Increased continental weathering flux during orbital-scale sea-level highstands: Evidence from Nd and O isotope trends in Middle Pennsylvanian cyclic carbonates

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ABSTRACT

Despite the common occurrence of orbital-scale (104–105 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 δ18O values (from conodont apatite) from Middle Pennsylvanian cyclic marine carbonates in the U.S. Southwest. Conodont δ18O 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° seawater temperature changes. Two additional sampled cycles show initially increasing, then decreasing δ18O trends. Based on these results, we suggest that δ18O better defines a eustatic sea-level curve, rather than a facies-derived curve. εNd 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 base-line position in this paleotropical location. These results highlight the use of combined εNd and δ18O analyses 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.

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1. 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 fluvial, lacustrine, and paleosol deposits (e.g. Anderson, 1982; Arthur et al., 1986; Goldhammer, 1987; Olson and Kent, 1999; 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 104–105 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 tephrochronology (e.g., Shishkin and Ochev, 1993; Lozovsky and Yarshenko, 1994; Arens and Jahren, 2000; Jahren et al., 2001; Mundil et al., 2003). 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 pCO2, 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 ($^{18}$O values) and continental weathering flux (O$\text{v}$s, 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 >10$^6$ yr oceanic residence time for Sr precludes its use in orbital-scale paleoclimate studies. The short oceanic residence time of Nd (10$^7$ yr) however, implies that Nd-isotopic ratios will be incorporated into marine sedimentary deposits before homogenization by oceanic mixing. In addition, Rb is 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 chemotstratigraphic reconstruction in carbonates. The objectives of this study are to describe and interpret changes in $^{18}$O 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).

2. Geologic background

The Pennsylvanian Earth system was dominated by the early formation of the Pangaean supercontinent, the large Panthalassa 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, 1997; Soreghan, 1997) 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 Galonka, 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 Ghelbian) (Dickinson and Lawton, 2003).

The Middle Pennsylvanian (Desmoinesian or Moscovian) Gray Mesa Formation accumulated in the Lucero Basin of central New Mexico (Fig. 1; Kelly and Wood, 1946; Martin, 1971; Kues and Giles, 2004) and comprised 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 (Fig. 1; 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; Wengert, 1959; Martin, 1971).

At the Mesa Sarca study area (Fig. 1), 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-beded, 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 $^{13}$C signatures, calcrites, and regolith breccias (Fig. 2; 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 $^{13}$C and conodont $^{18}$O, which together indicate that 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).

3. 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).

3.1. Oxygen isotopes

Analyses of conodont $^{18}$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. Emiliani, 1966; Epstein et al., 1953; Emiliani, 1955; Shackleton and Opdyke, 1973; Veizer et al., 1999). $^{18}$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; Jacobim et al., 1996; Wenzel et al., 1999; Joachimski et al., 2008). Conodont apatite has been shown to precipitate in equilibrium with ambient seawater when compared to coeval fish teeth (Amzey et al., 1998). In addition, conodont $^{18}$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 and 25 kg. Conodonts were extracted from whole rock limestones using conventional separation techniques of Sweet and Harris (1988).

Oxygen isotopic analyses were performed on ~500 $\mu$g of $\text{Ag}_3\text{PO}_4$ 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 $\text{Ag}_3\text{PO}_4$ in a continuous flow TC–EA and analyzed on a Finnigan Mat 253 mass spectrometer.
Oxygen isotope data are reported in ‰ with respect to SMOW (Table 1). Reproducibility of δ18O measurements was determined by replicate analyses of internal standards and with an uncertainty of ±0.3 ‰ (1σ).

3.2. 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/144Ndsample / 143Nd/144NdCHUR − 1) * 10,000, where CHUR is the 143Nd/144Nd 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 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 εNd = −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 (<105 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), δ18O 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; Puget 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 147Sm/144Nd, and one to be used for REE and Sm–Nd column separation for analysis of 143Nd/144Nd.

For this initial effort, we used a small aliquot of the supernate to determine the Sm/Nd ratio of the samples to calculate initial 143Nd/144Nd 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 143Nd/144Nd values were calculated using an age of 300 Ma (approximate depositional age of Gray Mesa Formation; Table 1). We have verified this initial method using a total spiking method, whereby a calibrated spike with known 147Sm/150Nd was added to sample supernate to determine sample 147Sm/144Nd.
with 1N HNO₃. REE were collected using a modified method of Asmerom (1999). REE fractions were dried down and dissolved in 250 μL 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 1N 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 250 μL 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 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 εNd was determined using replicate analyses and is reported for each sample, ranging between 0.05 and 0.26 ε-units and averaging 0.11 ε-units (2σ) (Table 1, Fig. 2). Error bars of less than 0.20 ε-units are smaller than data points and therefore not shown in Fig. 2. The La Jolla Nd isotopic standard was run with each batch, obtaining a mean value of 143Nd/144Nd ratio of 0.511825 ± 4 (2σ). The supernate used for analysis of 143Nd/144Nd was dried down and the εNd value was calculated.

4. Results

δ¹⁸O values range between 18.0 and 19.5‰. The change in δ¹⁸O values across individual sampled cycles ranges between 0.5‰ and 0.9‰ (Table 1, Fig. 2). Cycles 5, 6, and 12 show progressively up-cycle increases in δ¹⁸O. Data for cycle 12 comes from Scott and Elrick (2004). Cycles 7 and 8 show initially increasing, then decreasing δ¹⁸O trends.

εNd values (t = 300 My; estimated age of Grey Mesa cycles) range between −10.9 and −7.4 (Table 1, Fig. 2). The change in εNd values across individual sampled cycles ranges between 0.2 and 2.0 ε-units. Five of the eight sampled cycles are characterized by initially decreasing, then increasing εNd values. Because only 2 samples were recovered for cycle 5, no trend is specified. Cycle 6 shows progressively decreasing εNd values. Cycle 8 shows initially increasing, then decreasing εNd values.

δ¹⁸O vs. εNd do not covary (Fig. 3). Systems in which the supply of continental weathering flux co-varies with δ¹⁸O 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 δ¹⁸O vs. εNd 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).

5. Discussion

5.1. δ¹⁴O trends

The systematic up-cycle increase in δ¹⁴O 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) (Fig. 2). 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 and 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...
Changes. However, Ca/Mg ratios and change (Fairbanks and Matthews, 1978).

Nd(ppm)

Identified cycles, assuming the relationship of 0.11

Nd at the time of deposition.

The estimated >30–50 m magnitudes record minimum values and are less than those (60–140 m) reported by Erick 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 δ18O values, with maximum values near mid cycle (Fig. 2).

Based on traditional facies analysis, which is used to interpret relative sea-level changes, these δ18O 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 δ18O versus facies relationships using Fig. 4, 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, 2003).

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 δ13C signatures, which can only form when absolute sea level falls and exposes the seafloor to meteoric waters and soil formation.

Increasing, then decreasing δ18O 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 generated by greater δ18O values. However, this hypothesis is unlikely because the greatest δ18O values are recorded during the mid- to late regression when eustatic sea-level is high (Fig. 4). 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 δ18O values.

### 5.2. Nd-isotope trends

Five of the eight sampled cycles are characterized by εNd trends that are initially high at cycle base (maximum flooding), lowest near the mid-cycle (mid-regression), and return to high εNd values at the cycle top (late regression; Figs. 2 and 4). These trends suggest increasing

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Sample Location</th>
<th>Age (My)</th>
<th>εNd at Cycle Base</th>
<th>εNd at Cycle Top</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>MS 15.25</td>
<td>7–12</td>
<td>13.64 ± 0.471</td>
<td>10.37 ± 0.186</td>
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<td>6</td>
<td>MS 15.75</td>
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<td>14.09 ± 0.541</td>
<td>10.56 ± 0.195</td>
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<td>7</td>
<td>MS 17.5</td>
<td>7–12</td>
<td>13.07 ± 0.273</td>
<td>9.76 ± 0.197</td>
</tr>
<tr>
<td>8</td>
<td>MS 17.65</td>
<td>7–12</td>
<td>11.84 ± 2.543</td>
<td>8.56 ± 1.588</td>
</tr>
<tr>
<td>9</td>
<td>MS 18.5</td>
<td>7–12</td>
<td>14.40 ± 0.495</td>
<td>10.90 ± 0.885</td>
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<td>14.86 ± 0.273</td>
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<td>13.44 ± 0.958</td>
<td>9.56 ± 0.186</td>
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<td>12.93 ± 2.075</td>
<td>9.19 ± 0.185</td>
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<td>12.06 ± 0.635</td>
<td>8.30 ± 0.193</td>
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<tr>
<td>14</td>
<td>MS 20.5</td>
<td>7–12</td>
<td>11.12 ± 1.000</td>
<td>7.39 ± 0.189</td>
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<td>12.20 ± 0.008</td>
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<tr>
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<td>13.60 ± 0.728</td>
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<td>13.47 ± 1.138</td>
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<td>14.18 ± 0.298</td>
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<td>39</td>
<td>MS 32.2</td>
<td>7–12</td>
<td>14.22 ± 0.483</td>
<td>9.66 ± 0.189</td>
</tr>
<tr>
<td>40</td>
<td>MS 32.3</td>
<td>7–12</td>
<td>12.27 ± 0.826</td>
<td>8.65 ± 0.189</td>
</tr>
</tbody>
</table>

*ε* values 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).
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 εNd 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 εNd trends, each within the context of orbital-scale glacio-eustatic sea-level fluctuations. Fanton et al. (2002) interpret that εNd 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 εNd) was exposed during regression and submerged during transgression, which resulted in regressive marine deposits with low εNd values and transgressive deposits with higher εNd values. Applying this principle to the Lucero Basin, the observed εNd trends could be produced if influx from older continental crust (with lower εNd values) occurred during high sea level (interglacial maximum), whereas influx from younger continental crust (with higher εNd 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 εNd at the time of deposition of Gray Mesa cycles is ~ -30 to ~25 calculated from measured 143Nd/144Nd and 147Sm/144Nd 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 εNd trends opposite to those observed.

A second potential explanation for the observed εNd trends would be changes in regional marine circulation patterns. The observed εNd trends would result from regional marine currents transporting lower εNd values from older continental source areas flowing into the Lucero Basin during rising and high sea level (interglacial), whereas marine currents transporting higher εNd 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 $\epsilon_{\text{Nd}}$ values (Bennett and DePaolo, 1987), it is unlikely that the Mesa Sarca $\epsilon_{\text{Nd}}$ 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 $\epsilon_{\text{Nd}}$ values. This would be followed by increasing eolian influx due to increasing winds/aridity during highest sea-levels (interglacial maxima or mid-cycles), resulting in low $\epsilon_{\text{Nd}}$ values. During subsequent sea-level fall (early glacial), eolian input would decline with decreasing wind intensity and/or aridity and a return to higher $\epsilon_{\text{Nd}}$ 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. van Zeist, 1967; Janecek and Rea, 1983; Wasson et al., 1984; Rea et al., 1991; Nanson et al., 1992; Wang, 1993; Rea, 1994; Rincón-Martínez 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 $\epsilon_{\text{Nd}}$ 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 $\epsilon_{\text{Nd}}$ values), increasing during maximum sea-level rise rates (early interglacial), and were greatest, signaled by lower $\epsilon_{\text{Nd}}$ values, during sea-level highs (interglacial maxima): fluvial influx and/or weathering rates would then decrease (rising $\epsilon_{\text{Nd}}$ values) during the subsequent fall in sea level (early glacial) (Fig. 4). We suggest that the systematic changes in fluviatile 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$_2$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, 1997) and Pleistocene–Holocene (e.g. van Zeist, 1967; Janecek and Rea, 1983; Wasson et al., 1984; Rea et al., 1991; Nanson et al., 1992; Wang, 1993; Rea, 1994; Rincón-Martínez et al., 2010). In particular, planktonic foraminifera from the Bay of Bengal demonstrate cyclic variations in $\epsilon_{\text{Nd}}$ on glacial–interglacial timescales over the past 150 kyr due to variations in continental weathering flux (Burton and Vance, 2000). Each of these examples is characterized by cooler, drier climates during glacial maxima with a relatively low flux of fluvially-derived material (reflected by higher $\epsilon_{\text{Nd}}$) and warmer, wetter interglacial intervals, in which flux of fluvially-derived material increases (reflected by lower $\epsilon_{\text{Nd}}$ (Burton and Vance, 2000; Naimo et al., 2005; Kettner and Syvitski, 2009; Lewis et al., 2009).

Vance et al. (2009) suggest that the products of chemical weathering on glacial–interglacial timescales are 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 $\epsilon_{\text{Nd}}$ supports the assumption that $\epsilon_{\text{Nd}}$ values are locally-derived (Fig. 3).

One of the eight sampled cycles (cycle 6) records a progressive increase in $\epsilon_{\text{Nd}}$ values from cycle base to top and one cycle (cycle 8) shows an initial increase to peak $\epsilon_{\text{Nd}}$ values in the middle of the cycle followed by a decrease in values within the cycle cap (Fig. 2). These variable trends may be due to fluctuations in sedimentation rate, thus recording an incomplete eustatic sea-level curve over cycle development (Fig. 4). 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 $\epsilon_{\text{Nd}}$ between the acid soluble (AS) and acid insoluble (AIS) fraction of samples may elucidate whether $\epsilon_{\text{Nd}}$ values were incorporated into the crystal structure of carbonate minerals (suggesting chemical weathering dominated) or whether $\epsilon_{\text{Nd}}$ 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 $\Delta_{\text{Nd}}$. 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 increased $\Delta_{\text{Nd}}$) coincide with intervals of sea-level rise and highstand (interglacial), followed by decreased fluvial incision and/or flux (shown by decreasing $\Delta_{\text{Nd}}$) during sea-level fall/lowstand (glaciation) (Fig. 4). 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 $\Delta_{\text{Nd}}$ and $\delta^{18}O$ 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 Pennsylvaniaan paleotropical continental weathering flux is generally in-phase with glacioeustatic 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.

6. 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 $\Delta_{\text{Nd}}$ analysis display trends indicating maximum continental weathering flux during interglacial maxima (sea-level highstands) when local paleotropical precipitation rates and/or paloetemperatures 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.

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