Legacy amino acid ratios from terrestrial snails in alluvial deposits in Colorado show >8-10°C average Quaternary temperature depression but inconsistent river-terrace correlations

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Objectives and Analysis

Following on the success of using amino acid ratios measured on marine mollusks in the late 1970s and early 1980s as a relative or calibrated-numerical dating method (e.g., Mitterer et al., 1975; Miller and Hare, 1980; Belknap and Wehmiller, 1980; Miller, 1985; Miller and Brigham-Grette, 1989), during 1976-1982 we obtained samples of terrestrial gastropods from a series of Quaternary sediment sequences in the intermountain west of the United States and measured D-alloisoleucine/L-isoleucine (alle/Ile) ratios on the shells at INSTAAR (University of Colorado) using high-performance liquid chromatography (Miller et al., 1979; Miller et al., 1982). Here we summarize the results from three of the most extensive collections of gastropod shells: from alluvial terrace sediments in the Denver region (Scott, 1960; 1963; Madole, 1998), from alluvial terrace sediments along the Yampa River in northwestern Colorado (Madole, 1989; 1991a; 1991b), and from alluvial terrace sediments along the White River 100 km southwest of the Yampa River terraces (Evanoff, 1983; Madole, 1989). The results of our analyses of alle/Ile ratios on some other collections of gastropods during this same period can be found in publications listed in a database at: https://doi.org/10.7910/DVN/JLDPAD. The relevant pages of those references, a table listing locations and ratio data for the Colorado samples (Table D1), and additional data can also be found in the database.

Our objectives in analyzing the Colorado gastropods were: (1) to use the ratios on shells from terraces of differing heights to determine terrace relative ages (Figs. 1, 2, and 3), and then (2) to correlate major terraces among the three Colorado study areas (Fig. 4). A third objective was to use ratios on shells collected stratigraphically near the Lava Creek B ash (~631 ka; Mathews et al., 2015), and others from terraces inferred at the time to be at least as old as oxygen-isotope stage 6 (150 ka), to estimate an average effective Quaternary diagenetic temperature (EDT; e.g., McCoy, 1987; Wehmiller, 1993) for the Colorado sites. To do so we used our laboratory-determined alle/Ile epimerization kinetics for *Vallonia* (Fig. 5) and the kinetics determined by Oches et al. (1996) for *Succinea-Catinella*. Results for the third objective were summarized in an abstract (Nelson et al., 1984; reproduced to the right), with data in Table 1 below.

Gastropod samples were identified and processed largely following methods described by Clark et al. (1989) and Oches et al. (1996; our preparation procedures are in the database). We did 3-4 preparations of most samples (range 2-6) and ran most preparations on the amino acid analyzer 3-6 times (range 2-7), averaging acceptable results (Table D1 in database). Alle/Ile ratios were hand measured from peak heights, as was common at the time. More recent comparisons (Dahl and Meyer, 1999), as well as our own on the original data (Fig. D1 in database), show that peak-height ratios on good-quality chromatograms do not differ significantly or systematically from peak-area ratios measured on the same samples. We determined the Arrhenius equation and activation energy for isoleucine epimerization in *Vallonia* (Fig. 5) through laboratory heating analyses and radiocarbon-dated shells as described by Oches et al. (1996) for *Succinea-Catinella*. As free fraction alle/Ile ratios were more variable than the ratios on the total acid hydrolysate fraction, we limit our calculations and comparisons to the hydrolysate fractions.

Through evaluation of our amino acid chromatograms (1977-1984), we did not use alle/Ile ratios for those showing low concentrations of D or L diastereomers of isoleucine (perhaps due to leaching of amino acids), unusually high concentrations of threonine or serine (which suggest contaminated samples), or poorly resolved amino acid peaks (e.g., Miller and Brigham-Grette, 1989; Dahl and Meyer, 1999).

We also discounted unusually low or high ratios compared with those measured on other shells from the same samples as possibly being leached of amino acids or reworked from older deposits, respectively (e.g., Wehmiller, 1993; Oches and McCoy, 1995). Because epimerization in mollusks is commonly genus dependent (Miller and Hare, 1980; Wehmiller, 1993) we compared alle/Ile ratios in our most common genera (*Vallonia*, *Succinea-Catinella*, and *Pupilla*). In our samples, ratios for *Pupilla* are very similar to those for *Vallonia* (Fig. 6). However, because of greater differences between *Succinea-Catinella* and *Vallonia* ratios, we converted *Succinea-Catinella* ratios to *Vallonia*-equivalent ratios using a regression equation (Fig. 7; Table D1 in database).

Compared with our third objective of estimating an EDT for our Colorado sequences (Nelson et al., 1984; Table 1), our first and second objectives of using alle/Ile ratios for relative dating and correlation were largely unsuccessful. Even in our two areas where mean annual temperatures (MAT) are similar (~6°C), ratios are too variable to support correlations of individual terraces between the two areas. For most of our samples, analyses are too few to show the <10% precision among ratios for multiple genera required for aminostratigraphic correlation (Wehmiller, 1993). Although similar ratios suggest that the 18-m terrace along the White River correlates with some 32-35-m terraces along the Yampa River, and the 31-m terrace on the White River may correlate with a 37-m terrace on the Yampa, higher ratios for other nearby samples (e.g., 23-m and 42-m terraces along the Yampa River; Figs. 1 and 2) suggest that shells from the latter terraces are reworked, or perhaps have had differing temperature histories. Because the ratio for the highest shells along the White River, collected from a gravel bed containing the 631-ka Lava Creek B ash, is much higher than ratios for lower terraces, the latter are probably much younger (<<500 ka).

A greater unresolved issue is that ratios for shells collected by Glenn Scott in the late 1950s and early 1960s from sediments on the terraces along the Front Range are dramatically lower than expected considering the present MAT in the area (10°C). Considering the 4°C higher MAT along the Front Range than in northwestern Colorado, Front Range ratios should be much higher—not lower—than those from equivalent-aged terraces in northwestern Colorado (Fig. 4). Recent work shows that Front Range surfaces and sediments are of variable—largely older than previously thought—ages, and are far more stratigraphically complex than inferred in the mid-twentieth century (Riihimaki et al., 2006; Diihnfourth et al., 2012; Foster et al., 2016). Glenn Scott (oral communication, 1976) was not certain that analyzed shells from the uppermost sections of the Louviers Alluvium were as old as the adjacent Louviers terraces; much lower than expected Louviers ratios suggest that they are, in fact, much younger (Fig. 3). Similarly, Rich Madole (written communication, 1976) was unsure if shells from gravel beneath the Broadway terrace near Boulder (Madole, 1998) were the same age or older than the terrace; ratios on the shells indicate the latter. These, and other unrecognized interpretative issues, such as variable long-term depths of burial of samples (e.g., McCoy, 1987; Wehmiller, 1993; Oches and McCoy, 1995), preclude using our Front Range ratios for relative-age dating and correlation. However, the much lower than expected ratios for all Front Range shells suggest that EDTs along the Front Range were likely lower than suggested by the present differences between Front Range MAT and the MATs of other areas where alle/Ile ratios have been measured on terrestrial gastropods.

References here and on figures and the table are listed in the database.

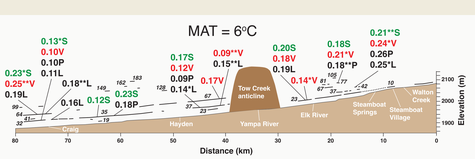
1984 Abstract- Quaternary Temperature Depression in Colorado

Amino-acid ratios (D-alloisoleucine/L-isoleucine of the total hydrolysate fraction) that we measured on shells of the terrestrial gastropod genera *Vallonia, Pupilla,* and *Succinea-Catinella* from fluvial terrace deposits in Colorado confirm several independent estimates of about 8-10°C lowering of temperature in the Rocky Mountain region during middle and late Quaternary glaciations.

D/L ratios from the analysis of three shell samples stratigraphically near the Lava Creek B ash at three sites in western Colorado allow us to estimate the average EDT (effective diagenetic temperature) for the last 631 ka. D/L ratios from *Vallonia, Pupilla,* and *Succinea-Catinella* from the same shell samples collected at a number of sites show that isoleucine in all three genera epimerizes at about the same rate. Using ratios from pyrolysis experiments and from sites where radiocarbon ages permit calibration, we have calculated a first-order kinetic equation for the epimerization rate in *Vallonia* (Fig. 5). Ratios on *Vallonia* from a Lava Creek B ash bed near Carbondale, Colorado, on *Succinea-Catinella* from just above the same ash near Meeker, Colorado, and on *Succinea-Catinella* from just beneath the same ash near Baggs, Wyoming, when used with this equation, yield an EDT of 7-11°C lower than the present MAT (mean annual temperature) at these sites (Table 1). This EDT assumes a linear epimerization rate from 0-631 ka, but studies on other mollusks indicate that this rate may decrease significantly in samples that have ratios >0.3-0.4. The gastropods from our Lava Creek B calibration sites yield ratios of 0.34-0.50. Thus, EDT's derived using a kinetic equation that may be valid only when used with younger samples will tend to overestimate the amount the temperature is lowered from modern values (yielding minimum estimates of paleotemperature).

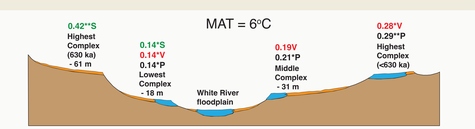
Evaluation of the accuracy of our EDT is complicated by the lack of accurately dated calibration sites with gastropods in the age range of 100-500 ka. However, by assuming reasonable minimum ages for gastropods from terrace deposits from two widely separated alluvial sequences, we show that 8-10°C is a reasonable EDT. *Succinea-Catinella* from deposits of the 37-m terrace along the Yampa River in northwestern Colorado (Fig. 1) give D/L ratios of 0.17±0.01. Stratigraphic relationships between moraines, loess, and terrace deposits along the river near Steamboat Springs indicate that this terrace is at least as old as oxygen-isotope stage 8 (>250 ka). Using this minimum age with our kinetic equation yields a maximum EDT of 8.0°C lower than MAT (Table 1). We have also obtained D/L ratios (0.18±0.01) on *Succinea-Catinella* from the Slocum Alluvium along the Front Range Piedmont (Fig. 3), which soil development and uranium-series ages on bone show to be significantly older than the last interglacial. Assuming a minumum age of 150 ka for these gastropods yields a similar maximum EDT of 9.2°C lower than MAT. Although there is considerable uncertainty in these calculations, because both maximum and minimum estimates are similar, we conclude that 8-10°C is a reasonable regional EDT for 0-631 ka. Because our EDT is estimated from an equation in which the reaction rate is exponentially dependent on temperature, the arithmetic mean temperature for the period 0-631 ka must have been lower than our EDT.

Nelson, A.R., Madole, R.F., Evanoff, Emmett, Scott, G.R., and Piety, L.A., 1984, Quaternary paleotemperature estimates using amino-acid ratios measured on terrestrial gastropods from fluvial sequences in Colorado [abs.]: American Quarternary Association, Program and Abstracts, 8th Biennial Meeting, University of Colorado, Boulder, p. 92.



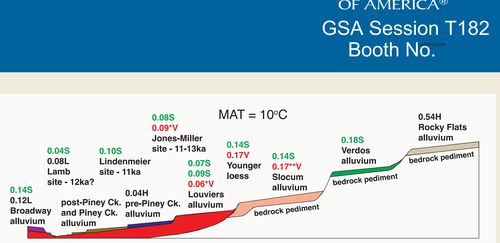
Yampa River

Figure 1. Mean total fraction alle/Ile ratios for gastropods collected from alluvial terrace sediments along the Yampa River (Madole,1989; 1991a; 1991b). V = *Vallonia* sp., S = *Succinea-Catinella*, P = *Pupilla* sp., L = *Lymnea* sp. Standard deviations for ratios are ±0.01, except as marked with * (* = ±0.02-0.03, ** = ±0.04-0.06). *Succinea-Catinella* ratios were converted to *Vallonia* equivalent ratios (Fig. 7). Elevations of terrace surfaces along the river (black lines) are marked with small numbers (m).



White River

Figure 2. Mean total fraction alle/Ile ratios for gastropods collected from alluvial terrace sediments along the White River (Evanoff, 1983). V = *Vallonia* sp., S = *Succinea-Catinella*, P = *Pupilla* sp. Standard deviations for ratios are ±0.01, except as marked with * (* = ±0.02-0.03, ** = ±0.04-0.06). Succinea-Catinella ratios were converted to *Vallonia* equivalent ratios (Fig. 7). Elevation of terraces of different relative age (as labeled for terraces in meters) is shown only schematically (not to scale).



Front Range piedmont

Figure 3. Mean total fraction alle/Ile ratios for gastropods collected from Front Range alluvial sediments shown on the classic alluvial terrace framework of Scott (1963). Ratios of shells from 3 ^{14}C-dated archeological sites in the area are also shown. V = *Vallonia* sp., S = *Succinea-Catinella*, H = Hawaia sp., L = *Lymnea* sp. Standard deviations for ratios are ±0.01, except as marked with * (* = ±0.02-0.03, ** = ±0.04-0.06). *Succinea-Catinella* ratios were converted to *Vallonia* equivalent ratios (Fig. 7). Elevation of terraces of different relative age is shown only schematically (not to scale).

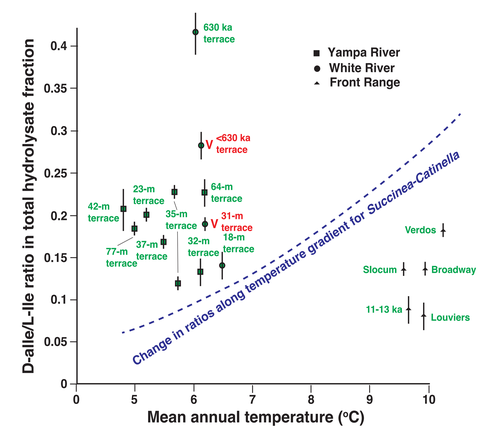


Figure 4. Comparison of hydolysate fraction alle/Ile ratios for gastropods collected from alluvial terrace sediments from the three field areas (Figs. 1, 2, 3) versus MAT (mean annual temperatures) for those areas. We limit the comparison to *Succinea-Catinella* ratios (green labels) except for two samples from the White River (red labels, V = *Vallonia*). Extrapolating from Figure 11 in Oches and McCoy (1995), we use a dashed line to show how ratios would be expected to change from an area with a present MAT of 10°C (ratios of ~0.28) to an area of 6°C MAT (ratios of ~0.09), assuming the kinetics for *Succinea-Catinella* determined by Oches et al. (1996, their Fig. 5). The trend of the dashed line is based on the assumption that the differences in MATs in the three areas are estimates of the difference in EDTs (effective diagenetic temperatures) for samples from the three areas. Because the ratios from the Front Range are dramatically lower than suggested by the trend of the line, based on inferred ages for sediments on Front Range terraces, the assumption about MATs approximating EDTs is unreasonable.

Table 1. Data used to calculate effective diagenetic temperatures (EDT) from alle/Ile ratios on terrestrial gastropods

Estimated sample age (ka)[a]	Alle/Ile ratios[b]	Gastropod genera[c]	Locality[d]	MAT (αC)$_0$	Calculated EDT (αC) $_T$	MATEDT (αC) $_E$	Sample weights (mg)	Univ. Colorado Amino Acid Laboratory no.[b]
>631	**0.50±0.03**	***Succinea-Catinella***	**B-5 near Baggs, Carbon County,WY**	**6.1**	**-0.9**	**7.0**	**5.1-47.7**	**AAL-341**
<631	**0.34±0.09**	***Succinea-Catinella***	**B-4 near Baggs, Carbon County,WY**	**6.1**	**-3.0**	**9.1**	**5.8-7.1**	**AAL-340**
<<500?	0.29±0.02	*Succinea-Catinella*	GM-1, Summit County,CO	9.5	-2.7	12.2	5.2-35	AAL-339
~631	0.44±0.02	*Vallonia*	CR-2, Barbers Gulch, Carbondale County, CO	7.2	-4.6	11.8	1.8-2.0	DAN-122
~631	**0.42±0.06**	***Succinea-Catinella***	**terrace Q5-1, White River, Meeker, CO**	**6.2**	**-1.9**	**8.1**	**2-15**	**DAN-232**
<<500?	0.28±0.02	*Vallonia*	terrace QV-1, White River, Meeker, CO	6.2	-5.9	12.1	1.8-4.1	DAN-111
<<500?	0.29±0.06	*Pupilla*	terrace QV-1, White River, Meeker, CO	6.2	-5.7	11.9	2.8-3.0	DAN-110
>150	0.18±0.01	*Succinea-Catinella*	Slocum terrace, Kassler Quadrangle, Jefferson Douglas Counties, CO	10.1	0.9	9.2	2.3-4.8	AAL-356
>250	**0.17±0.01**	***Succinea-Catinella***	**37-m terrace, Yampa River, Moffat County, CO**	**6.0**	**-2.0**	**8.0**	**4.7-10.3**	**DAN-145**
631	0.62±0.03	*Vallonia*	Cudahey Ash Mine, Meade County, KS	13.0	-2.5	15.5	7.3-9.1	AAL-720

[a]Age estimate based on stratigraphic relations with the 631-ka Lava Creek B ash (Mathews et al., 2015), and as explained in 1984 Abstract for >150-ka and >250-ka samples. [b] Alle/Ile ratio (peak height) measured using methods of Miller and Hare (1980). Mean ratios include one standard deviation. Extraneous ratios, or those whose chromatograms show high serine/glutamic acid or threonine/glutamic acid ratios, were excluded using the methods of Dixon (1965; see Table D1 in database URL). [c] *Succinea* sp. and *Catinella* sp. are indistinguishable using shell morphology (Oches et al., 1996). [d]Detailed locations in Table D1 in the database: https://doi.org/10.7910/DVN/JLDPAD.

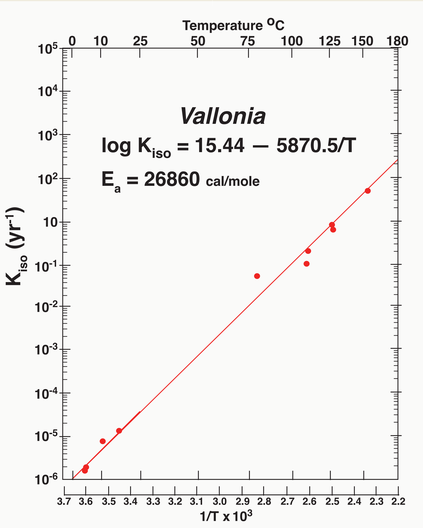


Figure 5. Arrhenius plot and equation for the relation between the rate of isoluecine epimerization in the terrestrial gastropod *Vallonia* sp. and temperature (Miller et al., 1982; Nelson, 1984) obtained through shell heating experiments and ^{14}C dated samples (e.g., Oches et al., 1996).

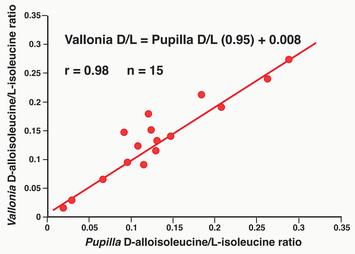


Figure 6. Comparison of D-alloisoleucine/L-isoleucine ratios for fossil shells of *Vallonia* sp. and *Pupilla* sp. from the same alluvial terrace sediments. Because ratios are so similar, we did not convert *Pupilla* ratios to equivalent *Vallonia* ratios (as we did for *Succinea-Catinella* ratios, Fig. 7) when attempting to correlate terrace beds from site to site.

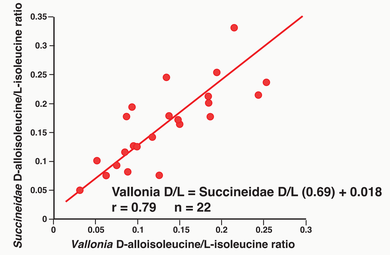


Figure 7. Comparison of D-alloisoleucine/L-isoleucine ratios for fossil shells of *Vallonia* sp. and *Succinea-Catinella* from the same alluvial terrace beds.We used this regression equation to convert *Succinea-Catinella* ratios to equivalent *Vallonia* ratios when attempting to correlate terrace beds from site to site.

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