Orbital-scale fluctuations in continental weathering flux and continental ice-volume during greenhouse and icehouse climate intervals: evidence from oxygen and neodymium isotopes

Bethany Theiling

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ORBITAL-SCALE FLUCTUATIONS IN CONTINENTAL WEATHERING FLUX AND CONTINENTAL ICE-VOLUME DURING GREENHOUSE AND ICEHOUSE CLIMATE INTERVALS: EVIDENCE FROM OXYGEN AND NEODYMIUM ISOTOPES

BY

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DISSEONATION

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DEDICATION

I would like to dedicate this work to my husband, Mark Theiling, and my father, John Purdin.

To my father, thank you for opening my eyes to the wonders of the world we live in. You taught me to question, to explore, and to love every moment of it. You are a shining example of what it is to be an excellent teacher and mentor.

To Mark, thank you for showing me the world has more to offer than I ever dreamed. You taught me to love the journey, not just the destination. You are my inspiration.

On my grey days, you both helped lift the fog to show me how colorful the world really was.
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10^4-10^5 YEAR FLUCTUATIONS IN CONTINENTAL WEATHERING FLUX AND CONTINENTAL ICE-VOLUME DURING GLOBAL GREENHOUSE CLIMATE INTERVALS: EVIDENCE FROM OXYGEN AND NEODYMIUM ISOTOPES WITHIN THE CONTEXT OF CYCLOSTRATIGRAPHY

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ABSTRACT

Rapid changes in global and local climate and weather, noticeable over our lifetimes, have spurred heated public and political debate over the cause of these climatic changes, whether or not we can reverse, stop or slow down this process, and how to create adequate models that can predict Earth’s changing climate. To create the most accurate models of future climate, many researchers look to past greenhouse intervals for insight; intervals of time identified by high modeled atmospheric CO₂, a lack of glacial deposits, and geologic evidence of globally high sea-levels—all of which suggest little to no glacial ice and a relatively monotonous climate. However, recent stratigraphic and geochemical evidence from the Cretaceous ‘supergreenhouse’ interval document compelling evidence to support dynamic greenhouse climates.

The goals of the studies hereafter described are to document and describe orbital-scale (10^4-10^5 yr) climate fluctuations recorded by δ^{18}O as a proxy for glacio-eustasy and sea surface temperature and ε_{Nd} as a proxy for continental weathering and wet/warm or dry/cool climate during two global greenhouse intervals: the Late Silurian and Late Devonian.
The first study (Chapter 1) explores whether glacio-eustasy was the driver for orbital-scale shallowing-upward cycles developed in Late Silurian and early Late Devonian tropical and subtropical greenhouse climates. Two intra-cycle $\delta^{18}$O conodont apatite trends were observed: asymmetric trends demonstrating progressive $\delta^{18}$O increases coincident with facies shallowing, or symmetric trends demonstrating initially decreasing, then increasing $\delta^{18}$O values. These isotopic trends and intra-cycle magnitudes support the hypothesis that these cycles developed in response to glacio-eustasy during glacial stages, implying that Late Silurian and Late Devonian greenhouse climates were more dynamic than traditionally assumed.

Relationships between orbital-scale continental weathering flux and glacial-interglacial marine cycles was first assessed comparing intra-cycle $\varepsilon_{\text{Nd}}$ and $\delta^{18}$O values from Middle Pennsylvanian icehouse cycles (Chapter 2). Observed conodont $\delta^{18}$O trends support previous interpretations that sampled cycles were generated by glacio-eustasy (30-50 m magnitudes) combined with $<$1° sea surface temperature changes. $\varepsilon_{\text{Nd}}$ trends typically demonstrate lower $\varepsilon_{\text{Nd}}$ values during interglacial intervals and higher $\varepsilon_{\text{Nd}}$ during glacial intervals, supporting claims that increases in precipitation and/or air temperatures during interglacial intervals result in increased continental weathering rates and/or increased flux to marine basins.

Using this initial continental weathering flux study and Pleistocene Nd-isotope studies as a model, we tested the phase-relationships of continental weathering flux and sea-level change in Upper Silurian and Upper Devonian greenhouse cycles (Chapter 3). Upper Silurian $\varepsilon_{\text{Nd}}$ demonstrates relatively uniform intra-cycle values, due to averaging out of far-field source variations in continental weathering flux, relatively uniform Late
Silurian sub-tropical climate, and/or subdued continental weathering and flux due to the absence of upland and inland vascular land plants. Upper Devonian $\varepsilon_{\text{Nd}}$ demonstrate greater intra-cycle variation in $\varepsilon_{\text{Nd}}$, which may be due to enhanced chemical weathering as a result of upland and inland colonization of land plants with large root systems and an intensified hydrologic cycle due to evapotranspiration. Observed $\varepsilon_{\text{Nd}}$ trends support the hypothesis that these greenhouse cycles record increases and decreases in continental weathering due to increases and decreases in precipitation and/or air temperature. $\varepsilon_{\text{Nd}}$ and $^{147}\text{Sm}^{144}\text{Nd}$ values for Upper Silurian and Upper Devonian cycles support previous claims of far-field transport of Caledonian Mountain Belt material via trans-Laurentian fluvial systems.
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CHAPTER 1
OXYGEN ISOTOPIC EVIDENCE FOR ORBITAL-SCALE GLACIAL ICE-VOLUME CHANGES DURING MIDDLE PALEozoic (SILURIAN AND DEVONIAN) GREENHOUSE TIME INTERVALS

Bethany P. Theiling, Maya Elrick

ABSTRACT

Observations of rising pCO$_2$, sea levels, and global temperatures motivates a more comprehensive understanding of greenhouse climate analogues throughout Earth’s history. This study explores whether glacio-eustasy was the driver for orbital-scale (10$^4$-10$^5$ yr) shallowing-deepening marine cycles developed in Late Silurian and early Late Devonian greenhouse climates. $\delta^{18}$O$_{conodont}$ apatite values from 14 Upper Silurian and Upper Devonian cycles record two intracycle trends: progressive $\delta^{18}$O increases coincident with facies shallowing, or initially decreasing, then increasing $\delta^{18}$O values; average intracycle magnitudes are 1.5‰. These isotopic trends support the hypothesis that these cycles developed in response to glacio-eustasy, sea surface temperature changes, and potentially local increases in subtropical evaporation rates during glacial stages. These data suggest that glacial ice existed and fluctuated on orbital timescales during Late Silurian and early Late Devonian greenhouses, adding to an increasing body of evidence that illustrate greenhouse climates were not as uniformly warm and stable as previously thought.

INTRODUCTION

The past 100+ years of observations describing increasing pCO$_2$, rising sea-levels, retreating continental glaciers and sea ice, increasing global temperatures, and perturbations in regional global climate stimulate detailed characterization of global greenhouse climates. The Cretaceous ‘supergreenhouse’ is often considered the closest
analogue to Earth’s next greenhouse interval, typified by significantly higher pCO2 than present and a comparable continental configuration to the modern. Nevertheless, while Cretaceous sea surface temperatures (SST) calculated using a variety of methods exceed ~35°C for tropical (Forster et al., 2007; Bornemann et al. 2008) and ~20°C for polar latitudes (Herman and Spicer, 1996), an increasing body of work communicates compelling stratigraphic and δ18O evidence for glacio-eustatic fluctuations occurring on orbital (10^4-10^5 yr) timescales (e.g. Miller et al., 1999; Gale et al., 2002; Bornemann et al., 2008). Such data suggest that the Cretaceous was not as uniformly warm and ice free as previously thought.

Although modeled atmospheric paleo-pCO2 illustrates higher than present concentrations for other Phanerzoic greenhouse intervals (Cambrian-Early Ordovician, Late Silurian-Late Devonian and the Late Permian-Jurassic) (Berner, 2001), a growing body of research documents significant δ18O changes associated with eustatic sea-level fluctuations and glacial dropstones (Stoll and Schrag 2000; Bornemann et al. 2008). These findings imply that some greenhouse time intervals accommodate continental ice, in direct opposition to traditional greenhouse climate models. If greenhouse intervals can include both high-latitude glacial ice and very warm tropical SST, climate prediction models must reflect the large pole-to-equator temperature gradients and address the feedback mechanisms required to create such atmospheric and oceanic conditions.

The focus of this study is to test the hypothesis that continental ice was present and growing and melting over orbital timescales during portions of two Paleozoic greenhouse time intervals—the Late Silurian and early Late Devonian. We utilize marine conodont
apatite from two different successions of subtropical, shallow-water platform carbonates for $\delta^{18}$O analyses.

**GEOLOGIC SETTING**

**Upper Silurian**

Traditionally, the Silurian has been interpreted as a greenhouse interval based on a wide latitudinal distribution of reefs (Copper, 2002), shallow-water carbonates (Lubeseder, 2008) and tropical and temperate biota (Copper and Scotese, 2003), a lack of glacial deposits (Lehnert et al., 2006), globally high sea levels, and low $\delta^{18}$O (Veizer et al., 1999). However, recent data from Upper Silurian marine deposits record a range of geochemical and stratigraphic evidence indicating dynamic climatic/paleoceanographic conditions, including large positive $\delta^{13}$C excursions (Joachimski et al., 2002; Munnecke et al. 2003; Saltzman, 2005), My-scale $\delta^{13}$C and $\delta^{18}$O fluctuations (Samtleben, 2000; Munnecke et al., 2003), and the occurrence of repeated orbital-scale upward-shallowing marine sedimentary cycles (or parasequences) (Calder and Gibling, 1994; Brett et al., 1998; Cotter, 1998; Dorning and Harvey, 1999; Al-Shaieb et al., 2001; Bourque, 2001; Anderson and Goodwin, 2003; Skompski et al., 2008; Cramer, 2009).

Sampled Upper Silurian cycles (Pridolian-Ludlovian) of the Haragan-Henryhouse Formation (HHF) were deposited on a tectonically quiescent, southeastward-dipping carbonate ramp ~20-30°S of the paleo-equator (Al-Shaieb et al., 2001; Cocks and Torsvik, 2002) (Figure 1). Observed HHF subtidal cycles are characterized by thinly bedded shale and nodular argillaceous skeletal mudstone/wackestone (substorm wave base) overlain by medium-bedded skeletal wackestone-packstone (near fairweather wave base) which show no evidence of subaerial exposure (Figure 2).
Upper Silurian (Pridolian-Ludlovian) conodont samples were collected from the *Oulodus elegans detorta* conodont Zone (Barrick, 1975) (Figure 1), and are primarily *Belodella* elements, though sample 6.0 was a mixture of *Belodella* (coniform) and *Icriodus* (platform). Age control is based on conodont and graptolite biostratigraphy (Barrick et al., 1990). Coeval Upper Silurian cycles are found worldwide (e.g. Cotter, 1998; Dorning and Harvey, 1999; Samtleben et al., 2000); those with adequate biostratigraphic time control reveal cycle durations of between ~20-120 ky (Jeppsson, 1997; Crick et al., 2001; Cramer et al., 2009), suggesting orbital climate influences during this time.

**Upper Devonian**

Evidence for Early through early Late Devonian greenhouse climates is based on similar characteristics as that for the Silurian. Similar to the Silurian, the Late Devonian also records large, positive $\delta^{13}$C excursions (Joachimski and Buggisch, 1993; Joachimski
Figure 2. Cyclostratigraphy and associated $\delta^{18}$O trends. A) Upper Devonian (Frasnian; *hassi* conodont Zone) cycles from Devil's Gate Formation, central Nevada (~10 km northwest of Eureka, Nevada). B) Upper Silurian (Pridolian-Ludlovian; *Kockelella crassa-Ozarkodina snajdri* conodont Zone) cycles from the Henryhouse Formation, central Oklahoma Arbuckle Mountains (~10 km south of Davis, Oklahoma). Long horizontal lines indicate cycle boundaries. m/s=lime-mudstone/shale, w=wackstone, p=packstone, g=grainstone
et al., 2002; Saltzman, 2005; van Geldern et al., 2006), My-scale δ18O fluctuations (Joachmiski et al., 2009), and common orbital-scale upward-shallowing cycles (LaMaskin and Elrick, 1997; Gong et al., 2001; Yiming et al., 2001; Chen and Tucker, 2003; Ma et al., 2008; Zamanzadeh 2009; Whalen and Day, 2010).

Sampled Upper Devonian (Frasnian) cycles were deposited along a westward-deepening carbonate ramp ~10-20°S of the paleo-equator (Stampfl and Borel, 2002). Sampled subtidal cycles are characterized by thin, interbedded limestone and shale (rhythmites) or thin-bedded skeletal mudstone-wackestone (below storm wave base) overlain by medium- to thick-bedded skeletal mudstone-packstone, some of which contain in-growth-position Amphipora-type and/or lenticular stromatoporoids (near fair-weather wave base likely within photic zone) (Figure 2).

Figure 3. A) Late Devonian paleogeographic reconstruction of North America with major uplifts and orogenic front labeled in comparison to the estimated paleoequator. Grady shaded area indicates the positions of Nevada and Utah (United States). Inset outlines Nevada and Utah, showing locations of major faults and the Devil’s Gate Pass study area (gray square)(modified from Sandberg et al., 2003). B) Middle-Late Devonian chronostratigraphy of the study area (modified from Johnson and Murphy, 1984; LaMaskin and Elrick, 1997). Abbreviations: Lst = Limestone, Fm = Formation. Vertical lines = unconformity. Age of Middle-Upper Devonian boundary from Gradstein et al. (2004).
Upper Devonian (Frasnian) conodont samples were collected from the *hassi* conodont Zone of the Devil’s Gate Formation (Figure 3), and are primarily *Polygnathus* taxa. Age control is based on conodont biostratigraphy (e.g. Sandberg and Ziegler, 1996; Morrow and Sandberg, 2003). Coeval Upper Devonian cycles east of the study area record ~30-165 ky durations (LaMaskin and Elrick, 1997) and in other global localities record ~20 ky durations (Chen and Tucker, 2003).

Determining the magnitude of water-depth change responsible for cycle development in these and other ancient cyclic deposits is difficult, particularly because depth-diagnostic facies are lacking. However, interpretations from previous studies of meter-scale cycles from various Paleozoic successions composed of similar facies changes and from epicontinental seaway settings suggest magnitudes of less than 10-20 meters for sampled Upper Silurian and Upper Devonian cycles (e.g., Osleger, 1991; Immenhauser and Scott, 2002; Immenhauser, 2009).

**METHODS AND RESULTS**

Isotopic ratios were determined by reducing Ag₃PO₄ in a continuous flow TC-EA connected to a Finnigan Mat 253 mass spectrometer using a method modified from O’Neil et al. (1994) and Bassett et al. (2007). δ¹⁸O data are reported in ‰ with respect to SMOW (Table 1). Reproducibility of δ¹⁸O measurements was determined by replicate analyses of internal standards and uncertainty is ±0.3‰ (1σ).

δ¹⁸O analyses from sampled Upper Silurian and Upper Devonian cycles yield two major trends. Three of four sampled Silurian cycles and two of five sampled Devonian cycles demonstrate a progressive increase in δ¹⁸O in-phase with shallowing-upward facies trends (asymmetric cycles; Figure 1). The range in magnitude of intracycle
isotopic change for these cycles is 1.0-3.2‰, analogous to magnitudes recorded across Pleistocene glacial-interglacial cycles (e.g., Shackleton et al., 1988; Lisiecki and Raymo, 2005). Three of five sampled Upper Devonian cycles demonstrate an initially decreasing, then increasing $\delta^{18}O$ into the cycle cap (Fig.1). The total magnitude of intracycle isotopic change for these symmetric $\delta^{18}O$ trends is <0.5‰. One Silurian cycle records progressively decreasing $\delta^{18}O$ trends.

<table>
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<tr>
<th>distance from stratigraphic base (m)</th>
<th>$\delta^{18}O$ (%)</th>
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<tbody>
<tr>
<td><strong>Upper Silurian</strong></td>
<td></td>
</tr>
<tr>
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Table 1. Table of conodont $\delta^{18}O$ values with stratigraphic depth (m) separated into Upper Silurian and Upper Devonian ages.
DISCUSSION

Those Silurian and Devonian cycles that display δ¹⁸O trends coincident with water-depth changes support the hypothesis that these cycles were generated by orbital-scale climate changes--namely glacio-eustasy combined with SST changes. We preclude tectonic origins for cycle development because while some type of recurrent, high-frequency subsidence/uplift has been argued for particular cycles deposited in tectonically active regions (Cisne, 1986), there are no realistic explanations as to why tectonically induced water-depth changes would control systematic δ¹⁸O trends similar to those observed in this study.

Measured asymmetric δ¹⁸O trends could be generated by thermo-eustasy, groundwater storage/release, or glacio-eustasy. Orbital-scale SST changes driving thermo-eustasy (thermal expansion/contraction of seawater) could explain the observed relationships between isotopic and intracycle facies trends under ice-free conditions; however, calculated estimates on the magnitude of sea-level change caused by 4-14°C shift (Silurian) or 0.5-7°C shift (Devonian) in SST (Kolodny et al., 1983; Pucéat et al., 2011) are <5 m (Schulz and Schäfer-Neth, 1998), assuming δ¹⁸O_seawater of -1‰. Such small thermo-eustatic magnitudes are insufficient to explain the observed range of water-depth changes estimated by facies changes.

Periodic and climatically-controlled storage and release of groundwater may explain δ¹⁸O shifts and associated sea-level fluctuations (Hay and Leslie, 1990; Faure et al., 2002), in which increased groundwater storage of low δ¹⁸O meteoric waters lowers global sea-level and locally increases surface seawater δ¹⁸O values, and release of groundwater raises sea levels and decreases δ¹⁸O. While this model is attractive to explain greenhouse
cycles, we cannot use this mechanism to explain observed cyclic facies and $\delta^{18}O$ changes without a process-oriented model to rationalize cyclic groundwater storage.

Therefore, we suggest that the growth and melting of continental and alpine glaciers combined with SST variations generated observed $\delta^{18}O$ and sea-level changes (Figure 2). In the following discussion, we estimate the potential magnitudes of paleoclimate and sea-level changes necessary to create the observed isotopic shifts. Because independent temperature proxies are limited for pre-Cretaceous marine deposits, it is difficult to estimate the relative effects of ice-volume versus SST changes. Under Neogene icehouse conditions, ~70% of observed $\delta^{18}O$ values are due to ice-volume and ~30% are due to SST effects (Fairbanks and Matthews, 1978). Applying this 70:30 proportionality to these greenhouse data results in glacio-eustatic sea-level fluctuations of ~65-200 m for Upper Silurian cycles and 8-80 m for Upper Devonian cycles with coeval SST fluctuations of ~4°C and <2°C, respectively. Such large magnitudes of eustatic change are unreasonable because subaerial exposure features are not observed in these subtidal cycles and observed facies changes suggest <10-20 m of sea-level change. Assuming a smaller ice-volume contribution (e.g., 30:70; Pekar et al., 2005) results in smaller glacio-eustatic estimates (~20-90 m for Silurian cycles, ~10-35 m for Devonian cycles) but unrealistic SST changes for subtropical paleolatitudes (up to 10°C for Silurian cycles, and ~5°C for Devonian cycles). These results suggest that an additional mechanism influenced the observed intracycle isotopic trends.

Glacial intervals (low sea level) are typified by globally higher $\delta^{18}O_{\text{seawater}}$ values, drier/windier subtropical climates (e.g., van Zeist, 1967; Janecek and Rea, 1983; Rea, 1994), and associated increased evaporation rates. These increased evaporation rates,
particularly in subtropical paleolatitudes, may have further enriched local surface $\delta^{18}O_{\text{seawater}}$ values, resulting in accentuated glacial-interglacial isotopic shifts. While these local evaporation effects may explain increased intracycle isotopic shifts, the contribution of evaporation to the $\delta^{18}O$ values must have been small because the diversity and abundance of typically open-marine fauna is similar throughout Silurian and Devonian cycle development. In addition, the measured isotopic values lie within the range of conodont $\delta^{18}O$ previously reported in coeval Silurian and Devonian successions (Joachimski et al., 2004; Žigaitė et al., 2010). Most importantly, while local orbital-scale evaporation variations may explain some of the observed greenhouse $\delta^{18}O$ isotopic shifts, only glacio-eustasy can account for the observed intracycle water-depth changes.

If our glacio-eustatic hypothesis is correct, then symmetric (decreasing, then increasing upward) $\delta^{18}O$ trends within asymmetric (shallowing-upward) cycles chronicle a more complete record of the glacial-interglacial climate transition, where decreasing and low $\delta^{18}O$ values represent the transition into maximum interglacial intervals and $\delta^{18}O$ increases record the transition into full glacial intervals, while asymmetric cycles with asymmetric $\delta^{18}O$ trends record only the interglacial to glacial portion of the climatic transition. We suggest that asymmetric cycles with symmetric $\delta^{18}O$ trends are generated as a result of the interplay between sedimentation rate, subsidence and eustasy; i.e., sedimentation outpaced accommodation gains and peak interglacial conditions (sea-level highstand) occurred just below the subtidal cycle caps (Jervey, 1988).

CONCLUSIONS

Intracycle $\delta^{18}O$ trends support the hypothesis that glacio-eustasy, combined with some SST and local seawater evaporation changes, generated these Upper Silurian and
Upper Devonian cycles. These results combined with previous studies suggest very warm subtropical SSTs for the Late Silurian and early Late Devonian, but imply that polar/high latitudes provided suitable climates for some glacial ice growth during particular orbital configurations. Furthermore, these data suggest that pole-to-equator temperature gradients may have been steeper than previously assumed for portions of some greenhouse time intervals and that significant ocean-atmosphere feedbacks should be included in greenhouse climate models. In order to revise the current paradigm for greenhouse (ice-free) and icehouse (large ice sheets) time intervals, we emphasize the significance of glacial ice as a driver for orbital-scale sea-level change during both greenhouse and icehouse intervals and suggest that orbital cyclicity in portions of some greenhouse climates permit the growth of polar and alpine glaciers.
CHAPTER 2

INCREASED CONTINENTAL WEATHERING FLUX DURING ORBITAL-SCALE SEA-LEVEL HIGHSTANDS: EVIDENCE FROM ND AND O ISOTOPE TRENDS IN MIDDLE PENNSYLVANIAN CYCLIC CARBONATES

Theiling, Bethany P., Elrick, Maya, and Asmerom, Yemane

Abstract

Despite the common occurrence of orbital-scale ($10^4$-$10^5$ yr) sedimentary cycles in a wide range of Proterozoic through Neogene marine and non-marine depositional systems, understanding the effects and phase relationships of orbital-scale climate drivers on time-equivalent marine and non-marine deposits is difficult mainly due to correlation limitations between the geographically isolated deposition settings. Results from this study assess the relationships between orbital-scale continental weathering flux and glacial-interglacial marine cycles using Nd isotopes (from whole rock limestones) and $\delta^{18}$O values (from conodont apatite) from Middle Pennsylvanian cyclic marine carbonates in the U.S. Southwest.

Conodont $\delta^{18}$O trends from 2 of 4 sampled glacial-interglacial carbonate cycles support previous interpretations that observed water-depth changes were controlled by glacio-eustasy (30-50 m magnitudes) combined with $<1^\circ$ seawater temperature changes. Two additional sampled cycles show initially increasing, then decreasing $\delta^{18}$O trends. Based on these results, we suggest that $\delta^{18}$O better defines a eustatic sea-level curve, rather than a facies-derived curve.

$\varepsilon_{Nd}$ trends in 5 of 8 sampled cycles are higher during regressive intervals (early glacial phase) and lower during sea-level highstands (interglacial phase), supporting the
hypothesis that increases in precipitation and/or air temperatures during interglacial intervals result in increased continental weathering rates and/or increased flux of weathered solutes to the Middle Pennsylvanian marine basin. This hypothesis is in contrast to traditional sequence stratigraphic interpretations (increased siliciclastic shedding into marine basins during falling sea level/lowstands) and suggests that climatically-controlled precipitation and/or air temperature fluctuations influenced continental weathering flux more than sea level-controlled shoreline or baseline position in this paleotropical location. These results highlight the use of combined εNd and δ18O analysis as a tool for evaluating the response of marine and coeval non-marine systems to orbital-scale climate changes, particularly in deep-time depositional systems.

Keywords: cycles, orbital-scale, neodymium, oxygen, sea-level, glacioeustasy, glacio-eustasy, continental weathering, δ18O, εNd, glacial-interglacial

**Introduction**

Sedimentary cycles (or parasequences) recording orbitally-driven climate changes are documented in a wide range of Precambrian through Phanerozoic marine and continental deposits including shelf, slope, and open-ocean marine environments and fluviial, lacustrine, and paleosol deposits (e.g. Anderson, 1982; Arthur et al., 1986; Goldhammer et al., 1987; Olsen & Kent, 1996; Gale et al., 2002; Laurin et al., 2005; Culver et al., 2011). The widespread occurrence of such cycles across a range of geologic time periods and settings suggests that orbitally-forced climate changes are a major driver of sedimentation patterns at 10^4-10^5 yr timescales.

Despite the common occurrence of orbital cycles in the sedimentary record, it has been difficult to assess the effects and phase relationships of orbital forcing on time-
equivalent marine and non-marine deposits, particularly in deep-time systems (pre-Cenozoic). These difficulties are due mainly to limitations related to correlating between marine and geographically isolated non-marine successions at the orbital and sub-orbital timescales using conventional correlation tools such as biostratigraphy, magnetostratigraphy, carbon-isotope stratigraphy, and/or tephrachronology (e.g., Shishkin and Ochev, 1993; Lozovsky and Yarshenko, 1994; Arens and Jahren, 2000; Mundil et al., 2003; Jahren et al., 2001). An additional complexity is that many deep-time marine successions lack coeval continental deposits due to erosion, nondeposition, and/or later deformation. Understanding the flux and timing of continental material (solid and dissolved load) to adjacent marine basins in the context of orbitally-driven climate changes has important implications for evaluating global oceanic elemental and nutrient budgets, biologic productivity, carbon cycling, and $p$CO$_2$, with its associated climatic effects.

Some previous attempts to understand the effects of and relationships between orbital-scale climate change and deep-time marine and coeval continental deposits were conducted on interbedded marine and non-marine facies (Soreghan, 1994; Miller et al., 1996; Rankey, 1997). Continental climate interpretations were based on the nature and occurrence of climatically sensitive non-marine facies (i.e., eolian, paleosols, fluvial deposits), whereas sea-level interpretations tracking glacial-interglacial climate phases and glacio-eustasy were made from interbedded cyclic marine deposits. Soreghan (1994) and Rankey (1997) interpreted wetter Pennsylvanian continental climates during interglacial phases (sea-level highstands) with drier conditions during glacial phases (sea-level lowstands). In contrast, Miller et al. (1996), working on Permian deposits, report
wetter or more seasonally variable conditions during glacial phases (sea-level lowstands). These opposing interpretations are due in part to the fact that the analyzed successions contained interbedded continental and marine deposits which are not strictly time-equivalent and therefore cannot track coeval climatic responses to orbital forcing.

Alternative approaches to evaluating the effects of orbital climate change in marine and coeval non-marine systems include combined analysis of geochemical proxies for sea surface temperature (SST) and glacio-eustasy (δ¹⁸O values) and continental weathering flux (Os, Sr, and/or Nd isotopes) that occur in marine strata. The use of these proxies within fully marine successions removes potential effects of miscorrelation between marine and non-marine strata and does not require the presence of coeval non-marine successions. Although Sr isotopes have been utilized in a variety of studies to track changes in mantle versus continental flux, the >10⁶ yr oceanic residence time for Sr precludes its use in orbital-scale paleoclimate studies. The short oceanic residence time of Nd (10² yr) however, implies that Nd-isotopic ratios will be incorporated into marine sedimentary deposits before homogenization by oceanic mixing. In addition, REE are immobile (insoluble) and therefore, relatively unsusceptible to diagenesis (McLennan, 1989; Banner, 2004). Therefore, Nd isotopes can be utilized for regional-scale continental weathering flux studies to evaluate orbital- and suborbital-scale climate changes across varying climate zones/belts.

Recent advances in multi-collector inductively coupled mass spectrometry (MC-ICPMS) have made possible the rapid high-precision isotopic analysis of small quantities of Nd, opening the use of Nd isotopic data for high-resolution chemosтратigraphic reconstruction in carbonates. The objectives of this study are to describe and interpret
changes in δ¹⁸O values from conodont apatite and Nd-isotopes from cyclic whole rock limestones to assess the effects and timing relationships between orbitally driven glacial-interglacial marine cycles and continental weathering flux (a term we use to refer to continental weathering rates and/or transport to a basin).

**Geologic Background**

The Pennsylvanian Earth system was dominated by the early formation of the Pangaean supercontinent, the large Panthalassic ocean, and by major fluctuations in continental ice-volume centered in high-latitude Gondwana (Caputo and Crowell, 1985; Veevers and Powell, 1987; Frakes and Francis, 1988; Crowell, 1999; Scotese, 2001; Isbell et al., 2003; Fielding et al., 2008). Growth and melting of glaciers caused sea-level fluctuations of >50 m (e.g. Heckel, 1977; Goldhammer and Elmore, 1984; Soreghan, 1994; Joachimski et al., 2006; Rygel et al., 2008; Elrick et al., 2009) which generated orbital-scale cycles (Heckel 1977, 1994, 1997; Soreghan and Giles, 1999) and million year (My)-scale depositional sequences (Algeo et al., 1991; Soreghan, 1994; Wiberg and Smith, 1994; Scott and Elrick, 2004, Elrick and Scott, 2010).

During the Pennsylvanian, New Mexico was located approximately 5-10° south of the paleoequator (Scotese and Golonka, 1992). Tectonic subsidence rates related to Ancestral Rocky Mountain deformation were minimal during the Early and Middle Pennsylvanian and highest during the Late Pennsylvanian (Virgilian or Gzhelian) (Dickinson and Lawton, 2003).

The Middle Pennsylvanian (Desmoinesian or Moscovian) Gray Mesa Formation accumulated in the Lucero Basin of central New Mexico (Figure 4; Kelley and Wood, 1946; Martin, 1971; Kues and Giles, 2004) and is comprised of nearly 300 m of cyclic,
mixed carbonate-siliciclastic marine deposits (Martin, 1971, Scott and Elrick, 2004; Elrick and Scott, 2010). The Lucero Basin was surrounded by relatively low-relief Precambrian crystalline uplifts (~1.4-1.65 Ga; Karlstrom et al., 2004) associated with formation of the Ancestral Rocky Mountains (Figure 4; Kluth and Coney, 1981; Ye et al., 1996). Within the Lucero Basin, northward increases in both siliciclastic sediment abundance and grain size suggest sourcing from the nearby Penasco Uplift to the northeast (Martin, 1971; Scott and Elrick, 2004). Age control for the Grey Mesa
Formation is based on limited fusulinid and conodont biostratigraphy (Kelly and Wood, 1946; Wengerd, 1956; Martin, 1971).

At the Mesa Sarca study area (Figure 4), the Gray Mesa Formation is composed of ~75 orbital-scale upward-shallowing subtidal cycles (or parasequences) (Scott and Elrick, 2004). Subtidal cycles provide a more continuous record of deposition relative to peritidal cycles because of relatively uninterrupted deposition in subtidal marine environments. Typical Gray Mesa subtidal cycles (1.5-5 m) are characterized by thinly bedded, argillaceous, skeletal mudstone/wackestone or covered intervals at cycle bases (deeper subtidal facies), thin- to medium-bedded, bioturbated skeletal wackestone/packstone in the middle of cycles (shallow subtidal facies), with medium- to thick-bedded, skeletal wackestone/packstone and rare grainstone cycle caps (shallowest subtidal facies). Approximately 40% of cycle caps display evidence of subaerial exposure, including meteoric δ¹³C signatures, calcretes, and regolith breccias (Figure 5; Scott and Elrick, 2004; Elrick and Scott, 2010).

Previous studies of Gray Mesa cycles in the study area document orbital-scale sea-level fluctuations and systematic up-cycle increases in whole rock δ¹³C and conodont δ¹⁸O, which together indicate high-amplitude (>50 m) glacio-eustasy was responsible for cycle development and subaerial exposure during sea-level fall/lowstands (Scott and Elrick, 2004; Elrick and Scott, 2010).

**Methodology**

This study focuses on samples collected from 8 successive, subtidal cycles in the lower 35 m of the Gray Mesa Formation (highstand systems tract of Sequence 1; Scott and Elrick, 2004).
Figure 5. Cyclostratigraphy of the targeted lower Gray Mesa Formation versus relative water depths (dashed line) determined from facies analysis and eustatic sea-level (solid line) estimated from the combined effects of sedimentation, subsidence, and sea-level change, $\delta^{18}O_{apatite}$, and $\varepsilon_{Nd}$ trends. Cycle numbers are based on previous work by Scott and Elrick (2004). $\delta^{18}O$ data from cycle 12 is taken from Elrick and Scott (2010). Error bars for $\varepsilon_{Nd}$ are smaller than the size of the data point, when not shown suggesting that small isotopic variations recorded in cycle 10 are significant.
Oxygen Isotopes

Analyses of conodont δ\textsuperscript{18}O were used to verify that Gray Mesa cycles sampled for Nd isotopes formed in response to orbital-scale glacio-eustasy. Oxygen isotopes from marine calcite are a well-established tool for determination of seawater temperature changes and ice-volume effects (e.g. Epstein et al., 1953; Emiliani, 1955, Shackleton and Opdyke, 1973; Veizer et al., 1999). δ\textsuperscript{18}O from conodont apatite is considered more reliable for pre-Mesozoic studies than calcite because it is less susceptible to diagenetic alteration (Bryant et al., 1996; Iacumin et al., 1996; Wenzel et al., 2000; Joachimski et al., 2004). Conodont apatite has been shown to precipitate in equilibrium with ambient seawater when compared to coeval fish teeth (Amzy et al., 1998). In addition, conodont δ\textsuperscript{18}O values demonstrate smaller isotopic variability than coeval calcite (Wenzel et al., 2000).

Samples for conodont analyses were collected at 0.1-0.5 m intervals depending on observed facies changes, with individual samples weighing between 10-25 kg. Conodonts were extracted from whole rock limestones using conventional separation techniques of Sweet and Harris (1988).

Oxygen isotopic analyses were performed on \textsim500 \mu g of Ag\textsubscript{3}PO\textsubscript{4} crystals, formed from the conversion of conodont apatite using a method modified from O’Neil et al. (1994) and Bassett et al. (2007). Isotopic ratios were determined by reducing Ag\textsubscript{3}PO\textsubscript{4} in a continuous flow TC-EA and analyzed on a Finnigan Mat 253 mass spectrometer at the University of New Mexico Stable Isotope Laboratory. Oxygen isotope data are reported in ‰ with respect to SMOW (Table 2). Reproducibility of δ\textsuperscript{18}O measurements was
determined by replicate analyses of internal standards and with an uncertainty of ±0.3‰ (1σ).

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aSample numbers represent distance (m) above underlying sequence boundary, identified by Scott and Elrick (2003).

bValue of εNd at present day.

cεNd during estimated time of deposition (300 My), where 147Sm/144Nd = Sm(ppm)/Nd(ppm)^b

Natural abundance of 147Sm/144Nd. Atomic weight of Nd/Sm, then 143Nd/144Nd(300 My) = 143Nd/144Nd(measured(εt=1)*147Sm/144Nd, εNd(t=300 My) = (143Nd/144Nd(300 My)^b/143Nd/144Nd(subchur)^b)*10000

Table 2. 143Nd/144Nd, apparent εNd (value at present), Sm and Nd concentrations (ppm), εNd (t=300 My), and δ18O data for sampled intervals. t=300 My is assumed as an approximate age for deposition of Gray Mesa cycles to determine εNd at the time of deposition.

Neodymium Isotopes

143Nd is the decay product of 147Sm (t1/2 = 106 Ga). Variations in 143Nd/144Nd are typically expressed by εNd values, defined as (143Nd/144Nd(sample)/143Nd/144Nd(CHUR)^b -
where CHUR is the \(^{143}\text{Nd} / ^{144}\text{Nd}\) ratio of the chondritic undifferentiated reservoir at the time of interest. Because Nd has a larger ionic radius than Sm, Nd is considered ‘more incompatible’ than Sm. More incompatible elements will be preferentially partitioned into the crust during mantle melting and differentiation. Consequently, the continental crust has a lower Sm/Nd ratio than the depleted mantle (as sampled by mid-ocean ridge basalts [MORB]) and as a result, a less radiogenic Nd-isotopic composition (typically \(\varepsilon_{\text{Nd}} = -20\) for crust with a mean age of 2 Ga; Goldstein and Jacobsen, 1987) compared to MORB (typically > +8; Shirey, 1991). The short oceanic residence time of Nd (<10\(^2\) yr) however, implies that Nd-isotopic ratios will be incorporated into marine sedimentary deposits before homogenization by oceanic mixing (oceanic mixing time ~1000 yrs). In addition, REE are immobile (insoluble) and therefore, relatively unsusceptible to diagenesis (McLennan, 1989; Banner, 2004). Therefore, Nd isotopes can be utilized for regional-scale continental weathering flux studies to evaluate orbital- and suborbital-scale climate changes across varying climate zones/belts. Because the seawater REE budget is dominated by continental input (Goldstein and Jacobsen, 1987), \(\varepsilon_{\text{Nd}}\) in marine deposits can serve as a proxy for changes in the regional continental weathering flux, and can be used to track paleo-ocean circulation (e.g. Martin and Macdougall, 1995; Reynolds et al., 1999; Thomas, 2004; Piotrowski et al., 2005; Puceat et al., 2005; Scher and Martin, 2006; Via and Thomas, 2006; MacLeod et al., 2008) and emergence/flooding of continental landmass (Fanton et al., 2002).

Nd-isotopic analyses were performed on powdered whole-rock limestones collected at a 0.1-1 m sampling resolution. Approximately 500 mg of powder was drilled from
each sample using a diamond-bit Dremel© in order to avoid stylolites, intraclasts, large skeletal grains, and veins. The powder was dissolved in 6N HCl. The soluble and insoluble fractions were then centrifuged and the supernate was separated into two Teflon© beakers, one to be used to analyze concentrations of Sm and Nd for calculation of $^{147}\text{Sm}/^{144}\text{Nd}$, and one to be used for REE and Sm-Nd column separation for analysis of $^{143}\text{Nd}/^{144}\text{Nd}$.

For this initial effort, we used a small aliquot of the supernate to determine the Sm/Nd ratio of the samples to calculate initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. The Sm/Nd fraction was dried down, dissolved in 200 μL 7N HNO₃, capped, and left overnight. The sample was then dissolved in 50 mL of 10 ppb In + 3% HNO₃, and was analyzed on a Thermo X-series II inductively coupled plasma quadrupole mass spectrometer (ICPQMS) at the University of New Mexico Radiogenic Isotope Laboratory. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ values were calculated using an age of 300 Ma (approximate depositional age of Gray Mesa Formation; Table 2). We have verified this initial method using a total spiking method, whereby a calibrated spike with known $^{147}\text{Sm}/^{150}\text{Nd}$ was added to sample supernate to determine sample $^{147}\text{Sm}/^{144}\text{Nd}$.

The supernate used for analysis of $^{143}\text{Nd}/^{144}\text{Nd}$ was dried down and dissolved sequentially in 7N HNO₃ and 15N HNO₃, drying after each acid addition. The sample was then dissolved in 4 mL 1N HNO₃, centrifuged, and the supernate was added to 250μL cation exchange columns filled with TRU-SP resin, cleaned, and conditioned with 1N HNO₃. REE were collected using a modified method of Asmerom (1999). REE fractions were dried down and dissolved in 200 μL 0.18N HCl and were added to REE exchange columns cleaned and conditioned with 0.18N HCl. Nd was separated and
collected using a modified method of Asmerom (1999). The sample solution was dried and dissolved in 1 mL 3% HNO₃ for analysis on a Thermo Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at the University of New Mexico Radiogenic Isotope Laboratory.). Reproducibility of $\varepsilon_{\text{Nd}}$ was determined using replicate analyses and is reported for each sample, ranging between 0.05 and 0.26 $\varepsilon$-units and averaging 0.11 $\varepsilon$-units ($2\sigma$) (Table 2, Figure 5). Error bars of less than 0.20 $\varepsilon$-units are smaller than data points and therefore not shown in Figure 5. The La Jolla Nd isotopic standard was run with each batch, obtaining a mean value of $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511825± 4 ($2\sigma$), which is within the accepted range of values for the standard (Pier et al., 1989).

**Results**

$\delta^{18}O$ values range between 18.0-19.5‰. The change in $\delta^{18}O$ values across individual sampled cycles ranges between 0.5‰ and 0.9‰ (Table 2, Figure 5). Cycles 5, 6, and 12 show progressive up-cycle increases in $\delta^{18}O$. Data for cycle 12 comes from Scott and Elrick (2004). Cycles 7 and 8 show initially increasing, then decreasing $\delta^{18}O$ trends.

$\varepsilon_{\text{Nd}}$ values ($t=300$ My; estimated age of Grey Mesa cycles) range between -10.9 and -7.4 (Table 2, Figure 5). The change in $\varepsilon_{\text{Nd}}$ values across individual sampled cycles ranges between 0.2-2.0 $\varepsilon$-units. Five of the eight sampled cycles are characterized by initially decreasing, then increasing $\varepsilon_{\text{Nd}}$ values. Because only 2 samples were recovered for cycle 5, no trend is specified. Cycle 6 shows progressively decreasing $\varepsilon_{\text{Nd}}$ values. Cycle 8 shows initially increasing, then decreasing $\varepsilon_{\text{Nd}}$ values.

$\delta^{18}O$ vs. $\varepsilon_{\text{Nd}}$ do not covary (Figure 6). Systems in which the supply of continental weathering flux co-varies with $\delta^{18}O$ suggest that both isotopic systems were influenced
by the same process on the same spatial or temporal scale, namely global glacial-interglacial climate changes (Vance et al., 2009). That $\delta^{18}O$ vs. $\varepsilon_{Nd}$ do not covary suggests that these proxies were influenced by either different processes or that they are affected on a different spatial scale (e.g. global vs. regional changes).

![Figure 6. $\varepsilon_{Nd}$ vs. $\delta^{18}O$ for sampled Gray Mesa cycles. The lack of co-variance suggests that continental weathering flux ($\varepsilon_{Nd}$) is locally-derived. Co-variance of $\varepsilon_{Nd}$ and $\delta^{18}O$ would suggest that changes in continental weathering flux were influenced by either the same process (i.e. glacio-eustasy and SST change) or that changes in continental weathering flux occurred on the same spatial scale (i.e. global vs. regional).](image)

**Discussion**

$\delta^{18}O$ trends

The systematic up-cycle increase in $\delta^{18}O$ values in 3 of 5 cycles supports the expected relationship between sea level and glacial growth and melting recorded in the Pleistocene-Holocene (e.g., Shackleton et al., 1988; Zachos et al., 2001; Lisiecki and Raymo, 2005; Raymo et al., 2006; Massari et al., 2007) and previous interpretations that these Pennsylvanian cycles were generated by glacio-eustatic sea-level change combined with some SST change (Joachimski et al., 2006; Elrick and Scott, 2010) (Figure 5). Without the aid of independent temperature proxies such as foraminiferal Mg/Ca ratios, we cannot separate the effects of changes in glacial ice volume versus seawater temperature.
If the measured isotopic shifts were due entirely to SST change, then the estimated temperature change across individual cycles would range between 2-4°C, applying the phosphate-water fractionation and temperature equations from Kolodny et al. (1983) and Pucéat et al. (2010). This range of temperature change would produce only a <0.5 m thermo-eustatic sea-level change (thermal expansion/contraction of seawater; deWolde et al., 1995; Schulz and Schäfer-Neth, 1998). Such low magnitudes are unreasonable given the >50 m estimates based on facies analysis, extent and depth of subaerial exposure features, and stratal geometries (e.g. Heckel, 1977; Rygel et al., 2008). Conversely, if we assume isotopic shifts were due only to ice-volume effects, the measured 0.5-0.9‰ changes in δ\(^{18}\)O during cycle development equate to ~45-80 m glacio-eustatic changes for the sampled cycles, assuming the relationship of 0.11‰ per 10 m sea-level change (Fairbanks and Matthews, 1978).

Using the Pleistocene as an analog, we assume a combination of ice-volume and SST effects controlled the measured isotopic variations, and assume SST and ice-volume effect contributions of ~30% and ~70%, respectively (Fairbanks and Matthews 1978; Fairbanks, 1989). Using this method, we estimate that the sampled Gray Mesa cycles were generated by >30-50 m glacio-eustatic changes accompanied by <1°C SST changes. However, Ca/Mg ratios and δ\(^{18}\)O data from planktonic foraminifera over the past 350 kyr suggest glacial-interglacial SST changes on the order of 3-5°C (Lea et al., 2000;2002). If we apply 3-5°C SST change as a minimum to sampled Pennsylvanian cycles, then the remaining isotopic shift equates to <25 m glacio-eustatic sea-level fluctuations, which would imply that SST change contributed ~70% of the total δ\(^{18}\)O value, double the
estimated contribution over the last few million years (Fairbanks and Matthews, 1978; Fairbanks, 1989).

The estimated >30-50 m magnitudes record minimum values and are less than those (~60-140 m) reported by Elrick and Scott (2010). The absence of lowstand and early transgressive deposits and variability in the extent of subaerial exposure and facies changes observed at Mesa Sarca indicate that this locality did not record the full extent of sea-level rise and fall and imply that the full magnitude of glacial-interglacial isotopic shift was even larger. Much like the Pleistocene, \(10^5-10^6\) yr fluctuations in the volume of glacial ice during the Pennsylvanian likely contributed to the variability of sea-level change between successive cycles (Rygel et al., 2008).

It is unclear why cycles 7 and 8 show initially increasing, then decreasing \(\delta^{18}O\) values, with maximum values near mid cycle (Figure 5). Based on traditional facies analysis, which is used to interpret relative sea-level changes, these \(\delta^{18}O\) versus facies relationships suggest that maximum glaciation occurred just above mid-cycle or below cycle tops, before deposition of the shallowest water facies at the cycle top. However, a more reasonable interpretation is that these cycles were generated in response to eustasy. We discuss \(\delta^{18}O\) versus facies relationships using Figure 7, which outlines the differences between relative sea-level interpreted from facies analysis versus eustatic sea-level interpreted from a theoretical understanding of the combined effects of subsidence, sea-level change, and sedimentation (Jervey, 1988; Coe and Church, 2000). Shallowing-upward facies could be generated by sedimentation rates greater than eustatic sea-level rise rates. However, this hypothesis is unlikely because the tops of cycles 7 and 8 display evidence of prolonged subaerial exposure, including pedogenic calcretes and meteoric
δ^{13}C signatures, which can only form when absolute sea level falls and exposes the seafloor to meteoric waters and soil formation.

Increasing, then decreasing δ^{18}O in cycles 7 and 8 could also be generated by changes in evaporation rate and/or basin restriction, whereby increases in evaporation rate and/or basin restriction are recorded by greater δ^{18}O values. However, this hypothesis is unlikely because the greatest δ^{18}O values are recorded during the mid- to late regression when eustatic sea-level is high (Figure 7). If evaporation rates increased during this interval, exchange with the open ocean would have also increased due to sea-level rise, dampening the effect of evaporation rate on δ^{18}O values.

![Figure 7](image)

Figure 7. A) Simplified sinusoidal eustatic sea-level (SL) curve with labeled inflection points and maximum glacial-interglacial intervals. B) Stratigraphic nomenclature used in text with schematic asymmetric cycles similar to those observed in the Gray Mesa Formation with a narrower column representing deeper water facies and a wider column representing shallower water facies. Note that no deposition/erosion occurs during the late...
eustatic fall, lowstand and early rise (diagonal lines) and a disconformity develops; subaerial exposure features develop at the cycle top during subaerial exposure (black triangles). During a single glacial-interglacial sea-level cycle, deposition during the initial transgression as the glaciers begin to melt is not recorded within the study area due to lack of accommodation space. Once accommodation space is created due to subsidence and rapid (maximum) SL rise rates, deposition occurs and is represented by deeper water deposits at the cycle base. SL continues to rise with additional glacial melting and reaches its highest position at the interglacial maximum (mid-regression). Because SL is rising at a slower rate after the maximum rate of SL rise inflection point (and assuming constant sedimentation rate), sediments above the maximum flooding zone reflect loss of accommodation space and is termed the early regressive interval. After the interglacial maximum, SL fall rates increase and is represented by the shallowest water deposits of the late regressive interval. The maximum regression is therefore defined in this study as the maximum regressive deposits recorded at the sampling locality.

Nd-isotope trends

Five of the eight sampled cycles are characterized by $\varepsilon_{\text{Nd}}$ trends that are initially high at cycle base (maximum flooding), lowest near the mid-cycle (mid-regression), and return to high $\varepsilon_{\text{Nd}}$ values at the cycle top (late regression; Figures 5 and 7). These trends suggest increasing continental weathering flux into the Lucero Basin during times of maximum flooding when sea-level was rising the fastest and until sea level reached its highest position at the interglacial maximum (mid-cycle). Subsequent increases in $\varepsilon_{\text{Nd}}$ values suggest a reduction in continental weathering flux into the basin during initial sea-level fall. During sea-level lowstand, this inner shelf location was subaerially exposed (depositional hiatus) and no record of Nd-isotopes is available.

Four possible interpretations are explored to explain these dominant $\varepsilon_{\text{Nd}}$ trends, each within the context of orbital-scale glacio-eustatic sea-level fluctuations. Fanton et al. (2002) interpret that $\varepsilon_{\text{Nd}}$ increases and decreases recorded in Ordovician marine deposits represent influx from significantly different continental source areas during My-scale regression and transgression. In their scenario, the low-relief Precambrian shield (with low $\varepsilon_{\text{Nd}}$) was exposed during regression and submerged during transgression, which resulted in regressive marine deposits with low $\varepsilon_{\text{Nd}}$ values and transgressive deposits with higher $\varepsilon_{\text{Nd}}$ values. Applying this principle to the Lucero Basin, the observed $\varepsilon_{\text{Nd}}$ trends could be produced if influx from older continental crust (with lower $\varepsilon_{\text{Nd}}$ values) occurred
during high sea level (interglacial maximum), whereas influx from younger continental crust (with higher $\varepsilon_{Nd}$ values) reached the basin during sea-level fall (glacier growth). This scenario is not reasonable for this study because the Lucero Basin was surrounded by Precambrian uplifts (Ancestral Rocky Mountains), all with similar ages of ~1.7 Ga whose $\varepsilon_{Nd}$ at the time of deposition of Gray Mesa cycles is ~30 to -25 calculated from measured $^{143}\text{Nd} / ^{144}\text{Nd}$ and $^{147}\text{Sm} / ^{144}\text{Nd}$ reported in Bennett and DePaolo (1987); see Table 1 for calculations. Maximum exposure of these Precambrian uplifts during falling and low sea levels (glacier growth and glacial maximum) would have generated $\varepsilon_{Nd}$ trends opposite of those observed.

A second potential explanation for the observed $\varepsilon_{Nd}$ trends would be changes in regional marine circulation patterns. The observed $\varepsilon_{Nd}$ trends would result from regional marine currents transporting lower $\varepsilon_{Nd}$ values from older continental source areas flowing into the Lucero Basin during rising and high sea level (interglacials), whereas marine currents transporting higher $\varepsilon_{Nd}$ isotope values (sourced from younger continental crust or more open-ocean waters) would flow into the Lucero Basin during falling and low sea level (early, maximum, and late glacial intervals). Because Precambrian Ancestral Rocky Mountain uplifts throughout the U.S. Southwest have relatively uniform $\varepsilon_{Nd}$ values (Bennett and DePaolo, 1987), it is unlikely that the Mesa Sarca $\varepsilon_{Nd}$ trends record changes in influx from significantly different continental crust source areas and it is unlikely that the same marine circulation patterns would have occurred for six successive cycles formed during variable magnitude sea-level changes.

Instead, we explore two alternative mechanisms that can explain changes in continental weathering flux on orbital timescales. In a scenario in which eolian transport
dominated continental influx into the Lucero Basin, rising sea levels (early interglacials or cycle bases) are characterized by low eolian influx due to low wind intensities and/or greater humidity/wetter climate, and resultant high $\varepsilon_{\text{Nd}}$ values. This would be followed by increasing eolian influx due to increasing winds/aridity during highest sea-levels (interglacial maximums or mid-cycles), resulting in low $\varepsilon_{\text{Nd}}$ values. During subsequent sea-level fall (early glacial), eolian input would decline with decreasing wind intensity and/or aridity and a return to higher $\varepsilon_{\text{Nd}}$ values. While a few studies from tropical and temperate Pacific Ocean cores report increased eolian input during Pleistocene or Holocene interglacial intervals (Rea et al., 1986; Hovan et al., 1991), the majority of findings from these studies suggest that glacial intervals are characterized by drier climates and greater wind intensities, whereas interglacial intervals have wetter climates and lower wind intensities globally (e.g. Zeist, 1967; Janecek and Rea, 1983; Wasson et al., 1984; Rea et al., 1991; Nanson et al., 1992; Wang, 1993; Rea, 1994; Rincón-Martinez et al., 2010). Without a process-oriented model explaining windier/more arid conditions during interglacial intervals, it is not reasonable to expect that wind behavior during glacial Pennsylvanian intervals opposed the dominant Pleistocene regime.

We suggest that the observed $\varepsilon_{\text{Nd}}$ trends were likely controlled by orbitally-driven changes in continental weathering rates and/or fluvial sediment influx. Accordingly, the observed trends would develop if fluvial influx and/or chemical weathering rates were low (resulting in higher $\varepsilon_{\text{Nd}}$ values), increasing during maximum sea-level rise rates (early interglacial), and were greatest, signaled by lower $\varepsilon_{\text{Nd}}$ values, during sea-level highs (interglacial maxima); fluvial influx and/or weathering rates would then decrease (rising $\varepsilon_{\text{Nd}}$ values) during the subsequent fall in sea level (early glacial) (Figure 7).
suggest that the systematic changes in fluvial influx and/or chemical weathering rates were controlled by orbitally-forced changes in paleotropical precipitation and/or air temperature, in which increases in precipitation and/or air temperature resulted in increased fluvial influx and/or chemical weathering rates and decreases in precipitation and/or air temperature resulted in decreased fluvial influx and/or weathering rates.

Many modern watersheds are shown to be ‘weathering limited’, characterized by thinner soils with readily available unaltered minerals, such that weathering flux is limited by mineralogy (susceptibility to chemical weathering), precipitation, soil-water pH, and temperature (Stallard and Edmond, 1981; 1983; 1987; Kump et al., 2000). Global continental chemical weathering rates are shown to increase with rises in temperature and precipitation demonstrated by increases in fluvial discharge cation concentrations, Ca, Mg, K, HCO$_3^-$, and H$_4$SiO$_4$ (e.g., Bluth and Kump, 1994; White and Blum, 1995; Berner et al., 1998; Kump et al., 2000; Frank, 2002; West et al., 2005; Schmidt et al., 2006; Gislason et al., 2009; McKay et al., 2009; Kuwahara et al., 2010; Williams et al., 2010). Indeed, positive coupling of chemical weathering rates with precipitation and temperature is also demonstrated over orbitally-driven glacial-interglacial cycles (e.g. Burton and Vance, 2000; Piotrowski et al., 2005; Bokhorst et al., 2009; Kuwahara et al., 2010). Because air temperature often co-varies with precipitation, evaporation rates, and vegetation cover, it is difficult to separate the effects of temperature and precipitation on chemical weathering rates (Kump et al., 2000). To separate the effects of temperature and precipitation, White and Blum (1995) fit an Arrhenius-type equation to SiO$_2$ and Na fluxes. Although plots of weathering fluxes versus temperature correlate reasonably well, they significantly underestimate chemical
weathering rates, suggesting that precipitation dominates chemical weathering rates and that precipitation and temperature are positively coupled.

The relationship between drier glacials and wetter interglacials is consistent with results from paleoequatorial regions in the Late Pennsylvanian (Soreghan, 1994; Rankey et al., 1997) and Pleistocene-Holocene (e.g. Zeist, 1967; Janecek and Rea, 1983; Wasson et al., 1984; Rea et al., 1991; Nanson et al., 1992; Wang, 1993; Rea, 1994; Rincón-Martinez et al., 2010). In particular, planktonic foraminifera from the Bay of Bengal demonstrate cyclic variations in \( \varepsilon_{\text{Nd}} \) on glacial-interglacial timescales over the past 150 kyr due to variations in continental weathering flux (Burton and Vance, 2000). Each of these examples are characterized by cooler, drier climates during glacial maxima with a relatively low flux of fluvially-derived material (reflected by higher \( \varepsilon_{\text{Nd}} \)) and warmer, wetter interglacial intervals, in which flux of fluvially-derived material increases (reflected by lower \( \varepsilon_{\text{Nd}} \)) (Naimo et al., 2005; Kettner and Syvitski, 2009; Lewis et al., 2009, Burton and Vance, 2000).

Vance et al., (2009) suggest that the products of chemical weathering on glacial-interglacial timescales is moderated by post-glacial weathering pulses (fine-grained physical weathering products produced by subglacial grinding underneath continental glaciers; Bell and Laine, 1985; Anderson, 2007) released during glacial melting and retreat. Post-glacial weathering pulses are more likely to be observed in ferromanganese nodules in post-glacial lakes (Vance et al., 2009), deep-ocean ferromanganese crusts (Reynolds et al., 1999; Piotrowski et al., 2005), and marine sediments along high-latitude continental shelves (Scher et al., 2011). Low-latitude shelf localities are less likely to record post-glacial pulses because global transport of REEs such as Nd and Sm occur via
large-scale ocean circulation (i.e., modern transport from the Labrador Surface Water current to the North Atlantic Deep Water current and then the Antarctic Bottom Water current; e.g., Burton et al., 1997; Piotrowski et al., 2005; Scher and Martin, 2006; Via and Thomas, 2006). Due to their low mobility, REEs will likely be scavenged by particulates before a high-latitude post-glacial weathering pulse can be recorded in marine sediments accumulating on a low-latitude shelf. In addition, the lack of co-variance between $\delta^{18}$O and $\varepsilon_{\text{Nd}}$ support the assumption that $\varepsilon_{\text{Nd}}$ values are locally-derived (Figure 6).

One of the eight sampled cycles (cycle 6) records a progressive increase in $\varepsilon_{\text{Nd}}$ values from cycle base to top and one cycle (cycle 8) shows an initial increase to peak $\varepsilon_{\text{Nd}}$ values in the middle of the cycle followed by a decrease in values within the cycle cap (Figure 5). These variable trends may be due to fluctuations in sedimentation rate, thus recording an incomplete eustatic sea-level curve over cycle development (Figure 7). Long-term variations in the magnitude of Pliocene through Pleistocene orbital-scale climate forcing are a possible explanation for variations in continental weathering flux, if changes in the magnitude of climatic forcing control the proclivity of chemical versus mechanical weathering. Differences in $\varepsilon_{\text{Nd}}$ between the acid soluble (AS) and acid insoluble (AIS) fraction of samples may elucidate whether $\varepsilon_{\text{Nd}}$ values were incorporated into the crystal structure of carbonate minerals (suggesting chemical weathering dominated) or whether $\varepsilon_{\text{Nd}}$ is a primary signature of the detrital component (suggesting mechanical weathering dominated). Such a test may also explain why sediments deposited during the interglacial maximum do not necessarily possess the greatest detrital (AIS) fraction.

It is important to note that if our hypothesis of increased continental weathering flux during sea-level highstands (interglacials) is due to increased precipitation (and as a
result, increased fluvial flux), then it opposes traditional sequence stratigraphic interpretations, where sea-level controls shoreline and fluvial base-level positions and by implication, the flux of continentally-derived sediment into the marine basin (e.g. Van Wagoner et al., 1988; Coe and Church, 2003). In the traditional sequence stratigraphic model, sea-level fall/lowstands are characterized by fluvial incision and increased fluvial transport to the marine basin, which would be recorded by an up-cycle increase in $\varepsilon_{\text{Nd}}$. In contrast, our hypothesized model suggests that increased fluvial incision and/or transport of physical weathering products (solids) and dissolved chemical weathering products (dissolved load) (shown by decreased $\varepsilon_{\text{Nd}}$) coincide with intervals of sea-level rise and highstand (interglacial), followed by decreased fluvial incision and/or flux (shown by increasing $\varepsilon_{\text{Nd}}$) during sea-level fall/lowstand (glaciation) (Figure 7). Increased fluvial incision is indeed more likely to occur during maximum regression due to lowering of fluvial base level, however the type of weathering (physical versus chemical), the mechanism of transport (fluvial versus eolian) and weathering rates to generate transportable particles is dominated by local/regional, climatically controlled changes in precipitation and/or air temperature.

Results from this study highlight how orbital to suborbital variations in $\varepsilon_{\text{Nd}}$ and $\delta^{18}\text{O}$ within marine strata can detect the response of continental weathering flux to orbitally-forced climate change and eliminates potential miscorrelations between geographically separated marine and coeval non-marine successions. These results demonstrate that Middle Pennsylvanian paleotropical continental weathering flux is generally in-phase with glacio-eustatic sea-level change and glacial growth/melting, and suggest that local/regional paleotropical continental weathering may be dependent upon climatically
controlled changes in fluvial flux due to fluctuations in precipitation and/or air temperature. These results highlight a promising new technique utilizing nearshore marine successions to evaluate regional continental weathering flux and climate change within the context of global sea-level and glacial-interglacial cycles.

Conclusions
1) $\delta^{18}$O trends across targeted orbital-scale subtidal cycles support previous interpretations that these cycles formed in response to glacio-eustasy with magnitudes of between 30 and 50 m combined with ~1°C SST changes.

2) The majority of cycles sampled for $\varepsilon_{\text{Nd}}$ analysis display trends indicating maximum continental weathering flux during interglacial maxima (sea-level highstands) when local paleotropical precipitation rates and/or paleotemperatures were the highest, facilitating maximum weathering rates and/or fluvial transport of weathered solutes to the study area. During lower sea-level stands (early and late glacial stages), continental weathering flux decreased, suggesting drier and/or cooler paleotropical climates. Because these cycles were deposited at an inner shelf location, no record is available for lowest sea-level positions (glacial maximum).

3) Our hypothesis of increased continental weathering influx during sea-level highstands (interglacials) is in contrast to traditional sequence stratigraphic interpretations and suggests that climatically controlled precipitation and/or air temperature fluctuations influenced continental weathering flux more than sea-level controlled shoreline/base line position in this paleotropical location.
CHAPTER 3
FLUCTUATIONS IN CONTINENTAL WEATHERING FLUX DURING TWO
PALEOZOIC GREENHOUSE INTERVALS

Theiling, B.P., and Elrick, M.

Abstract

Previous utilization of Nd isotopes in marine successions as a proxy for evaluating regional-scale changes in continental weathering flux under icehouse global climate regimes typically describe a binary mixing model between relatively unradiogenic continental rocks and relatively radiogenic oceanic waters and demonstrate that increases in continental weathering flux occur during interglacial intervals as a result of increases in precipitation and/or air temperature. This study compares icehouse Nd isotope trends to those generated during two separate global greenhouse intervals of the Late Silurian and early Late Devonian. Upper Silurian \( \varepsilon_{Nd} \) ranges from -8.4 to -10.9 and show no consistent intra-cycle trend, due to averaging out of far-field source variations in continental weathering flux, relatively uniform Late Silurian sub-tropical climate, and/or subdued continental weathering and flux due to the absence of upland and inland vascular land plants. Upper Devonian \( \varepsilon_{Nd} \) ranges from -12.9 to -6.6, and demonstrate increased intra-cycle variation in \( \varepsilon_{Nd} \), most likely due to enhanced chemical weathering due to widespread colonization of land plants with large root systems and an intensified hydrologic cycle due to evapotranspiration. The range in \( \varepsilon_{Nd} \) for Upper Silurian and Upper Devonian cycles support previous claims that the widespread transition from weathering of relatively unradiogenic Canadian Shield and Transcontinental Arch to the radiogenic Caledonian Mountain Belt had occurred by the Pridolian in mid-Laurentia and
the Frasnian in western Laurentia. Cycle-scale comparison of $\varepsilon_{\text{Nd}}$ from sampled greenhouse cycles to an icehouse continental weathering-climate model suggests that only a portion of the complete transition from warmer and/or wetter climate to cooler and/or drier climate intervals may be recorded. Partial $\varepsilon_{\text{Nd}}$ records observed in most Upper Devonian sampled cycles are likely produced as the result of the interplay between sedimentation rate, accommodation space, and eustasy.

**Introduction**

Recently, Nd isotopes have been used to detect significant orbital-scale or high-frequency ($10^4$-$10^5$ yr) changes in continental weathering flux during icehouse climates (Burton and Vance, 2000; Theiling et al., 2012)(Chapter 2), intervals characterized by large climate shifts and large changes in continental ice volumes. Observed continental weathering flux variations imply concurrent fluctuations in nutrient supply to oceans and pCO$_2$ uptake related to silicate weathering rate changes, both of which have important affects on the global carbon budget, climate, and marine biologic productivity.

As our global climate shifts to warmer, or greenhouse, modes, a question arises as to whether continental weathering flux changes occur on orbital-timescales during warmer climates and if so, are these flux changes enhanced by warmer temperatures and an intensified hydrologic cycle or damped by more stable/uniform climatic conditions? Furthermore, are fluctuations in continental weathering flux recorded in marine basins the result of local, regional, or far-field changes in weathering and erosion?

The objectives of this study are to 1) describe orbital-scale Nd isotope trends during two different cyclic greenhouse marine successions of Late Silurian and Late Devonian age, 2) compare these greenhouse Nd isotope trends to those recorded in Pleistocene and
Pennsylvanian icehouse orbital-scale cycles, and 3) evaluate continental weathering flux provenance using absolute Nd and Sm/Nd isotope ratios.

Climatic and Geologic Setting

Upper Silurian

Traditionally, the Late Silurian has been interpreted as a greenhouse interval based on high latitudinal reef (Copper 2002) and carbonate (Lubeseder 2008) distribution, a lack of glacial deposits (Lehnert et al. 2006), globally high sea levels (Copper 2002), and low δ¹⁸O (Veizer et al. 1999). However, recent data from Upper Silurian marine deposits record a range of geochemical and stratigraphic fluctuations that indicate widespread and dynamic climatic conditions, including large positive δ¹³C excursions (e.g. Joachimski et al., 2002; Munnecke et al. 2003; Saltzman, 2005), My-scale δ¹³C and δ¹⁸O fluctuations (Samtleben, 2000; Munnecke et al., 2003; Saltzman), and worldwide distribution of cyclic, orbital-scale upward-shallowing marine sedimentary cycles (parasequences) (Calder and Gibling, 1994; Brett et al., 1998; Cotter, 1998; Dorning and Harvey, 1999; Al-Shaieb et al., 2001; Bourque, 2001; Anderson and Goodwin, 2003; Skompski et al., 2008; Cramer, 2009).

During the Late Silurian, much of the Earth’s continental mass was situated in the southern hemisphere, leaving the northern hemisphere largely covered by the Panthalassic Ocean. The Late Silurian saw the closure of the Iapetus Ocean, culminating in the collision of Laurentia with the newly-combined Baltica-Avalonia Terrane (Caledonide Orogengy: 425-420 Ma; Cocks and Torsvik, 2002). The resultant Laurussian continent was largely covered by an epeiric sea. Successive continental collisions from the Taconic (Late Ordovician), Caledonide (Late Silurian) and Acadian
(Late Silurian-Early Devonian) Orogenies generated ~2000 km of uplifted accreted terranes to the north and northeast portions of Laurentia. Although the timing of the Romanzof Orogeny is still debated to have begun in the Early-Middle Devonian (Embry, 1991; Trettin, 1991), the Romanzof and Klakas Orogenies may have generated uplifts along the northern edge of Laurentia as early as the Late Silurian (Bazard et al., 1995; Butler et al., 1997; Soja and Antoshkina, 1997; Soja et al., 2000; van Staal et al., 2009). Carlson (1999) suggests the relatively low relief Transcontinental Arch (extending from Minnesota to New Mexico) was exposed during the Late Silurian. The Southern Oklahoma Rift and Reelfoot Rift (Proterozoic) basins intersected the southern margin of Laurussia. (Cocks and Scotese, 1991; Golonka et al., 1994; Cocks and Torsvik, 2002). Carbonate ramps and platforms extended along this southern edge from present-day New Mexico to central Tennessee (Baarli et al., 2003).

Sampled Upper Silurian cycles (Pridolian-Ludlovian) of the Haragan-Henryhouse Formation were deposited in the Anadarko Basin of south-central Oklahoma on a tectonically quiescent, southeastward-dipping carbonate ramp, positioned ~20-30°S of the paleoequator (Figure 1) (Cocks and Scotese, 1991; Golonka et al., 1994; Cocks and Torsvik, 2002). The Haragan-Henryhouse Formation is unconformably underlain by the Clarita Formation (Wenlockian) and unconformably overlain by the Mississippian and Devonian Woodford Shale (Figure 1). Observed subtidal cycles are characterized by thinly bedded shale and nodular argillaceous skeletal mudstone/wackestone (substorm wave base) overlain by medium-bedded skeletal wackestone-packstone (near fairweather wave base) which show no evidence of subaerial exposure (Figure 8), though subaerial exposure features and karsting are observed in landward positions (Al-Shaieb et al.,
Age control is based on conodont and graptolite biostratigraphy (Barrick et al., 1990). Those coeval Upper Silurian cycles with adequate biostratigraphic time control reveal cycle durations of between ~20-120 ky (Jeppsson, 1997; Crick et al., 2001; Cramer et al., 2009), suggesting orbital climate influences during this time.

Possible sources of continental weathering flux to the Anadarko Basin are the Transcontinental Arch to the north and northwest of the study locality and uplifts to the north and northeast due to the Caledonide Orogeny (Avalonia, Baltica, Meguma, Malverns, Cadomia, and Alexander Terranes) (Figure 1) (Nance and Murphy, 1996; Murphy, 2000; 2007; Baarli et al., 2003; Cocks and Torsvik 2011). Detrital zircons and Upper Silurian sedimentary rocks sourced from terranes accreted during the Caledonide
and Acadian Orogenies document variable Nd isotopic ratios ($\varepsilon_{\text{Nd}}$) and Nd model ages ($\tau_{\text{DM}}$) (Figure 9; $\varepsilon_{\text{Nd}}$ at $t=410$ Ma: $-12.0$ to $+7.0$, $\tau_{\text{DM}}$: $0.9$ to $2.0$ Ga) (Clarke and Halliday, 1985; Gleason et al., 1985; Andre et al., 1986; Thorogood et al., 1990; Clarke et al., 1992; Pimental and Fuck, 1992; Nance and Murphy, 1996; Murphy et al., 1999; 2000; 2008; Murphy and Nance, 2002; Tull, 2002; Linnemann et al., 2012). $\varepsilon_{\text{Nd}}$ ($t=410$ Ma) for the Canadian Shield and Transcontinental Arch ranges from $-25$ to $-8$ (Miller et al., 1986).

Figure 9. $\varepsilon_{\text{Nd}}$ vs. $^{147}\text{Sm}^{144}\text{Nd}$ of possible sources of continental weathering flux compared to other Upper Silurian sedimentary rocks and results from this study. Possible reservoirs and isotopic data include the Caledonian Mountain belt, which includes the Avalonian Terrane (Murphy and MacDonald, 1993; Murphy et al., 1996; 1999; 2000; 2008) and the Meguma Terrane (Clarke and Halliday, 1985; Clarke et al., 1993), the Canadian Shield and Transcontinental Arch (Canadian Shield: Miller et al., 1986). Upper Silurian sedimentary rocks shown for comparison from Thorogood (1990) and Gleason et al. (1995). Inset shows the same comparison, centered on the results from this study.
**Upper Devonian**

Evidence for Late Devonian greenhouse climates is based on comparable characteristics as that for the Late Silurian. Similar to Upper Silurian deposits, the Upper Devonian greenhouse interval records large, positive $\delta^{13}$C excursions (e.g. Joachimski and Buggisch, 1993; Joachimski et al., 2002; Saltzman, 2005; van Geldern et al., 2006), My-scale $\delta^{18}$O fluctuations (Joachmiski et al., 2009), and common orbital-scale upward-shallowing cycles (LaMaskin and Elrick, 1997; Gong et al., 2001; Yiming et al., 2001; Chen and Tucker, 2003; Ma et al., 2008; Zamanzadeh 2009; Whalen and Day, 2010).

The Late Devonian marks northward movement of Gondwana and initiation of Rheic ocean closure, ultimately ending in Pangean formation. Continuing continental collision from the Acadian Orogeny generated arc magmatism along the northeastern edge of Laurussia (Murphy et al., 1999). The Devonian also marks a shift from passive to active margin tectonics along the western edge of Laurussia, demonstrated by ophiolites, island arc rocks (Brouxel et al., 1987; Brouxel and LaPierre, 1988; Rouer et al., 1989; Dickinson, 2000; Nokleberg et al., 2000; Nelson and Colpron, 2007; Colpron and Nelson, 2009) and overthrust assemblages from the Romanzof (Late Silurian-Middle Devonian), and Antler and Ellesmerian (Late Devonian-Carboniferous) Orogenies (Embry, 1991; Trettin, 1991; Dickinson, 2000; Dickinson, 2009). Much of Laurussia’s interior was covered by an epeiric sea after a major transgression in the Middle Devonian (Taghanic Onlap; Johnson, 1970), broken by small exposures of the Transcontinental Arch (Boucot et al., 2008).

Sampled Upper Devonian (late Givetian-Frasnian) cycles of the Guilmette and Devil’s Gate Formation were deposited along a westward-deepening carbonate ramp which extended from Canada to Mexico. Central Nevada was positioned 10-20°S of the
paleo-equator during Late Devonian time (Torsvik and Cocks, 2004). The Devil’s Gate Formation and coeval Guilmette Formation are underlain by the Bay State Dolomite (Givetian) and overlain by the Pilot Shale (Fammenian) (Figure 3). Of the many cycles observed at Devil’s Gate and Gap Mountain, eight sampled subtidal cycles are characterized by thin, interbedded limestone and shale (rhythmites) or thin-bedded skeletal mudstone-wackestone (below storm wave base) overlain by medium- to thick-bedded skeletal mudstone-packstone, some of which contain in-growth-position Amphipora-type and/or lenticular stromatoporoids (near fair-weather wave base likely within photic zone). Half of the cycles record some initial deepening, followed by shallowing-upward facies trends (Figure 10).

Age control is based on conodont biostratigraphy, with samples coming from the hassi conodont Zone (e.g. Sandberg and Ziegler, 1996; Morrow and Sandberg, 2003). Coeval Upper Devonian cycles east of the study area record ~30-165 ky durations (LaMaskin and Elrick, 1997) and in other localities record ~20 ky durations (Chen and Tucker, 2003).

Possible sources of continental weathering flux (calculated at t=380 Ma) are immature ophiolites ($\varepsilon_{\text{Nd}} = +3$ to $+8$: Brouxel et al., 1987; Brouxel and LaPierre, 1988) and more mature arc volcanic ($\varepsilon_{\text{Nd}} = -3$ to $-9$: Rouer and LaPierre, 1989; Rouer et al., 1989) to the west, Grenville-aged crust from the Canadian Shield and Appalachian-Caledonian mobile belt to the north ($\varepsilon_{\text{Nd}} = -27$ to $-8$: Patchett et al., 1999; Dickinson, 2000), or the exotic Arctic Chukotka and Alexander terranes ($\varepsilon_{\text{Nd}} = -8$ to $-0.5$: Samson et al., 1989; Natal’in et al., 1999; Amato et al., 2009) to the northeast (Figure 11).
Figure 10. Cyclostratigraphy with interpreted changes in water depth based on facies changes and associated $\varepsilon_{Nd}$ trends. A) Upper Devonian (Frasnian; hassi conodont Zone) cycles from the Devil’s Gate Formation, central Nevada (Devil’s Gate Pass, ~10 km northwest of Eureka, Nevada). B) Upper Devonian (Givetian-Frasnian; norrisi conodont Zone) cycles from the Guilmette Formation, southeastern Nevada (Gap Mountain, ~150 km southeast of Eureka, Nevada). Long horizontal lines indicate cycle boundaries. m/s = lime-mudstone/shale, w = wackstone, p = packstone, g = grainstone

**Vascular land plant evolution**

Fossil evidence of tetrads demonstrates that the emergence of primitive vascular land plants was established by the Middle Ordovician (Strother et al., 1996). The first
vascular plant, *Cooksonia*, appeared by the Middle Silurian, having a distinctive rigid body (due to development of lignin and cellulose), a vascular system (with vesicles and pathways for transporting water and nutrients through the body), and cellulose (used for preventing desiccation and blocking UV radiation) (Gerrieme et al., 2001). Yet, these early vascular land plants were rootless and spore-bearing, requiring water for reproduction. Between the Late Silurian and Late Devonian, land plants developed roots, leaves, secondary growths, and seeds (Sanderson et al., 2004). The production of seeds allowed plants to move inland and upland; invading land through streams, rivers, and lakes, then moist environments, and finally to hinterland and harsher regions (Yaalon, 1990; Park and Gierlowski-Kordesch, 2007).

Figure 11. εNd vs. 147Sm/144Nd of possible sources of continental weathering flux compared to other Upper Devonian sedimentary rocks from the Cordilleran miogeoclone and results from this study. Possible reservoirs and isotopic data include the Caledonian Mountain Belt (Franklinian Mobile Belt; Patchett et al., 1999), the Canadian Shield (Miller et al., 1986), and western North American volcanics from the Trinity ophiolite (Brouxel et al., 1988; Brouxel and LaPierre, 1988), the Alexander Terrane (Samson et al., 1989), or the Arctic-Chukokta terrane (Natal’in et al., 1989; Amato et al., 2009). Data for the Cordilleran miogeoclone from Boghossian et al.
Evolution and habitat diversification of vascular land plants had a profound effect on continental weathering. Chemical weathering by plants is due to four major processes: secretions of oxalic acid from roots, organic acids secreted by mycorrhizal symbionts, bacterial decay of plant litter, and production of carbonic acid from the respiration of CO$_2$ by plant roots (Berner, 1992; Drever, 1994; Algeo et al., 1998). Berner (1992) suggests that the production of carbonic acid by root respiration is the most important in terms of continental weathering and the long-term carbon cycle. Therefore, the development of large root systems increased chemical weathering rates due to greater acid production from CO2-pumping into soils (Retallack, 1992) and a greater contact area of rootlets with soils (Fogel, 1985). The evolution of land plants resulted in rapid and dramatic drawdown of $p$CO$_2$ from the Silurian-Carboniferous, causing a decrease in average global temperature, increasing atmospheric O$_2$, and contributed to episodic anoxia in ocean bottom-waters (Berner, 1992; Cannfield, 1994; Algeo et al., 1995; 1998; Berner, 1998; Edwards and Scott, 1998; Malkowski and Racki, 2009).

**Previous Work**

Marine apatite collected from cycles sampled in this study record two intra-cycle $\delta^{18}$O trends (Theiling and Elrick, in prep., Chapter 1). The first trend illustrates a progressive increase in $\delta^{18}$O coincident with facies-shallowing, similar in magnitude (1.3-3.1‰) to $\delta^{18}$O trends observed in icehouse cycles generated by glacio-eustasy. Theiling and Elrick (in prep., Chapter 1) describe this result as an asymmetric $\delta^{18}$O trend within an asymmetric cycle. The second trend observed illustrates initially decreasing, then increasing $\delta^{18}$O values with <0.5 ‰ total magnitude of change, described as a
symmetric trend within an asymmetric cycle. They conclude that both isotopic trends support the hypothesis that these Late Silurian and Late Devonian greenhouse cycles developed in response to glacio-eustasy, but that recorded δ\(^{18}\)O are produced by the combination of changes in ice-volume, sea surface temperature, and changes in evaporation rate over orbital (glacial-interglacial) timescales.

Theiling and Elrick (in prep., Chapter 1) suggest that the interplay between sedimentation rate, subsidence and eustasy (Jervey, 1988) may cause only a portion of the total glacial to interglacial transition to be recorded. In typical, asymmetrical icehouse cycles with asymmetrical, increasing upward δ\(^{18}\)O, sedimentation rate outpaces accommodation gains as a result of lowering sea-level from glacial growth. However, sedimentation rate that outpaces accommodation gains during peak interglacial conditions could generate low δ\(^{18}\)O in shallow-water facies (Figure 7; Jervey, 1988). Applying this model, Theiling and Elrick (in prep.) suggest that symmetric δ\(^{18}\)O trends within asymmetric cycles chronicle a more complete record of the glacial-interglacial climate transition, where decreasing and low δ\(^{18}\)O values represent the transition into maximum interglacial intervals and δ\(^{18}\)O increases record the transition into full glacial intervals (Figures 2, 5, and 7). In contrast, asymmetric cycles with asymmetric (increasing upward) δ\(^{18}\)O trends record only the interglacial to glacial portion of the climatic transition.

**Methodology**

REE systems such as Sm-Nd are ideal for studies of continental weathering flux in marine successions because the seawater REE budget is dominated by continental input (Goldstein and Jacobsen, 1988). Due to the short oceanic residence time of Nd (\(<10^2\) yr),
Nd-isotopic ratios will be incorporated into marine sedimentary deposits before homogenization by oceanic mixing (oceanic mixing time $\sim 10^3$ yrs). In addition, REE are immobile (insoluble) and therefore, relatively unsusceptible to diagenesis (McLennan, 1989; Banner, 2004). The slightly larger ionic radius of Nd over Sm (lanthanide contraction) makes Nd ‘more incompatible,’ resulting in preferential partitioning of Nd into the crust during mantle melting and differentiation. As a result, Sm/Nd for the continental crust is $\sim 40\%$ lower than the depleted mantle and imparts significantly different isotopic ratios for each reservoir.

The decay of $^{147}\text{Sm}$ to $^{143}\text{Nd}$ results in emission of an alpha particle ($t_{1/2} = 106$ Ga). Measurements of $^{143}\text{Nd}/^{144}\text{Nd}$ are typically expressed in comparison to the bulk earth $^{143}\text{Nd}/^{144}\text{Nd}$ (chondritic undifferentiated reservoir (CHUR)) as $\varepsilon_{\text{Nd}}$, where $\varepsilon_{\text{Nd}} = (\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{sample}}/\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{CHUR}} - 1) \times 10,000$. Due to preferential partitioning of Nd versus Sm in the continental crust, continental crust is typified by more unradiogenic $\varepsilon_{\text{Nd}}$ ($-20$ for crust with a mean $\tau_{\text{DM}}$ of $2$ Ga; Goldstein and Jacobsen, 1987) compared to more radiogenic mid-ocean ridge basalts (MORB) ($> +8$; Shirey, 1991). $\tau_{\text{DM}}$ represents the weighted average of the sample’s crustal residence time, which can include many compositional and aged sources. Therefore, Nd isotopes can be utilized for regional-scale continental weathering flux studies to evaluate orbital- and suborbital-scale climate changes across varying climate zones/belts. $\varepsilon_{\text{Nd}}$ in marine deposits can serve as a proxy for changes in the regional continental weathering flux, and can be used to track paleo-ocean circulation (e.g. Martin and Macdougall, 1995; Reynolds et al., 1999; Thomas, 2004; Piotrowski et al., 2005; Puceat et al., 2005; Scher and Martin, 2006; Via and
Thomas, 2006; MacLeod et al., 2008) and emergence/flooding of continental landmass (Fanton et al., 2002; Theiling et al., 2012).

These previous utilisations of Nd isotopes make several important assumptions: 1) rare earth elements (REE) such as Sm and Nd are immediately scavenged by particulates; the Sm/Nd ratio was recorded during or very soon after sedimentary deposition, 2) isotopic evolution of Sm and Nd is linear, 3) no isotopic exchange occurred after deposition, 4) Sm/Nd record the weighted average of all sources of REE (Thorogood, 1990), and most importantly, 5) fluctuations in Nd isotopic ratios are the result of a simple binary mixing line between a source of continental weathering flux (low Sm/Nd) and a relatively homogenous (higher Sm/Nd) local ocean/epeiric sea value. As a result, increases in continental weathering flux or changes in weathering source generate changes in Sm/Nd. Therefore, the Sm-Nd system is best utilized on sea floor ferromanganese crusts and/or nodules (Piotrowski et al., 2004; 2005) or on passive margin platform marine deposits because these environments are distant enough from singular sources of weathering material that the recorded marine Sm and Nd isotopic ratios will reflect a weighted average of binary mixing.

Neodymium isotopic analyses were performed on whole rock, collected at 0.1-1 m increments using a modified method of Theiling et al. (2012) (Chapter 2). Determination of $^{147}\text{Sm}/^{144}\text{Nd}$ was accomplished using a spike of known $^{147}\text{Sm}/^{150}\text{Nd}$. $^{147}\text{Sm}/^{144}\text{Nd}$ was calculated from measurements of $^{147}\text{Sm}/^{152}\text{Nd}$. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ values were calculated using approximated ages of deposition of 410 Ma (Henryhouse-Haragan Formation), 385 Ma (Guilmette Formation), and 380 Ma (Devil’s Gate Formation). All analyses were performed on a Thermo Neptune multi-collector inductively coupled plasma mass
spectrometer (MC-ICPMS) at the University of New Mexico Radiogenic Isotope Laboratory. The La Jolla Nd isotopic standard was run with each batch, obtaining a mean $\frac{^{143}\text{Nd}}{^{144}\text{Nd}}$ of 0.511825 ± 4e-5 (2σ), which is within the accepted range of values for the standard (Pier et al., 1989). An internal REE standard spiked with $\frac{^{147}\text{Sm}}{^{150}\text{Nd}}$ was run with each batch to check Sm isotope measurement accuracy, obtaining a mean value of 0.575496 ± 9e-5 (2σ), which is within the accepted range of values for this standard. Error is reported on initial $\varepsilon_{\text{Nd}}$ (t = estimated age of deposition) for each sample, calculated by combining the error on replicate analyses of $\frac{^{143}\text{Nd}}{^{144}\text{Nd}}$ and $\frac{^{147}\text{Sm}}{^{152}\text{Nd}}$. $\varepsilon_{\text{Nd}}$ error ranges between 0.04 and 0.49 ε-units and averages 0.10 ε-units (2σ) (Table 3, Figure 8, 10). Error bars of less than 0.30 ε-units are smaller than data points and are therefore not shown in Figures 8 and 10.

**Results**

*Upper Silurian*

Arbuckle Mountains

Sm and Nd isotopic results for Upper Silurian cycles are presented in Table 3 and Figure 8. $\varepsilon_{\text{Nd}}$ (t=410 My) over the entire sampled ARB section range from -8.4 to -10.9. Trends and offsets of $\varepsilon_{\text{Nd}}$ within each sampled cycle vary. $\varepsilon_{\text{Nd}}$ trends of cycle 1 show a slight shift to higher values in the middle of the cycle. Nd values in cycle 2 are initially low, then increase into the cycle cap. $\varepsilon_{\text{Nd}}$ from cycle 3 shows slight increases and decreases with a shift to lower values at the cycle cap. Cycle 4 has limited samples but shows a shift to lower values into the mid cycle. is initially high and decreases by 0.7 ε-units. Cycle 5 records a symmetric shift from high to low then back to high values in the cycle cap.
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<th>$^{147}$Sm/$^{144}$Nd</th>
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54

Table 3. Measured $^{143}\text{Nd}/^{144}\text{Nd}$, apparent $\varepsilon_{\text{Nd}}$ (value at present), measured $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{143}\text{Nd}/^{144}\text{Nd}$, $\varepsilon_{\text{Nd}} (t)$, and $f_{\text{Sm/Nd}}$ where $t$ = estimated time of deposition.

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In total, the Upper Silurian samples exhibit an up-section increase in $\varepsilon_{\text{Nd}}$ of 2.7 $\varepsilon$-units and an up-section decrease in $^{147}\text{Sm}/^{144}\text{Nd}$. $^{147}\text{Sm}/^{144}\text{Nd}$ versus $\varepsilon_{\text{Nd}} (t = 410 \text{ My})$ are shown in Figure 8 and are compared to terranes and crustal material accreted to Laurentia during the Caledonide and Acadian Orogenies. Calculated $\tau_{\text{DM}}$ for Upper Silurian samples is 1.6-2.1 Ga.
Upper Devonian

Gap Mountain

Neodymium isotopic results for Upper Devonian cycles at Gap Mountain (GM) are presented in Table 3 and Figure 10. $\varepsilon_{\text{Nd}}$ (t=385 My) over the entire sampled GM section ranges from -10.7 to -8.0. Trends and offsets of $\varepsilon_{\text{Nd}}$ within each sampled cycle vary. $\varepsilon_{\text{Nd}}$ of cycle 1 records a symmetric trend of initially high, then decreasing values toward mid-cycle, then increases progressively into the cycle cap. Cycle 2 demonstrates essentially stable values with a small shift to lower values in the cycle cap. Cycle 3 shows a large up-cycle increase in $\varepsilon_{\text{Nd}}$ values.

Devil’s Gate

Neodymium isotopic results for Upper Devonian cycles from Devil’s Gate (DG) are presented in Table 3 and Figure 10. $\varepsilon_{\text{Nd}}$ (t=380 My) over the entire sampled DG section ranges from -12.9 to -6.6 and decreases by ~3.2 e-units from the base to the top of the sampled section. Trends and offsets of $\varepsilon_{\text{Nd}}$ within each sampled cycle vary. Cycle 1 records an initial increase in $\varepsilon_{\text{Nd}}$ values followed by relatively stable values to the cycle cap. $\varepsilon_{\text{Nd}}$ from cycle 2 demonstrates an abrupt increase, then decrease in values into the cycle cap. Cycle 3 shows an abrupt decrease to lower values, then a steady increase up-cycle. Although incompletely sampled, cycle 4 cap records an anomalously high $\varepsilon_{\text{Nd}}$ value of -6.6. Cycle 5 records a relatively symmetric trend of decreasing values followed by increasing and high values in the cycle cap.

Discussion

Provenance
Middle Silurian-Upper Devonian sedimentary rocks from across the United States and Canada record a transition from unradiogenic source rocks ($\varepsilon_{\text{Nd}} = -27$ to -15) to a more radiogenic source ($\varepsilon_{\text{Nd}} = -10$ to -5) (Figure 12). This transition is observed in the Canadian Cordilleran miogeocline and mid-continental United States during the Silurian (Gleason et al., 1994; 1995; Patchett et al., 1999) and in the western United States Cordilleran miogeocline during the Middle and Upper Devonian (Boghossian et al., 1996; Garzione et al., 1997; Patchett and Gehrels, 1997). $\varepsilon_{\text{Nd}}$ from all three sampled successions from this study lie between -12 and -8, with the exception of one sample from the Devil’s Gate Formation (-6.4; Figure 10), supporting the claim that this source change had occurred by the at least the Pridolian (Oklahoma study area) and Frasnian (Nevada study area) (Figure 12).

Figure 12. $\varepsilon_{\text{Nd}}$ vs. age (Ma) for sampled Upper Silurian and Upper Devonian cycles compared to other sedimentary rocks, indicating that the shift from relatively unradiogenic to radiogenic $\varepsilon_{\text{Nd}}$ had occurred in each of the sampled marine basins by the time of deposition. $\varepsilon_{\text{Nd}}$ data from the Canadian Cordilleran (Garzione et al., 1997; Patchett and Gehrels, 1998), United States Cordilleran (Boghossian et al., 1996), and mid-United States (Gleason et al., 1995).
Accretion, uplift, and weathering of relatively radiogenic crustal material from the Caledonide Orogeny (Figure 9) during the Late Silurian-Late Devonian are the most likely sources of continental weathering flux that generated the observed range in $\varepsilon_{\text{Nd}}$ (Figures 9 and 11). Two processes may have generated this range: mixing of a radiogenic and unradiogenic source, or introduction of a source with similar isotopic ratios to those observed. The most probable sources of large-scale binary mixing are the strongly unradiogenic Canadian Shield and Transcontinental Arch ($\varepsilon_{\text{Nd}} = -25$ to -15; Miller et al., 1986) and strongly radiogenic terranes of the Caledonian-Appalachian mobile belt ($\varepsilon_{\text{Nd}} = -5$ to +7; Murphy et al., 1996; 1999; 2000; 2008) (Figure 9). To estimate the contributions of these end-members to sampled Upper Silurian limestones, we utilize the mixing model equations of Langmuir et al. (1978), assuming an average $^{143}\text{Nd}/^{144}\text{Nd}$ value for radiogenic Caledonide terranes (Murphy et al., 1996; 1999; 2000; 2008) and Archean-aged Canadian Shield and Transcontinental Arch rocks (Miller et al., 1999). Binary mixing between these sources suggests that approximately 45% of all Nd was sourced from strongly radiogenic Caledonide terranes (i.e. Avalonia terrane) and 55% was sourced from the Canadian Shield and/or Transcontinental Arch. Due to the inner-shelf position of the sampled successions, deposition is biased toward highstand through lowstand deposition. As a result, the Transcontinental Arch was likely submerged during much of the recorded intervals, implying that enormous quantities of unradiogenic material would have been sourced from intermittent exposures of the Transcontinental Arch or Canadian Shield. The greater weathering ability of exposed terranes and overlap in Nd values with samples from a mixture of strongly radiogenic and more unradiogenic terranes within the Caledonide mobile belt (Figures 9 and 11)
suggests introduction of continental weathering flux from these far-field accreted and uplifted terranes (e.g. Stallard and Edmond, 1983; Raymo et al., 1988; Berner, 1994).

Eolian and fluvial processes demonstrate transport over remarkable continental distances. Prevailing southwestwardly winds for southern hemisphere subtropical latitudes suggest eolian-derived detritus is a possible component to mid-southern Laurentia during the Late Silurian. However, Late Devonian northwestward prevailing winds for western Laurentia render wind-blown material an unlikely source of Nd for the studied Upper Devonian successions.

Basins ranging from Ordovician-Carboniferous age across Laurentia contain detrital zircons (Dickinson and Gehrels, 2003), sedimentary $\varepsilon_{\text{Nd}}$ and paleocurrents (Gleason et al., 1994; 1995; Patchett et al., 1999; Boghossian et al., 1996; Garzione et al., 1997; Patchett and Gehrels, 1997) traceable to the Caledonian-Appalachian orogenic belt, invoking large fluvial systems that traversed the width of Laurentia. The modern Amazon River basin encompasses a similarly large continental area ($\sim 2.5-3 \times 10^6$ km$^2$: Revenga et al., 1998), traveling $\sim 3000$ km from the Andes Mountains to the Atlantic Ocean. Immature Amazonian Quarternary-aged quartz sands demonstrate transport of continental weathering flux over $\sim 3000$ km in a single phase (Johnsson et al., 1988; Potter, 1978), implying single-phase transport for trans-continental paleo-rivers.

Boghossian et al. (1996) and Patchett et al. (1999) suggest a multi-phase transport of Caledonian-Appalachian detrital material across Laurentia, whereby extensive weathering of the Caledonian-Appalachian orogenic belt, beginning in the Ordovician, deposited material in an extensive foreland basin that was later uplifted, eroded, transported further and re-incorporated into younger deposits. Indeed, crystallization
ages, paleocurrent directions, and comparison of observed $\varepsilon_{\text{Nd}}$ to Caledonian basement $\varepsilon_{\text{Nd}}$ demonstrate that Siluro-Devonian sedimentary rocks from the Canadian miogeoclone were sourced from the Caledonian orogeny via the Franklinian mobile belt of northern Canada, suggesting multi-phase transport of Caledonian weathered material (Patchett et al., 1999). Similarly, Grenville-aged detrital zircons suggest that trans-Laurentian river systems were established by at least the Neoproterozoic and demonstrate a multi-phase process of weathering, deposition, lithification and reworking of detrital material (Ross and Parrish, 1991; Rainbird et al. 1992; 1997; Stewart et al., 2001).

*Intracycle-scale Nd-isotope trends*

Source area changes

If our far-field Caledonian source area interpretations are correct, then this implies that any potential variations in the source material(s) would have been averaged out by the time continental weathering flux reached the studied marine basins, whether transport and deposition was single or multi-phase. Therefore, it is not unreasonable to assume binary mixing would occur between an average Caledonian source and ocean waters and/or the Canadian Shield/Transcontinental Arch over orbital timescales.

Cyclic $\varepsilon_{\text{Nd}}$ trends due to changes in source material are demonstrated in an Upper Ordovician mixed carbonate-siliciclastic succession (Fanton et al., 2002). In their study, platform emergence due to My-scale sea-level fall exposed low $\varepsilon_{\text{Nd}}$ Precambrian basement rocks from the Canadian Shield and Transcontinental Arch, generating lower marine $\varepsilon_{\text{Nd}}$ values in the sampled marine succession. Platform flooding due to My-scale sea-level rise submerged low $\varepsilon_{\text{Nd}}$ rocks, increasing $\varepsilon_{\text{Nd}}$ values in the sampled marine succession. This scenario is unlikely in either Upper Silurian or Upper Devonian
sampled successions because observed $\varepsilon_{\text{Nd}}$ are not low enough to suggest periodic sourcing from the adjacent unradiogenic Transcontinental Arch or Canadian Shield. Likewise, the similar range in $\varepsilon_{\text{Nd}}$ of our samples with Caledonian source rocks, suggests that observed cycle-scale variation in $\varepsilon_{\text{Nd}}$ trends are not a result of source area changes, but rather are generated by binary mixing with ocean waters.

**Orbital-scale climate changes**

If our binary mixing interpretation is correct then we can compare observed Upper Silurian and Upper Devonian greenhouse $\varepsilon_{\text{Nd}}$ trends to those observed in icehouse cycles of Burton and Vance (2000), Piotrowski et al. (2005), and Theiling et al. (2012). $\varepsilon_{\text{Nd}}$ trends from previously studied icehouse cycles demonstrate decreasing $\varepsilon_{\text{Nd}}$ into interglacial intervals and increasing $\varepsilon_{\text{Nd}}$ into glacial intervals due to increases and decreases, respectively, in continental weathering and/or transport. Theiling et al. (2012) proposed a climate-weathering model for platform marine sedimentary systems in which decreases in $\varepsilon_{\text{Nd}}$ into mid-cycle deposits (sea-level highstand or interglacials) are generated by increases in continental weathering flux that result from increases in precipitation and/or air temperature. Increases in $\varepsilon_{\text{Nd}}$ into cycle caps are generated by decreases in continental weathering flux from decreases in precipitation and/or air temperature. Hypothesized fluctuations in precipitation and/or air temperature may manifest as climatically-driven fluctuations in fluvial and/or eolian input to a marine basin. The Theiling et al. (2012) climate-weathering model is shown in comparison to the stratigraphic-eustatic model of Jervey (1988) in Figure 13, which illustrates schematic intra-cycle $\varepsilon_{\text{Nd}}$ trends produced during wet/warm (interglacial) and dry/cool (glacial) intervals.
Figure 13. A) Simplified sinusoidal eustatic sea-level (SL) curve with labeled inflection points and maximum glacial-interglacial intervals. B) Stratigraphic nomenclature with schematic asymmetric cycles similar to those observed in sampled Upper Silurian and Upper Devonian cycles with a narrower column representing deeper water facies and a wider column representing shallower water facies. Note that no deposition/erosion occurs during the late eustatic fall, lowstand and early rise (diagonal lines) and a disconformity develops; subaerial exposure features develop at the cycle top during subaerial exposure (black triangles). During a single glacial-interglacial sea-level cycle, deposition during the initial transgression as the glaciers begin to melt is not recorded within the study area due to lack of accommodation space. Once accommodation space is created due to subsidence and rapid (maximum) SL rise rates, deposition occurs and is represented by deeper water deposits at the cycle base. SL continues to rise with additional glacial melting and reaches its highest position at the interglacial maximum (mid-regression). Because SL is rising at a slower rate after the maximum rate of SL rise inflection point (and assuming constant sedimentation rate), sediments above the maximum flooding zone reflect loss of accommodation space. After the interglacial maximum, SL fall rates increase and is represented by the shallowest water deposits. C) Schematic of d18O trend due to changes in ice-volume and sea surface temperatures (SST) over successive glacial-interglacial intervals. D) Schematic of eNd due to changes in precipitation and/or air temperature as a direct result of glacial-interglacial cycles. Modified from Theiling et al. (2012).

Most sampled Upper Silurian cycles demonstrate relatively steady intra-cycle $\varepsilon_{Nd}$, with the exception of cycles 2 and 5 (Figure 8), as opposed to larger variations in $\varepsilon_{Nd}$.
observed in sampled Upper Devonian cycles (Figure 10). Such small cycle-scale $\varepsilon_{\text{Nd}}$ variations in this succession suggest orbital-scale changes in continental weathering flux were not as profound during the Late Silurian in relation to the Late Devonian. Smaller Upper Silurian intra-cycle variations may be generated by a lag between the time of climate fluctuation and subsequent continental weathering, and the time required to transport continental weathering flux from a far-field Caledonide source, which could average out any initial variations in continental weathering flux.

This scenario is in opposition to continental weathering sources of Fanton et al. (2002) and Theiling et al. (2012). In these studies, changes in climate and continental weathering flux were readily apparent because flux was sourced from uplifts <100 km away from sampled marine basins. Furthermore, these sampled successions were sometimes subaerially exposed, suggesting these localities were sometimes directly fed by local fluvial waters from nearby uplifts. While the proposed lag time between weathering and deposition is likely for such far-field transport to the sampled Upper Silurian basin, larger intra-cycle variations observed in similarly-sourced Upper Devonian cycles suggest that averaging out of far-field flux did not generate small Upper Silurian variation.

A relatively uniform $\varepsilon_{\text{Nd}}$ trend may also be generated by a relatively constant warm and/or wet Late Silurian subtropical climate. Modeling of, and proxy data from greenhouse intervals suggest that increased greenhouse temperatures intensify the hydrologic cycle (Pagani et al., 2006; Clementz and Sewall, 2011; Berra, 2012), leading to overall increased rainfall patterns. An intensified greenhouse hydrologic cycle implies more intense and relatively constant continental weathering and flux. However, this
scenario is inadequate because Upper Devonian $\varepsilon_{\text{Nd}}$ shows greater intra-cycle variation, implying that fluctuations in continental weathering flux may occur during greenhouse intervals.

Perhaps the most likely scenario is that the lack of inland and upland vascular land plants during the Late Silurian contributed to relatively uniform weathering. Vascular plants prior to the Middle Devonian were rootless, contributing to chemical breakdown of rock/proto-soil due to production of oxalic, humic, and carbonic acids, but providing little stabilization of the land-surface (Algeo et al., 1998). Therefore, before upland and inland land plant colonization, continental weathering was primarily a product of erosion and mass-wasting. As plants developed large root systems, chemical weathering increased due to both greater acid production from pumping of CO$_2$ into soil (Retallack, 1992) and a greater contact area of rootlets with soils (Fogel, 1985).

In the modern record, we observe that fluctuations in climate have a profound effect on plants. During wetter and/or warmer intervals, roots penetrate deeper and generate increased chemical weathering, while plant roots are smaller during drier and/or cooler intervals, generating decreased weathering. As a result, changes in continental weathering rates as a result of fluctuations in climate may not have been as pronounced before the evolution of land plants with large root systems and colonization of upland and inland land areas (Middle-Late Devonian). Instead, erosion due to tectonic uplift (Stallard and Edmond, 1983) may have dominated continental weathering flux before the Middle-Late Devonian.

It is also possible that minimal plant colonization of land during the Late Silurian contributed to a relatively suppressed greenhouse hydrologic cycle. Increased
atmospheric instability typical of warmer climates is enhanced by evapotranspiration, whereby water is transferred directly from a plant to the atmosphere. Therefore, the effect of plants on the hydrologic cycle is to promote recirculation of water in the atmosphere, increasing cloud-cover and precipitation (Algeo et al., 1998; Shuckle and Mintz, 1982). Without widespread distribution of land plants, the Late Silurian hydrologic cycle may have been less intense than the Late Devonian.

In opposition to the relatively steady record of continental weathering flux observed in these Upper Silurian cycles, sampled upper Devonian cycles record greater variability in $\varepsilon_{\text{Nd}}$. 5 of 7 cycles record high $\varepsilon_{\text{Nd}}$ values (low continental weathering flux) during falling/lowstand sea-level and low $\varepsilon_{\text{Nd}}$ values (high continental weathering flux) during sea-level highstands. 2 of 7 cycles show symmetric $\varepsilon_{\text{Nd}}$ trends within asymmetric cycles, one of which demonstrates an in-phase symmetric $\delta^{18}$O trend (Theiling and Elrick, in prep., Chapter 1). Similar to symmetric $\delta^{18}$O intra-cycle trends, these symmetric $\varepsilon_{\text{Nd}}$ trends argue that these particular cycles preserve a more complete transition from glacial-interglacial-glacial stages (Figure 13). Both trends and these magnitudes are similar to Pennsylvanian and Pleistocene studies, suggesting that increases in precipitation and/or air temperature generate increases in continental weathering flux and decreases in precipitation and/or air temperature generate decreases in continental weathering flux.

We suggest that these two trends are generated as a result of the interplay between sedimentation rate, subsidence and eustasy, illustrated by combining the sedimentation-eustasy model of Jervey (1988) and the $\varepsilon_{\text{Nd}}$-weathering-climate model of Theiling et al. (2012). Symmetric $\varepsilon_{\text{Nd}}$ trends will be recorded in asymmetric cycles under the following conditions: if sedimentation rate outpaces accommodation gains during peak cool and/or
dry conditions, lowest $\varepsilon_{\text{Nd}}$ will be recorded when sea-level is highest, between maximum flooding and mid-regression and high $\varepsilon_{\text{Nd}}$ will be recorded in shallow-water facies during maximum sea-level fall (Figure 13). However, an asymmetric $\varepsilon_{\text{Nd}}$ trend may be recorded in an asymmetric cycle if accommodation gains outpaced sedimentation rate during the transition from peak glacial to peak interglacial (highest sea-level position). After the maximum interglacial (highest sea-level), sedimentation rate begins to outpace accommodation gains, recording only the top half of the idealized $\varepsilon_{\text{Nd}}$ trend (Figure 13).

Increased variation in continental weathering flux during the Late Devonian is likely due to the more widespread distribution and diversification of land plants, increasing chemical weathering rates (Knoll and James, 1987; Johnson, 1993; Drever, 1994) and precipitation from evapotranspiration, leading to dramatic drawdown in $p\text{CO}_2$ and cooling global climate (Shukla and Mintz, 1982; Berner, 1992; 1998; Edwards and Scott, 1998; Algeo et al., 1998; Malkowski and Racki, 2009). Indeed, Algeo et al. (1995) describe a critical shift in continental weathering flux and oceanic nutrient influx occurring in the Devonian as a result of inland and upland habitation of vascular land plants and increased root penetration. Late Devonian climate changes are expected given the appearance of well-documented ice sheets in South America within a few million years (e.g., Veevers and Powell, 1987; Frakes and Francis, 1988; Frakes et al., 1992; Ziegler et al., 1997; Hyde et al., 1999; Isbell et al., 2003; Blakey, 2008; Fielding et al., 2008; Buggisch et al., 2011; Isbell et al., 2012).

Conclusions
1) $\varepsilon_{\text{Nd}}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ values for both Silurian and Devonian successions suggest far-field Caledonide source area, which implies trans-Laurentian fluvial systems transported weathered material.

2) Silurian intra-cycle $\varepsilon_{\text{Nd}}$ trends are relatively steady across individual orbital-scale cycles, implying relatively constant continental weathering flux. Constant flux may be related to a) a lag between the time of weathering and the time of deposition, effectively averaging out initial variations, b) relatively constant continental weathering flux due to warm and/or wet sub-tropical climate, or c) lower chemical weathering rates and precipitation due to the absence of widespread upland and inland vascular land plants.

3) Devonian record increased intra-cycle $\varepsilon_{\text{Nd}}$ variability similar in appearance and magnitude to icehouse $\varepsilon_{\text{Nd}}$ trends, with higher continental weathering flux (lower $\varepsilon_{\text{Nd}}$ values) during sea-level highstand (warmer/wetter stages) and lower continental weathering flux (higher $\varepsilon_{\text{Nd}}$ values) during falling sea-levels (cooler/drier stages). Increased $\varepsilon_{\text{Nd}}$ variability may have resulted from evolution and inland and upland colonization of land plants, increasing chemical weathering rates due to evolution of large root systems and increasing precipitation as a result of evapotranspiration.
SUPPLEMENTAL A

OXYGEN ISOTOPE DATA AND INTERPRETATIONS FROM UPPER SILURIAN APATITIC BRACHIPODS AND CONODONT PEARLS COLLECTED FROM THE ARBUCKLE MOUNTAINS, OKLAHOMA

Introduction

Oxygen isotopic data from Theiling and Elrick (in prep., Chapter 1) suggests that sea-level fluctuations observed from facies changes of Upper Silurian and Upper Devonian marine greenhouse successions were glacially-driven, implying that greenhouse intervals can support both very warm sea surface temperatures (SST) and polar glacial ice. Due to the difficulty in recovering sufficient coniform conodonts at each Upper Silurian sampling interval (typically ~100-300 elements), apatitic inarticulate brachiopod fragments and conodont pearls were collected in addition to conodont elements whenever possible. The stronger PO$_4$ bond in apatite as opposed to the weaker CO$_3$ bond found in most calcitic and aragonitic brachiopod or whole-rock samples suggests that biogenic apatites are less susceptible to diagenetic recrystallization (Longinelli and Nuti, 1973; Kolodny et al., 1983; Luz et al., 1984; Lécuyer et al., 1996) and that biogenic apatite is precipitated in equilibrium with ambient seawater (Longinelli and Nuti, 1973; Kolodny et al., 1983; Lécuyer et al., 1996). Although some studies have demonstrated offsets in apatitic inarticulate brachiopod versus conodont (Luz et al. 1984; Kastner et al., 1990; Kolodny and Luz, 1991; Wenzel et al., 2000) and fish tooth apatite (Zigate et al., 2010) δ$^{18}$O due to partial recrystallization, the similarity of brachiopod to conodont and fish δ$^{18}$O imply that apatitic brachiopods may be used to evaluate relative changes in δ$^{18}$O.
The purpose of this study is to compare δ¹⁸O data from coniform conodont elements of *Belodella* condonts collected from the Upper Silurian (Haragan-Henryhouse Formation) in the Arbuckle Mountains of central Oklahoma (Theiling and Elrick, in prep.; Chapter 1) with coeval conodont pearls and apatitic inarticulate brachiopods to assess whether these brachiopods and pearls generate similar δ¹⁸O trends to coniform conodont elements. The geologic setting, sampling intervals and analytical techniques are described in Theiling and Elrick (in prep.; Chapter 1).

![Figure 14. Upper Silurian (Pridolian-Ludlovian) cyclostratigraphy with interpreted changes in water depth based on facies changes and associated δ¹⁸O trends. Sampled section is within the *Oulodus elegans detorta* conodont Zone from the Haragan-Henryhouse Formation of central Oklahoma (~5 km south of Davis, Oklahoma). All δ¹⁸O data points are single analyses and/or averaged from replicate analyses. Coniform conodont δ¹⁸O data (filled circles) from Theiling and Elrick (in prep). δ¹⁸O data symbols: open squares = phosphatic brachiopods, open circles = conodont pearls. Long horizontal lines indicate cycle boundaries. m/s = lime-mudstone/shale, w (or wkst) = wackstone, p (or pkst) = packstone, g = grainstone.](image-url)
Results

Conodont Pearls

Oxygen isotopic results from conodont pearls are presented in Table 4 and Figure 14. δ^{18}O over the entire sampled section ranges from 18.1‰ to 20.0‰. Only cycle 5 contained sufficient conodont pearls throughout the cycle to generate a trend; decreasing δ^{18}O toward mid-cycle, followed by increasing δ^{18}O into the cycle cap. The total intra-cycle change in δ^{18}O over this cycle is 1.9‰.

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<th>distance from stratigraphic base (m)</th>
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Table 4. δ^{18}O from sampled apatitic inarticulate brachiopods and conodont pearls with stratigraphic depth.
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**Phosphatic brachiopods**

Oxygen isotopic results from phosphatic brachiopods are presented in Table 4 and Figure 14. δ\(^{18}\)O from brachiopods over the entire sampled section ranges from 16.3‰ to 19.5‰. Only two samples contained sufficient brachiopods from cycle 1 to measure δ\(^{18}\)O, suggesting decreasing δ\(^{18}\)O up-cycle of 3.0‰. Cycle 2 demonstrates decreasing δ\(^{18}\)O upward with a total intra-cycle change of 0.7‰. Cycle 3 demonstrates a zig-zag pattern; initially decreasing δ\(^{18}\)O, followed by an increase toward mid-cycle deposits, then a decrease in δ\(^{18}\)O into cycle cap deposits. The total intra-cycle change for cycle 3 is 1.8‰. Cycle 4 demonstrates a decrease upward with a total intra-cycle change of 0.5‰. Cycle 5 exhibits initially decreasing, then increasing δ\(^{18}\)O with a total intra-cycle change of 0.9‰.

**Discussion**

**Conodont pearls**

Only one of the five sampled cycles (cycle 5) contained sufficient conodont pearls to generate an intra-cycle trend, which is similar to brachiopod data but opposes platform conodont data (Figure 14). A trend of decreasing, then increasing δ\(^{18}\)O for analyzed pearls and brachiopods suggests increasing SST and/or decreasing ice-volume into mid-cycle deposits, followed by decreasing SST and/or increasing ice-volume. If the hypothesis proposed by Theiling and Elrick (in prep., Chapter 1) and Chapter 3 is correct, whereby decreasing, then increasing δ\(^{18}\)O is indicative of a more complete record of the transition from glacial-interglacial-glacial, then these brachiopod and pearl data demonstrate a more complete climatic record than coniform conodont data (Figure 7). However, because this result was produced in only one sampled cycle, it is equally or
more plausible that conodont pearl and brachiopod trends from cycle 5 were generated as a result of diagenetic recrystallization.

**Apatitic inarticulate brachiopods**

Two comparative trends between coniform conodont and apatitic brachiopods emerge from these analyses: in-phase or opposing δ¹⁸O. Conodont and brachiopod δ¹⁸O trends are similar and in-phase in cycles 3 and 4, with conodont δ¹⁸O enriched by -0.8‰ to +2.5‰ (+1.4‰ average). This offset is also observed between conodont pearl and brachiopod samples in cycle 5 (although the trends oppose platform conodont δ¹⁸O), where pearls are enriched by +0.5‰ to +1.7‰. Similar enrichment of conodont δ¹⁸O versus brachiopod δ¹⁸O is widely observed (Luz et al. 1984; Kastner et al., 1990; Kolodny and Luz, 1991; Lecuyer et al., 1996; Wenzel and Joachimski, 1996; Wenzel et al., 2000; Elrick et al., 2011). Lower δ¹⁸O of coeval apatitic brachiopods may be the result of post-mortem phosphate addition (Lecuyer et al., 1998) from the degradation of chitinous organic layers that alternate with fibrous carbonate-fluorapatite (francolite) (Iijima and Moriwaki, 1990; Williams et al., 1992; Cusack et al., 1997).

Partial recrystallization of apatitic brachiopods is also suggested by higher SST estimated from brachiopods; brachiopod samples estimate SST of 30-38°C (34°C average) whereas coeval conodonts estimate 21-37°C SST (27°C average) (ocean δ¹⁸O assumed at -1‰; Kolodny et al., 1983). Estimations of SST using the equation of Puceat et al. (2011) produce unreasonably high SSTs ~8°C higher than estimations using the equation of Kolodny et al. (1983). However, these SST estimations support the hypothesis that brachiopod trends may be used to assess relative changes in δ¹⁸O, supporting the claim that these Upper Silurian cycles were generated by glacio-eustasy.
Opposing $\delta^{18}O$ trends between conodont pearl and brachiopod versus coniform conodonts observed in cycles 1 and 5 may be described by vital effects, diagenetic recrystallization, differing water temperature due to deep or shallow-water habitats, or out-of-phase climate transitions recorded by conodonts versus apatitic brachiopods. Due to the lack of data documenting similar isotopic inconsistencies between pearls and elements of conodonts, we cannot further comment on whether conodont pearls are subject to vital effects or recrystallization. To avoid possible interspecies differences in $\delta^{18}O$ (Bassett et al., 2005), all conodont samples were composed of coniform elements of *Belodella*. However, due to the fragmentary preservation of apatitic brachiopod samples recovered, we were unable to separate brachiopods by species. As a result, brachiopod $\delta^{18}O$ may include a component of interspecies biologic fractionation of $\delta^{18}O$.

The benthic nature of brachiopods versus nektonic conodonts may suggest differences in $\delta^{18}O$ result from water temperatures at the sea-floor as opposed to surface waters (Picard et al., 1998). However, the shallow water depths estimated for this platform are < 100 m (Theiling and Elrick, in prep., Chapter 1), implying any differences in water temperature between brachiopod and conodont habitats are insignificant (Adlis et al., 1988; Levitus and Boyer, 1994).

If opposing brachiopod and conodont $\delta^{18}O$ trends indeed record a climatic transition, cycle 2 implies that warmest SST and smallest glacial ice-volumes occurred when the sea-level fall rate was near or at a maximum and that coolest SST and largest glacial ice-volumes occurred when sea-level rise rate was near or at a maximum (Figure 7). Similarly, brachiopod $\delta^{18}O$ from cycle 5 may demonstrate an as a more complete record of the glacial-interglacial climate transition that is out-of-phase with conodont $\delta^{18}O$. 

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Conclusions

$\delta^{18}O$ data from the sampled Upper Silurian greenhouse section demonstrate that apatitic brachiopods and conodont pearls generate both similar and opposing trends to coniform conodont $\delta^{18}O$. Because apatitic brachiopods recovered from these deposits were too fragmentary to allow for species separation, variable $\delta^{18}O$ trends may be due to vital effects or partial recrystallization. If analyzed brachiopod and conodont pearl samples were not subject to vital effects or recrystallization, these samples suggest that brachiopod and conodont pearl samples sometimes record $\delta^{18}O$ out-of-phase with coniform conodont element $\delta^{18}O$. 
SUPPLEMENTAL B

RARE EARTH ELEMENT AND SM-ND CATION EXTRACTION COLUMN EXPERIMENT

Introduction

Separation of Sm and Nd from carbonates in the studies presented in previous chapters were accomplished through ion exchange chromatography. Ion exchange chromatography methods for rare earth elements (REE) are typically generated for use with silicate materials, which require strong acids (e.g. HF) to dissolve sample powders and rocks. Carbonate rocks sampled for these studies however, may be dissolved using weak acids (e.g. HCl). Carbonate samples collected for the preceding studies are typified by very low concentrations of REE relative to silicate rocks. Due to the low REE concentrations expected for these samples, it was necessary to determine a more precisely the amount of eluent required to elute REE in the first phase of extraction and Sm and Nd in the second phase of extraction using the ion exchange columns and resins available in the clean lab at the Radiogenic Isotope Laboratory at the University of Mexico. Here I present the results of two ion extraction experiments and a revised methodology for extraction of REE and Sm and Nd at the Radiogenic Isotope Laboratory at the University of New Mexico.

Methodology

Ion Exchange chromatography

In liquid ion exchange chromatography, a sample dissolved in a weak acid (mobile phase) is introduced (loaded) onto an ion exchange resin (stationary phase), typically composed of a sulfonic or carboxylic acid. TRU Resin is used for REE extractions
(Horwitz et al., 1993). Sequential addition of eluent induces downward movement of the mobile phase while increasing the partitioning between ions in the solution based on ion charge, size, and $K_D$ (distribution coefficient). Small, lesser charged ions with low $K_D$ will elute first. In the first stage of extraction, REE are separated from $^{+2}$Ca, $^{+2}$Mg, and $^{+2}$Sr ions that dominate carbonate samples. Sm and Nd are separated and collected in a second stage extraction utilizing long TRU Resin filled columns, which allows REE to partition from small additions of 0.18 N HCl eluent.

*Traditional Sm and Nd extraction method*

Each whole-rock sample was prepared using the method described in Theiling et al. (2012). REE were extracted using a method modified from Asmerom et al. (1999). The soluble fraction of powdered whole-rock samples were dissolved in 4mL 1N HNO₃, centrifuged, and the supernate was loaded onto 250 μL cation exchange columns filled with TRU-SP resin, cleaned and conditioned with 1N HNO₃. Each addition of eluent was allowed to drip completely through the columns to ensure reproducibility of the methodology and precision of separations. After sample loading, 2mL 1N HNO₃ was added to columns to partition REE from ions that dominate carbonate samples (primarily $^{+2}$Ca, $^{+2}$Mg, and $^{+2}$Sr). REE were then collected during addition of 2mL 0.1% HNO₃.

Longer exchange columns were used for partitioning REE using a method modified from Asmerom et al. (1999). Columns were cleaned by allowing 10 mL 6N HCl to drip through; a strong acid ensures effective removal of any ions from previous separations. This cleaning procedure was also performed at the end of each sample separation. 0.18N HCl were added to REE columns in two separate increments, such that the mobile and stationary phases have the same pH when the sample is introduced, termed conditioning.
The sample was loaded onto the columns in a 0.2mL solution of 0.18N HCl. Each addition of eluent was allowed to drip through the column completely to ensure precision and reproducibility of REE partitioning. To partition REE, two increments of 0.2mL 0.18N HCl were added to columns, followed by 0.5mL 0.18N HCl, 1mL HCl, and 16mL 0.18N HCl. Nd was then collected by adding 8mL 0.18N HCl. 2 mL 0.5N HCl were then added to move Sm ions downward in the resin. Sm was collected by adding 4mL 0.5N HCl to columns.

![REE extraction phase table]

Table 5. Counts per second (cps) of $^{146}$Nd and $^{147}$Sm for each aliquot collected during both REE and Sm and Nd extraction phases of experiment #1. Aliquots collected are compared to traditional method eluent addition. Traditional collection intervals are indicated by gray shaded areas.

**Sm and Nd extraction experiment #1**

Efficiency of REE extraction was tested using a REE standard of known concentration. 1mL increments of 0.1% HNO$_3$ eluent were added to columns during the collection step to determine which increment contained the highest concentrations of Sm and Nd. Each 1mL aliquot was collected and analyzed separately on a Thermo Finnigan
X-Series II ICPQ-MS at the University of New Mexico Radiogenic Isotope Laboratory. Amounts of Sm and Nd collected are expressed in counts per second (cps) of $^{146}$Nd and $^{147}$Sm because these isotopes are not subject to isobaric interferences. The results of this experiment are detailed in Figure 15 and Table 5. The 3$^{rd}$ and 4$^{th}$ aliquots of eluent produced maximum cps, suggesting the traditional method will not sufficiently collect REE in carbonate samples. As a result, we altered the method to add two aliquots of 2mL 0.1% HNO$_3$. REE are now collected during the second addition of 0.1% HNO$_3$.

![Graph](image)

Figure 15. Histogram of counts per second (cps) for each sample collection aliquot taken during extraction experiment #1. Nd = open triangles, Sm = open squares. Traditional collection intervals are indicated by shaded rectangles. Eluent amounts for each sample are given in Table 1. a) REE extraction experiment. b) Sm and Nd extraction experiment.
Determination of the separation and collection efficiency of Sm and Nd during the second phase of extraction was performed similarly to the REE extraction experiment. In the traditional method, Nd is collected during addition of 8mL 0.18N. We separated this collection phase into four increments of 2mL 0.18N HCl. Likewise, Sm is traditionally collected in a later phase using 4mL 0.5N HCl, but was similarly separated into 2mL increments for this experiment. The results of this experiment are shown in Figure 15 and Table 5 and indicate that Nd collection may be sufficient, but that Sm collection needs modification.

<table>
<thead>
<tr>
<th>Sm-Nd extraction phase</th>
<th>traditional method</th>
<th>eluent added</th>
<th>sample $^{146}$Nd (cps)</th>
<th>$^{147}$Sm (cps)</th>
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<tr>
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<td>load sample</td>
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<tr>
<td>0.2 mL 0.18N HCl</td>
<td>0.2 mL 0.18N HCl</td>
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<tr>
<td>0.2 mL 0.18N HCl</td>
<td>0.2 mL 0.18N HCl</td>
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<tr>
<td>0.5 mL 0.18N HCl</td>
<td>0.5 mL 0.18N HCl</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 mL 0.18N HCl</td>
<td>1 mL 0.18N HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 mL 0.18N HCl</td>
<td>8 mL 0.18N HCl</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 mL 0.18N HCl</td>
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<td>300000</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>4 mL 0.18N HCl</td>
<td>2</td>
<td>1200000</td>
<td>150</td>
</tr>
<tr>
<td>8 mL 0.18N HCl</td>
<td>1 mL 0.18N HCl</td>
<td>3</td>
<td>1600000</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>1 mL 0.18N HCl</td>
<td>4</td>
<td>1800000</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>1 mL 0.18N HCl</td>
<td>5</td>
<td>2000000</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>1 mL 0.18N HCl</td>
<td>6</td>
<td>2200000</td>
<td>300</td>
</tr>
<tr>
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<td>7</td>
<td>2200000</td>
<td>300</td>
</tr>
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<td>1 mL 0.18N HCl</td>
<td>8</td>
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<td>200</td>
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<td>9</td>
<td>2000000</td>
<td>250</td>
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<tr>
<td></td>
<td>1 mL 0.18N HCl</td>
<td>10</td>
<td>2000000</td>
<td>250</td>
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<tr>
<td>2 mL 0.5N HCl</td>
<td>1 mL 0.5N HCl</td>
<td>11</td>
<td>1800000</td>
<td>250</td>
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<tr>
<td></td>
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<td>10000</td>
</tr>
<tr>
<td>4 mL 0.5N HCl</td>
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<td>13</td>
<td>1700000</td>
<td>1200000</td>
</tr>
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<td></td>
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<td>5000000</td>
</tr>
<tr>
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<td>180000</td>
<td>5000000</td>
</tr>
<tr>
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<td>95000</td>
<td>5000000</td>
</tr>
<tr>
<td>clean columns/</td>
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<td></td>
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<tr>
<td>discard waste</td>
<td>discard waste</td>
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</tr>
<tr>
<td>1 mL 0.5N HCl</td>
<td>1 mL 0.5N HCl</td>
<td>17</td>
<td>50000</td>
<td>2200000</td>
</tr>
<tr>
<td></td>
<td>1 mL 0.5N HCl</td>
<td>18</td>
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<td>3900000</td>
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<td>2000</td>
<td>500000</td>
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<tr>
<td></td>
<td>1 mL 0.5N HCl</td>
<td>20</td>
<td>1500</td>
<td>130000</td>
</tr>
</tbody>
</table>

Table 6. Counts per second (cps) of $^{146}$Nd and $^{147}$Sm for each aliquot collected during only the Sm and Nd extraction phase of experiment #2. Aliquots collected are compared to traditional method eluent addition. Traditional collection intervals are indicated by gray shaded areas.
Sm and Nd extraction experiment # 2

Results from the REE extraction efficiency in the first experiment promoted alteration of the REE extraction methodology whereby REE are collected during a second aliquot addition of 2mL 0.1% HNO3. We used this altered extraction during the first phase of REE collection for the second experiment. In this experiment, traditional collection intervals of Nd and Sm (second extraction phase) were further subdivided to determine the most accurate collection phase for each cation (Table 6). The 16mL 0.18N HCl eluent addition was subdivided into 8mL, 4mL and 4mL additions. The 8mL 0.18N HCl Nd collection phase, 2mL 0.5N HCl intermediary phase, and 4mL 0.5N HCl Sm collection phase were each subdivided into 1mL increments. Each aliquot was analyzed for cps $^{146}$Nd and $^{147}$Sm similar to the first experiment. The results of this experiment are shown in Figure 16 and Table 6. This experiment demonstrates that Nd is eluted from the column earlier than predicted using the modified REE extraction method and that Sm

![Figure 16](image-url)  

**Figure 16.** Histogram of counts per second (cps) for $^{146}$Nd and $^{147}$Sm of each sample collection aliquot taken during Sm and Nd extraction experiment #2. Nd = open triangles, Sm = open squares. Traditional collection intervals are indicated by shaded rectangles. Eluent amounts for each sample are given in Table 2.
continues eluting after collection ends using the traditional method. As a result of these observations, 15.5 mL 0.18N HCl is now added to the column before Nd collection. Nd is collected using 8.5 mL 0.18N HCl. Likewise, Sm is now collected with 5 mL 0.5N HCl instead of the traditional 4mL.

**Revised Sm and Nd extraction methodology**

*Carbonate sample preparation for REE extraction*

1) Drill ~250 mg of powder from clean whole rock samples, taking care to avoid stylolites, intraclasts, large skeletal grains, veins and heavily weathered surfaces with a diamond Dremel© drill bit. Clean drill bit with 5-10% HCl, dionized water, then ethanol between samples to avoid contamination.

2) Take powder vials into clean lab contained inside a Ziploc© bag to minimize dust contamination in the lab.

3) Label a clean 15mL Teflon© collection beaker and obtain mass (g).
   a) After placing beaker inside scale, use static gun 2-3 times.
   b) Close doors to scale before obtaining mass measurement.

4) Tare scale with collection beaker on scale, then remove collection beaker from scale.

5) Carefully tap sample powder into collection beaker.

6) Use static gun on sample powder in beaker before closing collection beaker with lid.

7) Place closed collection beaker + sample onto the scale, use static gun, close doors, and obtain mass.

8) Clean up any sample powder that may have fallen onto table with a clean Kimwipe© and ethanol.

9) Place sample under fume hood onto the glass plates on the left side of the fume hood.
10) Add 6N HCl dropwise to each sample until dissolved. Begin by adding ~10 drops, allowing the reaction to begin violently. Then, add drops until the reaction has completed.

11) Transfer acid soluble (AS) and acid insoluble (AIS) fractions to a labeled 15 mL centrifuge tube, using 6N HCl in squeeze bottle to remove AIS fractions if necessary. Cover centrifuge tube with small squares of Parafilm®.

12) Place tubes into centrifuge containers. Make sure that centrifuge containers are within ~0.025 g of each other so that the centrifuge is well-balanced. Use the large scale in the cabinet underneath the table scale for this measurement. If extra mass is needed, use scraps of weigh paper (often found near the centrifuge from previous users).

13) Turn on centrifuge. This will take ~4 min.

14) During this time, clean collection beakers using the following method:

   a) Turn on tap water. Use 18MΩ water to rinse beakers. Use a clean Kimwipe® to wipe out any excess sample material.

   b) Rinse with 18MΩ 3 times.

   c) Pour a small amount (2-3 mL) of 6N HCl from the bottle labeled: “For cleaning purposes only”

   d) Screw cap back on tightly, place on hotplate on setting 2 for 5-10 min. Do not increase temperature on hotplate above setting 3 because it will melt Teflon beakers.

   e) Place beakers on glass plate under hood until cool enough to handle.

   f) Turn back on tap water, shake beaker, remove cap, and pour liquid down drain.

Rinse beaker 3 times with 18MΩ water.
g) Fill ~halfway with 18MΩ, screw cap tightly, and place beaker back on hotplate for 5-10 min.

h) Take off hotplate as before, pour liquid down drain, and rinse 3 times with 18MΩ water.

i) Fill again halfway with 18MΩ, screw cap tightly, and place beaker back on hotplate for 5-10 min.

j) Take off hotplate as before, pour liquid down drain, and rinse 3 times with 18MΩ water.

k) Your collection beaker is now clean only for future use with its labeled sample.

15) Remove centrifuge tube containers from centrifuge. Carefully peel back Parafilm®, taking care not to disturb the AIS fraction at the bottom.

16) Very carefully pour the AS (liquid) sample into your newly cleaned labeled collection beaker.

17) Place the Parafilm® cover back on the centrifuge tube in the event that you want to analyze AIS fractions later.

18) Take collection beaker + AS fraction to hotplate. Remove lid. Let sample dry down on hotplate setting 3 (2+ hours).

19) Once dry, remove from hotplate onto glass plate, and dissolve sample dropwise in 7N HNO₃. (~10-15 drops or until reaction is complete).

20) Place back on hotplate until dry.

21) Once dry, remove from hotplate onto glass plate, and dissolve sample dropwise in 15N HNO₃. (~10 drops or until reaction is complete). This phase often does not completely dissolve until placed back on the hotplate.
22) Place back on hotplate until dry.
23) Once dry, remove from hotplate onto glass plate and dissolve in 2mL 1N HNO₃
24) Bring sample (in 2mL 1N HNO₃) into weigh room. Obtain mass of each sample using procedure outlined above in steps #3-4 as a guideline.
25) Weigh Sm-Nd spike before and after use on large scale in lower cabinet and record masses in Spikes and Standards Book.
26) Add 2 drops of Sm-Nd spike to sample and obtain spike mass (g) for each sample.
27) Screw lid on tightly and allow sample to flux on hotplate for a few minutes (lower heat setting ~1-2).
28) Carefully pour spiked sample into clean 20mL centrifuge tube, cover with parafilm, and centrifuge, using procedure outlined in step #12-13 above.
29) Carefully remove centrifuge tube from container and pipette 2/3 to ¾ of the AS liquid from the tube and load into cleaned and conditioned REE columns.

REE extraction

1) Add TRU-SPS resin powder to a 15mL Teflon collection beaker.
2) Add 18MΩ water to resin powder in beaker and stir.
3) Obtain 250μL columns at equilibrium with 2N HCl acid. Rinse with 18MΩ water:
   a) Turn tap water on.
   b) Turn 18MΩ water on and rinse column, first shaking column to remove 2N HCl, then rinsing with 18MΩ water and shaking out water 3 times.
   c) Fill entire column with 18MΩ water. Using thumb and forefinger, pinch top of column closed and flick column to ensure that no air bubbles are present in narrow part of column.
d) Bring column (still filled with 18MΩ) to lab station and place in column holder, with a small glass waste beaker underneath each column.

4) Mix resin powder and water by gently swirling a clean pipette tip in mixture. Then, pipette resin/water mixture in 0.5-1 mL increments into clean 250mL columns. This entire process should be done before the 18MΩ water already in the columns drips through, which may take several seconds.

5) After the first pipette increment of resin/water, wait for resin to settle into column to determine whether additional resin/water is needed. Only the stem of the column should be filled with resin. The amount of acid used in future steps is calibrated for having to travel through the amount of resin contained in only the stem of the column. If too much resin is added to column, use pipette to remove excess resin and discard in waste beaker underneath column. To avoid possible contamination of resin, do not put excess resin back into Teflon beaker with clean resin/water mixture.

6) Add additional resin/water as needed until only narrow column is filled with resin. Allow 18MΩ water to drip through into waste beaker.

7) Add 3mL 0.1% HNO₃ to columns to clean resin. Allow to drip through completely.

8) Add 1mL 1N HNO₃ to condition columns. Allow to drip through completely.

9) Add the top 2/3 to ¾ of the supernate from centrifuged sample (see step #28-29 from “Sample prep for REE columns”) to your cleaned and conditioned REE columns. This will be approximately 1.5mL. Allow to drip through completely.

10) Add 2mL 1N HNO₃. Allow to drip through completely.

11) Replace waste beaker underneath column with cleaned and labeled collection beaker.

12) Add 2mL 0.1% HNO₃. Allow to drip through completely.
13) Add 2mL 0.1\% HNO3 and COLLECT REE’s in collection beaker.

14) Dry down collected sample on the hotplate or by leaving uncovered under the fume hood overnight.

15) Clean waste beakers:
   a) Turn on tap water.
   b) Pour acid mixture down drain, using tap water to dilute.
   c) Rinse beakers 3 times in 18M\(\Omega\) water.
   d) Place upside down on towel next to sink.

16) Clean columns:
   a) Turn on tap water.
   b) Using 18M\(\Omega\) water, fill and rinse columns until all resin is gone from column.
   c) Place column back into bottle with other 250\(\mu\)L columns. Add more 2N HCl if necessary. Replace cap tightly. Shake bottle so that 2N HCl may fill columns inside bottle.

17) Clean lab station with ethanol.

*Sm and Nd extractions*

1) Remove columns from containers filled with 6N HCl. Place beakers (acid waste beaker) under each column and secure column through upper and lower holes in rack. Wash column and resin by adding 10mL 6N HCl.

2) While columns are being washed, add 0.2mL 0.18N HCl to dried REE separate sample in collection beaker. Screw cap on tightly and flux on hotplate setting ~1 for ~10min. Take off hotplate and set onto glass to continue dissolution until columns are ready.

3) Add 3mL 0.18N HCl to columns to condition.
4) Add 2 mL of 0.18N HCl to columns to condition.

4) Bring sample (in 0.2mL 0.18N HCl) to workstation. Using a clean pipette for every sample, load sample onto column.

5) Add 0.2 mL of 0.18N HCl to column.

6) Add 0.2 mL of 0.18N HCl to column.

7) Add 0.5 mL of 0.18N HCl to column.

8) Add 1 mL of 0.18N HCl to column.

9) Add 15.5 mL of 0.18N HCl.

10) Clean collection beakers using the method described in “Sample prep for REE columns”.

11) Replace waste acid beaker with clean, labeled collection beaker (Adding to your original label: “Nd”).

12) Add 8.5 mL of 0.18N HCl and COLLECT Nd in clean collection beaker.

13) Remove collection beaker with Nd separate and place on hotplate (setting 3) to dry.

14) Place waste acid beaker underneath column, and add 2 mL of 0.5N HCl.

15) Label a new 15mL collection beaker with sample designation + “Sm”. Replace waste acid beaker with “Sm” collection beaker, add 5 mL of 0.5N HCl and COLLECT Sm in clean collection beaker.

16) Remove collection beaker with Sm separate and place on hotplate to dry.

17) Add 10mL 6N HCl to clean columns. After adding 10mL, use the squirt bottle for 6N HCl to squirt around inside of column to remove any possible contaminants.
18) Rinse acid waste beakers 3 times with 18MΩ water. Place Sm-Nd columns back into containers filled with 6N HCl, nested inside cleaned acid waste beakers. Clean lab station if necessary.

18) When Nd and Sm separates are dry (usually next day or another day), add 1 mL of 3% HNO₃ to each. Cover tightly and flux (hotplate setting 1-2) for ~10 min. Remove and place on glass plate. Allow to sit for a few hours, if possible, to maximize voltage signal on Neptune.

19) Carefully pour into labeled sample vials and cap tightly. Bring to lab with Neptune for analysis.
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