Stratigraphic expression and numerical modeling of meteoric diagenesis in carbonate platforms during the Late Paleozoic Ice Age

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Abstract

The history of life on Earth is intricately tied to the coevolution of the biosphere, atmosphere, and lithosphere over billions of years. Ancient sediments are the fragmented historical record of the interactions among these systems. The Late Paleozoic Ice Age (LPIA) is an interval of extreme climate change and variability that is expressed in the physical and chemical stratigraphy of tropical sediments. The focus of this thesis is refining strategies to extract information about global and local sea level from carbonate-rich sedimentary basins.

The second chapter explores the impact sea level had on the stratigraphic expression of carbonate cycles from the late Pennsylvanian. These carbonate cycles classically are interpreted as the sedimentary response to Milankovitch-style orbital forcing of climate in the Late Paleozoic, but the lateral synthesis of sedimentary facies and their carbon isotopic values suggests that sea level change was a minor component to sedimentary expression in the basin. Therefore, late Pennsylvanian ice sheets were relatively stable and not responding rapidly to changes in orbital forcings.

The third chapter investigates a globally expressed sedimentary unconformity near the middle Carboniferous boundary. Glacial expansion and subsequent sea level fall results in sedimentary hiatus and meteoric diagenesis of the carbon isotopes in the exposed carbonates. The observations of negative carbon isotopes in the carbonate platforms motivates the exploration of the impact on the global carbon cycle, and suggests that the $\delta^{13}C$ of the ocean may be elevated during glacioeustasy of the LPIA. This result offers a much needed improvement on global biogeochemical models that have struggled to provide a congruent solution to the high $\delta^{13}C$ of the LPIA. The final chapter provides numerical methods to interpret superimposed seawater and meteoric diagenetic isotopic signals in the stratigraphy. The merger of these numerical methods and the carbon and calcium isotopic excursions beneath the middle Carboniferous unconformity offers insight into the processes by which sea water chemistry, carbonate weathering, meteoric diagenesis, and local platform hydrology contribute to the composite stratigraphic record.

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The path that led me to the geosciences and to pursue a PhD focusing on carbonates in deep time is filled with so many inspirational scientists, teachers, and friends. This accomplishment is a testament to the combined effort of all these people that have impacted my life and their commitment to the pursuit of scientific curiosity. To all those mentioned below, and to those I forgot, I sincerely thank you.

I first became aware of the geosciences during freshman orientation week at Rice University. I was walking through an academic fair where departments try to get the interest of incoming students. I remember that I was certain that I would become a theoretical physicist and had absolutely no interest in other departments. Somehow this jovial Swiss man with a giant inviting smile caught my attention. Within minutes of sitting down with Andrè Droxler of the Earth Science department, I was convinced that Earth Science was the only discipline for me. Little did I know at the time that a few years later Andrè would be the one to give me my first close encounter with carbonates through a fantastic field trip to the reef in Belize.

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Chapter 1

Introduction

1.1 The Stratigrapher’s Undertaking

The fundamental task of stratigraphy is to reproduce an environmental message from the past. This environmental information is transmitted into sediments, buried, and sometimes returned to the surface for the stratigrapher to receive, but the successful decoding of that message requires a complete comprehension of the processes involved in the recording, transmission, and degradation of that information over millions of years. The target of this thesis is to infer environmental change from tropical carbonate-dominated sedimentary basins that were deposited during the Late Paleozoic Ice Age (331–260 million years ago) under the influence of extreme variations in climate and sea level.

Classic communication theory offers an insightful analogy to the problem of stratigraphy (Figure 1.1; Shannon 1948). The information source is the environment of the past Earth, and the information of interest may be some combination of climate, sea level, or the evolution and extinction of species. These properties of the planet currently are changing at rates that we can observe on human timescales: climate is warming, sea level is rising, and many species on land are facing extinction (Barnosky et al., 2011). The present offers a narrow perspective on the magnitude and rates of environmental change, while the information
Figure 1.1: The diagram and text in black correspond to a figure on communication theory from Shannon (1948) illustrating the flow of information. This framework is used as an analogy for the job of the stratigrapher. Environmental information is transmitted into sediments through various predictable mechanisms as physical and chemical properties. Geologic time can introduce less predictable, noisy degradation of the original message before the stratigrapher receives it in the present.

recorded in the sedimentary record presents the full range of naturally occurring variability in the past environment. Therefore, the endeavor of reproducing the environmental information stored in Earth’s sedimentary shell provides the baseline to differentiate naturally occurring change from human induced change.

Past environmental information is transmitted into sediments as physical and chemical properties through many mechanisms. For example, variations in climate can impart changes in the chemistry of the ocean, and these changes can be observed in chemical sediments that precipitate from the water column, such as carbonates (e.g., Hayes et al. 1999; Zachos et al. 2001). The distribution of the fossilized remains of animals may document local habitat change, preservation, or biological evolution. However, those same animals may burrow through sediments and reorder or destroy some of the information previously recorded, and chemical reactions between sediments and rainwater may overprint the record of seawater chemistry. These destructive processes, and many others, reveal new information about the past environment while overprinting other environmental signals. In the above
examples, burrows may indicate that the sediment-water interface had enough oxygen to support animals, and meteoric diagenesis reveals that the local sea level went down. Typically, diagenetic processes are viewed as purely destructive, but the inference of sea level change from the evidence of meteoric water–mineral reactions is a central theme in each of the chapters presented in this thesis. The complexity in the stratigraphic expression of past environments is a result of competition among many such simultaneously destructive and transcriptive processes that are subsequently filtered through the physics and chemistry of sedimentary transport and burial. In addition to this complexity, there is some degree of less predictable geologic noise added to the environmental message as it passes through the *channel* of time. The Late Paleozoic Ice Age (LPIA) is an interval of extreme climate change and variability that is expressed in the physical and chemical stratigraphy of tropical sediments. The environmental messages stored in these rocks offer the perfect natural setting to refine strategies to extract information about global and local sea level from carbonate stratigraphy.

### 1.2 The Late Paleozoic Ice Age

In the time leading up to the first evidence of Late Paleozoic Ice sheets, the major continental land masses were converging into the super continent known as Pangea (Morel and Irving, 1981; Irving, 2004; Van der Voo et al., 1984; Domeier et al., 2011). The coincidence of this major plate tectonic restructuring and the evolution and expansion of terrestrial forests has inspired many theories about the mechanisms driving late Paleozoic cooling. Some of the glaciation observed during the Late Paleozoic Ice Age may be due to the rise of land along wet convergent margins above elevations where snow can accumulate and persist throughout a full year (Eyles, 1993). This uplift also could increase the efficiency in the removal of CO$_2$ from the atmosphere through reactions with newly exposed mineral surfaces (Siever, 1968; Broecker, 1971), and CO$_2$ is a greenhouse gas that regulates the surface tem-
temperatures through the partial absorption Earth’s outgoing infrared radiation (Owen et al., 1979). This interval of tectonic convergence also corresponds with the evolution and geographic expansion of forest ecosystems. These plants may have led to increased nutrient supplies to the ocean through more efficient chemical weathering, leading to the transfer of carbon from the atmosphere into a growing biosphere and the cooling of the atmosphere (Schwartzman and Volk, 1991). The validity of many of these ideas still remains to be tested with the stratigraphic record of Late Paleozoic climate. The specific timing and distribution of Late Paleozoic ice, as recorded by the sediments deposited adjacent and beneath ice sheets (the nearfield sedimentary record), offers one perspective on the climate history. In contrast, sediments accumulating in the paleo-tropics at the time (the farfield sedimentary record) may record the environmental message through different mechanisms. Therefore, the combination of observations from both records is a necessary tool to discover the climate forcings that underpin the complete stratigraphic story. The importance of considering both records is demonstrated by studies from the Pleistocene, where resolving northern hemisphere glaciation required a synthesis of the spatially and temporally discontinuous nearfield glacial records and the more continuous deep sea records (Imbrie and Imbrie, 1986; Emiliani, 1995).

1.2.1 Nearfield Record of Glaciation

The Initiation of the Ice Age

The work of many stratigraphers has been synthesized in a set of compilations that provide a level of detail to the glacial history that reveals a world of dynamic relatively short-lived (1-8 million years) ice sheets that are punctuated by periods of warmer climate (Frakes and Crowell, 1969, 1970; Frakes et al., 1971; Crowell and Frakes, 1971a,b, 1972; Crowell, 1978; Visser, 1997; Isbell et al., 2003; Fielding et al., 2008b; Gulbranson et al., 2010; Montañez and Poulsen, 2013). Basins from Brazil and Peru contain some of the first sedimentary evidence for glaciation starting at the end of the Visean (346.7–330.9 Ma) (Caputo et al.,
Figure 1.2: This figure depicts the complete published nearfield geologic record of glaciation during the Carboniferous (adapted from Montañez and Poulsen 2013). Dark blue boxes correspond to intervals where sediments or features associated with grounded ice have been observed, and the light blue boxes correspond to intervals where there sedimentary record suggests possible ice sheets. Chapter 2 in this thesis focuses on the Late Carboniferous, and Chapters 3 and 4 focus on the middle Carboniferous, and these time intervals are highlighted on the figure by the numbers circles.

2008). Tournaisian (358.9–346.7 Ma) and Visean stratigraphy from nearby Bolivia is more complex, where coals that formed in temperate climates are truncated by a sedimentary hiatus at the end of the Visean that spans the Serpukhovian (330.9–323.2 Ma) (Isaacson and Martinez, 1995). The 3rd and 4th chapters of this thesis focus on the farfield expression of this same interval of hiatus (Figure 1.2 and 1.3).

The Pulse of the Ice Age

In the Parana basin of Brazil, sediments from the middle Serpukhovian to the end of the Carboniferous (298.9 Ma) reveal glacial pulses interrupted by regionally coincident non-deposition and valley incision (Rocha-Campos et al., 2008; Holz et al., 2008). The timing of glacial advance and retreat in the upper Carboniferous as inferred from these sequence boundaries roughly agrees with observations from southern Africa, Oman, Australia, Antarctica, and India (Veevers and Tewari, 1995; Stollhofen et al., 2008; Martin et al., 2008; Mory et al., 2008; Fielding et al., 2008a; Isbell et al., 2008). The 2nd chapter of this thesis is a
Figure 1.3: This photograph portrays the end Visean unconformity in the Arrow Canyon section of southern Nevada, USA. The white line corresponds to the exposure surface that spans the western United States, and forms the backbone of chapters 3 and 4 in this thesis.
focused investigation of the farfield record during this period of dynamic glacial advance and retreat.

1.2.2 Farfield Record of Glaciation

Shelf sediments on all major continents contain a significant hiatus during the Serpukhovian, and many carbonate sequences in the tropics are replaced by siliciclastics prior to this hiatus (Saunders and Ramsbottom, 1986). Where the stratigraphy around the hiatus is more complete, the age of fossils in the sediments reveal that the hiatus begins near the end of the Visean and deposition resumes a few million years later in the Serpukhovian. Deep sedimentary environments lack a long lived hiatus at this interval (Cantabrian Mountains, Spain (Sanz López et al., 2006; Nemyrovska et al., 2011)) and can consist of repeating deep to shallow sedimentary cycles (Donets Basin, Ukraine (Eros et al., 2012)). The global correspondence of hiatus in shelf sediments and the continuous nature of deep water sections is consistent with a drop in sea level near the end of the Visean. In North America, this stratigraphic gap famously is known as the Mississippian–Pennsylvanian boundary. In the west, this boundary sits above extensive stable crinoidal and coralline carbonate banks (bottom of Figure 1.3), and is expressed as limestone karst towers, solution collapse breccia pits, red terra rossa, dolomitization, caves, and pervasively recrystallized carbonates capped in fossilized tree roots. Chapter 3 of this thesis integrates five years of field work aimed at providing a coherent regional and global context to the physical and chemical features associated with this interval of hiatus, and the results presented therein offer new evidence for the expansion or initiation of the Late Paleozoic Ice Age at that time.

Above the middle Carboniferous unconformity, the tropical sedimentary basins of the Late Paleozoic are comprised of cyclic stacks of meter-scale upward-shallowing parasequences (cyclothsems; Figure 1.4). These parasequences are bounded by flooding surfaces, and the facies within often exhibit a progression from low to high energy sedimentary facies. Variations in sea level or climate, as a result of predictable orbitally driven ice volume changes, may
Figure 1.4: The fresh snowfall in this photograph of classic cyclic carbonate parasequences in Utah, USA highlights the differential erosion between the recessive sedimentary facies that correspond to the bottom of cycles and resistant sedimentary facies at the tops of cycles.
be responsible for forming many of these cyclothems (Wanless and Shepard, 1936; Ross and Ross, 1985; Heckel, 1994). However, sea-level change estimates from different Late Paleozoic basins and authors vary by up to 150 meters (see compilation in Rygel et al. 2008). This variability could arise from an incomplete understanding of the process by which sea level is recorded in tropical sediments (Figure 1.1), or it could indicate that the cycles are not generated by a single, global sea level signal.

The relationship between cyclothems and glacioeustasy is complicated because ordered sedimentary cycles may form from either random or periodic inputs. Sediment supply, accommodation space, biological productivity, and prevailing atmospheric forces all vary periodically with glacial-interglacial change and may be recorded as ordered sedimentary cycles. Sedimentary transport ultimately is responsible for the stratigraphic record, and all environmental inputs are filtered through the physical thresholds of transport mechanisms. This sedimentary process may obscure periodic forcings in the resulting stratigraphy, or generate patterned stratigraphy where no periodic forcing exists (Jerolmack and Paola, 2010). The extensive cyclic sediments and the potentially large environmental forcing of the Late Paleozoic icehouse make it the ideal place to study the relationship between sea level change and carbonate parasequences. Chapter 2 of this thesis provides new insights into the sea level history from regional integrated high resolution stratigraphy of the most famous of Late Paleozoic carbonate cyclothems, which are photographed in Figure 1.4.

1.3 Conclusions

The environmental messages stored in the carbonate sediments of the Late Paleozoic Ice Age include information about the rates and magnitudes of sea level and climate change that are more extreme than those observed in Cenozoic records of climate (Zachos et al., 2001; Montañez and Poulsen, 2013). Therefore, these sediments are the perfect target to reproduce the environmental signal of natural variability in Earth’s sea level and climate from carbonate
stratigraphy. In Chapters 2 and 3, the geochemical observations of carbonate–rainwater reactions at exposure surfaces reveal information about sea level change and glacioeustasy during the Late Paleozoic Ice Age. These observations motivated questions about the potential ramifications these mineral–fluid reactions may have on the global carbon cycle. Chapter 3 expands on this question through box modeling of the global carbon cycle to help explain the abnormally high $\delta^{13}C$ of the upper Carboniferous ocean. The numerical modeling presented in Chapter 4 of mineral–fluid reactions offers a new perspective on the process by which local fluid flow, weathering, and sea level fall are recorded in the carbon and calcium isotopes beneath exposure surfaces.
References


Holz, M., Souza, P., and Iannuzzi, R., 2008, Sequence stratigraphy and biostratigraphy of the Late Carboniferous to Early Permian glacial succession (Itararé subgroup) at the eastern-southeastern margin of the Paraná Basin, Brazil: Resolving the late Paleozoic ice age in time and space, p. 115.


Isaacson, P. and Martinez, E. D., 1995, Evidence for a middle-late Paleozoic foreland basin and significant paleolatitudinal shift, Central Andes.


REFERENCES


Martin, J., Redfern, J., and Aitken, J., 2008, A regional overview of the late Paleozoic glaciation in Oman: Resolving the late Paleozoic ice age in time and space, p. 175.


Mory, A., Redfern, J., and Martin, J., 2008, A review of Permian–Carboniferous glacial deposits in Western Australia: Resolving the late Paleozoic ice age in time and space, p. 29.


Ross, C. and Ross, J., 1985, Late Paleozoic depositional sequences are synchronous and worldwide: Geology, v. 13, p. 194.


Chapter 2

Physical and Chemical Stratigraphy Suggest Small or Absent Glacioeustatic Variation During Formation of the Paradox Basin Cyclotherms

2.1 Abstract

The Paradox Basin cyclotherms previously have been interpreted as Milankovitch style glacial-interglacial cycles from the Late Paleozoic Ice Age, but an unambiguous test for a glacioeustatic origin has not been conducted. A high resolution coupled chemical and physical stratigraphic analysis of two outcrop sections and three core segments provides

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new evidence that supports either minor sea level change of several meters or an autocyclic mechanism for parasequence formation. High amplitude sea level change is ruled out by the scale of thin top-negative isotopic meteoric diagenesis trends associated with parasequence tops and subaerial exposure fabrics. Isotopic gradients from shelf (light) to basin (heavy) indicate that parasequences are deposited diachronously, with isotopes of the more distal sections recording a more restricted basin. These results support the idea that the late Pennsylvanian was a prolonged period of relatively static eustasy, agreeing with recent studies in the western USA. The methods provide a new set of tools and context for extracting environmental information from cyclic upward shallowing carbonate parasequences.

2.2 Introduction

Ice sheets intermittently covered the south pole for nearly 70 million years (330 ma to 260 ma) during the late Paleozoic ice age (LPIA) (Veevers and Powell, 1987). In the LPIA tropics, ubiquitous cyclic sedimentary basins recorded the onset, dynamics, and eventual demise of this icehouse period. These records provide a basis for understanding the climate, vegetation, and glacial dynamics of a long term warming trend during an icehouse interval, which may be relevant to understanding and predicting the consequences of modern climate change (Stocker et al., 2013). The sedimentary record is fundamentally complex, incorporating information about climate, tectonics, and biology as well as the internal forcings of the sedimentary system, all recorded through the physics and chemistry of sediment transport. Comprehensive basin- and global-scale studies of the physical and chemical stratigraphy allow one to deconvolve this record into each of its components. These components have been used to reconstruct a rich history of the LPIA (Montanez and Poulsen, 2013), but further research on the sensitivity of the sedimentary system to the unique boundary conditions of that time can improve estimates of associated ice volume and eustatic changes.
Throughout Euramerica, LPIA sedimentary basins are comprised of cyclic stacks of meter-scale upward-shallowing parasequences (cyclothems). These parasequences are bounded by flooding surfaces, and the facies within often exhibit a progression from low to high energy sedimentary facies. Variations in sea level or climate, as a result of predictable orbitally driven ice volume changes, may be responsible for forming many of these cyclothems (Wanless and Shepard, 1936; Ross and Ross, 1985; Heckel, 1994). However, sea-level change estimates from different LPIA basins and authors vary by up to 150 meters (Rygel et al., 2008). This variability could arise from the noise introduced by the sedimentary system, or it could indicate that the cycles are not generated by a single, global sea level signal.

The relationship between cyclothems and glacioeustasy is complicated because ordered sedimentary cycles may form from either random or periodic inputs. Sediment supply, accommodation space, biological productivity, and prevailing atmospheric forces all vary periodically with glacial-interglacial change and may be recorded as ordered sedimentary cycles. Since sedimentary transport is ultimately responsible for the stratigraphic record, all environmental inputs are filtered through the physical thresholds of transport mechanisms. This sedimentary process may obscure periodic forcings in the resulting stratigraphy, or generate patterned stratigraphy where no periodic forcing exists (Jerolmack and Paola, 2010). The extensive cyclic sediments and the potentially large environmental forcing of the late Paleozoic icehouse make it the ideal place to study the relationship between sea level change and carbonate parasequences.

### 2.2.1 The Paradox Basin

The Paradox Basin (Figure 2.1) is a foreland basin formed by flexure adjacent to the Uncompahgre uplift that is filled with cyclic marine sediments and evaporites from the Pennsylvanian subperiod (Barbeau, 2003). Stacked upward-shallowing carbonate parasequences exist along the margins of the basin, and the interior sediments are salt and sapropel interbeds (Hite and Buckner, 1981). Peterson and Hite (1969) identified 29 salt-sapropel basinal cy-
cles that are thought to correlate to major carbonate sequences developed on the peripheral bulge. The correspondence of these lithologically distinct cycles implies that a single mechanism is responsible for cyclicity on the shelf and in the basin. These carbonate sequences are separated by regionally extensive black sapropel shales that are easily identified in analog core logs due to their contrasting gamma ray signal with carbonates and evaporites. Each of these roughly 30 meter thick (4th order) sequences is comprised of 4-6 meter-scale (5th order) upward-shallowing parasequences. This relationship is illustrated in Figure 2.2A. Since these parasequences lack a significant fluvio-deltaic siliciclastic component, it is unlikely that the parasequences were generated by cyclic wet to dry climate changes as discussed in Cecil (2003), although the larger scale sequences may be partially controlled by regional climate.

Goldhammer et al. (1991) used the spectral properties of the thickness distribution of these meter-scale cycles to argue that a hierarchical stacking of these sequences may have been generated by the modulation of obliquity (41 ka) and long term eccentricity (413 ka). However, since non-random stratigraphy does not provide unambiguous origin for the cycles, it is necessary to seek new independent evidence of a causal mechanism that will support or reject the idea that glacioeustasy is responsible for the generation of cyclothems in the Paradox Basin. Only a successful positive test that glacioeustasy is responsible for the parasequences can allow the use of the Milankovitch model to understand the frequency and amplitude of ice volume change in the Pennsylvanian. During the modern icehouse, large sea level drops of up to 120 meters exposed the Bahama bank, and meteoric waters significantly altered the carbon and oxygen isotopes of the carbonates (Swart and Eberli, 2005). Top-down early meteoric diagenesis can be preserved in the isotopes of ancient carbonates (Allan and Matthews, 1982), and this signature would be expected for carbonate platforms that were exposed during sea level fall. Oxygen isotopes in carbonate phases are subjected to isotopic exchange with subsurface fluids, and may not reliably preserve ancient primary or early diagenetic signals (Jacobsen and Kaufman, 1999). Carbon isotopes, on the other hand, are generally more resistant to diagenetic changes and often are used as a proxy for the isotopic
composition of the dissolved inorganic carbon (DIC) of ancient seawater. However, early
diagenesis during exposure to CO$_2$ rich meteoric fluids has high potential for preservation
if the sediments are not eroded away during exposure. These altered sediments may be
targeted by proximity to exposure surfaces and through physical evidence of dissolution and
recrystallization, and the correspondence of anomalously light carbon isotopes and these
physical features could indicate meteoric diagenesis.

Coupled high resolution chemical and physical stratigraphic data from two shelf carbonate
outcrops and three basinward cores are presented below. Small (< 5 meter) scale meteoric
diagenesis associated with some cycle caps might indicate that if sea level were changing, the
amplitude is small. Additionally, very heavy carbon isotopes in the basin-ward cores suggests
increased restriction of the basin and diachronous deposition of parasequences from the
peripheral bulge to the basin interior. Carbonate buildup in the shallow seaways connecting
the Paradox Basin to the global ocean is the simplest mechanism to explain the observed
geochemistry, and the diachronous depositional cycles without requiring large changes in
global sea level.

2.3 Methods

In the field, the sediments of the Honaker Trail and Paradox formations were classified into
ten lithofacies based on environmentally sensitive sedimentary structures and the Dunham
classification scheme for carbonate sediments (Dunham, 1962). Parasequences were identified
as a sedimentary sequence that shallow upwards and is bounded by flooding surfaces. 55
upward-shallowing parasequences between 0.9 and 28.4 meters thick were identified in a 350
meter section measured along the Honaker Trail (Figure 2.4). At a second shorter outcrop
section, the Raplee syncline east of Mexican Hat, 33 parasequences were identified. Where
these sections overlap, only 3 parasequences were not identified in both sections, and in
all three cases the interval in the other section is covered and has no outcropping strata.
Figure 2.1: Pennsylvanian Isopach map of the Paradox Basin region with core and outcrop study locations. Isopachs are 150 meter intervals from Peterson and Ohlen (1963). The orange region represents the extent of carbonate facies during the Desert Creek and Ismay sequences based on labeled cores from the USGS Core Research Center and from Peterson and Ohlen (1963).
Additionally, three core segments at the USGS Core Research Center in Denver, CO were described and sampled for isotopic analysis. These cores segments span the Ismay sequence, as identified by the basal Gothic Shale.

Nearly 3000 carbonate samples, from roughly every 20-30 cm in each section and core studied, have been analyzed for $\delta^{13}$C and $\delta^{18}$O. These samples were slabbed and polished to selectively microdrill micrite for isotopic analysis. All carbonate powders were heated to 110 °C to remove water. Samples were then placed in individual borosilicate reaction viles and reacted at 72 °C with 5 drops of H$_3$PO$_4$ before the CO$_2$ analyte was sent to the IRMS. Measured precision is $\pm 0.1$‰ for carbon and $\pm 0.2$‰ for oxygen. The samples were analyzed with either a Thermo DeltaPlus continuous flow IRMS or a Sercon IRMS coupled with a GasBench II sampling device. An additional subset of samples were analyzed in the University of Michigan Stable Isotope Laboratory on a Finnigan MAT 251 triple collector isotope ratio mass spectrometer with a Kiel I preparation device. $\delta^{18}$O and $\delta^{13}$C data are reported in the standard delta notation relative to the Vienna Pee Dee Belemnite (VPBD) standard.

Figure 2.2: (Next Page) (A) Honaker Trail and Raplee sections with corresponding $\delta^{13}$C and $\delta^{18}$O of carbonate. Parasequence tops are marked in red or orange. Orange parasequence tops correspond to parasequences with strata that have physical evidence of dissolution or recrystallization. Red parasequences lack obvious physical signs of diagenesis, and were identified by flooding surfaces and facies progressions. Dark green or dark red sample symbols mark samples collected from beds that were identified in the field with potential diagenetic features. The 4th order sequences from Goldhammer et al. (1991) are labeled on the left. (B) Select parasequences from the Honaker Trail and Raplee syncline that exhibit top-negative isotopic $\delta^{13}$C trends associated with exposure such as brecciation, root traces, and dissolution features. Parasequences from the Honaker Trail section have been slightly stretched (< 1 meter) so that the tops in each section align.
2.4. RESULTS

Figure 2.2
2.4 Results

Grammer et al. (1996) and Goldhammer et al. (1991) have described the facies in the Paradox basin in great detail. Deep, low energy environments favor the accumulation of silt and mud, often have thin planar bedding, and lack bioturbation. More energetic wackestones and packestones contain abundant skeletal material, bioturbation, scours, low silt and mud fraction, and fossil assemblages composed of: bryozoa, brachiopods, crinoids, rugose corals, and fusilinids. These features indicate a normal marine depositional environment, perhaps between storm wave base and fair weather wave base. Cross-bedded, mud-free grainstones formed as high energy shoals above fair weather wave base where wave energy abraded skeletal remains, winnowed away carbonate muds, and coated grains with layers of micrite. Coralline (*Chaetetes* and *Syringapora*) and stromatolitic patch reefs formed in the shallow low energy areas protected by these roaming carbonate shoals. Cryptagal laminites, often laterally transitioning into mud chip breccias and mudcracks, are partially dolomitized and represent deposition very near or in the intertidal zone (peritidal).

These facies are organized in meter-scale upward-shallowing carbonate parasequences that have been grouped into 4th order sequences bounded by regionally extensive black shales (Figure 2.2). These black shales can be traced into the basin through core records and gamma ray logs and correspond to sequence bounding units on salt-sapropel cycles (Peterson and Hite, 1969). Of the meter scale 5th order parasequences observed in outcrop along the San Juan River, 16 parasequences are capped by unequivocal exposure surfaces, evidenced by root fossils or desiccation cracks. In each of these exposure sequences, the cap facies often contain stylolites, fossilized root traces, calcite filled popcorn to fist sized vugs, or pervasive fabric destructive recrystallization. Carbon isotopes in the lower portions of these exposure-topped parasequences are between 2‰ and 4‰, the same range as other Pennsylvanian records (Saltzman, 2003). Up section, the carbon isotopes monotonically decline to values as low as -5‰ approaching the exposure surface (Figure 2.2), and there is a stronger positive covariance between $\delta^{13}C$ and $\delta^{18}O$ in these samples (Figure 2.3B).
Within tens of centimeters above the exposure surface, carbon isotopes abruptly return to the positive values of +2 to +4‰.

Of the 1087 outcrop samples analyzed, there are more light carbon isotopes in shallow facies (Figure 2.3A). However, when physical evidence of exposure, such as dissolution features, heavy recrystallization, dolomitization, root horizons, or mud cracks is used to filter the dataset for potential diagenesis, the carbon isotopic values of shallow, intermediate, and deep facies have similar distributions (Figure 2.3A). Since the isotopic value of the unaltered sediments is not changing rapidly in time, the lack of a gradient from shallow to deep facies indicates that there were no large vertical (water depth) or lateral gradients in the $\delta^{13}C$ of the Paradox basin.

All of the sedimentary lithofacies present in outcrop along the peripheral bulge are also present in 3 cores spanning a 120 km transect (Figure 2.1) towards the basin interior. However, wackestones are more abundant in sections closer to the basin interior, while grainstone and packestone are more abundant on the edge of the basin. 5th order parasequences can not be reliably traced into these cores, but the large scale sequences, such as the Lower Ismay interval, are easily identified by the corresponding basin-spanning black shales. During the Lower Ismay interval, the $\delta^{13}C$ of carbonate in outcrop along the shelf edge is between +2 and +4 ‰, which is in line with values reported by Saltzman (2003) from other locations along the Panthalassic margin. Approaching the foredeep, the $\delta^{13}C$ of carbonate increases to values of +5 to +6 ‰ (Figure 2.4).

2.5 Discussion

2.5.1 Diachronous Deposition

The carbon isotopic data from these sections is difficult to explain with synchronous deposition of cycles and sustained isotopic gradients in the Paradox basin. In modern carbonate environments, lateral gradients in the isotopic composition of dissolved inorganic carbon
result from two mechanisms. In the Bahamas, waters on the carbonate platform are continually scavenged of light carbon by grasses and algae, and in many places the mixing time is relatively slow compare to the residence time, resulting in sustained isotope gradients across the shelf (Broecker and Takahashi, 1966). This gradient is further enhanced because aragonite, which is heavier than calcite, dominates inner shelf deposition while the outer shelf and slope environments have more calcitic plankton. The combined effect accounts for isotopic gradients of 1-2‰, with heavier sediments deposited on the platform. Since this mechanism results in heavier nearshore deposition, it can not explain the distal enrichment observed in the Paradox Basin. Alternatively, in the Florida Bay, river water discharged from the Everglades is loaded with isotopically light remineralized organic which overwhelms the marine water chemistry and results in isotopically lighter carbonates deposited nearshore (Patterson and Walter, 1994). The resulting lateral gradient in carbon isotopes could explain the lighter
carbon isotopes deposited nearshore, but it cannot account for carbon isotopes further into the basin that are heavier than Pennsylvanian $\delta^{13}C$ from the rest of Laurentia (+3 to +4 ‰, Saltzman (2003)). The carbon isotopes from the two nearshore sections, Honaker trail and Raplee, are consistent with these Laurentia values, but the Ismay sequence in the most basinward cores is enriched up to +6‰, which is significantly heavier than any other open ocean carbonates deposited along the Panthalassic margin. It is also evident from the overlying Cutler formation that fluvial input to the Paradox Basin came from the Uncompaghre uplift in the northeast. Therefore, the most significant river input would be on the wrong side of the basin to explain the observed gradient. Furthermore, a lateral gradient of carbon isotopes would be preserved as offsets in the isotopes by facies from a single location. Marls and wackestones, deposited distally from carbonate tidal flats should be heavier than grainstones and packestones deposited nearshore. Figure 2.3 illustrates the distribution of carbon isotopes grouped by depositional environment for the Honaker trail and Raplee outcrop sections. For this figure, peritidal breccias and grainstones are considered shallow, packestones are intermediate, and subtidal marls, mudstones and wackestones are deep. The mean values for all three depth ranges are between 2.18 and 2.42 ‰, and the distributions are consistent enough to conclude that there are no facies dependent trends in the data. Since none of these mechanisms for maintaining lateral isotopic gradients fully explain the observations presented here, it is worth considering the possibility that parasequences in this basin were deposited diachronously. The carbonate platform could prograde from the foreland bulge towards the basin interior, and the chemistry of the carbonates would then track changes in basin seawater over this time period. Therefore, the enrichment in $^{13}C$ observed in the basinward sediments may be related to the same process driving the progradation of the carbonate tidal flats.

The Paradox is an intracratonic basin that may be highly sensitive to changes in shape or depth of shallow seaways that connect it to the Panthalassic ocean through a series of basins (See Figure 2.1). The Oquirrh basin is immediately to the northwest and the
San Juan Basin is to the southeast. The seaway connecting the Paradox to the Oquirrh is narrow (< 50 km) and the entire preserved Pennsylvanian accumulation in this region is less than 150 meters, whereas the connection to the San Juan basin may be up to 100 km wide and underwent greater subsidence during the deposition of the Honaker Trail and Paradox formations. Since the $\delta^{13}C$ of the carbonates along the basin margins matches the late Pennsylvanian Panthalassic ocean, these sediments were most likely deposited during a stage where the flux of waters into and out of the basin was high enough to keep the nutrients and dissolved inorganic carbonate composition in equilibrium with Panthalassia.

2.5.2 Basin Restriction

The presence of salt-sapropel cycles in the foredeep indicates a second state where the water in the basin is stratified or restricted enough for evaporite deposition. Marine evaporites today only occur in shallow environments such as sabkhas and lagoons. In deep, mostly land-locked basins, such as the Red Sea, salinities do not reach levels high enough for evaporites since any salt transported from the surface into the deep waters of these basins is carried out by countercurrents (Brongersma-Sanders, 1971). However, evaporite deposition in deep basins is well known in the geologic record, with examples such as the Messinian salinity crisis of the Mediterranean Ocean (Ryan, 1973; Hsu et al., 1977). The salts of the Paradox are located in the region of the basin with the greatest subsidence and accommodation space, and the edges of the basin, where the shallowest environments occur, do not have evaporites. The deep water evaporite model of Schmalz (1969) reconciles the thick distribution of cyclic evaporites in the deepest part of the Paradox Basin. Deep water evaporites only form if there exists a trap to keep dense deep water brines from escaping the basin, such as a shallow exit seaway in a mostly land-locked basin. When surface evaporation exceeds runoff, high salinity can lead to the precipitation of gypsum in the surface, and crystal settling drives the transport of $\text{CaSO}_4$ into the deep. The gypsum will dissolve in the undersaturated deep waters leading to an increase in salinity. If these deep waters can escape the basin and mix with the open
Figure 2.4: (A) Map inset of the Paradox Basin focused on the stratigraphic sections and cores highlighted for the lateral transect. Bold lines are Pennsylvanian-Permian isopach contours of 150 meters adapted from Peterson and Ohlen (1963). The base map is a digital elevation model, with grey 50 meter elevation contours. (B) Side by side comparison of the stratigraphy (Facies legend in Figure 2.2) and carbon isotopes of the Ismay Sequence $\delta^{13}$C along transect A-A'. Each plot contains the carbon isotopes from all 5 sections (gray), and the highlighted color data corresponds to the adjacent stratigraphy.
ocean, then the basin will remain undersaturated. However, a shallow obstruction connecting
the basin to the open ocean may amplify the halocline and lead to a vertically stratified
water column. If the export of organic matter from the surface productivity continues, the
stratified bottom waters will eventually become oxygen limited, and the burial of organic
matter in sapropels will occur. With less remineralized organic matter cycling back into
the surface waters, the DIC will become heavier through time. Eventually, the lack of new
upwelling nutrients will kill off the surface productivity, and the ever increasing salinity will
lead to the deep water precipitation of gypsum (Figure 2.5B). The entire system will reset as
soon as the oceanic conduits open back up, from the shallowing of the basin interior through
rapid salt deposition, or glacioeustatic sea level rise, or as the connecting seaways sufficiently
depen through continued flexural and/or thermal subsidence (Figure 2.5C). Slight changes
in relative sea level of the basin openings, especially if the geometry is wide and shallow, can
significantly alter the interior circulation of the basin and drive the cyclicity of both the deep
basin evaporites and the carbonate rich periphery. Glacioeustasy and carbonate build up are
two mechanisms that could periodically alter the sea level in these regions. If glacioeustasy
is responsible for the basin restriction, there should be physical and geochemical evidence of
deep, penetrative meteoric diagenesis at the fore bulge.

2.5.3 Meteoric Diagenesis

Isotopically light $\delta^{13}C$ of some parasequences tops that get gradually heavier with depth is
evidence of early meteoric diagenesis, but the depth of each diagenetic event at the Honaker
Trail and Raplee outcrops suggests minor or no sea level change. When sea level falls and
carbonate platforms are exposed, meteoric fluids (undersaturated in carbonate and charged
with atmospheric CO$_2$ or respired CO$_2$ from organic material) are driven through the plat-
form by gravity (Thrailkill, 1965, 1968; Matthews, 1974; Bögli and Schmid, 1980). The
freshwater saturated (phreatic) region of the platform experiences extensive dissolution and
often is characterized by the development of large solution cavities and openings, which even-
2.5. DISCUSSION

The mixing of undersaturated meteoric fluids and super saturated marine fluids along the fringes of the freshwater lens can result in the precipitation of new calcite that contains a mixture of carbon and oxygen from both the marine and meteoric systems. Carbon and oxygen from the meteoric system will have a unique isotopic signature derived from a combination of atmospheric values, dissolved marine carbonate, and CO$_2$ generated by the decay of marine and terrestrial organic matter and the respiration of nearby roots from living plants. Organic matter is light in carbon (-25‰) due to kinetic fractionation during photosynthesis, and dissolved atmospheric CO$_2$ is on the order of 10‰ lighter than seawater CO$_2$ due to the kinetics of exchange between atmosphere and water (Hayes, 2001). Marine values normally will be heavier than both of these light reservoirs, so dissolution and reprecipitation of carbonate in a karst system should drive marine carbonates to lighter values. The thickness of meteorically altered, isotopically light carbonate is indicative of the vertical extent of the phreatic zone. The depth of diagenesis in the phreatic zone is a function of the permeability of the vadose cap, and the flux of CO$_2$ charged meteoric waters through the rock. In dry conditions with low permeability sediments, the freshwater to marine isotopic transition will be shallow and sharp near mean sea level. Wet environments with permeable sediments may develop a deep meteoric profiles extending well below mean sea level in locations away from the coastline. Throughout the Pleistocene, the Great Bahama Bank has been exposed to rainwater during the sea level draw down associated with each stadial, and the isotopic values of bulk carbonate in the upper parts of the platform are much lighter than the carbonate precipitated from seawater on and around the bank today (Swart and Eberli, 2005). Clino core is on the shelf edge of the Bahama Bank in 10 m of water and the freshwater lens during the 120 m sea level drop of the last glacial maximum has been interpreted to be at least 100 meters deep based on the downcore isotopic profile. The 100 meter thick top-negative carbon isotope anomaly completely overprints at least 7 glacioeustatic parasequences within this interval that have been identified in the physical stratigraphy and are thought to correspond to Pleistocene glacial-interglacial cycles. Iso-
Figure 2.5: Three stages of the Paradox basin autocyclic model. In stage (A) the ocean is well connected to Panthalassia and the carbonate factory is very active. Carbonate is transported landward and trapped. In stage (B) the tidal flat has prograded over the productive carbonate factory, and restricted the flow through the shallow seaway connecting the basin to the open ocean. The restricted waters result in isotopically heavier carbonate deposition and eventually salt precipitation in the basin. With the carbonate factory turned off at the end of stage (B), subsidence is greater than sedimentation and the tidal flat is flooded. In stage (C), the carbonate factory has the nutrients, light, and time to re-establish itself on top of the old flooded tidal flats, and carbonate once again is transported landward to get trapped in prograding tidal flats. Model is adapted from Ginsburg (1971).

topic depletion with similar vertical scale from the Middle Carboniferous has been identified in Kazakhstan (Katz et al., 2013) and Nevada (Bishop et al., 2009). The meteoric isotopic profile from the Late Mississippian in Arrow Canyon, Nevada goes from $+3\%$ to $-7\%$, and penetrates 60 meters below the exposure surface.

The isotopic profiles of meteoric diagenesis in the Paradox basin are never more than a few meters deep, and stacked parasequences record independent meteoric events without overprinting underlying parasequences. The parasequences illustrated on the right of Figure 2.2B are good examples of these observations. The expectation based on the diagenesis
during the Pliocene is that high amplitude sea level change in the Paradox Basin cycles would result in a single large top negative isotopic anomaly that completely overprints the parasequences below. The mixing zone between the freshwater lens and seawater in coastal carbonate environments is a significant site for the development of porosity and permeability (Back et al., 1986), and repeated cycles of sea level change would subject the lithologic column over the entire range of sea level change to these dissolving forces. The mixing zone in coastal carbonates of the Yucatan peninsula within 1 km of the coastline is between 2 and 4 meters deep, and the $\delta^{13}C$ of the water above the mixing zone is between $-12\%_o$ and $-7\%_o$ (Stoessell et al., 1989). This mixing zone gets deeper further inland, and the shape ultimately is controlled by the amount of freshwater entering the system, the distance from the shoreline, and the permeability of the rock (Budd and Vacher, 1991). Therefore, unless the Paradox basin cycle tops, which are often coarse oolites or coated grainstones, were impermeable to meteoric water, then these shallow meteoric diagenesis profiles cannot be generated by high amplitude sea level change. In fact, sea level change is not a requirement to explain the exposure sequences or negative isotopic profiles. In the case of no sea level change, exposure surfaces are generated by hurricane type storm events that accumulate sediment above the mean sea level, and these local highs develop shallow freshwater lenses. Furthermore, low amplitude periodic sea level change should generate highly ordered parasequence thicknesses. Since the parasequence thicknesses in the Paradox basin are unpredictable and random (Lehrmann and Goldhammer, 1999), the most elegant model for their origin is one controlled entirely by intrinsic sedimentary processes.

2.5.4 Autocyclic Depositional Model

Ginsburg (1971) proposed a sedimentation model for generating regressive carbonate cycles based on observations in the Bahamas, Persian Gulf, and Florida that is completely controlled by the trapping of carbonate near the shore. In this model, carbonate that is produced over extensive open platforms is collected in intertidal lagoons (Figure 2.5A). These
nearshore traps prograde and decrease the carbonate production area, and eventually subsidence outpaces the sediment production, resulting in transgression (Figure 2.5B). In the Paradox basin, carbonate banks are present in core extending into the shallow seaways connecting to the ocean (See Figure 2.1). If the carbonate accumulating in these seaways is tied to the diachronous progradation observed in the shelf to basin transect, then there is a single mechanism that simultaneously explains the paradoxical alternations of sapropel-evaporite in the deep basin, the cyclic nature of carbonates on the peripheral bulge, the elevated δ\textsuperscript{13}C of the basinward sections, and the lack of deep meteoric diagenesis in any of the carbonates.

### 2.6 Conclusions

Isotopic evidence from three cores and two outcrop sections indicates that carbonate parasequences were deposited diachronously from the forebulge into the foredeep of the Paradox Basin. Heavier isotopes in the carbonates from the basin interior are evidence of the increasing anoxic bottom waters associated with stratification and restriction of the basin. Shallow meteoric diagenesis profiles associated with root filled exposure surfaces in some of the parasequences at the forebulge indicate that sea level change associated with the exposure was minor or nonexistent. Additionally, the lack of order in the parasequence thicknesses supports the idea that the stochastic sedimentary system, as opposed to environmental factors, imparted the greatest control on the formation of cycles in the Paradox Basin. Previous studies in the western United States, relying solely on physical stratigraphy, have found that the late Pennsylvanian is a time period of glacial minimum and relatively static eustasy (Bishop et al., 2010), which is consistent with the results presented here. Furthermore, this study demonstrates that laterally extensive coupled physical and chemical stratigraphy can be used to extract environmental information from cyclic upward-shallowing carbonate parasequences, and indicates that local sedimentary and regional basinal processes can significantly contribute to the apparent cyclicity in the stratigraphic record.
2.7 Acknowledgements

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References


Cecil, C. B., 2003, Climate controls on the stratigraphy of a Middle Pennsylvanian cyclothem in North America: Special Publications of SEPM.


Hite, R. and Buckner, D., 1981, Stratigraphic correlations, facies concepts, and cyclicity in Pennsylvanian rocks of the Paradox Basin.


Matthews, R., 1974, A process approach to diagenesis of reefs and reef associated limestones: Special Publications of SEPM.


Peterson, J. A. and Ohlen, H. R., 1963, Pennsylvanian shelf carbonates, Paradox basin:

Ross, C. and Ross, J., 1985, Late Paleozoic depositional sequences are synchronous and worldwide: Geology, v. 13, p. 194.


Chapter 3

Glacioeustasy, Meteoric Diagenesis, and the Carbon Cycle During the Mid-Carboniferous

3.1 Abstract

Mid-Carboniferous carbonates in the western United States have undergone Pleistocene Bahamas-style meteoric diagenesis that may be associated with expanding late Paleozoic ice sheets. Fourteen stratigraphic sections from carbonate platforms illustrate the regional distribution and variable intensity of physical and chemical diagenesis just below the mid-Carboniferous unconformity. Each section contains top-negative carbon isotope excursions that terminate in regional exposure surfaces that are associated with some combination of karst towers, desiccation cracks, fabric destructive recrystallization, or extensive root systems. The timing of the diagenesis is synchronous with similarly-scaled top-negative carbon

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isotope excursions observed by others in England, Kazakhstan, and China. The mass flux of negative carbon required to generate similar isotopic profiles across the areal extent of middle Carboniferous platform carbonates is a significant component of the global carbon cycle. We present a simple carbon box model to illustrate that the $\delta^{13}C$ of dissolved inorganic carbon in the ocean could be elevated by $\sim 1.4\%e$ as isotopically lower carbon from the terrestrial organic weathering reacts with exposed platforms before reaching the ocean and atmosphere. These results represent an improvement on global biogeochemical models that have struggled to provide a congruent solution to the high $\delta^{13}C$ of the late Paleozoic icehouse.

### 3.2 Introduction

Ancient sediments from the late Paleozoic record climate change from a time period with tectonic, evolutionary, and oceanic-atmospheric boundary conditions vastly different than the Cenozoic. This geologic history represents an important opportunity to investigate the forcings and feedbacks of the climate system that can not be gleaned from more recent archives. The ubiquitous diagenetic alteration of carbonates underlying a complex unconformable surface in the western US that spans the middle Carboniferous is presented here to constrain glacioeustatic change and to explore the potential impact that globally extensive meteoric diagenesis may have on the $\delta^{13}C$ of the ocean.

Extensive land ice during the Late Paleozoic led to striated pavements, diamictites, dropstones, and glacial deformation structures across Gondwana (Fielding et al., 2008). Glacially derived sediments in Brazil, Bolivia, and Peru contain pollen and other microfossils from the latest Devonian (Caputo et al., 2008; Isaacson et al., 2008), suggesting possible Gondwanan ice sheets 360 million years ago. These South American ice sheets are thought to be followed by a 30–40 million year long ice-free interval during the Tournaisian (358.9–346.7 Ma) and early Visean (346.7–330.9 Ma) (Isbell et al., 2003). By the start of the Serpukhovian (330.9–
3.2. INTRODUCTION

3.2.1 At 323.2 Ma, there is strong evidence of glaciation in both South America and Australia. Furthermore, detailed stratigraphic analysis of carbonate sections from the tropics indicate major facies distribution changes starting around this interval and persisting well into the Pennsylvanian (Bishop et al., 2009, 2010; Fielding and Frank, 2015).

The early nearfield glacial history could be explained by either large Gondwana-spanning ice sheets, or smaller ice sheets that were growing and shrinking in various locations (Isbell et al., 2003). The oldest radiometric constraints on late Paleozoic glaciation are 60 million years younger than the end Devonian glacial sediments in South America (Stollhofen et al., 2008; Cagliari et al., 2014), and the inconsistencies in the early glacial records could reflect the difficulties of determining the depositional age of glacial sediments from biostratigraphy. Dry coastal climates from icehouse intervals are known to contaminate glaciers and glacial sediments with specious, old microfossils that weather out of exposed coastlines (Hoffman and Maloof, 2003; Kellogg and Kellogg, 1996). Additionally, glaciers may erode and rework underlying stratigraphy before filling a basin with new sediments, and the resulting stratigraphic limits on glacial processes will be too old. Combining the observations from glacial sediments with farfield, tropical marine sediments is a necessary tool for discovering the underlying climate forcings that underpin both records. The importance of considering both records is demonstrated by studies from the Pleistocene, where resolving northern hemisphere glaciation required a synthesis of the discontinuous nearfield glacial records and the more continuous deep sea records (Imbrie and Imbrie, 1986; Emiliani, 1995).

The sedimentary record of Antarctic glaciation during the early Oligocene provides specific predictions for the response of platform carbonates during icehouse initiation. Carbonates on passive margins experienced 15–80 meters of apparent sea level fall and largely were replaced by prograding deltas (Miller et al., 2005). In response to ice growth and cooling, oceanic $\delta^{18}O$ shifted 1–1.5‰ heavier, and an increase in ocean fertility (Baldauf, 1992) and major drop in the calcium carbonate compensation depth (Van Andel et al., 1975) may have lead to 1–2 My of oceanic $\delta^{13}C$ enrichment by 1‰ (Zachos et al., 2001). In the early
Carboniferous, carbon and oxygen isotopic shifts in platform carbonates mimic the observations from the Oligocene (Saltzman, 2002). If analogous, this isotopic record suggests a Tournaisian initiation of the late Paleozoic ice age. However, the timing of this excursion overlaps with the 30–40 million year ice-free interval following the end Devonian glacial sediments from South America, indicating that that the Gondwanan sedimentary record from the mid-Tournaisian is incomplete or that the $\delta^{13}C$ enrichment is not related to glaciation.

If the late Paleozoic icehouse began in the early Carboniferous, then the globally extensive paleotropical sedimentary hiatus in the middle Carboniferous may be evidence of land ice expansion. During the expansion of northern hemisphere glaciation during Plio-Pleistocene ($\sim$3 Ma), global sea level experienced an additional drop of 50 meters (Miller et al., 2005), and the new lower latitude ice albedo dynamics lead to unstable ice sheets that varied periodically with orbitally driven solar insolation changes (Huybers, 2006). The Bahama bank was exposed during the Plio-Pleistocene transition and after subsiding was subsequently flooded during each glacial-interglacial cycle. During exposure, meteoric fluids carrying isotopically lower carbon and oxygen from the overlying soil system reacted with the calcium carbonate of the platform below (Swart and Eberli, 2005). If the mid-Carboniferous hiatus is comparable to ice expansion in the Cenozoic, then the diagenetic reactions observed in the Bahama bank might be expected in carbonates below the stratigraphic horizon marking the expansion of late Paleozoic ice sheets.

### 3.2.1 Mid-Carboniferous Hiatus

Shelf sediments on all major continents contain a significant hiatus during the Serpukhovian, and many carbonate sequences are replaced by siliciclastics prior to this hiatus (Saunders and Ramsbottom, 1986). In the most complete sections, hiatus begins near the end of the Visean and deposition resumes in the Serpukhovian or Bashkirian (322.8–314.6 Ma). Deep basins lack a long lived sedimentary hiatus (Cantabrian Mountains, Spain (Sanz López et al., 2006; Nemyrovska et al., 2011)) and can consist of repeating deep to shallow sedimentary
Figure 3.1: Regional map of the western US during the Mississippian subperiod. Blank regions represent highlands or regions with no Mississippian sediment preservation, and block texture represents marine carbonate deposition. Stratigraphic Sections studied are highlighted and color coded in correspondence with Fig. 3.2. Diagonal lines are paleolatitude (Domeier et al., 2012).
cycles (Donets Basin, Ukraine (Eros et al., 2012)). The global correspondence of hiatus in shelf sediments and the continuous nature of deep water sections is consistent with a drop in sea level near the start of the Serpukhovian, and the deeper section cycles could indicate variable sea level during this interval. In North America, this interval famously is known as the Mississippian–Pennsylvanian boundary, and some regions of the shelf sediments in the western US contain only 2–4 Ma of hiatus.

The middle Carboniferous unconformity in the western US caps extensive Tournaisian and Visean stable crinoidal and coralline carbonate banks known as the Madison Limestone in the north, the Leadville and Redwall limestones in the southeast, the Monte Cristo Group limestones in the southwest, and the Lake Valley Formation of southern New Mexico (Fig. 3.1). The end Visean and early Serpukhovian is always missing in the unconformity, and hiatus in many sections spans a much wider range of time both above and below this interval (Fig. 3.2). The unconformity is expressed as limestone karst towers and solution collapse breccia pits (Fig. 3.3D) in Colorado, red terra rossa (Fig. 3.3E), collapse breccia, dolomitization, and caves in Wyoming, pervasively recrystallized carbonates capped in Stigmarian roots (Fig. 3.3B), soils, sand filled pits, and dissolution collapse breccias (Fig. 3.3A) in southern Nevada (Bishop et al., 2009).

These large scale karst features indicate the importance of erosional processes inland and north of the Nevada sections, which could explain the wide range of ages for the immediately underlying strata. Post hiatus deposition across the region would be controlled by local subsidence, leading to variable ages in overlying sediments as well. All of these observations are consistent with sea level fall, exposure, and erosion of the western US carbonate shelf during the end Visean and may indicate expansion of land ice during the end Visean and Serpukhovian.

Evidence for exposure and sea level fall is expressed in the physical and chemical stratigraphy of western US carbonates. In some areas, the regional unconformity is associated with at least 90 meters of meteoric diagenesis, and a global trigger for this large-scale meteoric
Figure 3.2: Carbon isotopes, depositional ages, and diagenetic reaction calculations for six stratigraphic sections from the upper Mississippian (see Fig. 3.1 for a map of section locations). Colored squares correspond to adjacent stratigraphy, while light grey squares indicate the data from all six sections. Dark grey small squares represent the upper 150 meters of $\delta^{13}$C from Clino core in the Bahamas which spans $\sim$3 Ma (Swart and Eberli, 2005). The diagenetic process is related to fluid flow from the upper exposure surface, and sections and data are hung by stratigraphic thickness from the exposure surface at 0 meters. The light blue bar adjacent to the age timeline represents the ice record from the glacial sedimentary compilation in (Montañez and Poulsen, 2013). Thick colored bars represent the biostratigraphic age of fossils contained in the rocks below and above the unconformity. Minimum mass exchange (pink area) calculations based on the percentage of soil carbon ($-22\%$) that would have to replace marine sourced ($2\%$) carbonate carbon to create the observed profile. The stratigraphic information have been simplified in this plot with high energy carbonates corresponding roughly to packstones and grainstones and low energy carbonates corresponding to micrites and wackestones. Recrystallized carbonates represent facies that have experienced significant coarse fabric-destructive recrystallization.
diagenesis is required to explain the presence of similarly-scaled top-negative carbon isotope excursions in contemporaneous platformal carbonates in the UK (Campion and Maloof, 2015), Kazakhstan (Ronchi et al., 2010), and China (Zhao and Zheng, 2014). Furthermore, the presence of $+2^{\circ}\delta^{13}C$ in continuous deep water carbonates of northern Spain that span this interval (Buggisch et al., 2008) is evidence that the altered shelf sediments elsewhere are not recording the global dissolved inorganic carbon (DIC) of the ocean.

Isotopically light carbon in these shelf sediments is instead sourced, in part, from remineralized organic matter incorporated by meteoric fluids moving through the overlying soil and vadose zone during exposure (Gross, 1964; Lohmann, 1988). Carbonate minerals are unstable in the CO$_2$ charged meteoric fluids, leading to the dissolution and reprecipitation of the platform minerals (Budd, 1988). The depth of this diagenetic freshwater lens is controlled by the distance from the coast, the local recharge rate, and the hydraulic conductivity of the carbonate rocks. As the underlying saltwater is pushed down, the freshwater lens can extend well below mean sea level (Vacher et al., 1990).

While diagenetically altered carbonate platforms and karst terrains in the modern world represent a small fraction of sedimentary basins, the early Carboniferous may have had the highest areal extent of neritic carbonates in Phanerozoic Earth history (Ronov, 1982; Walker et al., 2002; Peters, 2008). These massive carbonates are coincident with the longest icehouse interval in the Paleozoic, where glacioeustatic change provided the opportunity for extensive meteoric diagenesis. The middle Carboniferous unconformity may represent an initiation or major expansion of late Paleozoic glaciation, and the stratigraphy of this interval records the duration, lateral extent, and degree of diagenetic alteration of shallow carbonates. These observations, when coupled to carbon box modeling, provide a means to explore the impact of meteoric diagenesis on the $\delta^{13}C$ of the late Paleozoic ocean and atmosphere.
3.2. INTRODUCTION

DISSOLUTION COLLAPSE BRECCIA CONTACT, MEADOWS MOUNTAINS, NV.

STIGMARIAN ROOT CAST
ARROW CANYON, NV.

SILICIFIED ROOT
BATTLESHIP WASH, NV.

DISSOLUTION COLLAPSE BRECCIA,
LITTLE MOLAS LAKE, CO.

TERRA ROSSA
SALT RIVER RANGE, WY.

Figure 3.3
3.3. CARBON BOX MODEL

Figure 3.3: (Previous page.) Photographs of sedimentary features diagnostic of the middle Carboniferous unconformity in the western United States. A. The contact between the Battleship Wash formation carbonates and the dissolution collapse breccia cap at the unconformity. The hand sample in Fig. 3.4 was collected from within this breccia. B. Stigmarian root impression at the hiatus contact in Arrow Canyon. C. Photograph of the laterally continuous layer of black microcrystalline silica whose interior zonations are reminiscent of root. This layer is used as one of the stratigraphical tie points in Fig. 3.6. D. Dissolution collapse breccia at the unconformable contact between the grey Visean Leadville Limestone and the overlying red Bashkirian Molas Shale, Little Molas Lake, CO. E. Terra rossa surface diagnostic of hiatus surface of the platform carbonates exposed in the Salt River Range, WY (Strawberry Creek). Hammer-head is 17.5 cm, pencil is 14.5 cm, marker is 14 cm, and coin diameter is 1.8 cm.

3.3 Carbon Box Model

The mass flux of light carbon removed from the ocean and atmosphere and stored in altered carbonate rocks may have lead to carbon isotopic enrichment of the ocean. A small modification to the carbon box model of Kump and Arthur (1999) can be used to evaluate the impact that such a process would have on the long term evolution of ocean $\delta^{13}$C (Fig. 3.8). The effect is analogous to that proposed for an authigenic carbonate sink (Schrag et al., 2013), though in this case the respired organic carbon is derived from the terrestrial biosphere, and the forcing is linked to glacioeustasy. The long term isotope mass-balance of the ocean and atmosphere is controlled by the carbon entering the system through weathering ($F_w$) and volcanism ($F_{volc}$) and the carbon leaving the system through carbonate ($F_{b,carb}$) and organic carbon ($F_{b,org}$) sedimentation:

$$\frac{dM\delta}{dt} = F_w\delta_w + F_{volc}\delta_{volc} - F_{b,carb}\delta_{carb} - F_{b,org}(\delta_{carb} + \Delta_B)$$

(3.1)

The weathering term ($F_w\delta_w$) is a combination of carbonate weathering ($F_{w,carb}$), and the weathering of organic matter in sediments ($F_{w,org}$). In times of low sea level, isotope exchange reactions during meteoric diagenesis ($F_R$) exchange low $\delta^{13}$C terrestrial carbon with carbonate carbon, resulting in less isotopically light carbon ($F_{w,plat}$) entering the ocean and atmosphere. The dissolution of platforms ($F_D$) is allowed to exceed this reaction flux
(F_R) to explore the model sensitivity to increased carbonate weathering during lowstands.

\[ F_w \delta_w = F_{w,\text{carb}} \delta_{w,\text{carb}} + (F_{w,\text{org}} - F_R) \delta_{w,\text{org}} + F_D \delta_{w,\text{plat}} \]  \hspace{1cm} (3.2)

Mass in the system is conserved by allowing the carbonate burial term to incorporate excess dissolved carbonate from platforms (F_D).

\[ F_{b,\text{carb}} \delta_{\text{carb}} = (F_{b,\text{carb}} - F_R + F_D) \delta_{\text{carb}} \]  \hspace{1cm} (3.3)

In order to quantify the reaction flux term in this model (F_R), limits must be placed on the extent, depth, and duration of meteoric diagenesis in the middle Carboniferous.

### 3.4 Stratigraphy

Fourteen stratigraphic sections across the mid-Carboniferous unconformity in the western United States (Fig. 3.1) were studied to document patterns of regional physical and chemical exposure features. To assess the ~10 km scale variability in diagenetic intensity, seven of these sections are located within a 14 km study area in the Arrow Canyon region of southern Nevada (Fig. 3.6). Sediments were classified bed by bed into six lithofacies based on fossils, environmentally sensitive sedimentary structures, and the Dunham classification scheme for carbonates (Dunham, 1962). From these sections, 1579 samples were collected at a half meter resolution and analyzed for δ^{13}C and δ^{18}O analysis. The hand samples were slabbled and polished to drill out carbonate powders for isotopic analysis. When possible, grains and shells were avoided and micrite was selectively sampled. Samples were hand polished, photographed, and individual textures, clasts, and shells were micro-drilled to resolve millimeter-scale isotopic variations (Fig. 3.4 and 3.5). All carbonate powders were heated to 110 °C to remove water. Samples were then placed in individual borosilicate reaction vials and reacted at 72 °C with 5 drops of H_3PO_4 before the CO_2 analyte was
3.4. STRATIGRAPHY

Measures the precision is ±0.1‰ for carbon and ±0.2 ‰ for oxygen. The samples were analyzed with either a Thermo DeltaPlus continuous flow IRMS or a Sercon IRMS coupled with a GasBench II sampling device. δ¹⁸O and δ¹³C data are reported in the standard delta notation relative to the Vienna Pee Dee Belemnite (VPBD) standard.

3.4.1 Monte Cristo Group, Nevada

The upper 50 meters of the late Visean and early Serpukhovian carbonate shelf in southern Nevada hosts a gradual top-negative carbon isotope excursion (Bishop et al., 2009; Saltzman, 2005) that ranges from +2‰ at the bottom to -5‰ δ¹³C at the exposure surface. Stable, thick bedded crinoidal wackestones and packestones of the Yellowpine Formation are capped in a 10-15 meter thick Lithostrotionella coralline boundstone that can be traced for at least 14 kilometers. Abundant low energy fenestral mudstones and articulated brachiopod filled wackestones make up the next 10-15 meters of section. Two parallel beds, separated by less than a meter of coarsely recrystallized carbonate, contain dense, branching networks of black microcrystalline silica whose interior zonations are reminiscent of root interiors (Fig. 3.3C). These silicified root layers and the top of the Lithostrotionella coral beds were used as tie points for seven stratigraphic sections measured in the Arrow Canyon range and Meadows Mountains (Fig. 3.6). Above the silicified roots, the carbonate is mostly coarse grainstone and packstone where it has not been completely recrystallized. In addition to macroscale, outcrop based identification of recrystallization, Bishop et al. (2009) found three sets of calcite cements that correspond to vadose zone, meteoric, and compaction lithification processes.

Figure 3.3: (Next Page) Hand sample of dissolution-collapse breccia from the top of the Battleship Wash formation collected roughly 8 km north of Arrow Canyon, NV. Circles correspond to micro-drilled δ¹³C spot measurements, and the color scale indicates the isotopic value of that drill spot. Green data correspond to non-sparry brachiopods and crinoids. Large clasts are brecciated carbonate from the top of the Battleship Wash platform that have been coated by laminated black carbonate in a phytokarst environment. Uncoated shells, mud chips, and cements fill the interstitial space between large clasts.
3.4. STRATIGRAPHY

Figure 3.4

DISSOLUTION-COLLAPSE BRECCIA HAND SAMPLE
Figure 3.5: Carbon and oxygen isotope cross plot illustrating the high seawater $\delta^{13}$C values recorded in pristine shells, and the low meteoric values recorded in clasts from the breccia hand samples (Fig. 3.4) and in the 30 meters of carbonates directly below the unconformity in Arrow Canyon.
3.4. STRATIGRAPHY

in thin sections from this upper interval of the Battleship Wash formation. Sand filled pits and abundant meter-sized stigmarian root casts (Fig. 3.3B) mark the unconformity with the overlying Indian Springs Formation, which consists of 50-60 meters of siliciclastics, soils, and thin diagenetically altered skeletal packstone carbonate beds. Biostratigraphy (compiled in (Bishop et al., 2009)) indicates that this interval of hiatus corresponds to a single missing conodont zone that may represent up to 4 Ma (Fig. 3.2) when the biostratigraphic units are correlated with global, radiometrically constrained biostratigraphic boundaries (Davydov et al., 2012). Despite poor exposure of the unconformity surface, it appears that the carbonates of the Battleship Wash formation are immediately overlain by a thin, fine-grained, and distinctly rippled red-brown sandstone. This sandstone is found over the entire 14 km study area, and is illustrated by the red circle icon in Fig. 3.6. In the north, this rippled sandstone lies directly above carbonate breccia-filled channels and pits (Fig. 3.3A) of a phytokarst (Folk et al., 1973) terrain that corresponds to erosion of the upper Battleship Wash carbonates. The carbonate breccias contain clasts of limestone from the upper part of the Battleship Wash formation, and many clasts are coated by black, sub-millimeter laminated carbonate up to 5 cm thick. However, within the same breccia pits, some smaller clasts and intact shells are completely uncoated (Fig. 3.4).

Carbon isotopes at the bottom of the sections have low variance (Fig. 3.2 and 3.6) and match global estimates for Visean seawater (Fig. 3.12). Around 50 meters below the unconformity, the carbon isotopes start to gradually decrease upwards to minimum values of -4.5‰ just below the hiatus. The depth and intensity of carbon isotopic alteration generally increases from South to North in the Monte Cristo Group study area, and is not consistent from section to section. In Fig. 3.6, interpolation of carbon isotopic data between sections highlight the diagenetic pattern of the carbonate shelf. Some microdrilled shells from breccia hand samples (Fig. 3.4) at the top of this sequence just below the hiatus are isotopically similar to the values at the bottom of the excursion (+2‰ δ13C). The range of isotopic compositions for different features in the hand samples is larger than the outcrop variability...
3.4. STRATIGRAPHY

(Fig. 3.5). The large coated clasts have the lowest carbon isotopes (-5 to -8‰ δ13C), the black laminated coatings are slightly higher (-2.5 to -5‰ δ13C), and the shells are highly variable with values from -4.5‰ to +2.1‰ δ13C. Only the shells exhibit oxygen isotopes higher than -4‰ and carbon isotopes higher than -3‰ (Fig. 3.4), and shells that have have coarsely crystalline (sparry) textures have lower carbon isotopes than shells that have nearer to original biogenic textures.

3.4.2 Leadville Limestone, Colorado

The U956 and D751 cores through the Leadville Formation consist of interbedded limestone and dolomite wackestones where the dominant allochems are large articulated crinoids. The unconformity at the top of the formation is an irregular contact with limestone dissolution-collapse breccia containing interstitial red shale of the overlying Molas Formation. Around Little Molas Lake, Colorado, limestone karst towers and solution collapse breccia pits at this contact are well exposed. Biostratigraphy of the Leadville limestone indicates middle Tournaissian to middle Visean age (Fouret, 1996). The overlying Molas Shale is late Bashkirian, so the interval of time missing at the unconformity is roughly 20 million years (Fig. 3.2). Carbon isotopes of the carbonates below the unconformity in both U956 and D571 (30 km apart) are low (<0‰) for nearly 100 meters and get increasingly lower towards the upper contact with the dissolution-collapse breccia and Molas Formation.

3.4.3 Madison Shelf, Wyoming

A regional unconformity at the top of the Madison shelf is present throughout Wyoming. The western margin of the shelf is more continuous, and the unconformity is well constrained by conodont biostratigraphy to be end-Visean (Sando, 1988; Batt et al., 2007). The stratigraphic hiatus represented by the unconformity increases to the east due to a combination of both older underlying and younger overlying sediments (Fig. 3.2). This pattern could result
from a time-transgressive non depositional surface and increasing erosion inland (eastward) (Sando, 1988).

Sections from Strawberry Creek, Clark’s Fork Canyon, and Crazy Woman Creek span a range of 350 kilometers east to west and 200 kilometers north to south (Fig. 3.1). The western most section, measured along Strawberry Creek in the Salt River Range, is 93 meters of mostly wackestone. The upper 15 meters are increasingly brecciated and recrystallized, and the unconformable top is a 1 meter thick red, irregular, sand-filled pedogenic layer. The carbon isotopes of the section are consistently between +2 and +3‰ $\delta^{13}C$ with a slight decrease in the upper 10 meters to values as low as 0‰. At Clark’s Fork Canyon in northern Wyoming, 230 meters of Madison limestone outcrop along the northern canyon wall. The lower 120 meters are made up of stacked carbonate parasequences that contain the mid-Tournaisian double-peaked positive isotope excursion (Fig. 3.12) first documented in (Saltzman, 2002) (up to +7.3‰ $\delta^{13}C$). The textures and facies of the upper 110 meters have been completely erased by brecciation and recrystallization. The carbon isotopes in this interval are between +1 and +2‰, until the upper 16 meters where there is a top-negative carbon isotope excursion that goes from +2 to -4‰ $\delta^{13}C$. The unconformity at the top is irregular with several meters of pitted relief, including a 5 meter deep sand-filled paleo-sinkhole (described in (Sando, 1988)). The eastern extreme of the Madison Shelf, at Crazy Woman Canyon, is comprised of 130 meters of dolomite that terminates in brecciated carbonate, followed by red sandstones that are 15-20 million years younger (Sando, 1988). Meters 40-60 contain the double-peaked positive carbon isotope excursion of the Tournaisian (Fig. 3.12), followed by 35 meters of +2‰ $\delta^{13}C$. The remaining 20 meters contain a top-negative carbon isotope excursion that goes from +2 to -2‰ $\delta^{13}C$.

### 3.4.4 San Andres Canyon, New Mexico

Dark gray limestone mudstone to coarse-grained, cherty, crinoidal grainstone and packstone of the Lake Valley and Rancheria formations in the San Andres mountains are unconformably
overlain by 10-15 meters of black shale that contains conodonts from the end of the Visean. Exposure features such as mud cracks and root casts are present in the upper 60 meters of the underlying carbonates. Some medium to thick grainstone beds have silicified tops, but unlike the other sections described above, there is no pervasive, fabric destructive recrystallization apparent at the outcrop scale. However, three generations of meteoric, marine, and mixing zone cements in thin sections from the carbonate beds below the unconformity are attributed to reactions during fluid flow associated with sea level draw down (Meyers, 1985; Frank et al., 1996). Carbon isotopes in the lower 100 meters of this formation are highly variable with values ranging from -2‰ to 2‰. Carbon isotopes get progressively more negative over the 46 meters below the unconformity, with minimum values of -5‰ at the top.

3.5 Discussion

3.5.1 Primary versus Diagenetic $\delta^{13}C$

When changes in $\delta^{13}C$ are observed in time-correlative sections across 100s of kilometers and in different basins, it often is assumed that the carbonates are recording secular changes in the isotopic value of dissolved inorganic carbon in the global ocean. However, carbon isotopic variations in carbonate can be generated by diagenetic reactions associated with glacioeustasy (Swart and Eberli, 2005). Each of the late Paleozoic sections described in this paper has top-negative carbonate $\delta^{13}C$ excursions terminating in subaerial exposure surfaces (Fig. 3.2). The isotopic variation of 8-9‰ in $\delta^{13}C$ and 20-100 meter scale is comparable to the variation and scale observed in the Pleistocene of the Bahamas (Swart and Eberli, 2005) (Fig. 3.2). Despite these similarities, secular changes in DIC can not immediately be ruled out as environmental change and carbon isotopic excursions often are coincident. Diagenetically screened brachiopods from within the isotopic excursion in Arrow Canyon are isotopically much heavier than the micritic carbonate from the same stratigraphic intervals (Bishop et al., 2009; Brand et al., 2012). The presence of shells at the top of the excursion (Fig. 3.4 and
3.5) that have both high $\delta^{18}$O and $\delta^{13}$C values that match the carbonate values below the excursion (+2‰) is further indication that sea water DIC was high up to the unconformity. Additionally, these isotopically heavy shells have the same range of isotopic values that were measured by Buggisch et al. (2011) in time correlative deep pelagic carbonates in Spain (Fig. 3.12). The magnitude of isotopic variability observed between micrite and select shells throughout the isotopic excursion is inconsistent with the top negative excursion recording primary changes in global ocean DIC. Instead, the light isotopes can be explained by partial equilibration with diagenetic meteoric fluids, where locally decreased permeability around select shells, as well as their interior less permeable microstructure, allowed them to remain closed to the altering fluids.

### 3.5.2 Timing of Diagenesis

Sedimentary hiatus is a combination of erosion and non-deposition, and meteoric diagenesis below the unconformity could correspond to a single long diagenetic event or any number of short events spanning the interval of time missing. Diagenesis caused by glacioeustasy should be roughly synchronous around the world, and meteoric diagenesis should be recorded where that glacioeustasy resulted in exposure and sedimentary hiatus. Due to erosion and non-deposition during the hiatus, there is no unambiguous test for diagenetic synchronicity among the sections. However, glacioeustasy should lead to hiatus that span some common interval of time, and the smallest single interval of hiatus provides the best estimate for the timing of this glacioeustatic change.

As the global stratotype section and point (GSSP) for the Mississippian-Pennsylvanian boundary (Lane, 1999), the Arrow Canyon section has some of the best biostratigraphy in the late Paleozoic. This section is almost continuous through this interval, but a conodont zone that represents 2-4 million years of the end Visean is missing between Battleship Wash carbonates and the overlying Indian Springs formation (biostratigraphy compiled in (Bishop et al., 2009)). This timing is consistent with the Lake Valley carbonates from New Mexico.
Figure 3.6: Lateral (North to South) transect of the Battleship Wash Formation of southern Nevada, centered on Arrow Canyon. Sections are tied together by two laterally continuous stratigraphic units that are easily identified and were traced on foot over the study interval (grey lines). The regional exposure surface is identified by a combination of roots (Fig. 3.3B), recrystallized texture, blue-grey to brown coloration change, and a distinctive overlying current rippled fine sandstone. Circles correspond to isotopic measurements on carbonate from the adjacent stratigraphy, and the colored background is a smoothed 2-dimensional linear interpolation of these isotopic data. Refer to caption of Fig. 3.2 for facies description.
The carbonates below the unconformity contain middle Visean conodonts and the overlying Helms Shale contain conodonts from the end of the Visean and early Serpukhovian (Bachtel and Dorobek, 1998; Proske, 2013). While spanning much larger time intervals, hiatus in Leadville and the Madison Shelf sections overlap with this late Visean window (Fig. 3.2), so if the diagenetic excursions across the western US are from a single late Visean event, then erosion is responsible for older underlying sediments and variable non-deposition is responsible for younger overlying sediments. A glacioeustatic driver for meteoric diagenesis of the western US carbonate shelf explains similarly-scaled top-negative carbon isotopic excursions from platform carbonates in Kazakhstan (Ronchi et al., 2010), China (Zhao and Zheng, 2014), and the UK (Campion and Maloof, 2015) at the end of the Visean and early Serpukhovian (Fig. 3.12). This timing roughly corresponds to the turning on of near field glacial sedimentation in Australia and South America (Montañez and Poulsen, 2013). In addition, the ongoing formation of Pangea, may have played a role in the tectonic uplift of some of these carbonate platforms, perhaps resulting in meteoric diagenesis. Regardless of the mechanism behind the pervasive platform diagenesis, the presence of low $\delta^{13}$C in carbonates around the world over a narrow span of time likely had an impact on the global carbon cycle.

3.5.3 Constraining the Magnitude and Rate of Sea Level Fall

At the < 10km scale, the depth of meteoric diagenesis is controlled by local forcings, such as rainfall and rock permeability (Vacher et al., 1990). Over larger length scales the presence of diagenesis in many stratigraphic sections from the same exposure interval is evidence for regional changes in base level due to glacioeustasy or tectonics. When the same diagenesis is observed globally (Figure 3.12) at a time period when polar sedimentary basins are filled with glacially derived sediments (Fielding et al., 2008), then a glacioeustatic forcing for the diagenesis is probable. Ideally, the average depth of diagenesis across many stratigraphic sections would offer some insight into the scale of glacioeustatic fall. However, given the 10–
Figure 3.7: Cumulative stratigraphic thickness of sediments through time in the region of Arrow Canyon, beginning above with the Great Unconformity of the Cambrian. Cambrian and Ordovician accommodation space is dominated by post-rifting thermal subsidence (Bond et al., 1985). Accommodation in the Antler Orogeny foreland basin through the Devonian and Carboniferous (Dickinson, 2006) lead to constant accumulation rates during the middle Carboniferous. Assuming linear subsidence during the middle Carboniferous of Arrow Canyon, where biostratigraphy constrains the maximum length of hiatus to be $4 \pm 1$ Ma, sea level fall is calculated by the difference between post-hiatus accumulation thickness and the modeled expected subsidence (inset A). By including the biostratigraphic uncertainties for each boundary during this interval, sea level fall can be estimated to $30 \pm 8$ meters (inset B). Inset C illustrates the relationship between age uncertainty and the range of sea level fall estimates.
100 meters of variability in the depth of diagenesis at the regional (Fig. 3.2) and kilometer (Fig. 3.6) scale observed in the sections presented here, the local forcings in each location appear to overshadow information about the magnitude of glacioeustatic change.

If the subsidence of a sedimentary basin can be constrained, base level change potentially is recorded in the duration of stratigraphic hiatus. The biostratigraphic timescale from Arrow Canyon places limits on the duration of exposure at the end of the Visean. When coupled to a subsidence model, these limits can be used to estimate the drop in global sea level and infer the corresponding change in land ice volume at this time. Carbonates of the western US during the Devonian and early Carboniferous were deposited on a broad forebulge associated with the Antler Orogeny (Dickinson, 2006). Subsidence during the early and middle Carboniferous in the Arrow Canyon region is slow and constant (Fig. 3.7A), suggesting that a simple linear model for subsidence may provide some insight into the change in base level at the unconformity. Assuming that Indian Springs formation was deposited at sea level, and deposition initiated as soon as the exposed carbonates subsided to the new mean sea level, then the difference between the accumulated thickness of sediments and the linear fit subsidence model should correspond to a change in sea level. If this assumption is incorrect and the deposition of the Indian Springs begins below sea level, then the sea level change calculated here is an underestimate. Most likely, the biostratigraphic age uncertainty outweighs this depositional height uncertainty. To simulate the uncertainties associated with the biostratigraphy, this calculation was performed 10,000 times allowing each biostratigraphic interval to vary with a normal distribution over individually assigned uncertainties. The estimated sea level drop required to explain the difference between accumulation and the subsidence model from these calculations is 29.8±7.8 meters (Fig. 3.7B). In order to evaluate the sensitivity of this calculation to the assigned uncertainties, forty new sets of 10,000 calculations were performed for 2σ errors for 0.1 Ma intervals from 0–4 Ma (Fig. 3.7C). From the sensitivity test it is clear that if biostratigraphic uncertainties are ±4 Ma, then this calculation can not resolve changes in sea level. However, if the biostratigraphy is
accurate to 2-σ between 0.5 and 1.5 Ma, the sea level change estimate and calculated errors are robust for this simplified linear subsidence model.

The sea level change estimates of 30±8 meters are comparable to the glacioeustasy associated with the initiation of northern hemisphere glaciation (Miller et al., 2005), suggesting that the analogy to the Plio-Pleistocene expansion of the Cenozoic icehouse may be relevant for the middle Carboniferous. With almost no northern hemisphere continents at this time, all of the glacioeustasy would have been accommodated by expansion of the southern hemisphere Gondwanan ice sheets. Accounting for continental shelf isostatic effects that result from glacioeustasy (Hughes and Denton, 1981), an ice volume growth of 12.5–21.4 × 10^6 km^3 is required to account for these estimates of glacioeustasy. The upper end member overlaps with the maximum ice volume estimated from the late Paleozoic glacial sedimentary record of 20±2 × 10^6 km^3 (Montañez and Poulsen, 2013), suggesting that ice volume in the middle Carboniferous may have approached maximum ice volumes for the late Paleozoic icehouse or that the nearfield records have underestimated global ice volume.

### 3.5.4 Carbon Cycle Budget

Meteoric diagenesis of subaerially exposed carbonate platforms in the middle Carboniferous likely was a global phenomenon, and the total amount of light carbon exchanged with each sedimentary section presented in the bottom of Fig. 3.2. Reaction percentages are calculated by a simple two-component mixing of original +2‰ δ^{13}C and organically derived carbon (-22‰ δ^{13}C). The reaction mass flux (F_R) is estimated by multiplying the reaction percentages by a volume of reacted carbonate (based on areal extent of platforms and depth of diagenesis) and dividing by the timescale of diagenesis. Figure 3.9A shows the temporal evolution of three model simulations with a constant reaction flux (F_R) and a range of platform dissolution fluxes (F_D) to simulate the sensitivity to potential increased weathering from newly exposed carbonates. Figure 3.9B depicts the results of 100,000 model simulations where carbonate platform area, platform dissolution, duration and depth of diagenesis, and
Figure 3.8: Carbon box model after Kump and Arthur (1999) (solid flux arrows). During glacial lowstand, remineralized soil derived organic matter reacts with exposed carbonate platforms before entering the ocean and atmosphere (dashed flux arrows). This removal of light carbon from the ocean and atmosphere system leads to an enrichment in the $\delta^{13}C$ of the ocean DIC pool.
Figure 3.9: A. Carbon box model simulation with a reaction flux ($F_R$) of $2700 \times 10^{12}$ mol C per ky with variable platform dissolution ($F_D$). B. 2D histogram of 100,000 iterations of the carbon box model with variable carbonate platform area, platform dissolution, duration and depth of diagenesis, and reaction percentages. Each parameter was randomly drawn from the distributions illustrated on the right. The estimated probability density function corresponding to the model results for the diagenesis of late Mississippian carbonate platforms is illustrated in blue (Area from Walker et al. (2002)).
reaction percentages all are allowed to vary. The duration of diagenesis is based on the duration of hiatus at Arrow Canyon, and is input into the simulations as a normal distribution with a mean of 2 Ma and a standard deviation of 0.5 Ma. The distributions for the depth of diagenesis and reaction percentages are conservative estimates based on the geochemical data from each stratigraphic section plotted in the lower panel of Fig. 3.2, and the platform dissolution flux is allowed to vary with a uniform distribution between 0 and 2 times the diagenetic reaction flux. Using a minimum estimate for late Mississippian carbonate platform area of 39 million km$^2$ (Walker et al., 2002), there is a 95% probability that the ocean DIC was 0.6–2.9‰ heavier due to meteoric diagenesis, with a maximum probability peak at +1.4‰. When the same model parameter distributions are applied to the much smaller carbonate platform areas of the Pliocene (Walker et al., 2002), there is a 95% probability that the change in ocean DIC associated with meteoric diagenesis is less than 0.3‰.

3.5.5 Implications for biogeochemical models

Positive excursions in the carbonate $\delta^{13}C$ record commonly are interpreted as increases in the global fraction of organic carbon buried (relative to carbonate), and the burial of organic carbon decreases the oxygen removed from the ocean and atmosphere during remineralization, leading to an increase in oxygen concentrations through time (Berner, 2006). While the coals of the upper Carboniferous indicate significant organic carbon burial on land (Phillips and Peppers, 1984; Cleal and Thomas, 2005), the model presented above suggests that meteoric diagenesis also may contribute to the observed isotopic enrichment of oceanic DIC (Fig. 3.12). This enrichment could be sustained if these reactions remain important throughout the late Paleozoic, perhaps primarily during intervals of high amplitude glacioeustasy (Fig. 3.10).

The high $\delta^{13}C$ of the ocean is a major component in Phanerozoic atmosphere oxygen models such as GEOCARBSULF (Berner, 2006). This model determines atmospheric oxygen concentrations during the late Paleozoic as high as 30%, but concentrations much higher
than 25% would result in strong negative feedbacks in the fire system that should result in the collapse of terrestrial plant ecosystems (Belcher et al., 2010). While there is some evidence of increased fire during the Carboniferous (Scott and Glasspool, 2006; Glasspool and Scott, 2010), the presence of coal swamps and forests throughout the Pennsylvanian and Permian indicate that oxygen levels were probably not much higher than 25%. The COPSE biogeochemical model (Bergman et al., 2004) uses a set of six biological and geological forcings (volcanic degassing, tectonic uplift, land plant colonization, land plant weathering enhancement, deep pelagic carbonate sink, and solar luminosity) to estimate the pO$_2$ reservoir (and many others) through the Phanerozoic and provides more reasonable oxygen compositions during the Carboniferous (∼25%). Rather than using the δ$^{13}$C record as an input, this model predicts δ$^{13}$C, and comparison to the record provides a good test for the model. While generally the model predictions match the ancient record very well, it severely underestimates (1–3‰) the carbonate δ$^{13}$C record during the late Paleozoic Ice Age (Fig. 3.12). High oxygen estimates from GEOCARBSULF and underestimated δ$^{13}$C of DIC from COPSE can be reconciled if the high δ$^{13}$C of late Paleozoic oceans (Fig. 3.12) is in part caused by light carbon reacting with carbonate platforms during meteoric diagenesis (Fig. 3.8).

3.5.6 A Global Perspective from Compiled Carboniferous δ$^{13}$C

Fig. 3.12 depicts 5225 compiled Carboniferous δ$^{13}$C datapoints from this study and published literature (Batt et al., 2007; Buggisch et al., 2011, 2008; Mii et al., 1999; Saltzman, 2005; Ronchi et al., 2010; Zhao and Zheng, 2014; Bruckschen et al., 1999; Koch et al., 2014) with all age boundaries remapped into a single up-to-date timescale (Davydov et al., 2012). Negative isotopic excursions associated with meteoric diagenesis introduce significant scatter in the carbon isotopic record. Meteoric diagenesis is expressed over length scales of 0 to 100s of meters, and a single diagenetic event will overprint very different stratigraphic ages in sections containing different accumulation rates. Fig. 3.11 illustrates this concept with a computer generated synthetic basin where ocean DIC increases from 0–4‰ over arbitrary
Figure 3.10: GEOCARBSULF $pO_2$% estimates from Berner (2006). Meteoric diagenetic reactions of exposed carbonates during the late Paleozoic glaciation would result in lower $pO_2$ estimates for this time interval.

time-steps $t_0$ to $t_4$. Thus, assuming that the diagenetic $\delta^{13}C$ of the rock corresponds to the depositional age of that rock will lead to spurious carbon isotope based correlations in time (see Leadville in Fig. 3.12).

With high enough sampling density, spurious low $\delta^{13}C$ data can be filtered out by placing more weight on high carbon isotopic values. Diagenetic fluids are unlikely to drive carbon isotopes to values higher than ocean water, so high carbon isotopic values from open marine settings provide the best estimate for global ocean DIC. These ideas can be applied to the vast record of published Carboniferous $\delta^{13}C$. Means were calculated by weighted bootstrap resampling of the data within 0.5 Ma bins across the dataset. Two sets of weights were designed for the dataset to recreate global seawater DIC estimates. One weighting gives all datapoints within 1‰ of the maximum in that bin a uniform weight, and the distance below this 1‰ window leads to exponentially less probability to be resampled. To remove differences in the chemostratigraphic sampling resolutions among datasets, the second set of weights are inversely proportional to the sample density in time-$\delta^{13}C$ space. Histograms of the weighted bootstrap means for each time bin are illustrated as red boxes, where color
3.5. DISCUSSION

**Figure 3.11:** Synthetic basin illustrating how spatial diagenetic signals manifest in datasets based on depositional times. Timelines correlate sections of variable sedimentation rates. Similarly scaled diagenetic profiles cover longer intervals of stratigraphic time in sections with low sedimentation rates (orange) when compared to sections with higher sedimentation rates (blue). Insets at the top depict the relationship of each section when the isotopic values are plotted versus either stratigraphic time (left—potentially derived from biostratigraphy or radiometric ages from interbedded ashes) and stratigraphic depth (right).

Intensity represents probability. While this weighted bootstrap approach may overlook potential isotopic differences between ocean basins (Mii et al., 1999), it serves to highlight the first order differences between the late Mississippian and Pennsylvanian oceans.

Platform sediments in North America, Kazakhstan, and China contain significantly lower δ¹³C than global sea water estimates during the middle and late Carboniferous (Fig. 3.12). Meteoric diagenesis is not limited to the end Visean as presented in this study. Unstable ice sheets and the resulting glacial-interglacial cycles may be a mechanism for meteoric diagenesis throughout the late Paleozoic Ice Age. Small scale (1–5 meter) meteoric diagenesis has been documented in Upper Carboniferous sections from the western US (Elrick and Scott, 2010; Dyer and Maloof, 2015). Expanding on the model relationships illustrated above, a sustained meteoric diagenesis flux that begins at the end Visean could explain some portion of the observed ∼2‰ increase in global seawater DIC in the upper Carboniferous (Fig. 3.12).
Figure 3.12: Estimated (red) $\delta^{13}C$ of DIC from data presented here and literature compilation. All data has been remapped into the age boundaries found in (Davydov et al., 2012). Monte Carlo weighted bootstrap resampling of the data with uncertainties is used to generate seawater $\delta^{13}C$ DIC estimates. Seawater estimates increase at the mid-Carboniferous unconformity, and platform carbonates from three continents contain low carbon isotopic values throughout the Serpukhovian. Leadville carbonates are an example of diagenesis that spans stratigraphic intervals that do not match the timing of alteration (Fig. 3.11).
3.5.7 Groundwater–Rock Reactions and Plant Evolution

The evolutionary developments of forest and soil ecosystems during the middle Devonian seem to mark a fundamental change in the way meteoric diagenesis is recorded in carbonates. Phases reacting with meteoric fluids at the top of a platform are in open exchange with atmospheric carbon, dissolved rock carbon, and remineralized terrestrial organic carbon. Further away from atmospheric and terrestrial carbon inputs (downwards) the fluids are rock-buffered. For meteoric diagenesis to lead to carbon isotopic excursions, the open system inputs must be isotopically distinct from the ocean and atmosphere system that the carbonates precipitated from.

During the Devonian, the increase of tree distribution and depth of root penetration resulted in a large increase in the thickness and areal extent of soils (Algeo and Scheckler, 1998), which are a source of isotopically distinct carbon to subsurface freshwater systems. Exposed platform carbonates from before the Devonian that contain many of the same karst-terrain features documented in the middle Carboniferous are not associated with carbon isotopic excursions (Jones et al., 2015), suggesting that the open system fluids of that time (Hirnantian) lacked significant isotopically distinct carbon. Older isotopically light carbonates from the Neoproterozoic have been interpreted to have derived their low $\delta^{13}C$ values from Earth’s first terrestrial photo-synthesizers (Knauth and Kennedy, 2009; Swart and Kennedy, 2012). While these carbonates rest below glacial unconformities, they lack top-negative carbon isotopic excursions, and both platform chemostratigraphies and carbonate clasts from overlying diamictites indicate that the carbonate platforms acquired their $\delta^{13}C$ anomalies prior to glacial truncation (Halverson et al., 2002; Rose et al., 2012). If Cryogenian carbonates like the Trezona Formation (Rose et al., 2012) were altered during glacioeustatic drawdown, then the altering meteoric fluids were not carrying significant amounts of isotopically light carbon.
3.6 Conclusions

A long hypothesized period of land-ice expansion in the middle Carboniferous is supported by the observations of globally synchronous meteoric diagenesis of carbonate platforms. This climate change corresponds to a $2\%$ increase in the $\delta^{13}C$ of DIC and a shift from stable, monotonous shallow carbonate sediments that pervade the Visean to cyclic stacks of shallowing upwards parasequences in the Serpukhovian and Bashkirian. Such a change in shelf sedimentation could reflect an increased glacioeustatic sedimentary forcing caused by large, unstable ice sheets that formed during the the middle Carboniferous unconformity.

The burial flux of organic carbon exerts a dominant control on atmospheric $CO_2$ and $O_2$ on long geologic timescales. The isotopic value of the dissolved inorganic carbon in the ocean is recorded in carbonates through time, and secular changes in this value frequently are interpreted as changes in the burial flux of organic carbon. The isotopically light carbonate platforms from the middle Carboniferous are inconsistent with this simple model because remineralized, light, organic carbon has been removed from the ocean and atmosphere (buried) through diagenetic reactions. During the late Paleozoic Ice Age, meteoric diagenesis could reasonably account for $\sim 1.4\%$ increase in global DIC. These findings improve biogeochemical models that have difficulties reconciling the high $\delta^{13}C$ of the ocean at this time, resulting in lower atmospheric oxygen estimates in GEOCARBSULF (Berner, 2006), and more accurate $\delta^{13}C$ predictions in COPSE (Bergman et al., 2004).

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References


REFERENCES

Buggisch, W., X. Wang, A. S. Alekseev, and M. M. Joachimski (2011), Carboniferous-Permian carbon isotope stratigraphy of successions from China (Yangtze platform), USA (Kansas) and Russia (Moscow basin and Urals), *Palaeogeogr Palaeocl*, 301(1-4), 18–38.


Rose, C. V., N. L. Swanson-Hysell, J. M. Husson, L. N. Poppick, J. M. Cottle, B. Schoene, and A. C. Maloof (2012), Constraints on the origin and relative timing of the Trezona


Chapter 4

A Probabilistic Perspective on the C and Ca Isotope Stratigraphic Expression of Meteoric Diagenesis During the Late Paleozoic Ice Age

4.1 Abstract

We develop a simple dissolution-precipitation reactive transport forward model to investigate the meteoric diagenesis of carbonates that were subaerially exposed during an expansion of the Late Paleozoic Ice Age. The forward model probabilistic parameter space that defines geologic and isotopic data from seven middle Carboniferous stratigraphic sections is determined using a Markov Chain Monte Carlo sampler and a Bayesian statistical inverse model. The data and analysis indicate that the average carbonate reaction rates during long-term...
freshwater diagenesis are $7 - 31 \times 10^{-3}$ moles of carbonate per year. The stratigraphic expression of the isotopic reaction front in each section is controlled by the ratio of rate of mass fluxing through the carbonate platform to the rate of mass fluxing between mineral and fluid phases. This ratio of advection to reaction is used to estimate a minimum carbonate mass flux from above through the platform across the western US mid Carboniferous karst terrain. These carbonate weathering rates are insignificant in the Last Glacial Maximum world of 120 m of glacioeustasy due to the small area of tropical carbonate platforms, but in the Carboniferous may have contributed to a 20-50% increase in the CaCO$_3$ input to the ocean. Calcium isotopes from these stratigraphic sections indicate that meteoric diagenesis fractionates the rock towards more negative values, and we demonstrate that these observations are consistent with alpha of precipitation of 0.9996±0.002. This fractionation factor would require that the calcium entering the ocean in fluids that have equilibrated with carbonate platforms through meteoric diagenesis will be elevated up to 0.4‰ higher than the background silicate or carbonate calcium weathering flux.

4.2 Introduction

The sedimentary record of seawater chemistry drives our understanding of the coevolution of the atmosphere, lithosphere, and biosphere through deep time. Chemical sediments, such as carbonates, precipitate from the water column and form layered archives from which secular changes in seawater chemistry are inferred (e.g., Hayes et al. 1999; Zachos et al. 2001). These carbonate sediments often are deposited in a shallow environment that can be subjected to diagenetic reactions during local sea level fall or uplift (Allan and Matthews, 1982; Swart and Eberli, 2005; Dyer et al., 2015). Without proper identification, this diagenetic window may lead to false inferences about seawater chemistry as some of the chemical information imparted during the precipitation from sea water is erased (Gross, 1964; Lohmann, 1988; Swart and Eberli, 2005). However, the stratigraphy of meteoric diagenesis of carbonates is
also a rare glimpse into the weathering, fluid transport, and biological productivity of ancient Earth’s near-surface terrestrial Critical Zone (Brantley et al., 2007). The carbon and calcium isotopic expression of meteoric diagenesis trace interactions among the soil, carbonate rocks, and the ocean and atmosphere. This paper merges stratigraphic observations of meteorically altered carbonate platforms that were exposed during the expansion of southern hemisphere glaciation during the middle Carboniferous (Dyer et al., 2015) with numerical fluid–mineral reactive transport modeling to infer the local mass flux rates of carbon and calcium through the exposed platforms, and the calcium isotope fractionation during meteoric diagenesis.

4.2.1 Meteoric Diagenesis of Carbonates

When sea level falls and carbonate platforms are exposed, meteoric fluids (undersaturated in carbonate and charged with atmospheric CO$_2$ or respired CO$_2$ from organic material) are driven through the platform by gravity (Thrailkill, 1965, 1968; Matthews, 1974; Bögli and Schmid, 1980). The vadose region of the platform experiences extensive dissolution and often is characterized by the development of large solution cavities and openings, which eventually collapse. The transfer of carbon from the vadose zone to the underlying freshwater phreatic realm leads to a top-negative carbon isotopic excursion that propagates downwards from the exposure surface (Allan and Matthews, 1982). The light carbon altering the rocks is sourced, in part, from remineralized organic matter incorporated by meteoric fluids moving through the overlying soil and vadose zones during exposure (Gross, 1964; Lohmann, 1988). Carbonate minerals are unstable in the CO$_2$ charged meteoric fluids of the freshwater phreatic zone, leading to the dissolution and re-precipitation of the platform (Budd, 1988), and during that process isotopes exchange between the fluid and mineral phases.

Developing an isotope based transport and fluid–rock reaction model offers a way to investigate the extrinsic forcings that determine the isotopic expression and extent of diagenetic alteration of carbonate phases during sea level fall (Lasaga, 1984; Lichtner, 1988), and establishes a framework to extract information from isotopic profiles associated with
ancient meteoric diagenesis (Brantley and Lebedeva, 2011). Observations of carbon and calcium isotopic profiles through carbonates record information about the total mass flux of carbon and calcium through exposed carbonate platforms, and these fluxes provide context to understand potential changes in carbonate weathering rates with glacioeustatic change. Furthermore, this analytical framework can be used to investigate the behavior of calcium isotopes during dissolution and precipitation in a freshwater weathering environment. If there is a significant fractionation factor corresponding to the precipitation of meteoric calcite phases, then constraining these fluxes is of vital importance to understanding the long term calcium isotopic budget of the ocean during periods of glacioeustasy (Farkas et al., 2007; Blättler et al., 2012). Additionally, calcium isotopes may be a more useful isotopic fingerprint for meteoric diagenesis in pre-Silurian carbonates that lack negative carbon isotope excursions due to the scarcity of organic derived carbon in the freshwater diagenetic system, perhaps resulting from the absence of extensive terrestrial plants at the time (Rose et al., 2012; Jones et al., 2015).

In addition to recording information about the mass and isotopic fluxes through the carbonate platform, the isotopic excursion also depends on the duration of diagenesis and rate at which reactions between the fluid and rock occur. If the reaction rate between carbonates and meteoric fluids were known, then the geologic observations of isotopic excursions could be used to estimate the duration of time missing at exposure surfaces in ancient sediments. The carbonate geologic record is filled with instances of parasequence bounded meter-scale meteoric diagenesis at exposure surfaces (Elrick and Scott, 2010; Dyer and Maloof, 2015), and placing limits on the duration of exposure can test hypotheses linking the carbonate parasequence architecture to orbital forcings on climate (Goodwin and Anderson, 1985; Grotzinger, 1986; Read, 1998; Goldhammer et al., 1990) In this study, long term reaction rates in meteoric diagenetic settings are derived by modeling the carbon isotopic excursion in stratigraphy where fossil distribution places limits on the duration of time missing at the
exposure surface. This result is a first step towards establishing a tool for estimating the missing time at any meteorically altered exposure surface in carbonate rocks.

4.3 Physical and Chemical Stratigraphy

4.3.1 Carbon Isotopic Analysis

852 carbonate hand samples were collected at a 1-meter resolution and analyzed for $\delta^{13}C$ and $\delta^{18}O$ analysis. The hand samples were slabbed and polished to drill out carbonate powders prior to isotopic analysis. When possible, grains and shells were avoided and micrite was selectively sampled. All carbonate powders were heated to 110 °C to remove water. Samples were then placed in individual borosilicate reaction vials and reacted at 72 °C with 5 drops of H$_3$PO$_4$ before the CO$_2$ analyte was sent to the IRMS. Measured analytical precision is ±0.1‰ for carbon and ±0.2 ‰ for oxygen. The samples were analyzed with either a Thermo DeltaPlus continuous flow IRMS or a Sercon IRMS coupled with a GasBench II automated injection periphery. $\delta^{18}O$ and $\delta^{13}C$ data are reported in the standard delta notation relative to the Vienna Pee Dee Belemnite (VPBD) standard.

4.3.2 Calcium Isotopic Analysis

Carbonate powders for calcium isotopic analysis were milled from slabbed and polished hand samples from Arrow Canyon and Leadville (U956). 5 mg of powder was dissolved under sonication for 4 hours in 5 mL of (pH 5) solution containing acetic acid buffered by ammonium hydroxide. This dissolution technique effectively liberates carbonate phases, while leaving clays and oxides undissolved (Tessier et al., 1979). The solution was then centrifuged for thirty minutes under 2500 rpm, and the supernatant was transferred to a new container. Calcium ions were then separated from these solutions using a Thermo Dionex 5000+ ion chromatography (IC) system. 200 µl of 20-40 ppm Ca solutions pass through an in-line CS16 cation exchange column where collection windows are specified to
collect pure calcium. This fraction was then dried down in Teflon on a hot plate at 50 °C, dissolved in concentrated HNO₃, dried down again, and then re-dissolved in 2% HNO₃ immediately before preparation for isotopic analysis on a Thermo Neptune Plus inductively-coupled plasma mass spectrometer (ICP-MS) at Princeton University.

The calcium measurements are run in a sample-standard-sample bracketing sequence to correct for mass fractionation within the instrument over the analytical session, and the samples and standards are diluted so that concentrations match within 10% to minimize concentration-dependent isotope effects. The bracketing standard is a single-element high purity ICP Ca standard (HPS). The solutions are introduced to the plasma through an ESI Apex-IR system, which helps reduce hydride interferences, and the ions enter the mass spectrometer through a medium resolution slit so that the pure $^{42}$Ca beam can be differentiated from $^{42}$Ca+ArH$_2^+$ beam. $^{86}$Sr$^{2+}$ and $^{88}$Sr$^{2+}$ are also potential interferences on the Ca measurement. The $m/z = 43.5$ beam is measured to use the concentration of $^{87}$Sr$^{2+}$, if any, in the sample to correct for the other Sr interferences on Ca.

The external precision of the analyses is monitored by the long term reproducibility of carbonate standards that are processed through the same steps as each carbonate powder. The accuracy of the measurements is determined by the comparing measured offsets of external standard SRM-915b and modern sea water to offsets reported in the literature. The standards and modern sea water in the analyses reported here have a long term external reproducibility of ±0.12 on the $\delta^{44}$Ca/$^{40}$Ca scale (full data table in the supplement). The measured offset between the SRM-915b standard and seawater is -1.22‰ $\delta^{44}$Ca/$^{40}$Ca, which is within uncertainty of the −1.25‰ offset reported by Fantle and Tipper (2014).

4.3.3 Middle Carboniferous Karst Terrain

During the middle Carboniferous, glacioeustasy, perhaps in concert with widespread tectonism associated with the formation of Pangea, led to the exposure of many carbonate sequences around the world (Saunders and Ramsbottom, 1986). In the western United States,
the duration of hiatus at this unconformity is always greater than a few million years, and the carbonates underlying the exposure surface have undergone extensive meteoric diagenesis (Dyer et al., 2015). These carbonates contain top-negative carbon isotope excursions that terminate at exposure surfaces that are associated with some combination of karst towers, desiccation cracks, fabric destructive recrystallization, and extensive root systems (Bishop et al., 2009, 2010; Dyer et al., 2015). This vast karst terrain spanned all of the western United States, and the best modern analogs are tropical to subtropical carbonate terrains in Florida, the Yucatan or south east China karst terrains (Back and Hanshaw, 1970; Zhao et al., 2015). Water in these modern systems flows through a deep freshwater aquifer, which lies beneath 10 to 100s of meters of cave-filled vadose zone (Back and Hanshaw, 1970; Plummer, 1977; Gulley et al., 2014). In the Carboniferous karst terrain, this vadose zone easily is eroded and rarely is preserved, but the underlying carbonates contain extensive fabric destructive recrystallization and top-negative carbon isotope excursions that likely were generated as these rocks were hosting the meteoric derived groundwater moving through this terrain.

4.4 Reactive Transport Model and Bayesian Inference Framework

4.4.1 Forward Reactive Transport Model

Phreatic freshwater diagenesis occurs beneath the intense dissolution and mass loss (through the formation of caves) of the vadose zone. Large caves or macroporosity rarely are present in the phreatic realm, yet isotopic exchange between fluids and rocks clearly persists (e.g. Swart and Eberli 2005; Dyer et al. 2015). For carbonate terrains that have not been significantly buried prior to exposure and maintain their primary porosity (eogenic karst, Vacher and Mylroie 2002), fluids flow through the interconnected pore space rather than along joints, fractures, and bedding planes (Budd and Vacher, 2004). To predict and investigate the first
order environmental forcings responsible for the range of isotopic expression of meteoric diagenesis, a forward model must capture persistent isotopic exchange between mineral phases and a flowing fluid that is dispersed throughout the rock porosity (Lassey and Blattner, 1988; Blattner and Lassey, 1989).

The rock record of meteoric diagenesis offers insight into the physical and chemical mechanism controlling the exchange of mass between minerals and fluids in the freshwater system. Phreatically altered carbonates frequently contain pervasive fabric destructive recrystallization that is associated with a phase shift from high Mg calcite or aragonite to low Mg calcite...
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(Budd, 1988). These observations, when coupled to the lack of caves or other macro porosity in the phreatic zone, indicate that mass is mostly conserved in the host rocks during diagenesis. Recrystallization may occur through either solid state diffusion, or by the dissolution and reprecipitation mediated through super saturated interfacial boundary layers along crystal surfaces. Aqueous solutions are known to dissolve super saturated insoluble mineral phases, and the precipitation of new minerals in the resulting interfacial boundary layers can drive autocatalytic dissolution–reprecipitation (Putnis and Ruiz-Agudo, 2013; Ruiz-Agudo et al., 2014). The preservation of crystal morphology often is used to argue that solid state diffusion governs exchange between fluids and minerals. However, observations of nm-sharp gradients in chemical composition that are coincident with similarly sharp contacts between crystal and amorphous interfacial boundary layers are strong evidence that fluid–mineral interactions are controlled by dissolution–reprecipitation and that solid state diffusion is negligible (Putnis and Putnis, 2007; Hellmann et al., 2012). Furthermore, recent isotope labeling experiments observing the phase transitions from amorphous calcium carbonate to calcite show no evidence for solid state diffusion of isotopes between fluids and minerals (Giuffre et al., 2015). These findings motivate the use of a dissolution-reprecipitation reaction mechanism to predict the isotopic expression of carbonates altered by meteoric diagenesis.

The meteoric diagenesis model is composed of a cartesian grid in two dimensions, where each cell represents a volumetric geometry of 1 m$^3$ (Figure 4.1A). In each grid cell, the mass and isotopic value of carbon, oxygen, and calcium are tracked for a fluid and rock phase that are distributed according to a fixed porosity parameter (Figure 4.1B). With each step forward in time, the mass and isotopic values of the fluid move between adjacent grid cells according to a prescribed 2D divergence free flow field. During the same time-step, mass and isotopic values also move between the rock and fluid phases at a fixed reaction rate, which represents the long-term average dissolution and re-precipitation rates (over $10^5 – 10^6$ yr). At initiation, a selected set of grid cells serves as injection points for the altering fluid, which reacts with the rock as it moves through the cartesian grid. For meteoric diagenesis
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simulations, the injection point is the surface, and the isotopic values and composition of the fluids are based on modern karst systems (Zhao et al., 2015).

4.4.2 Advection

The advection of mass and isotopic compositions of each fluid parcel is solved for, to the first order, with a forward marching Euler numerical scheme to solve a continuity equation (Equation 4.1). \( C_i \) is the property of interest, such as the \( \delta^{13}C \) of the fluid, for a single mesh cell at the current time step, and the \( i + 1 \) subscript represents the property at one time step (\( dt \)) forward. \( C_{ix} \) and \( C_{iy} \) correspond to the upstream boundary conditions for the mesh cell in the \( x \) and \( y \) directions, and \( u \) and \( v \) are the \( x \) and \( y \) components to the velocity field. The system this model is solving always has advection rates much higher than diffusion rates, and the observations exist over relatively large length scales (10-100s of meters). Therefore, a diffusion term is not included in this model. In other words, the Peclet number of the diagenetic system being modeled always is significantly greater than 1, so advection is the dominant process by which mass moves around (Berner, 1980).

\[
C_{i+1} = C_i - v_i \frac{dt}{dy} (C_i - C_{iy}) - u_i \frac{dt}{dx} (C_i - C_{ix})
\]  

(4.1)

4.4.3 Reaction

With each step forward in time (\( dt \)), the fluid parcels in every mesh cell react with the rock in that cell through a mass balanced (equation 4.2) dissolution-precipitation reaction step. The reaction rate, \( R \), determines the mass flux (\( F_{in/out} \)) between the fluid and rock phases. The rock mass values for carbon, oxygen, and calcium (denoted as subscript \( j \)) are set to a calcite composition, forcing the reaction steps to proceed forward for carbon, oxygen, and calcium at a fixed stoichiometric ratio (equation 4.3). Since the reaction step is mass balanced, the change of the isotopic value of each element in the fluid and rock is a function of the isotopic mass flux between the two phases and the fractionation factor (\( \alpha \)) for each
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Element \( j \) (equations 4.4 and 4.5). The parameter \( \alpha \) is the isotopic fractionation factor for a given element associated with the precipitation process, where an alpha of 1 corresponds to no isotopic fractionation between the fluid and the rock at equilibrium.

\[
\frac{dM_{\delta}}{dT_{\text{rock}}} = -\frac{dM_{\delta}}{dT_{\text{fluid}}} = F_{\text{in}}\delta_{\text{in}} - F_{\text{out}}\delta_{\text{out}} \quad (4.2)
\]

\[
F_{\text{in},j} = F_{\text{out},j} = R \times M_{\text{rock},j} \quad (4.3)
\]

\[
\frac{d\delta}{dt_{\text{rock},j}} = \frac{F_{\text{in},j} (\delta_{\text{fluid},j} + (\alpha_j - 1.0) \times 10^3) - F_{\text{out},j}\delta_{\text{rock},j}}{M_{\text{rock},j}} \quad (4.4)
\]

\[
\frac{d\delta}{dt_{\text{fluid},j}} = -\frac{F_{\text{in},j} (\delta_{\text{fluid},j} + (\alpha_j - 1.0) \times 10^3) - F_{\text{out},j}\delta_{\text{rock},j}}{M_{\text{fluid},j}} \quad (4.5)
\]

4.4.4 The Reaction Front

As the infiltrating fluids react with the host rock a transient reaction front develops and propagates in the direction of flow. This reaction front is the region over which the isotopic values of the host rock are transitioning between original isotopic composition and diagenetic fluid isotopic composition. The modeling of mass loss and fluid rock interactions in porous media by Lichtner (1988) derives a physical basis for the thickness of the reaction front. The thickness of the front is determined by the ratio of mass transport to the ratio of mineral dissolution (mass reaction). The isotope based model presented in this work captures the same phenomenon of a quasi-steady state reaction front propagating through the rock with a shape that is determined by the ratio of the mass of a given element advecting through the pore space in a fluid to the mass of that same element moving between the fluid and rock phases (Figure 4.1D). Additionally, the time pathway of a single rock in multiple isotope space diverges from the canonical 'J' curve of Banner and Hanson (1990) without invoking any differences in fluid chemistry (Figure 4.1C). The 'J' curve results from the
faster equilibration of oxygen than carbon isotopes between the rock and the fluid. When advection of the fluid is coupled to a dissolution-reprecipitation where mass exchange rates are based on the mass ratio of elements in the mineral phase, the ‘J’ isotopic expression is only valid for slow advection rates. Meteoric diagenesis of carbonates often results in carbon and oxygen isotopic values that cover a region much wider than the canonical ‘J’, perhaps indicating that dissolution-reprecipitation reaction mechanism for the exchange of major elements between rock and fluid may be warranted (Swart and Eberli, 2005; Bishop et al., 2014; Liang and Jones, 2015; Dyer et al., 2015).

4.4.5 The Ratio of Advection to Reaction

Ultimately, the advection to reaction ratio determines the curvature and length of the reaction front along a single stream line. If the terrain is relatively constant over length scales comparable to the size of the observed reaction front in a stratigraphic section, then a 1D perspective from that stratigraphic data is a justified approximation for a minimum advection to reaction ratio. Large horizontal flow might indicate high mass flux through the system, but would be unobserved in 1D stratigraphic data. However, the minimum estimates on mass flux still provide interesting lower limits on the carbon and calcium moving through exposed carbonate platforms, and coupling the relative mass flux of multiple elements is a powerful tool to explore the chemical composition of the infiltrating fluids. Calcium in meteoric fluids in carbonate terrains largely is derived from dissolved calcite, which has isotopic values between $-1.1\%$ and $-1.0\%$. The calcium mass flux is a signal of the carbonate dissolution in the above vadose and soil zones, and thus provides a quantitative look at local carbonate weathering during exposure of the platform.

4.4.6 Bayesian Inverse Model

Bayes’ Theorem expresses the mathematical relationship between the prior belief about the set of parameters in this forward model and the geologic observations of stratigraphic sec-
Figure 4.2: This figure depicts a process diagram for the Bayesian inference problem. The forward reactive transport model is used to predict isotopic excursions, which are then compared to the observations from the middle Carboniferous karst terrain. The Markov Chain Monte Carlo sampling algorithm proposes new parameter values for each of the free parameters, and accepts or rejects the parameter set based on the likelihood that the observed isotopic data was generated by the model with those specific parameters.
rameter space and find broad regions of high probability. Then, the posterior distribution is described by randomly walking through the broad regions of high probability.

The general numerical approach is to draw a set of model parameters from their prior distributions based on the current state of the model. The relative likelihood that the observations correspond to current or proposed model state is used to accept or reject the proposal. Accepted parameters are stored, and rejected parameters return the model to the previous state. This process is then repeated many times. The MCMC sampler used for Bayesian inference in this work is a Metropolis-Hastings algorithm that sets the probability for accepting a proposal to the ratio of the likelihood of the proposal to the likelihood of the current state (Metropolis et al., 1953; Hastings, 1970; Patil et al., 2010). Therefore, parameter proposals that fit the data better are accepted, and proposals that are a worse fit to the data are still sometimes accepted based on their relative likelihood to the current state. To improve the speed of convergence on the posterior distribution, after 200 accepted proposals the sampler scales (tunes) the proposal distributions based on the rate of accepted proposals. High acceptance rates lead to expansion of the parameter proposal distributions to enable sampling of a wider region of parameter space, and low acceptance rates leads to a more focused proposal distribution. In theory, infinite samples of accepted proposals fully solve the analytical Bayesian inference problem. However, convergence to the point of usefulness often requires many fewer samples, and can be evaluated by inspecting the trace of accepted parameters.

4.5 Results

4.5.1 Testing the Bayesian Process model on Model Generated Data

Test datasets with known parameters can be generated from the forward model and run through the Bayesian inference model to determine the success of the inference model at
Figure 4.3: Datasets generated by the forward model with known parameters are passed to through the Bayesian inference model to explore the parameter estimation and its pitfalls. A. Carbon isotopic profiles from three test datasets generated by the forward model with normally distributed random noise added to each datapoint. B. Prior (box swatch) and posterior (filled color) distributions for the duration of diagenesis, reaction rates, advection to reaction ratios, and random noise. The colored vertical lines highlight the true value of each parameter used to generate the test dataset.
recreating the true parameter values. Figure 4.3 illustrates the results of the MCMC algorithm on three datasets generated from the model and normally distributed random noise. Test A and B are run with diagenetic durations that fall within the prior distribution for this parameter, which represents some geologic limits on exposure length. The posterior distributions for each test are nearly identical to the prior proposal, which indicates that the dataset does not inform that prior information very strongly. However, the inference on the data provides a range of reaction rates that are as good as the prior distribution used for the duration of diagenesis. For a third test (C), the model was run for a longer duration that falls beyond the prior distribution for duration of diagenesis. In this case, the MCMC algorithm fails to capture the true value within the posterior distribution for both reaction rate and duration of diagenesis. However, the posterior distribution for the ratio of advection to reaction in all three tests includes the true parameter used to generate the model. Therefore, the length scale and curvature of the reaction front do an acceptable job at informing the inference model about this advection to reaction ratio, regardless of a bad prior for the duration of diagenesis. Since the reaction rate serves to convert this ratio into a geologically meaningful carbonate mass flux, these estimates will only be as good as the posterior distribution on the duration of diagenesis. In the failed case of test C, the true duration of diagenesis is roughly four times longer than the posterior distribution, and thus reaction rates are also overestimated by four times.

4.5.2 Estimating the Reaction Rate from Arrow Canyon

The Arrow Canyon stratigraphic section is almost continuous through the interval of hiatus and diagenesis, and Bishop et al. (2009) compiled the biostratigraphy through this region which indicates that a conodont zone representing up to 4 million years (Gradstein et al. 2012; Davydov et al. 2012) of the end of the Visean is missing between the meteorically altered carbonates of the Battleship Wash formation and the overlying Indian Springs formation. Therefore the diagenesis must have occurred within this window which will be simulated in
Figure 4.4: A. Carbon isotopic data from seven stratigraphic sections spanning the western US hung from the regional unconformity surface at 100 meters (Dyer et al., 2015). B. Prior and posterior distributions for the duration of diagenesis, reaction rate, advection to reaction ratio, and geologic scatter for Arrow Canyon using 2.5±0.5 Ma as the prior distribution for the duration of diagenesis, and a flat uniform prior distribution for the other three parameters. C. Prior and posterior distributions for all of the stratigraphic sections, using the reaction rate posterior from Arrow Canyon as the prior for reaction rate in each of the other sections.

The models as a normal distribution centered at 2.5 Ma that extends from 1–4 Ma. Since the other stratigraphic sections presented here have a much more complex non-depositional history at the diagenetic unconformity (Dyer et al., 2015), the reaction rate for meteoric diagenesis in this terrain is generated using just the Arrow Canyon data and diagenetic duration window (Figure 4.4B). The reaction rate posterior distribution from Arrow Canyon is used as a prior distribution for the remaining stratigraphic sections (Figure 4.4C). The agreement between model fits (forward simulations of the posterior parameter space) and the data (Figure 4.4C) suggests that reaction rates as determined by the Arrow Canyon
data are consistent with the hypothesis that fluids and rocks in each of these stratigraphic sections were reacting for a similar period of time. Some of the variability in the posterior distributions might arise from erosion of the top of the diagenetic signal, which would remove the lightest isotopic data and lead to shorter durations of diagenesis. While it is not a very significant inference, the Leadville sections are both situated in an inland region with clear evidence of erosion prior to the deposition of the overlying sediments in the Pennsylvanian. Additionally, erosion of the Madison carbonate platform is presented in Sando (1988), where the erosional depth should increase to the east. The Crazy Woman Canyon section is the east-most section from the Madison shelf, and the posterior distribution for the duration of diagenesis is shorter than the other two Madison shelf sections, perhaps consistent with deeper erosion.

### 4.5.3 Ca Isotopic Expression of Meteoric Diagenesis

Calcium isotopic measurements from two stratigraphic sections offer the opportunity to explore the fractionation of calcium isotopes during dissolution and re-precipitation. Figure 4.5 illustrate the results of the same Bayesian inference process model used above for carbon isotopes with an additional free parameter, the fractionation factor $\alpha$. In both sections, there is a top-negative calcium isotopic excursion that covaries with the negative carbon isotopic profile (Figure 4.5B). The infiltrating fluid advects carbon and calcium through the system at the same rate, so the joint carbon and calcium isotopic expression is determined by the relative mass of calcium to carbon in the fluid. The data and modeling suggest that the fluids infiltrating Arrow Canyon carry significantly higher calcium to carbon ratios than Leadville (Figure 4.5B). There are three possible explanations for the top-negative calcium isotopic trend, 1) the calcium in the infiltrating fluid is isotopically lighter than the rock, 2) there is a fractionation factor, $\alpha$ associated with the dissolution and re-precipitation of calcite in these settings that preferentially removes lighter isotopes from the fluid ($\alpha < 1$), or 3) a combination of both effects.
Figure 4.5: A. Calcium isotopic profiles associated with meteoric diagenesis in Arrow Canyon and Leadville U956 (Dyer et al., 2015). B. The carbon and calcium isotopic cross plot illustrating the covariance of carbon and calcium isotopes. The region and pathway of diagenesis through the cross plot is set by the ratio of carbon to calcium in the fluid. The colored lines correspond to the 50th percentile model values given the posterior parameter space, and the filled colored region corresponds to the the 2.5%–97.5% model values for that same posterior parameter range. C. Posterior distributions on the $\alpha$ associated with dissolution and re-precipitation of calcite during meteoric diagenesis, or alternatively the calcium isotopic value that the infiltrating fluid must have had to generate the dataset.
In this mass balanced forward model, these two mechanisms impart the same stratigraphic expression when the fractionation factor $\alpha$ (2) matches the offset in calcium isotopes between the infiltrating fluid and the original rock (1). The modeling results indicate that this offset (or $\alpha$) corresponds to $\sim -1.4\%$ ($\alpha = 0.9996$). While this model alone can not differentiate the two processes responsible for the calcium isotope record, the discussion below will explore the feasibility of meteoric fluids carrying calcium isotopes as light as $\sim -1.4\%$.

## 4.6 Discussion

### 4.6.1 Calcium Isotope Weathering Flux and a Non-unity $\alpha$

In a karst terrain, the expected source for calcium in meteoric fluid largely is dissolved carbonate minerals from the soil and vadose zone, and there is no obvious significant source of calcium isotopes that are more negative than the carbonate minerals that comprise the platform. If the minerals in the Carboniferous platforms below the vadose zone are representative of the dissolving mineral distribution in the vadose zone, then the isotopic value of the incoming fluid would be unable to alter the underlying platform without a fractionation factor ($\alpha$) that is less than 1, and no isotopic excursion would exist. Moreover, the isotopic value of calcium weathering from silicate minerals should be close to $-1.1\%o \, \delta^{44}\text{Ca}/^{40}\text{Ca}$ (Skulan et al., 1997), and the weathering of calcium bearing salts in most cases should be identical to the weathering of carbonates (Blättler and Higgins, 2014). If the incoming fluid were isotopically lighter than the carbonate platform due to the preferential mobilization of light calcium by plants (Wiegand et al., 2005; Hindshaw et al., 2013) or faster dissolution of aragonite ($-2.0$ to $-1.5\%o \, \delta^{44}\text{Ca}/^{40}\text{Ca}$; Gussone et al. 2005) relative to calcite or silicate minerals ($-1.1\%o \, \delta^{44}\text{Ca}/^{40}\text{Ca}$; Skulan et al. 1997) in the vadose zone, then the fractionation factor may be on the higher side of posterior probability distributions presented in Figure 4.5C, but the simplest conclusion is that the infiltrating fluids carry calcium derived from calcite and
that the calcium isotope stratigraphic expression of meteoric diagenesis is driven entirely by an $\alpha$ that is less than 1.

In meteoric diagenetic systems in karst terrains, the infiltrating fluid isotopic values should be nearly identical to the platform minerals, and any isotopic variability in the altered rocks should isolate the effect of a mineral–fluid fractionation factor. Experimental approaches to derive this fractionation factor suggest that the value is close to 1 when the results are extrapolated to geologic reaction rates (Tang et al., 2008; DePaolo, 2011), but the experimental rates can not resolve small changes in $\alpha$ at these slower rates. The observation of calcium isotopes in sea floor carbonates that are reacting with sea water also indicates that fractionation factors must be very close to one (likely $> 0.9996$), and the preferred interpretation is that the fractionation factor at geologic reaction rates is 1 (Fantle and DePaolo, 2007; Blättler et al., 2015). However, the isotopic value of sea water is $0.0‰$, $\delta^{44}$Ca/$^{40}$Ca and carbonate sediments are close to $-1.0‰$ $\delta^{44}$Ca/$^{40}$Ca (Skulan et al., 1997; Schmitt et al., 2003), so this setting may not be the best place to resolve the potential fractionation associated with fluid–mineral reactions.

### 4.6.2 Carbonate Weathering Mass Flux and Climatic Implications

The posterior distribution for reaction rates spans $27\%-114\%$ of $1\text{ m}^3$ limestone reaction per million years, or between $7.3\times10^{-3}$ and $31.2\times10^{-3}$ moles of carbon per year. These rates are 2–30 times faster than estimates of fluid and carbonate mineral reactions in the sea floor (Richter and DePaolo, 1987; Fantle and DePaolo, 2006, 2007; Higgins and Schrag, 2012). Given that the CO$_2$ charged freshwater system has more potential to drive dissolution and precipitation of carbonate minerals, these high reaction rates may be expected. Considering the reaction rate in terms of percent of a cubic meter of limestone offers a more intuitive way to contextualize the conversion of the advection to reaction ratio to mass flux. For example, Arrow Canyon has an advection to reaction ratio of 7.5, and if the reaction rate is $1\text{ m}^3$ of
limestone per million years, then the carbon equivalent of 7.5 m$^3$ of limestone passed through that stratigraphic section in that time span.

The carbon in the fluid is a mixture of organic carbon ($-25\%$) and rock carbon ($+2\%$) from the overlying vadose and soil zone (Pearson and Hanshaw, 1970; Rightmire and Hanshaw, 1973). An isotopic value of $-8.0\%$ for the initial fluid is used based on observations of modern karst fluids in southeast China (Zhao et al., 2015), so 37% of the carbon flux is the result of dissolved carbonate rock. Therefore, in the Arrow Canyon example with a reaction rate of 1 m$^3$, a minimum of 2.7 m$^3$ of limestone has been dissolved in the overlying vadose zone. The lowest mass fluxes are in the Strawberry Creek section of the Salt River Range, where 0.5 – 1.5 m$^3$ of limestone dissolved per million years, and the highest mass flux in Leadville U956 corresponds to the dissolution of 19 – 80 m$^3$ of limestone per million years.

The dissolution of carbonate in the vadose zone primarily is driven by the mixing of fluids that have different CO$_2$ concentrations (Gulley et al., 2014). The saturation state of carbonate minerals is controlled by a power law, but the concentration of the reactants in the mixed fluid combine linearly (Wigley and Plummer, 1976; Drever, 1982). Vadose zone and soil CO$_2$ accumulates in and drives the expansion of cave systems in carbonates. When caves are well ventilated to the surface, this effect is minimalized. However, the air caves systems with large seasonal variations in outside air temperature (sub-tropical) tend to stagnate during summer months due to density contrasts in the air masses, and CO$_2$ from the fluids moving through the vadose and soil zones can build up in the cave system (Gulley et al., 2014). Additionally, organic acids and supercharged CO$_2$ fluids in the soil zone can lead to rapid dissolution of the upper carbonate surface from above, resulting in the classic karst terrain topography (Ford and Williams, 2013). The close link between CO$_2$ and dissolution suggests that the high weathering fluxes of carbonate in the Leadville region resulted from some combination of seasonality, a large local terrestrial biosphere, and relatively fast vertical fluid velocities through the freshwater system.
Carbonate accumulation in the modern interglacial ocean is estimated at $32 \times 10^{12}$ moles of CaCO$_3$ per year (Milliman and Droxler, 1996), which is a flux equivalent to dissolving 2000 cubic meters of limestone from the entire tropical carbonate platform area ($0.6 \times 10^6$ km$^2$; Walker et al. 2002) every million years. If the range of dissolution rates in the Carboniferous have any bearing on the modern terrestrial environment, the change in carbonate weathering from sea level high stand to sea level low stand in the modern ocean due to the addition of exposed carbonate platforms would be negligible. This conclusion is supported by observations that the carbonate compensation depth and carbonate accumulation rates did not change significantly from the Last Glacial Maximum through deglaciation (Catubig et al., 1998), despite the widespread exposure of shallow carbonates during the low stand. Carboniferous tropical shelf areas ($40 \times 10^6$ km$^2$) were much higher, and if the Carboniferous ocean carbonate accumulation were similar to today’s ocean, then the carbonate flux into the ocean may have increased by 20 – 50% whenever sea level fell. If the carbonate accumulation of the ocean could not keep up with the increased flux of CaCO$_3$, then carbon would move from the atmosphere to the ocean (Sigman and Boyle, 2000), and this loss in atmospheric pCO$_2$ would result in further cooling and a positive feedback with the glaciation. Through global subsidence of the newly exposed carbonate platforms, this carbonate pulse to the ocean would slowly turn off and the carbonate accumulation would once again match the inputs. Therefore, the complex feedbacks of carbonate weathering, glacioeustasy, and subsidence in the Carboniferous may play an unexplored role in the instability of climate that begins at this first major eustatic event in the middle Carboniferous and persists into the Permian (Fielding et al., 2008; Montañez and Poulsen, 2013).

### 4.6.3 Meteoric Diagenesis of the Bahama Bank

The carbonates of the Bahama Bank Clino core have experienced extensive meteoric diagenesis (Swart and Eberli, 2005). Since this diagenesis may have begun as early the Plio-Pliestocene expansion of northern hemisphere glaciation (~3 Ma), this duration window
provides a test for the reaction rates and model results from the Carboniferous terrain. One major difference between the two diagenetic environments is that the Bahama Bank sediments are altered in a freshwater lens that is sitting on top of and mixing with sea water below. Therefore, the reaction front in these settings is more complicated than a terrestrial freshwater system. However, the upper region of the isotope excursions likely were altered in just freshwater, and the isotopic values of these upper sediments can be generated by running the forward model a with a starting rock value equivalent to the bank top sediments today (+4.5 $\delta^{13}$C). Meteoric diagenesis only occurred during periods of sea level low stand (roughly 90% of the total maximum time of $\sim$3 Ma; Miller et al. 2005), and the carbon isotopic value of the fluids required to generate the values in the upper part of Clino core ($-1.0 \delta^{13}$C) over this time is roughly $-2 \delta^{13}$C. This value suggests that the fluids causing meteoric diagenesis in the Bahamas carry a larger dissolved carbonate carbon load than is observed in continental terrestrial karst systems (Zhao et al., 2015).

4.7 Conclusions

The modeling presented above offers a new perspective for extracting information about the paleo-environment from the isotopic expression of meteoric diagenesis in carbonates. Carbon and calcium isotopes have top-negative trends that truncate at the exposure surface (fluid source). As others have documented, the source of the negative carbon is remineralized organic matter in the soil and vadose zone. The calcium isotopic expression is generated by a fractionation factor slightly less than 1, estimated here as 0.9996±0.0002 (2σ). Geologic limits on the duration of exposure in Arrow Canyon provide a range of reaction rates that could generate the observed isotopic profiles, and these reaction rates are used to estimate the global CaCO$_3$ weathering flux associated with dissolution in the vadose zone of the mid Carboniferous carbonate platforms. This weathering flux is roughly equivalent to half of the CaCO$_3$ accumulation in the oceans today, suggesting that glaciation and subsidence may
have driven large scale changes in ocean surface saturation state in the Carboniferous. If the weathering of the Carboniferous platforms is analogous to the weathering of carbonates during low stand in the glacial periods of the Cenozoic, then the CaCO$_3$ additional weathering flux to the ocean is negligible.

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References


Brantley, S. L. and Lebedeva, M., 2011, Learning to read the chemistry of regolith to understand the critical zone: .


Fantle, M. S. and DePaolo, D. J., 2006, Sr isotopes and pore fluid chemistry in carbonate sediment of the Ontong Java Plateau: Calcite recrystallization rates and evidence for a rapid rise in seawater Mg over the last 10 million years: Geochimica et Cosmochimica Acta, v. 70, p. 3883–3904.


Liang, T. and Jones, B., 2015, Ongoing, long-term evolution of an unconformity that originated as a karstic surface in the Late Miocene: A case study from the Cayman Islands, British West Indies: Sedimentary Geology, v. 322, p. 1–18.


Matthews, R., 1974, A process approach to diagenesis of reefs and reef associated limestones: Special Publications of SEPM.


REFERENCES


