCO_3} \) values of -7.5‰, adjusted to -10.2‰, which are linked to maximum summer soil respiration. This strong positive correlation between \( \delta^{18}O_{CaCO_3} \) and \( \delta^{13}C_{CaCO_3} \) values recorded in these unionids throughout 4-5 annual cycles (Fig. 25) is likely in response to rainout during a summer monsoon during peak summer soil respiration. When plotted on a mixing diagram, isotopic values from these unionids
trend from wet-season monsoonal freshwater values toward WIS values (Fig. 26), supporting the presence of a summer monsoon. A summer monsoon is characterized by seasonally reversing wind patterns, with a wet warm-season and a dry cool-season (Ramage, 1971). Under these conditions, \( \delta^{18}O_{PCPN} \) values are decreased due to rainout during the summer wet-season and may also be increased by an amount effect during the dry season as shown in Figure 27 based upon \( \delta^{18}O_{PCPN} \) values for New Dehli (Rozanski et al., 1993; IAEA/WMO, 2016). The \( \delta^{18}O_{CaCO3} \) values of group B follow a similar trend and are, therefore, most likely recording a transition from a wet-season monsoon to a brackish dry-season conditions.

The lowest \( \delta^{13}C_{CaCO3} \) values of -8.2‰ recorded in group C, adjusted to -10.9‰, are associated with peak summer temperature and soil respiration. The highest \( \delta^{13}C_{CaCO3} \) values of -1.7‰, adjusted to -4.4‰, are enriched by 6.5‰ with respect to the lowest values in the group. This increase is likely the product of equilibration between river \( \delta^{13}C_{DIC} \) and \( \delta^{13}C_{atm} \), which occurs as rivers flow from their headwaters, with values increased up to 5‰ in modern North American rivers (Doctor et al., 2008). The highest \( \delta^{18}O_{CaCO3} \) values of -5.8‰ are depleted by -5.4‰ with respect to \( \delta^{18}O_{WIS} \) and do not appear to record marine values. The lack of a marine influence indicates the unionids in this group were positioned further inland on the coastal plain with respect to group B, reflecting continued eastward migration of the shoreline associated with regression of the WIS. In comparison to the patterns seen in group B, there is an alternating and random correlation between \( \delta^{18}O_{CaCO3} \) and \( \delta^{13}C_{CaCO3} \) values in this group (Fig. 25), indicating the loss of a strong summer monsoon between the two groups. The breakdown of the summer monsoon between the two unionid groups is likely in response to decreasing surface temperatures and global sea level regression. However, the lowest \( \delta^{18}O_{CaCO3} \) values of -10.5‰ are within 1‰ of the lowest \( \delta^{18}O_{CaCO3} \) values in group B, indicating a potential alternative source for these low values. When
plotted on a mixing diagram, group C values cluster near wet-season monsoonal freshwater values (Fig. 26). When compared to similar age, Hell Creek unionids from Dettman and Lohmann (2000) and Dennis et al. (2013), group C values plot near intermediate elevation precipitation values recorded in the 4 values of sample D&L-3192 (Fig. 28). The lowest $\delta^{18}$O$_{\text{CaCO}_3}$ values of group C may also be recording an influence from snowmelt at higher elevations within the catchment if significant dilution with lower elevation groundwater occurred as the river progressed toward the coast.

Figure 24: Mixing diagram displaying estimated freshwater and seaway values and the influence of snowmelt.
Figure 25: $\delta^{18}$O and $\delta^{13}$C plot.

Figure 26: Mixing diagram with group B and C values.
Figure 27: IAEA Global Network of Isotopes in Precipitation (GNIP) values for monsoonal precipitation in New Delhi.

Figure 28: Mixing diagram with values from this study (circles), Dettman and Lohmann (2000) (diamonds) and Dennis et al. (2013) (stars).
CHAPTER SIX: CONCLUSION

Bivalve $\delta^{18}O$ and $\delta^{13}C$ values reflecting coastal river compositions along the western shoreline of the late Maastrichtian WIS range from -10.5 to -2.8‰ and -8.2 to 5.6‰, respectively. A positive correlation between $\delta^{18}O$ and $\delta^{13}C$ values found in specimens lower in the section, reveals that the lowest $\delta^{18}O$ values occurred during times of peak summer soil respiration, whereas the highest $\delta^{13}C$ values of up to 5.6‰ record a marine influence. With the lowest $\delta^{18}O$ values occurring during peak summer convective rains and marine inundation during the dry season, these data support rainout during a summer monsoon as the cause for the lowest $\delta^{18}O$ values recorded by the unionids in this group. The two valves collected higher in the section have an alternating correlation between $\delta^{18}O$ and $\delta^{13}C$ and plot closer to high elevation rain values on a mixing diagram. The lowest $\delta^{18}O$ values of this group are likely recording rain or snowmelt values at a higher elevation in the catchment. The apparent loss of the summer monsoon between the two unionid groups is likely in response to decreasing surface temperatures and the retreat of the seaway. The deterioration of this temperature-sensitive phenomena during this cooling trend provides insight into the potential for increased intensity of modern monsoons in response to increasing surface temperatures and sea-level rise.
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APPENDIX

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