

# Elevation or alteration? Evaluation of isotopic constraints on paleoaltitudes surrounding the Eocene Green River Basin

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## ABSTRACT

Low oxygen isotope values ( $\sim -16\%$ , relative to Peedee belemnite standard) obtained from microbial carbonates of the Green River Formation have been interpreted as evidence for snowmelt and high elevations surrounding this early Eocene lake basin. However, low values from microbial precipitates could also represent a diagenetic overprint. We investigate these alternate hypotheses by measuring the oxygen isotope composition of altered and unaltered freshwater bivalves from the basin. We analyzed subannual samples from 3 individuals and bulk samples from 54 individuals. Subannual samples exhibit clear seasonal fluctuations in oxygen isotope values. These fluctuations are large enough to require seasonal shifts in temperature and/or the oxygen isotope value of the lake water. However, the lowest value of any unaltered sample (either bulk or high resolution) corresponds to lake-water  $\delta^{18}\text{O}$  of  $\sim -12\%$  (relative to standard mean ocean water) and is not low enough to require the addition of snowmelt to the lake. A few bulk samples exhibit very low oxygen isotope values, which would seem to suggest snowmelt. However, these samples also show clear evidence of calcite in X-ray diffraction patterns, demonstrating the presence of diagenetic precipitates. Given that (1) diagenetic alteration is a plausible explanation of very low  $\delta^{18}\text{O}$  values, (2) alteration has not been examined in microbial carbonates, and (3) unaltered aragonitic bivalves provide no independent evidence for low  $\delta^{18}\text{O}$  values for lake waters, we conclude that robust isotopic evidence for high elevations surrounding the Green River Basin during the Eocene is currently lacking.

**Keywords:** paleotopography, paleohydrology, Rocky Mountains, lacustrine sediments, stable isotopes.

## INTRODUCTION

Estimates of Cenozoic topography in the Rocky Mountains are important for reconstructing climate and for understanding the tectonic evolution of the region. Observations of low-relief Paleogene erosional surfaces led researchers to conclude that topography was subdued in the Rocky Mountains during the early Cenozoic and that present-day relief formed in the Neogene (Epis and Chapin, 1975; Burchfiel et al., 1992). However, analyses of structural and unroofing sequences (DeCelles et al., 1991; Hoy and Ridgway, 1997), fossil floras (Gregory and Chase, 1992; Chase et al., 1998; Wolfe et al., 1998), and oxygen isotopes in fossil bivalves (Dettman and Lohmann, 2000) suggest high altitudes in northern Wyoming and Montana during the early Cenozoic.

In southwestern Wyoming, low oxygen isotope ( $\delta^{18}\text{O}$ ) values in microbial carbonates from several levels in cores of the lacustrine Green River Formation (as low as  $\sim -16\%$ , relative to PDB) have been interpreted as evidence for high mountains surrounding the lake basin during the early to middle Eocene (Norris et al., 1996, 2000). (Note that  $\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}} \div ({}^{18}\text{O}/{}^{16}\text{O})_{\text{standard}} - 1] \times 1000$ . The units are per mil [‰]. Two standards are used: carbonates are often reported relative to a carbonate standard [VPDB, Vienna Peedee bel-

lemnite], whereas fluids are often reported relative to a water standard [VSMOW, Vienna standard mean ocean water]. Conversion between these scales is described by the equation  $\delta^{18}\text{O}_{\text{SMOW}} = 1.03086 \times \delta^{18}\text{O}_{\text{PDB}} + 30.86$ .) This inference is based on the observations that the  $\delta^{18}\text{O}$  of meteoric precipitation is correlated with local mean annual temperature (MAT) and that very negative precipitation  $\delta^{18}\text{O}$  values (i.e.,  $< -15\%$ , relative to SMOW) only occur in regions with cold temperatures (MAT  $< 3^\circ\text{C}$ ) and heavy snowfall (Rozanski et al., 1993). Because fossil plants in the basin suggest warm temperatures at the elevation of the lake (MAT  $\approx 15^\circ\text{C}$ ) (Greenwood and Wing, 1995), Norris et al. (1996, 2000) concluded that meltwaters from snow on high elevations surrounding the basin entered the lake and intermittently dominated its hydrologic budget.

Very low carbonate  $\delta^{18}\text{O}$  values may also result from high-temperature alteration during burial diagenesis or from meteoric diagenesis in the presence of  $^{18}\text{O}$ -depleted waters (Dickson and Coleman, 1980; Allan and Matthews, 1982). The presence of shortite in Green River cores suggests burial temperatures of  $>90^\circ\text{C}$  (Norris et al., 2000). Given an  $\sim 2\%$  decrease in calcite  $\delta^{18}\text{O}$  values for every  $10^\circ\text{C}$  increase in temperature (Friedman and O'Neil, 1977), diagenetic calcite  $\delta^{18}\text{O}$  values would be much lower than those at the surface. For example, in the Bighorn Basin (northern Wyoming), diagenetic spars from similar Paleogene sediments have  $\delta^{18}\text{O}_{\text{PDB}}$  values as low as  $-18.9\%$ , whereas pedogenic carbonates from the same deposits average  $\sim -8\%$  (Koch et al., 1995; Bao et al., 1998).

Here we reexamine the question of the isotopic composition of the Eocene Green River lake system to investigate the alternate hypotheses of diagenetic alteration versus high elevation. To do this we conducted two sets of analyses. First, we measured the  $\delta^{18}\text{O}$  of unaltered, lacustrine unionid bivalves from the Green River Formation. Unionid shells are composed of aragonite and form in oxygen isotope equilibrium with ambient fluids (Dettman et al., 1999). Very low  $\delta^{18}\text{O}$  values in bivalve aragonite would provide independent support for the snowmelt hypothesis. Second, we analyzed bivalve shells that had been altered from aragonite to calcite to determine the  $\delta^{18}\text{O}$  of the diagenetic end member in this system. Detection of very low  $\delta^{18}\text{O}$  values in altered bivalves would provide some independent support for the diagenetic hypothesis.

## MATERIALS AND METHODS

We collected unionid shells (superfamily Unionacea) from the Luman Tongue, Tipton Shale Member, and Laney Member of the Green River Formation in Wyoming and Colorado (Figs. 1 and 2). Each of these members was deposited in an open, freshwater lake known as Lake Gosiute (Roehler, 1993). Our collections were made at several locations in each of four sampling sites: Erickson-Kent Ranch (Luman Tongue), Shell Creek (Luman Tongue), Wamsutter (Luman Tongue and Tipton Shale Member), and Manila (Laney Member) (Table 1). Stratigraphic placement of our sampling sites was determined by using the detailed geologic maps and the measured sections of Roehler (1973, 1992) (Fig. 2).

The cores analyzed by Norris et al. (1996, 2000) sampled the upper Wilkins Peak Member and the lower Laney Member. We were unable to find bivalves within the Wilkins Peak Member, probably because lake salinity during the deposition of this member exceeded

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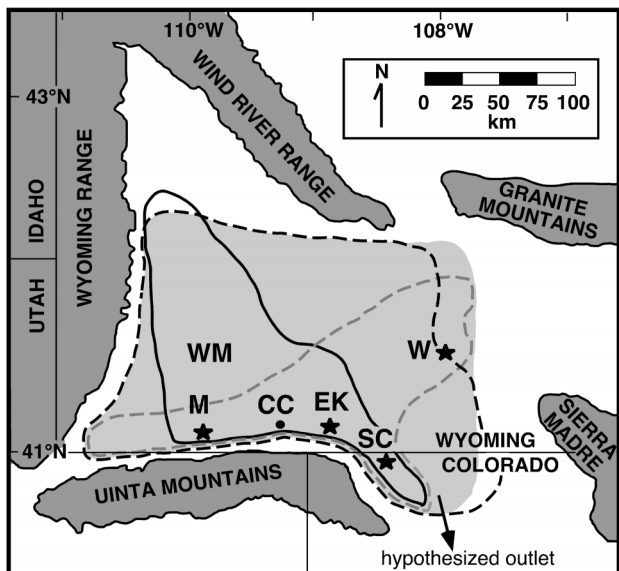


Figure 1. Map of Green River Basin showing bivalve sampling sites (EK—Erickson-Kent Ranch, M—Manila, SC—Shell Creek, W—Wamsutter) and locations of cores analyzed by Norris et al. (1996, 2000; CC—Currant Creek, WM—White Mountain). Lines and shading indicate estimated areal extent of Lake Gosiute during deposition of Luman Tongue (dashed gray line), Tipton Shale Member (dashed black line), upper Wilkins Peak Member (solid black line), and Laney Member (gray shading) (based on Roehler, 1993).

the tolerance of unionids. We did collect bivalves from the lower Laney Member, however, in which Norris et al. (1996, 2000) observed one negative  $\delta^{18}\text{O}$  excursion.

For bulk isotopic analysis, each shell was cleaned by rinsing with water and air drying; then a representative sample was ground in acetone by using a mortar and pestle. We determined the mineral content of each shell (i.e., calcite, aragonite, or mixed) by X-ray diffraction. Bulk sampling provides an average isotopic value for several years' growth.

To look for evidence of  $\delta^{18}\text{O}$  values that are low because of seasonal effects (perhaps associated with a spring meltwater plume), we collected intra-annual  $\delta^{18}\text{O}$  time series by micromilling unaltered bivalve shells (Dettman and Lohmann, 1995). Shells were cross-sectioned from umbo to commissure, thin-sectioned, then ground to 100  $\mu\text{m}$  thickness. Green-gold cathodoluminescence similar to that in modern unionids confirmed that sectioned shells were composed of unaltered aragonite. Each shell contained growth interruptions, which appeared as opaque bands in transmitted light, that we interpreted as annual features. Shells were sampled by micromilling parallel to growth increments at 50  $\mu\text{m}$  intervals. If we assume that growth interruptions are annual, the temporal resolution of isotopic sampling was up to monthly, although slower growth as the unionid aged led to lower resolution for later years. We microsampled three shells, which were chosen because they had among the lowest bulk  $\delta^{18}\text{O}$  values and be-

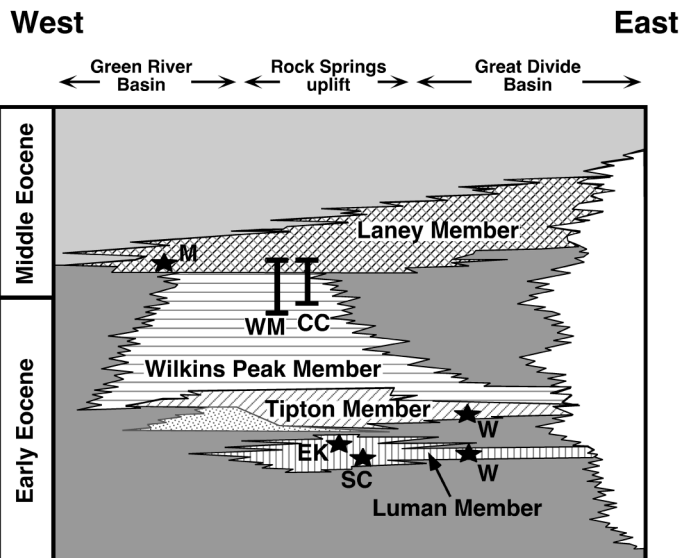


Figure 2. Schematic cross section of Eocene deposits of Green River Basin (after Roehler, 1993). Stars indicate stratigraphic positions of our sampling sites, and solid lines indicate extent of cores analyzed by Norris et al. (1996, 2000); abbreviations as in Figure 1.

cause they were relatively intact and thus could provide long time series.

Isotopic analyses were conducted by using a Micromass Isocar automated carbonate preparation device interfaced with either a Prism or an Optima mass spectrometer. In this method, samples are reacted in 100% phosphoric acid at 90 °C. The standard deviation for replicate isotopic analyses of carbonate standards (Carrara Marble, NSB 19) was <0.1‰.

## RESULTS

Unaltered aragonitic shells had  $\delta^{18}\text{O}_{\text{PDB}}$  values between -5‰ and -10‰ (Table 1). Altered calcitic shells had  $\delta^{18}\text{O}_{\text{PDB}}$  values ranging from -13‰ and -16‰. Partially altered shells had values intermediate between the aragonitic and calcitic end members.

To estimate the  $\delta^{18}\text{O}$  of ancient lake waters, we first converted carbonate values to the SMOW scale and then corrected for the temperature-dependent fractionation of oxygen isotopes during carbonate precipitation. For aragonitic unionid shells, we used the relationship of Grossman and Ku (1986) (as modified by Dettman et al., 1999):

$$1000 \ln \alpha_{\text{water}}^{\text{aragonite}} = 2.559 \times 10^6 T^{-2} - 0.715, \quad (1)$$

where  $T$  is temperature in kelvins and  $\alpha$  is the oxygen isotope fractionation factor between water and aragonite,

$$\alpha_{\text{water}}^{\text{aragonite}} = \frac{1000 + \delta^{18}\text{O}_{\text{aragonite}}}{1000 + \delta^{18}\text{O}_{\text{water}}}, \quad (2)$$

where both isotopic values are on the SMOW scale. To use these equa-

TABLE 1. ISOTOPIC AND SEDIMENTARY DATA FOR GREEN RIVER BIVALVES

Locality	Member	Sediment type	$\delta^{18}\text{O}_{\text{aragonite}}$	$\delta^{18}\text{O}_{\text{mixed}}$	$\delta^{18}\text{O}_{\text{calcite}}$
Erickson-Kent	Luman	Sandstone, shale	none	-11.22 ± 1.11 (2)	-15.40 ± 1.13 (8)
Shell Creek	Luman	Shale	-8.18 ± 0.76 (11)	-9.79 ± 1.27 (3)	none
Wamsutter	Luman	Shale	-7.10 ± 0.21 (2)	none	none
Wamsutter	Tipton	Shale	-5.72 ± 0.72 (3)	none	none
Manila	Laney	Limestone	-7.42 ± 1.90 (14)	-9.62 ± 2.31 (11)	none

Note: Data values are the mean ± 1 standard deviation in per mil relative to Peedee belemnite (PDB), followed by the number of specimens in parentheses. Shells were classified as aragonite, calcite, or mixed aragonite and calcite on the basis of X-ray diffraction patterns.

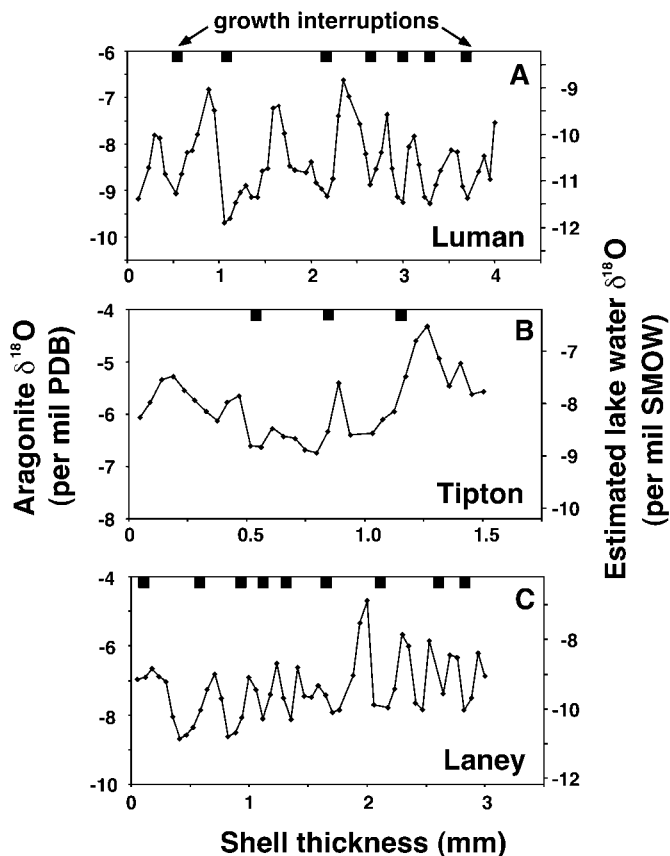


Figure 3. High-resolution measurements of  $\delta^{18}\text{O}$  from bivalve shells from (A) Luman Tongue, (B) Tipton Shale Member, and (C) Laney Member of Green River Formation. Solid black boxes indicate positions of growth interruptions, which are used to determine extent of annual cycle. Left axis shows measured  $\delta^{18}\text{O}_{\text{PDB}}$  and right axis shows estimates of lake-water  $\delta^{18}\text{O}_{\text{SMOW}}$  based on these measurements, crystallization temperature of  $10^\circ\text{C}$ , and equations described in text. PDB is Peedee belemnite, SMOW is standard mean ocean water.

tions, we must estimate the lake-water temperature. Modern unionids form their shells in the temperature range from  $\sim 10$  to  $30^\circ\text{C}$  (Howard, 1921; Negus, 1966; Dettman et al., 1999). We assumed a formation temperature of  $10^\circ\text{C}$  because this lowest-reasonable temperature yields the most negative estimated lake-water  $\delta^{18}\text{O}$  values and therefore offers the most permissive results for testing the snowmelt hypothesis. By using this approach for aragonitic shells, we estimated lake-water  $\delta^{18}\text{O}_{\text{SMOW}}$  values ranging from  $-7\text{‰}$  to  $-12\text{‰}$ .

Isotopic measurements from microsamples of aragonitic bivalves also show no evidence of very low  $\delta^{18}\text{O}$  values; the most negative values that we estimated for lake-water  $\delta^{18}\text{O}_{\text{SMOW}}$  were  $\sim -12\text{‰}$  (Fig. 3). The amplitudes of the annual cycle in shell  $\delta^{18}\text{O}_{\text{PDB}}$  are as large as  $3\text{‰}$ . If seasonal changes in crystallization temperature were the sole cause of the annual  $\delta^{18}\text{O}$  cycle, an  $\sim 15^\circ\text{C}$  temperature change would be implied. This is plausible given the  $\sim 20^\circ\text{C}$  temperature tolerance range of unionids and independent paleoclimatic information for seasonality in the Green River Basin (Wing and Greenwood, 1993). Alternatively, it is plausible that lake-water  $\delta^{18}\text{O}$  values varied seasonally by  $3\text{‰}$  or more owing to changes in the precipitation-evaporation balance or the  $\delta^{18}\text{O}$  value of the precipitation (Rozanski et al., 1993; Gat, 1995).

## DISCUSSION

None of our bulk samples or microsamples from unaltered aragonitic bivalves had  $\delta^{18}\text{O}$  values  $< -12\text{‰}$ . Thus they provide no in-

dependent support for the hypothesis that extremely  $^{18}\text{O}$ -depleted waters entered the Eocene Green River lake system. Yet this negative result does not falsify the snowmelt hypothesis outright for several reasons. First, the snowmelt signature in lake waters might have been obscured by evaporative enrichment or by dilution with less negative inputs from low-elevation precipitation. The effects of evaporation on lake-water  $\delta^{18}\text{O}$  should be low because we collected bivalves from deposits formed in an open lake. The  $\delta^{18}\text{O}$  of water in open lakes often reflects the  $\delta^{18}\text{O}$  of input water closely because these lakes lose water through overflow (a nonfractionating process) rather than solely by evaporation (Gat, 1995). If the evaporative enrichment was larger than several per mil, however, the lake-water  $\delta^{18}\text{O}$  values estimated from bivalve aragonite would begin to overlap the range indicative of snowmelt input to the lake. Because our bivalve  $\delta^{18}\text{O}$  values are not extremely low, without more specific information about the evaporative enrichment, it is impossible to determine conclusively if they are consistent with a significant contribution of snowmelt to the lake.

However, it is almost certainly true that some of the water entering the lake was derived from low-elevation precipitation. Dettman and Lohmann (2000) analyzed the  $\delta^{18}\text{O}$  of fluvial bivalves and estimated that basinal precipitation in northern Wyoming during the late Paleocene and early Eocene was  $\sim -9\text{‰}$  to  $-12\text{‰}$  relative to SMOW, nearly identical to values we estimated for lake water from unaltered bivalves. If we assume that the evaporative enrichment was small during the open phases of the lake (i.e.,  $< 2\text{‰}$ – $3\text{‰}$ ), this similarity suggests that lake waters in the intervals represented by unaltered bivalves were chiefly derived from basinal precipitation. By analyzing fluvial rather than lacustrine bivalves in their studies, Dettman and Lohmann (2000) were able to minimize the potential that a snowmelt signature had been altered by evaporation and dilution with low-elevation precipitation. Unfortunately, no unaltered fluvial bivalves are currently known from the Green River Formation, although it may be possible to examine river waters through analysis of gar scales (Fricke et al., 1998), which occur in fluvial deposits at the basin margins (P.L. Koch, personal observation).

We also note that we only sampled bivalves from several horizons in three members of the Green River Formation. This is problematic because Norris et al. (1996, 2000) observed only several short-lived intervals of extremely negative  $\delta^{18}\text{O}$ , and it is possible that none of our bivalves are representative of these intervals. In particular, we could not find bivalves in the lowstand deposits of the upper Wilkins Peak Member, which exhibited extremely low  $\delta^{18}\text{O}$  values at several levels in the study of Norris et al. (1996, 2000). It is possible that very negative  $\delta^{18}\text{O}$  values indicative of high-elevation precipitation may only be preserved in lake waters at extreme lowstands, when basinal rainfall is low. When the lake is deeper and less saline, the snowmelt signature may be diluted by basinal precipitation. If so, the lake system presents a difficult problem. Low  $\delta^{18}\text{O}$  values due to snowmelt may have occurred at lowstands when the lake contained only microbial laminates, for which robust tests of diagenesis are lacking, whereas at highstands, when the lake was able to support diagenetically robust aragonitic bivalves, it was dominated by basinal precipitation with higher  $\delta^{18}\text{O}$  values.

Our only attempt to address this issue is through analysis of microsamples, which provide “snapshots” of lake chemistry. If snow-covered mountains surrounded the basin throughout the interval, we might expect evidence for a seasonal meltwater plume entering the lake in the spring. Such a plume is most likely to be evident in the basin-margin settings from which we obtained bivalves. We view our failure to detect any extremely low  $\delta^{18}\text{O}$  values in microsampled bivalves as a troubling, although not fatal, failed test of the snowmelt hypothesis.

In contrast, altered bivalves provide strong support for the alternate hypothesis that low  $\delta^{18}\text{O}$  values in this system may have been

produced by diagenetic alteration. The only samples in our study that yielded extremely low  $\delta^{18}\text{O}_{\text{PDB}}$  values (i.e.,  $< -15\text{‰}$ ) were those from highly altered, calcitic shells. Even though these measurements were not obtained from micrite at the stratigraphic layers studied by Norris et al. (1996, 2000), these results and similar measurements obtained from soil nodules (Koch et al., 1995; Bao et al., 1998) lead us to believe that very negative  $\delta^{18}\text{O}$  values in this region can be the result of diagenesis. Strong support for this alternate hypothesis implies that the extent of alteration must be known before interpretations about the presence of snowmelt and high elevations can be made from carbonate  $\delta^{18}\text{O}$  values. We note, however, that most of the  $\delta^{18}\text{O}_{\text{PDB}}$  values measured by Norris et al. (1996, 2000) are less negative ( $-2.5\text{‰}$  to  $-5.0\text{‰}$ ) than those we obtained from bivalve aragonite. This implies that most of the microbial calcite analyzed by these authors had not undergone a significant amount of diagenetic alteration. However, this fact does not eliminate the possibility that restricted intervals with very low  $\delta^{18}\text{O}$  values have been diagenetically altered.

To summarize, study of unaltered bivalves provides no independent support for the hypothesis that Eocene lake waters had low  $\delta^{18}\text{O}$  values indicating the input of snowmelt. The  $\delta^{18}\text{O}$  values for bulk and high-resolution samples are in the range expected for low-elevation continental precipitation, and the annual cycles in  $\delta^{18}\text{O}$  observed in three shells can be explained purely through seasonal changes in evaporation, rainfall  $\delta^{18}\text{O}$ , or lake-water temperature. In contrast, isotopic measurements from altered bivalves provide support for the alternate hypothesis that diagenetic alteration produces very negative  $\delta^{18}\text{O}$  values for carbonates from the Green River Basin. No available petrographic, mineralogic, or sedimentologic information refutes this alternate hypothesis as the explanation for very negative  $\delta^{18}\text{O}$  values in Green River microbial carbonates. Without such information, we conclude that robust isotopic evidence for snowmelt, which would indicate high elevations surrounding the Green River Basin during the Eocene, is currently lacking.

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