

Amino acid estimates of latitudinal temperature gradients and geochronology of loess deposition during the last glaciation, Mississippi Valley, United States

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ABSTRACT

Principles of amino acid paleothermometry are used to estimate paleotemperatures and latitudinal temperature gradients for the period during and following the last glacial maximum in the Mississippi Valley. Gastropod shells were collected from the Peoria Loess for amino acid analysis, and Arrhenius parameters of isoleucine epimerization were determined experimentally for the gastropod genera *Catinella* and *Hendersonia*. There are 37 radiocarbon and 5 thermoluminescence ages that constrain the paleotemperature estimates and provide additional chronological data for loess deposition in the region.

Amino acid paleotemperature estimates suggest that the north-south temperature gradient was significantly depressed in the Mississippi Valley for a considerable period during the past ≈ 25 k.y. Effective diagenetic temperature estimates indicate that at some time during or following the last glaciation, the effective-temperature gradient was ≈ 0.3 – 0.6 °C/degree of latitude, which is significantly lower than the modern mean annual air-temperature gradient of ≈ 0.9 °C/degree of latitude. Calculated effective paleotemperatures for three localities in Tennessee and Mississippi suggest that temperatures were ≈ 7 – 13 °C lower than present during the period from ca. 24 to 16 ka in the lower Mississippi Valley. These results provide additional evidence for a significant cooling in southern United States continental temperatures during the last glacial maximum.

Data Repository item 9636 contains additional material related to this article.

INTRODUCTION

Independent quantitative temperature data are important for identifying mechanisms of climate change. In addition, the data can assist in the evaluation of climate models (COHMAP Members, 1988; Wright et al., 1993). Inferences of late Pleistocene paleoclimate in the Mississippi Valley have been derived from a variety of proxy data, including paleosols in loess (e.g., Follmer, 1983; Ruhe, 1983, 1984; Miller et al., 1986; Autin et al., 1991); vegetation reconstructions through pollen and plant macrofossils (e.g., Grüger, 1972; Delcourt et al., 1980; P. A. Delcourt and H. R. Delcourt, 1981; H. R. Delcourt and P. A. Delcourt, 1985; King, 1981; Watts, 1983; Givens and Givens, 1987; Baker et al., 1989; Baker, 1992; Webb et al., 1993); faunal reconstructions (e.g., Frest and Fay, 1980; Miller, 1984; Baker et al., 1986; Morgan, 1987); isotopic studies on speleothems (Harmon et al., 1978, 1979); and permafrost and other periglacial features (Péwé, 1983; Johnson, 1986, 1990). Many of these proxies, however, represent a composite of variables in the climate system and often offer conflicting interpretations.

In general, these diverse data suggest that the climate during the last glaciation varied from periglacial near the ice front to more temperate in the southern reaches of the Mississippi Valley, though somewhat cooler than present. Pollen-inferred temperature estimates indicate that mean January temperatures in the valley may have been as much as 12 °C colder in Wisconsin, Iowa, and northern Illinois (northern valley), and 16 °C colder in southern Arkansas, Tennessee, Mississippi, and Louisiana (southern valley) than present (Webb et al., 1993). Temperature reconstructions for July show a

cooling ranging from 12 °C in the north to 4 °C in the southern Mississippi Valley during the last glacial maximum (Webb et al., 1993).

The extent of amino acid racemization in the carbonate shells of mollusks is commonly used to derive relative and numerical age estimates of Quaternary deposits (e.g., Wehmiller, 1982; Miller and Mangerud, 1985; Clark et al., 1989; Mirecki and Miller, 1994; Oches and McCoy, 1995). If the numerical age can be independently established, the extent of racemization also provides a means by which paleotemperatures can be estimated for the period following deposition of the enclosing sediment. Fossil gastropods, the carbonate shells of which are suitable for amino acid analysis (Miller and Hare, 1980) and radiocarbon dating (Goodfriend and Hood, 1983; Goodfriend and Stipp, 1983), are abundant and well preserved in many places in the extensive late Pleistocene loess deposits blanketing the Mississippi River Valley. In this study we examine isoleucine epimerization in gastropod shells preserved in the late Wisconsin Peoria Loess in the Mississippi Valley (Fig. 1). We collected 43 samples of gastropod shells from the Peoria Loess at 25 localities throughout the Mississippi Valley from northwestern Illinois to south-central Louisiana (lat 42°–31°N) (Fig. 1). Models of racemization kinetics and independent dating techniques, including radiocarbon and thermoluminescence methods, are applied to quantitatively estimate paleotemperatures for intervals of time since ca. 25 ka. This investigation thus helps to further define climatic characteristics and provides additional chronostratigraphic data for loess deposition in the midcontinent of the United States during and following the last glacial maximum.

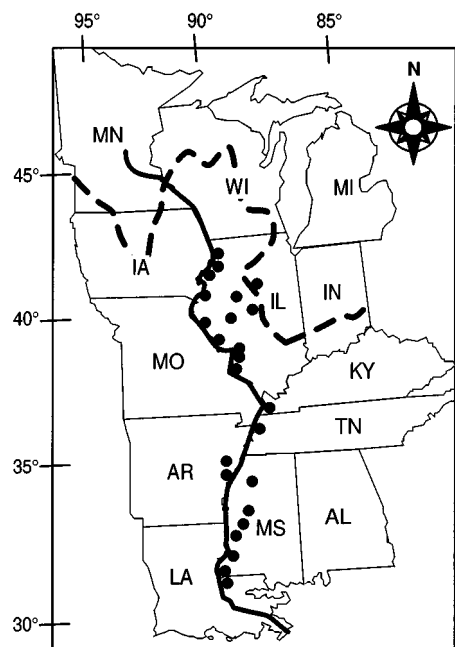


Figure 1. Map of the study region showing locations of sampling sites. The dashed line indicates the approximate position of the maximum extent of the late Wisconsin Laurentide ice sheet. The present course of the Mississippi River is indicated by the solid line.

GEOCHRONOLOGY OF LOESS DEPOSITION

The Peoria Loess is the thickest and most extensive loess unit in the Mississippi Valley, forming an essentially continuous sheet on the uplands adjacent to the Mississippi River from southwestern Wisconsin to south-central Louisiana. This loess began to accumulate ca. 25 ka in the northern valley, marking the end of the interstadial lull in glacial activity (McKay, 1979; Leigh and Knox, 1993, 1994). The base of the Peoria Loess is time transgressive; deposition began as late as 22 ka in the lower valley (Snowden and Priddy, 1968, p. 121; McKay, 1979). However, radiocarbon ages determined through this investigation suggest that loess deposition began ca. 24–25 ka in the lower valley as well (Table 1). Loess deposition appears to have ceased throughout the Mississippi Valley by ca. 10–12 ka (McKay, 1979; Forman et al., 1992).

Radiocarbon Chronology

To constrain the age of our samples for amino acid analyses, we obtained 37 radiocarbon age estimates from the Peoria Loess; all

but one were determined on terrestrial gastropod shell carbonate (Table 1). The single exception is a sample of wood from Illinois (sample #16, GX-13960, Table 1).

Radiocarbon dating of shell carbonate may yield unreliable ages due to different sources of carbon incorporated into the shell (Goodfriend and Hood, 1983). Studies to identify specific carbonate sources and their relative effects on radiocarbon age anomalies from land snail shells (Goodfriend and Hood, 1983; Goodfriend and Stipp, 1983; Goodfriend, 1987) indicate that the age may be too old because some of the land snail shell carbonate was derived from the ^{14}C -depleted substrate on which they live. Rubin et al. (1963), Evin et al. (1980), and Goodfriend and Stipp (1983) concluded that the possible radiocarbon age error in Pleistocene snails living on a carbonate substrate (Mississippi Valley loess is composed of only 10%–30% carbonate; McKay, 1979) may be acceptable “since it is on the same order as the counting error of (conventional) ^{14}C ” (Goodfriend and Stipp, 1983, p. 577).

Where Mississippi Valley radiocarbon ages on shells and wood from Pleistocene loess can be directly compared (Ives et al., 1964; Willman and Frye, 1970; Coleman, 1972; Coleman and Liu, 1975), they are statistically similar or in disagreement by <10%, lending further support to the proposed use of shell ages. Furthermore, Pye and Johnson (1988) reported modern terrestrial snail shells from the Natchez, Mississippi, area with ^{14}C activities of 135% modern, indicating “bomb” carbon but little influence of “dead” carbon derived from the underlying loess substrate.

Radiocarbon ages on shells from Peoria Loess obtained for this study range from $12\,010 \pm 90$ yr B.P. (AA-3620, Table 1) to $26\,670 \pm 710$ yr B.P. (GX-14659, Table 1); most of the ages are between 18 000 and 22 000 yr B.P. (Table 1; Appendix 1). Because the Peoria Loess is commonly leached of carbonate in its upper part, mollusk samples dating from the youngest period of deposition are rarely preserved. The oldest age, $26\,670 \pm 710$ yr B.P. (GX-14659, Table 1), is on a shell collection taken from the same stratigraphic interval as a shell sample dated as $24\,200 \pm 420$ yr B.P. (GX-13983, Table 1); the reason for the discrepancy in radiocarbon ages is not known.

Because Arrhenius parameters of isoleucine epimerization are determined based on calendar years, it is desirable to calibrate radiocarbon years appropriately. Calibration of radiocarbon ages is achieved using the radiocarbon age calibration software CALIB, Rev. 3.0.3 (Stuiver and Reimer, 1993) for samples younger than 18 360 ^{14}C yr B.P. For the re-

maining samples, calibration is accomplished using the Bard et al. (1993) U–Th versus ^{14}C comparison (calendar age B.P. = $1.24[^{14}\text{C}$ age B.P.] – 840) (Table 1).

Thermoluminescence Chronology

Five thermoluminescence (TL) ages were determined on the Peoria Loess by the (former) University of Colorado TL Laboratory (Table 2; Appendix 2). Previous studies in the Mississippi Valley have demonstrated the utility of TL for dating the younger loess record (Canfield and Pearson, 1985; Norton and Bradford, 1985; Canfield and Mickelson, 1986; Pye and Johnson, 1988; Forman et al., 1992), and results agree reasonably well with our radiocarbon chronology (except as noted below).

All five of the TL ages obtained in this study are in good agreement with accepted radiocarbon and stratigraphic chronologies. In one instance a calibrated radiocarbon age on a shell sample from the same horizon as sediment dated by TL offers a comparison of the methods. In this example the TL age is indistinguishable from the calibrated radiocarbon age ($23\,300 \pm 3000$ yr [TL] versus $24\,370 \pm 210$ yr [calibrated ^{14}C ; calibration by extension of Bard et al., 1993]). Two additional localities demonstrate stratigraphic continuity of superposed radiocarbon- and TL-dated samples. At the Cottonwood School section (Willman and Frye, 1970), near Beardstown, Illinois, we obtained an age of $15\,505 \pm 490$ ^{14}C yr B.P. (calendar age = $18\,400 \pm 480$ yr) on shells from directly above the Jules soil. Approximately 1 m above and 2 m below this interval, TL ages of $13\,200 \pm 1400$ yr and $25\,200 \pm 1900$ yr, respectively, were determined on loess. At Finley, Tennessee, a TL age of $19\,800 \pm 1600$ yr was obtained on a sediment sample ≈ 5 m stratigraphically above a shell sample radiocarbon dated at $24\,200 \pm 420$ yr B.P. (calendar age = $29\,170 \pm 520$ yr).

Pye and Johnson (1988) reported radiocarbon and TL ages on shell and sediment, respectively, from sections in the Vicksburg and Natchez areas in Mississippi. Shells were sampled for radiocarbon dating and amino acid analysis from the same sections (V1 and V2) near Vicksburg for this study. Snowden and Priddy (1968) carried out an extensive radiocarbon dating program on snails from an adjacent location (subsequently destroyed by road widening). Our radiocarbon ages from section V1 are in good agreement with those obtained by Snowden and Priddy (1968), but they differ significantly from TL and radiocarbon ages reported by Pye and Johnson (1988) (Fig. 2A). Similar trends in sedimentation rates are appar-

TABLE 1. RADIOCARBON AGES DETERMINED THROUGH THIS STUDY

Field number	Locality name	Latitude (°N)	Lab number	¹⁴ C age ± 1σ	Calibrated age range*			Calibration method†	Age used in study‡
					Min.	(Cal. age)	Max.		
1A	Coal Valley, Illinois	41.4	GX-15441	20120 ± 1130	25510	(24109)	22708	2	24110 ± 1400
1B	Coal Valley, Illinois	41.4	AA-3619	21072 ± 210	25550	(25289)	25029	2	25290 ± 260
3	Milan, Illinois	41.4	GX-15442	19660 ± 830	24568	(23538)	22509	2	23540 ± 1030
4	Bald Bluff, Illinois	41.0	GX-15443	14685 ± 460	18075	(17575)	17050	1	17560 ± 510
16	Farm Creek, Illinois	40.7	GX-13960	21470 ± 300	26155	(25783)	25411	2	25780 ± 370
5A	Lomax, Illinois	40.7	GX-15444	16190 ± 555	19760	(19068)	18528	1	19140 ± 620
5B	Lomax, Illinois	40.7	AA-3620	12010 ± 90	14169	(14004)	13850	1	14010 ± 160
8	Lima, Illinois	40.2	AA-3621	17530 ± 180	21166	(20866)	20550	1	20860 ± 310
17A	Cottonwood School, Illinois	40.0	GX-14775	15505 ± 490	18881	(18414)	17926	1	18400 ± 480
15A	Meredosia, Illinois	39.8	GX-14774	14870 ± 460	18258	(17777)	17263	1	17760 ± 500
10	Belleville, Illinois	38.6	GX-14044	21930 ± 340	26775	(26353)	25932	2	26350 ± 420
12	Hickman, Kentucky	36.6	AA-4073	20330 ± 170	24580	(24369)	24158	2	24370 ± 210
11A	Finley, Tennessee	36.1	GX-13983	24200 ± 420	29689	(29168)	28647	2	29170 ± 520
880515-30	Finley, Tennessee	36.1	AA-4392	21680 ± 175	26260	(26043)	25826	2	26040 ± 220
880515-31	Finley, Tennessee	36.1	GX-14659	26670 ± 710	33111	(32231)	31350	2	32230 ± 880
880507-28	S.Crowley's Ridge, Arkansas	34.6	GX-14658	22550 ± 445	27674	(27122)	26570	2	27120 ± 550
880513-26	West Helena, Arkansas	34.5	GX-14657	23485 ± 490	28889	(28281)	27674	2	28280 ± 610
880513-27	West Helena, Arkansas	34.5	AA-4391	17850 ± 145	21542	(21290)	21031	1	21290 ± 260
880511-25	Charleston, Mississippi	34.0	GX-14656	20360 ± 350	24840	(24406)	23972	2	24410 ± 430
880510-24	Tchula, Mississippi	33.1	AA-4390	24100 ± 260	29366	(29044)	28722	2	29040 ± 320
880508-23	Satartia, Mississippi	32.7	GX-14655	15570 ± 220	18697	(18474)	18252	1	18470 ± 220
880425-1	Vicksburg-1, Mississippi	32.4	ISGS-1884	23200 ± 450	28486	(27928)	27370	2	27930 ± 560
880425-2	Vicksburg-1, Mississippi	32.4	ISGS-1885	19810 ± 280	24072	(23724)	23377	2	23720 ± 350
880425-3	Vicksburg-1, Mississippi	32.4	ISGS-1886	18370 ± 270	22274	(21939)	21604	2	21940 ± 330
880426-4	Vicksburg-2, Mississippi	32.4	GX-14561	17530 ± 730	21829	(20866)	19806	1	20820 ± 1010
880426-5	Vicksburg-2, Mississippi	32.4	ISGS-1887	20560 ± 270	24989	(24654)	24320	2	24650 ± 330
880427-6	Vicksburg-2, Mississippi	32.4	GX-14562	20925 ± 1120	26496	(25107)	23718	2	25110 ± 1390
880508-22	Redwood, Mississippi	32.4	AA-4389	23945 ± 215	29118	(28852)	28585	2	28850 ± 270
880507-21	Alcorn, Mississippi	31.9	GX-14654	20940 ± 1105	26496	(25126)	23755	2	25130 ± 1370
880507-20	Lorman, Mississippi	31.7	GX-14653	19140 ± 870	23972	(22894)	21815	2	22890 ± 1080
880428-7	Natchez-1, Mississippi	31.6	GX-14563	21360 ± 425	26173	(25646)	25119	2	25650 ± 530
880505-15	Natchez-1, Mississippi	31.6	GX-14568	20740 ± 385	25355	(24878)	24400	2	24880 ± 480
880505-16	Doloroso, Mississippi	31.3	GX-14569	22470 ± 545	27699	(27023)	26347	2	27020 ± 680
880504-11	Pond, Mississippi	31.1	GX-14565	21330 ± 395	26099	(25609)	25119	2	25610 ± 490
880504-12	Pond, Mississippi	31.1	GX-14566	15340 ± 550	18779	(18259)	17686	1	18230 ± 550
880504-13	Pond, Mississippi	31.1	GX-14567	17540 ± 330	21351	(20880)	20376	1	20860 ± 490
880503-10	Tunica, Louisiana	31.0	GX-14564	21275 ± 400	26037	(25541)	25045	2	25540 ± 500

Note: All ¹⁴C ages were determined on terrestrial gastropod shells except field number 16 (GX-13960; wood).

*Calibrated ages are 1 σ (1 sigma) age ranges.

†(1) Ages calibrated using radiocarbon age calibration program CALIB Rev. 3.0.3 (Stuiver and Reimer, 1993). Applicable age range 0–18360

¹⁴C yr B.P. (2) Ages calibrated by extension of Bard et al. (1993) U-Th vs. ¹⁴C calibration [calibrated age B.P. = 1.24 (¹⁴C age B.P.) – 840].

‡Ages used in paleotemperature calculations are [median ± 0.5 (range)] of calibrated age ranges, rounded to 10.

TABLE 2. THERMOLUMINESCENCE AGE ESTIMATES FOR PEORIA LOESS SAMPLES

Field number	Locality name	TL lab number	ED method*	Temperature† (°C)	ED (Grays)	TL age estimate (ka)
11B	Finley, Tennessee	ITL-101	T. bleach—16 hr s.l.	300–350	69.29 ± 2.82	19.8 ± 1.6
14	Spankey, Illinois	ITL-100	T. bleach—16 hr s.l.	300–400	41.31 ± 2.16	17.0 ± 1.5
12	Hickman, Kentucky	ITL-104	T. bleach—16 hr s.l.	280–380	68.53 ± 8.76	23.3 ± 3.0
17B	Cottonwood School, Illinois	ITL-105	T. bleach—16 hr s.l.	300–400	48.83 ± 4.35	13.2 ± 1.4
17C	Cottonwood School, Illinois	ITL-106	T. bleach—16 hr s.l.	300–400	89.14 ± 3.54	25.2 ± 1.9

Note: All measurements were made with a Schott UG-11 and HA-3 filters in front of the photomultiplier tube.

All errors are 1 σ (1 sigma).

*ED = equivalent dose; s.l. = natural sunlight in Boulder, Colorado, used to define residual TL level; T. bleach = total bleach.

†Temperature = the temperature region of the ED plot corresponding to the plateau region.

ent, whereby slow rates characterize the initial phase of loess accumulation, followed by a significant increase in sedimentation rate, but the chronology differs by 2000–5000 yr between the Pye and Johnson (1988) study and this study. A similar disagreement is apparent from section V2, where our oldest age is the same as that reported by Pye and Johnson (1988), but our ages from higher in the section are older (Fig. 2B). The reason for this discrepancy may be related to the fact that their samples came

from auger holes drilled from the top of each section some distance back from the section face, whereas our samples were collected directly from cleaned surfaces of the exposure, and the stratigraphic positions of the samples are therefore not directly comparable. There is noticeable relief on the paleosurface on which Peoria Loess was deposited in this area (e.g., Priddy et al., 1964), and thus a sample collected some horizontal distance away from another sample may not be the same age. Note

that Pye and Johnson (1988) reported a radiocarbon age of 8760 ± 90 yr B.P. and TL ages of 5800 ± 400 and 5150 ± 360 yr, suggesting either their ages are too young, or loess continued to be deposited in the southern Mississippi Valley until a much later date than previously known. Pye and Johnson (1988) noted, however, that these youngest TL ages are believed to be minimum estimates, possibly reflecting the partial rezeroing of TL from bioturbation.

ISOLEUCINE EPIMERIZATION MEASUREMENT

Amino acids, which are present in the L-configuration in all living organisms, make up the proteinaceous structural matrix upon which the calcareous shells of mollusks are formed. After synthesis the protein within the carbonate shell begins to degrade through a series of complex diagenetic chemical reactions (Mitterer, 1993). Reactions of primary importance to amino acid geochronology and paleothermometry include hydrolysis of pep-

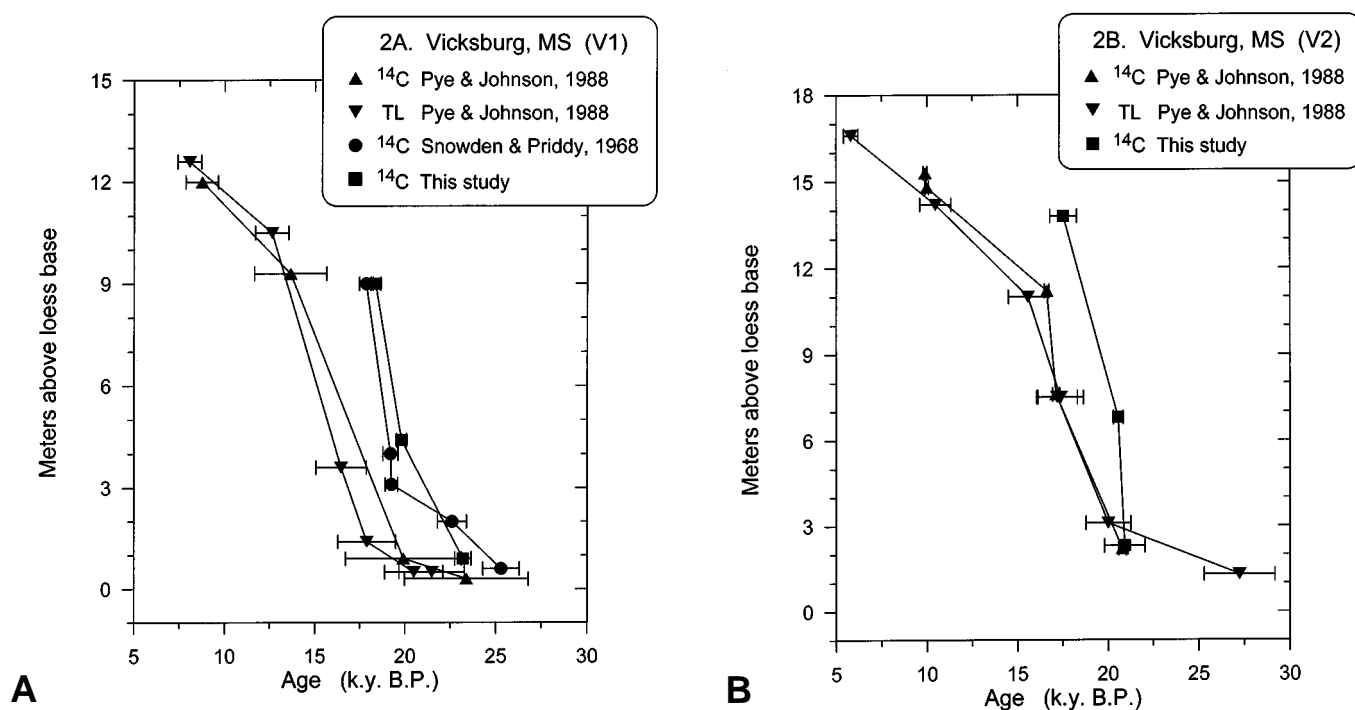


Figure 2. Radiocarbon and thermoluminescence ages plotted against depth for two exposures of Peoria Loess near Vicksburg, Mississippi. Plots compare ages obtained by Snowden and Priddy (1968), Pye and Johnson (1988), and this study. (A) Vicksburg section V1. (B) Vicksburg section V2.

tide bonds and racemization or epimerization of component amino acids.

In this investigation we evaluate the extent of isoleucine epimerization in fossil mollusk shells, as expressed by the ratio of the nonprotein amino acid alloisoleucine to its protein diastereomer isoleucine (alle/Ile). Combining alle/Ile measurements with independent numerical age data, laboratory-derived kinetic models of isoleucine epimerization can be developed for the quantitative estimation of paleotemperatures (Schroeder and Bada, 1976; Williams and Smith, 1977; McCoy, 1987; Wehmiller, 1984a, 1993).

Field Sampling Methods

Fossil gastropods are common in the extensive loess deposits along the Mississippi River and Illinois River valleys. Samples were collected from fossiliferous zones within the Peoria Loess, deposited mainly from ca. 25 to 10 ka. (Willman and Frye, 1970; McKay, 1979). Where single sections were of sufficient thickness, samples were chosen from different levels to estimate temperatures through time. We sampled only primary loess deposits. Sections were excavated ≈ 1 m back from exposed faces to uncover fresh, relatively unweathered material. Bulk samples were removed from intervals generally 10–30 cm in thickness, and

the material was sieved in the field to separate shells from the matrix.

Laboratory Methods

All amino acid analyses were completed at the Amino Acid Geochronology Laboratory at the University of Massachusetts, Amherst. Shells were separated and identified by reference to Pilsbry (1948), LaRouque (1970), Leonard and Frye (1960), Leonard (1959), and comparison to reference samples in the lab. The gastropod genera analyzed include *Succinea*, *Catinella*, *Hendersonia*, *Helicina*, and *Stenotrema*.

The rate of epimerization varies among different molluscan genera (Lajoie et al., 1980; Wehmiller, 1980). Previous investigations in the region have demonstrated that the five genera included in this study can be divided into two groups on the basis of relative rates of isoleucine epimerization (Clark et al., 1989; Oches, 1990). *Succinea* and *Catinella*, which are nearly indistinguishable on the basis of shell morphology alone, epimerize at a relatively fast rate and give similar alle/Ile values for coexisting samples. *Hendersonia*, *Helicina*, and *Stenotrema* yield comparable alle/Ile ratios within this second group, and they epimerize at a relatively slow rate. For this reason, heating experiments were conducted to determine the

Arrhenius parameters and establish the kinetics of the isoleucine epimerization reaction in *Catinella* and *Hendersonia* for subsequent paleotemperature calculations. Arrhenius parameters determined for *Catinella* are used in temperature calculations using *Succinea*–*Catinella* alle/Ile ratios, and *Hendersonia* Arrhenius parameters are used in the calculation of temperatures with *Hendersonia*–*Helicina* data and with *Stenotrema* alle/Ile values.

Whole shells, ideally free of visible alteration or recrystallization, were selected for analysis. From 10 to 20 mg of shell material are commonly required for adequate preparation and analysis. With sufficiently large individuals, such as *Succinea*, *Hendersonia*, *Helicina* or *Stenotrema*, a single shell was analyzed. For the smaller *Catinella*, three to five individuals were generally prepared for analysis. The shells were broken up for cleaning, foreign material was mechanically removed, and the samples were sonically cleaned repeatedly in distilled water and rinsed in ultrapure water. Three or more replicate preparations (subsamples) of each genus were made from each field sample. Subsamples were dried and weighed and then dissolved in a cold 7 N HCl + norleucine solution in the proportion of 1 ml HCl per 50 mg shell. A calibrating standard of the amino acid norleucine was added to the HCl so

that concentrations of amino acids within samples could be determined. For total acid hydrolysate analysis, samples were heated in a nitrogen atmosphere at 110 °C for 22 hr. This hydrolysis step was necessary to break down peptide bonds connecting chains of amino acids so that the total amino acid population of the sample could be measured. Samples were then dried in a vacuum. Immediately before analysis, samples were rehydrated with purified water adjusted with HCl to pH 2 in the proportion of 1 ml pH 2 H₂O per 25 mg shell.

Analysis was completed using high-performance liquid chromatography (HPLC). The amino acid analyzer used either a 25 or 30 cm (length) x 2.1 mm (bore) column packed with St. John Associates 6 µm sulfonated polystyrene resin. Step-wise elution with sodium citrate buffers was used to resolve alloisoleucine and isoleucine diastereomers as well as most other neutral and acidic amino acids. Detection was accomplished using ortho-phthalaldehyde (OPA) and 2-mercaptoethanol as a reagent and monitoring UV-excited fluorescence. Photomultiplier output was recorded by a Hewlett Packard HP3396A integrator. Ratios of alloisoleucine: isoleucine (alle/Ile) were calculated from peak-height values determined from chromatographic output.

Periodic analysis of the interlaboratory comparison sample standards (ILC) (Wehmiller, 1984b) was performed in order to compare results from the University of Massachusetts Amino Acid Geochronology Laboratory with results of other amino acid geochronology labs (Table 3). Consistent alle/Ile values have been determined for the Wehmiller ILC standards during the period of this study.

AMINO ACID PALEOTEMPERATURE STUDIES

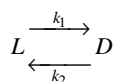
The extent of amino acid racemization in carbonate fossils can be used to estimate paleotemperatures for intervals of time during the Quaternary. Numerous studies have demonstrated the potential for amino acid paleothermometry in a variety of settings, including

coastal environments (e.g., Mitterer, 1975; Wehmiller, 1977, 1982; Brigham and Miller, 1983; Miller et al., 1983, 1987; Murray-Wallace et al., 1988) and continental interiors (e.g., McCoy, 1981; Miller et al., 1982).

Arrhenius Parameter Determination

In order to estimate paleotemperatures from alle/Ile ratios, knowledge of the kinetics of isoleucine epimerization is essential. Because this study is limited to material younger than ca. 25 ka, a linear model of epimerization kinetics is adequate. Older materials, with alle/Ile ratios >=0.3, involve more complicated, nonlinear kinetic models, which need not be considered in this study (Wehmiller, 1977, 1990, 1993).

The protein amino acid L-isoleucine epimerizes to its nonprotein diastereomer D-alloisoleucine, and the reaction in the total acid hydrolysate approximates a linear, first-order, reversible reaction at least up to an alle/Ile ratio of 0.3 (Schroeder and Bada, 1976; Williams and Smith, 1977; Bada, 1985):



where *L* and *D* represent the L- and D-diastereomers, and *k*₁ and *k*₂ are the forward and reverse rate constants, respectively, of the reaction.

Two basic equations are employed in the determination of paleotemperatures, including the integrated instantaneous rate equation (1) and the Arrhenius equation (2) (Schroeder and Bada, 1976; Williams and Smith, 1977; McCoy, 1987):

$$\ln \left[\frac{(1 + D/L)}{(1 - K' D/L)} \right] - \ln \left[\frac{(1 + D_o/L_o)}{(1 - K' D_o/L_o)} \right] = (1 + K')k_1 t \quad (1)$$

where *D/L* = ratio of D to L diastereomer (alle/Ile); *K'* = *k*₂/*k*₁ = 1/*K*_{eq} (the equilibrium constant) ≈ 0.77; *t* = time (age of the sample in years); and *D*_o/*L*_o = *D/L* ratio of sample at *t* = 0. Note that *D*_o/*L*_o, or the *D/L* ratio of a modern

sample, is ≠0 due to a small amount of laboratory-induced epimerization during sample preparation. Generally *D*_o/*L*_o ≈ 0.011 in the mollusks studied in this investigation (Oches, 1990).

The temperature dependence of the rate constant (*k*₁) may be expressed in terms of the Arrhenius equation (2):

$$k_1 = A \exp^{-E_a/RT} \quad (2)$$

where *A* = frequency or entropy factor; *E*_a = energy of activation (cal mol⁻¹); *R* = gas constant = 1.9872 cal kelvin⁻¹ mol⁻¹; and *T* = temperature in kelvin. *E*_a and *A* are the Arrhenius parameters of the epimerization reaction.

Taking the natural logarithm of both sides of the Arrhenius equation (equation 2):

$$\ln k_1 = \ln A - E_a/RT \quad (3)$$

A linear relationship is thus established among the variables. Values for *k*₁ can be determined experimentally (equation 1) by heating fossil shell samples over a range of controlled temperatures for fixed periods of time and measuring the resultant *D/L* values. A plot of ln *k*₁ versus 1/*T* is then made for each genus of interest, and the slope (*-E*_a/*R*) and intercept (ln *A*) of the regression line connecting the points determine the Arrhenius parameters, *E*_a and *A*.

McCoy (1987) described a somewhat modified approach in which a weighted least-squares regression is fit to the data. Weightings are proportional to the inverse of the variance of ln *k*₁. This method also allows for a multivariate error analysis in which the uncertainties in *E*_a and *A* can be estimated (Clifford, 1973). Uncertainties in the Arrhenius parameters, the equilibrium constant (*K*_{eq}), measured *D/L* ratios, and the independently known age of the sample are propagated through the temperature equation in order to establish the level of uncertainty on the paleotemperature estimates (McCoy, 1987).

In the course of this investigation, fossil shells of the gastropod genera *Catinella* and *Hendersonia* were heated at a number of controlled temperatures between 80 and 150 °C for periods of time ranging from several hours to >1 yr. Included in the *Catinella* data is a Holocene sample, the age and diagenetic temperature history of which were estimated and included in the Arrhenius plot. This sample comes from a terrace deposit of a post-Lake Algonquin stage of Lake Huron. Charcoal associated with the sample has a radiocarbon age of 9960 ± 210 yr B.P. (WAT-848). (The sample was provided by B. Miller, and the locality was described in Miller et al., 1985, locality 25.) An effective diagenetic temperature (EDT, see below) of 9 ± 1.5 °C was estimated on the basis of the present mean annual ground temperature at

TABLE 3. INTERLABORATORY COMPARISON SAMPLE STANDARDS

Standard number	Lab number	alle/Ile (total)	C.V.* (%)	Analyses (no.) [†]
81-ILC-A	AGL 1102	0.149 ± 0.004	2.7	9
81-ILC-B	AGL 1103	0.486 ± 0.021	4.3	9
81-ILC-C	AGL 1104	1.052 ± 0.021	2.0	9

Note: Results of analyses in University of Massachusetts Amino Acid Geochronology Laboratory for the period of this investigation.

*C.V. = coefficient of variation = [(standard deviation / mean) × 100].

[†]Number of analyses = the number of replicate analyses of a single preparation of each interlaboratory comparison standard sample.

1.5 and 3.0 m depth at Guelph and Elora Research Station, Ontario (Environment Canada, 1984), and a calibrated age of 11,060 yr (CALIB Rev. 3.0.3, Stuiver and Reimer, 1993) was used in the Arrhenius parameter analysis. Samples of this type have not become available for *Hendersonia*. Kinetics of the epimerization reaction at Earth-surface temperatures for that genus are thus estimated only by extrapolation from high-temperature laboratory studies.

Kinetic data for isoleucine epimerization have been determined for *Catinella* and *Hendersonia* (Data Repository Tables DR1 and

DR2, respectively¹), and a weighted least-squares estimation of the Arrhenius parameters is derived (Table 4; Fig. 3, A and B). Following the method of McCoy (1987), uncertainties in various measurements are propagated in the calculation of Arrhenius parameters to estimate uncertainties in the frequency factor (A) and the activation energy (E_a) (Table 5).

Calculation of Paleotemperatures

Equations 1 and 2 may be combined and rearranged to solve for T (temperature):

$$T = -E_a / \left(\text{Rln} \left[\ln \left(\frac{1 + D/L}{1 - K'D/L} \right) \right] \right. \\ \left. \left[-\ln \left(\frac{1 + D_o/L_o}{1 - K'D_o/L_o} \right) \right] / A t (1 + K') \right] \right) \quad (4)$$

Similarly, the temperature for an interval of time bracketed by independent age estimates can be estimated (McCoy, 1987):

TABLE 4. LEAST-SQUARES ESTIMATION OF ARRHENIUS PARAMETERS FOR ISOLEUCINE EPIMERIZATION IN *CATINELLA* AND *HENDERSONIA* SHELLS

1/T (kelvin)	Average k_1	Average $\ln(k_1)$	Std. dev. $\ln(k_1)$	Std. dev. 1/T	Tot. var. $(\ln k_1)$	w_1	Intercept	Slope	A	E_a (cal/mol)
<i>Catinella</i>										
0.003546	5.140E-06	-12.19262	0.18533	0.000019	0.10674	9.369				
0.002819	1.566E-01	-1.86078	0.12349	0.000009	0.03149	31.753				
0.002677	1.537E+00	0.42563	0.09648	0.000004	0.01252	79.896				
0.002536	6.950E+00	1.92888	0.15237	0.000002	0.02402	41.637				
0.002380	1.144E+02	4.73033	0.14766	0.000002	0.02260	44.239				
							38.853	-14407	7.477E+16	28630.2
<i>Hendersonia</i>										
0.002819	1.662E-01	-1.79743	0.07497	0.000009	0.02315	43.193				
0.002677	1.362E+00	0.29675	0.16090	0.000004	0.02935	34.070				
0.002536	8.358E+00	2.10433	0.21724	0.000002	0.04806	20.808				
0.002380	1.115E+02	4.70333	0.15247	0.000002	0.02411	41.470				
							39.649	-14712	1.658E+17	29235.5

Note: Parameters were calculated following the method of McCoy (1987). See text for explanation of parameters.

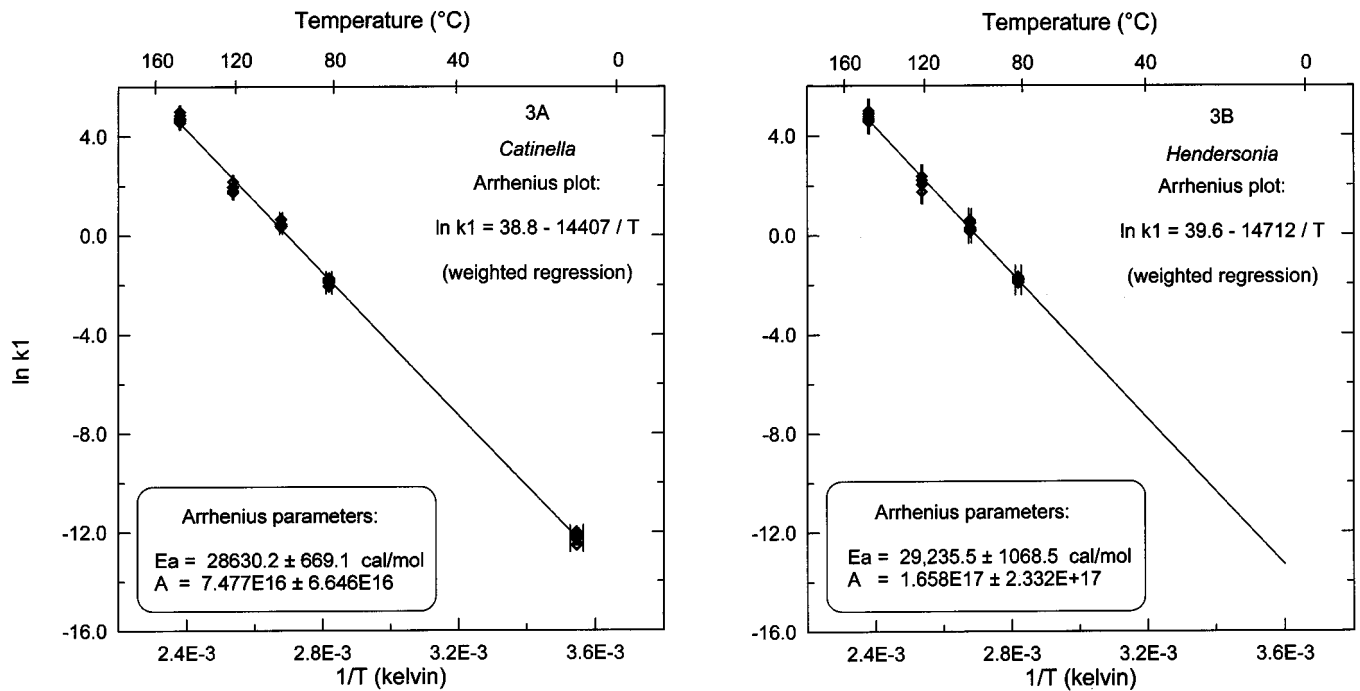


Figure 3. Arrhenius plot for (A) *Catinella* and (B) *Hendersonia*. The solid line, which determines the Arrhenius parameters of isoleucine epimerization, is a weighted least-squares regression through four sets of kinetic data (method of McCoy, 1987). See text for discussion of variables.

¹GSA Data Repository item 9636, Tables DR1 and DR2, is available on request from Document Secretary, GSA, P.O. Box 9140, Boulder, CO 80301.

TABLE 5. ERROR PROPOGATION IN THE CALCULATION OF ARRHENIUS PARAMETERS FOR ISOLEUCINE EPIMERIZATION IN *CATINELLA* AND *HENDERSONIA* SHELLS

Temperature (kelvin)	Average k_1	Std. dev. k_1	Tot. std. dev. k_1	w_i	dk_1 / dA	dk_1 / dE_a	Std. dev. A	Std. dev. E_a	r
<i>Catinella</i>									
282	5.140E-06	8.932E-07	1.958E-06	9.369	6.486E-23	-8.655E-09			
354.8	1.566E-01	1.861E-02	3.021E-02	31.753	2.308E-18	-2.448E-04			
373.5	1.537E+00	1.595E-01	1.812E-01	79.896	1.769E-17	-1.782E-03			
394.3	6.950E+00	1.082E+00	1.154E+00	41.637	1.353E-16	-1.291E-02			
420.2	1.144E+02	1.767E+01	1.839E+01	44.239	1.287E-15	-1.152E-01	6.646E+16	669.1	0.9968
<i>Hendersonia</i>									
354.8	1.662E-01	1.223E-02	2.724E-02	1348.082	9.796E-19	-2.303E-04			
373.5	1.362E+00	2.346E-01	2.514E-01	15.818	7.824E-18	-1.747E-03			
394.3	8.358E+00	1.718E+00	2.010E+00	0.247	6.250E-17	-1.322E-02			
420.2	1.115E+02	1.794E+01	1.853E+01	0.003	6.232E-16	-1.237E-01	2.332E+17	1068.5	0.9979

Note: Parameters were calculated following the method of McCoy (1987). See text for explanation of parameters.

$$T_{(t_2-t_1)} = E_a / R \ln(A/k), \quad (5)$$

$$k = (k_2 t_2 - k_1 t_1) / (t_2 - t_1), \quad (6)$$

$$= \ln(c/b) / \left\{ (1+K') (t_2 - t_1) \right\}, \quad (7)$$

$$\text{where } b = \left(1 + \frac{D_1}{L_1} \right) / \left(1 - K' \frac{D_1}{L_1} \right), \quad (8)$$

$$\text{and } c = \left(1 + \frac{D_2}{L_2} \right) / \left(1 - K' \frac{D_2}{L_2} \right). \quad (9)$$

In these equations, t_2 and t_1 refer to the ages of the older and younger samples, respectively, and D_2/L_2 and D_1/L_1 are the measured alle/Ile ratios of the older and younger samples, respectively. The uncertainty in the calculated T and $T_{(t_2-t_1)}$ is estimated following the method of McCoy (1987) and considers uncertainties in the ages, alle/Ile ratios, and the Arrhenius parameters.

The temperature history of a geological sample may be complex, so that T represents the integrated thermal history, including temperature fluctuations on time scales ranging from days to tens of thousands of years. Because the isoleucine epimerization reaction has a relatively high energy of activation (≈ 29 kcal mol⁻¹), the rate of epimerization is increasingly accelerated with increasing temperature. Therefore, the time spent by a sample at relatively high temperatures is disproportionately more important in increasing the D/L ratio than time spent at low temperatures, and the effective diagenetic temperature (EDT) undergone by a sample may be significantly greater than the simple mean temperature that it has undergone (Wehmiller, 1977).

In calculating latitudinal effective diagenetic temperature gradients, we included all samples dating between 22 and 16 ka. Samples in this age range were presumably buried relatively quickly during the period of rapid loess accumulation and have remained deeply buried through-

out their histories. Loess sedimentation rates were highly variable, depending on such factors as distance from source, wind direction, and topographic position. Data from the investigated region suggest that mean sedimentation rates ranged from <40 cm/k.y. to extreme values of >200 cm/k.y. (McKay, 1979; Pye and Johnson, 1988; Leigh and Knox, 1993; this investigation). In the southern valley, sedimentation rates appear to have decreased after 15 ka (Pye and Johnson, 1988). If significant loess sedimentation ceased by 12 ka, and if we consider, for example, a sedimentation rate of 60 cm/k.y., then a sample must have been deposited before ca. 15 ka in order to be buried to at least 2 m depth. Younger samples often have problems with relatively shallow depths of burial. Shallow burial can result in anomalously high EDTs related to effects of seasonal and diurnal temperature fluctuations penetrating the shallow subsurface. Shells close to the surface also are commonly leached or degraded, rendering them unsuitable for either amino acid analysis or radiocarbon dating.

RESULTS

We used alle/Ile ratios measured on samples collected from the Peoria Loess to calculate effective diagenetic temperatures for the period during and following the last glacial maximum throughout the Mississippi Valley. North-south effective-temperature gradients are determined for three sets of data, including the *Succinea-Catinella*, *Hendersonia-Helicina*, and *Stenotrema* sample groups. Calculated EDTs and EDT gradients are compared to current mean annual air temperatures (CMAT) and the modern air-temperature gradient of ≈ 0.9 °C/degree of latitude in the Mississippi Valley (Fig. 4).

The *Catinella-Succinea* data set yielded 12 samples in the appropriate age range (Fig. 4A). Calculated effective temperatures range from ≈ 6.4 °C in the north (lat 41.4°N, CMAT

≈ 10 °C) to ≈ 10.1 °C in the south (lat 31.6°N, CMAT ≈ 19 °C). A regression through the data yields a north-south EDT gradient of 0.3 °C/degree of latitude, with a correlation coefficient of 0.73 (Fig. 4A).

Hendersonia-Helicina data include 17 samples dated between 16 and 22 ka (Fig. 4B). Calculated EDTs in this data set range from 4.6 °C in the north (lat 41.4°N, CMAT ≈ 10 °C) to 11.2 °C in the southern reaches of the valley (lat 31.1°N, CMAT ≈ 19 °C). A regression line fitted through these points yields an EDT gradient of 0.6 °C/degree of latitude, with a correlation coefficient of 0.92 (Fig. 4B).

The final data set includes 11 samples of *Stenotrema*, which yield EDT estimates ranging from 4.8 °C (lat 40.7°N, CMAT ≈ 10 °C) to 11.4 °C (lat 31.1°N, CMAT ≈ 19 °C) (Fig. 4C). These data produce an EDT gradient of 0.6 °C/degree of latitude, with a 0.95 correlation coefficient.

Statistical hypothesis testing demonstrates that the calculated effective diagenetic temperature gradients are significantly different from the modern air temperature gradient of the Mississippi Valley. At the 0.01 significance level, t-tests indicate that all of the paleotemperature gradients that we calculated from the alle/Ile ratios are significantly less steep than the current mean annual air temperature gradient. Furthermore, the differences among the three calculated EDT gradients are not significant at the same level, emphasizing the consistency of the data (Fig. 5).

Latitudinal gradients of effective diagenetic ground temperatures calculated from each amino acid data set are significantly different from the modern air-temperature gradient. If it is assumed that mean annual ground temperature at depth shows a consistent relationship with mean annual surface air temperature, then these data suggest that there has been a major change in the north-south temperature regime at some time since the last glacial maximum. Speci-

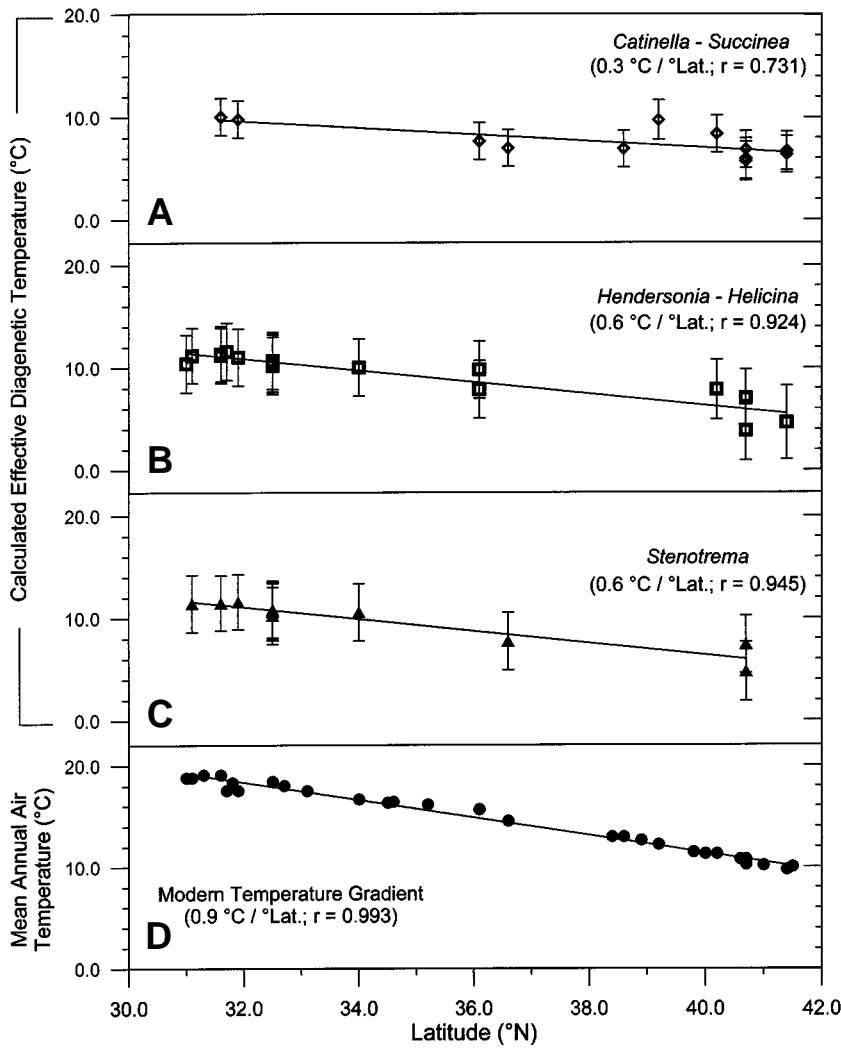


Figure 4. (A) Calculated *Catinella*–*Succinea* effective diagenetic temperature (EDT) gradient for sites in the Mississippi Valley plotted against latitude. (B) Calculated *Hendersonia*–*Helicina* EDT gradient for sites in the Mississippi Valley plotted against latitude. (C) Calculated *Stenotrema* EDT gradient for sites in the Mississippi Valley plotted against latitude. (D) Modern mean annual air temperature gradient for sampling sites (MATs; 1951–1980 data) in the Mississippi Valley plotted against latitude.

Finally, temperatures may have been depressed more in the southern part of the valley than in the north for a considerable portion of the past ≈20 k.y. However, it is unknown when this lowered temperature gradient may have existed, or how long it may have lasted. The phenomenon may have occurred as a relatively long-lived late-glacial event, when temperatures were still relatively low, or possibly as a relatively short-term, early Holocene event, after continental temperatures had increased. With additional sampling and numerical age dating, the timing and duration of this temperature depression may be further constrained.

In the southern valley, late Wisconsin loess deposits tend to be thicker than in the north, and deposition was more rapid due to the increased sediment supply from the northern valley and its tributaries. Higher southern valley temperatures caused the epimerization to progress at a faster rate than in samples of the northern valley. The precision of the amino acid method is thereby increased, whereas in the colder, northern Mississippi Valley, stratigraphic inversion of *alle/Ile* ratios sometimes resulted from relatively shallow burial of younger samples and relatively slow epimerization rates during glacial and immediate postglacial time.

Three localities in the lower Mississippi Valley have yielded sequences of samples which are deeply buried, have stratigraphically consistent *alle/Ile* values, and whose ages approximately bracket the last glacial maximum. Effective diagenetic temperatures are calculated for intervals of time (equation 5) which are bracketed by radiocarbon age estimates (Table 6). Two samples of *Succinea* have been analyzed from an ≈20-m-thick section of Peoria Loess near Finley, Tennessee (lat 36°04'N, CMAT = 15.7 °C). The

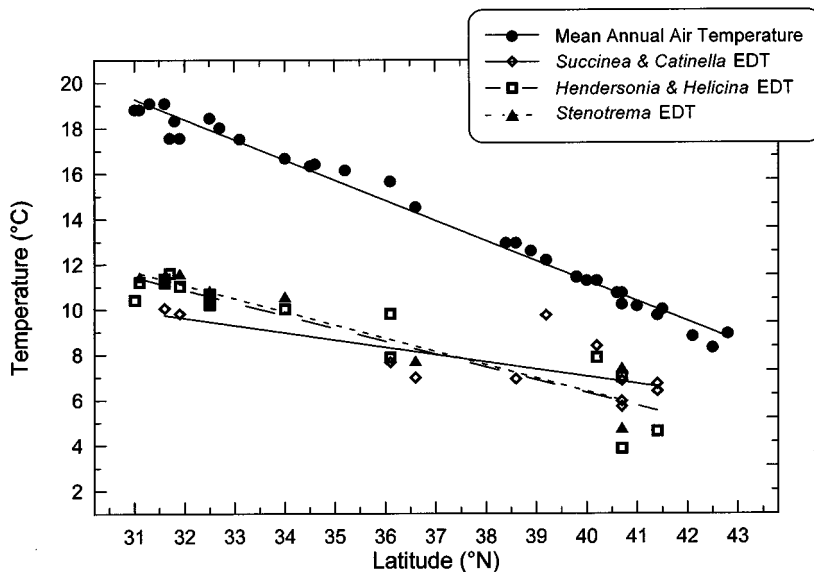


Figure 5. MAT (1951–1980) data gradient and calculated amino acid effective temperature gradients for all genera.

younger sample, ¹⁴C dated at 21 680 ± 175 yr B.P. (calendar age = 26 040 ± 220 yr), gave alle/Ile ratios of 0.114 ± 0.008. A second sample, from near the base of the loess, was radiocarbon dated at 24 200 ± 420 yr B.P. (calendar age = 32 230 ± 880 yr) and had alle/Ile values of 0.129 ± 0.005. An EDT calculated for the period between these two samples is 5.0 ± 3.9 °C, that is, ≈ 11 ± 4 °C lower than the present mean annual temperature (Table 6). The error on the EDT estimate is calculated following McCoy (1987), and reflects uncertainties in measured variables, including the ages, alle/Ile ratios, and the Arrhenius parameters.

Two sections were sampled at Vicksburg, Mississippi (lat 32°22'N, CMAT = 18.4 °C), at adjacent roadcuts. Three sets of samples were chosen for EDT calculations, including the youngest, dated at 17 530 ± 730 ¹⁴C yr B.P. (calendar age = 20 820 ± 1010 yr); the middle, dated at 20 925 ± 1120 ¹⁴C yr B.P. (calendar age = 25 110 ± 1390 yr); and the oldest, radiocarbon dated at 23 200 ± 450 yr B.P. (calendar age = 27 930 ± 560 yr) (Table 6).

Stenotrema from the youngest and middle sampling levels yielded alle/Ile ratios of 0.119 ± 0.013 and 0.131 ± 0.007, respectively. An effective temperature of 7.3 ± 7.5 °C is calculated for that period of time. *Hendersonia*, with alle/Ile values of 0.110 ± 0.003, were sampled from the youngest level, and alle/Ile ratios of 0.136 ± 0.015 were measured on *Helicina* from the middle level. An effective temperature of 11.5 ± 4.8 °C was calculated for that interval using these *Hendersonia*–*Helicina* data (Table 6).

An EDT was also calculated for a second interval, which spans the period from the youngest to the oldest sampling levels (ca. 18 000–24 000 ¹⁴C yr B.P.). An effective temperature of 9.0 ± 4.2 °C was calculated using *Helicina* with measured alle/Ile values of 0.137 ± 0.015 sampled from the lowest level and *Hendersonia* from the uppermost level with alle/Ile values of 0.110 ± 0.003 (Table 6).

Compared with the current mean annual air

temperature of 18.4 °C, these calculated values suggest a 7–11 °C temperature reduction at this locality during the last glacial maximum. Although there is considerable scatter in the EDT estimates, all three overlap at one standard deviation, and the temperature calculated for the second interval is in the middle of the two temperatures calculated for the first interval.

Thick Peoria Loess at Pond, Mississippi (lat 31°06'N, CMAT = 18.8 °C), presents a third opportunity to estimate an EDT for the period bracketing the last glacial maximum. Two levels, ¹⁴C dated at 15 340 ± 550 yr B.P. (calendar age = 18 230 ± 550 yr) and 21 330 ± 395 yr B.P. (calendar age = 25 610 ± 490 yr), yielded fossil gastropods. *Helicina* samples were recovered at both levels, and alle/Ile ratios of 0.142 ± 0.010 and 0.157 ± 0.008 were measured on the younger and older samples, respectively. An effective temperature of 5.6 ± 5.3 °C was estimated for the period bracketed by these two dated samples at that locality (Table 6). Compared to the modern air temperature of ≈19 °C, a temperature reduction of ≈13 °C is indicated for the period from ca. 16 to 22 ka.

DISCUSSION

Although the calculated temperatures have significant implications regarding the climate of the Mississippi Valley during the past ≈20 k.y., it is important to assess the relationship between EDTs calculated from samples buried deeply in the ground and mean annual air temperatures (MAT) at the surface (Wehmiller, 1977; McCoy, 1987; Stevenson et al., 1989).

Relatively little long-term ground temperature monitoring at depth, which would be useful in relating ground and air temperatures, has been undertaken in the United States (Fitton and Brooks, 1931; Chang, 1958; Labs, 1981). Complex relationships have been developed to predict and model ground temperature and thermal properties at various depths (e.g., de Vries, 1975; Labs, 1981; Horton et al., 1983). In the upper 1–2 m of soil, temperature varies greatly with

depth on hourly to seasonal time scales. Heat transfer in soils is affected by bulk density, composition, and moisture content. In the uppermost 0–1.0 m, wind, rain, snow cover, solar radiation, site aspect, and soil stratification are additional important variables (Stevenson et al., 1989). For deeply buried samples (>2–3 m), effects of seasonal and diurnal temperature fluctuations are minimized. Typically, mean annual ground temperature at depth (>≈2 m) can be estimated as 1–3 °C greater than mean annual air temperature (Chang, 1958; Smith et al., 1964). By selecting only samples buried >2 m in depth, we have attempted to avoid the complications of short-term, near-surface temperature variations.

Miller and Brigham–Grette (1989) suggested that the difference between EDT and mean annual ground temperature is <1 °C at the depth at which the amplitude of the temperature wave is <6 °C. This depth varies with soil and surface conditions, although it suggests that sampling from 2 m or greater depth should be adequate (Miller and Brigham–Grette, 1989).

The EDT represents an integrated thermal history, emphasizing the effects of warm periods, due to the exponential dependence of the rate constant of the epimerization reaction on temperature. For this reason the calculated EDT will always be somewhat higher, and never lower, than the mean temperature undergone by the sample during its postdepositional history. This would suggest that calculated effective temperatures are maximum values compared to mean ground temperatures or mean air temperatures, and temperature depressions estimated for the last glacial maximum are therefore minimum values; that is, it was at least 7–13 °C colder in the lower Mississippi Valley during the indicated period of time.

There is room for improvement in the Arrhenius parameter estimations. A major assumption implicit in the above effective diagenetic temperature calculations is that the kinetic relationship between time and elevated (e.g., 80–150 °C) temperatures holds true at normal Earth–surface temperatures. In the calculation of temperatures,

TABLE 6. SUMMARY OF EFFECTIVE DIAGENETIC TEMPERATURES (EDTs) CALCULATED FOR INTERVALS OF TIME BRACKETED BY INDEPENDENTLY DATED SAMPLES

Locality	M.A.T.* (°C)	Genus	D ₁ / L ₁ (alle/Ile)	Age 1† (yr)	D ₂ / L ₂ (alle/Ile)	Age 2† (yr)	Calculated EDT (°C)
Finley, Tennessee	15.7	<i>Succinea</i>	0.114 ± 0.008	26 040 ± 220	0.129 ± 0.005	32 230 ± 880	5.0 ± 3.9
Vicksburg, Mississippi	18.4	<i>Hendersonia</i> + <i>Helicina</i>	0.110 ± 0.003	20 820 ± 1010	0.136 ± 0.015	25 110 ± 1390	11.5 ± 4.8
Vicksburg, Mississippi	18.4	<i>Stenotrema</i>	0.119 ± 0.013	20 820 ± 1010	0.131 ± 0.007	25 110 ± 1390	7.3 ± 7.5
Vicksburg, Mississippi	18.4	<i>Hendersonia</i> + <i>Helicina</i>	0.110 ± 0.003	20 820 ± 1010	0.137 ± 0.015	27 930 ± 560	9.0 ± 4.2
Pond, Mississippi	18.8	<i>Helicina</i>	0.142 ± 0.010	18 230 ± 550	0.157 ± 0.008	25 610 ± 490	5.6 ± 5.3

Note: See text for explanation of variables.

*M.A.T. = mean annual air temperature (1951–1980 data) for the sampled localities.

†Ages shown are calibrated ¹⁴C ages (c.f. Table 1).

we are essentially extrapolating the $\ln k_1$ versus $1/T$ regression line from measured $\ln k_1$ values of $\approx +6$ to -3 down to values of -10 to -12 , corresponding to temperatures of ≈ 0 – 10 °C (cf. Fig. 3). The lower end of this line may be additionally constrained if suitable mid-Holocene shells can be recovered whose ages and effective diagenetic temperatures can be estimated. One set of samples has been obtained for *Catinella*. These data are consistent with heating experiment estimates of $\ln k_1$, and they are included in the *Catinella* Arrhenius parameter determinations (Fig. 3A). Additional samples would further constrain the *Catinella* Arrhenius plot and would be a valuable enhancement to the *Hendersonia* plot. Considerable attempts have been made toward obtaining such samples; however they have not yet become available. Future sampling of well-dated, deeply buried shells from Holocene fluvial deposits may provide samples to fill in these gaps on the Arrhenius plots.

CONCLUSIONS

Effective temperature gradients calculated from alle/le ratios measured in the gastropod genera *Catinella*, *Succinea*, *Hendersonia*, *Helicina*, and *Stenotrema*, independently dated by radiocarbon and thermoluminescence methods, indicate that temperatures may have been depressed to a larger degree in the southern Mississippi Valley than in the north for a considerable portion of the past ≈ 20 k.y. The timing of this lowered temperature gradient remains elusive, but it is hoped that through additional sampling of loess and perhaps alluvial sequences, new information will be gained toward resolving this issue.

Calculated effective temperatures for three localities in the lower Mississippi Valley suggest a minimum of 7–13 °C temperature reduction for the period during the last glacial maximum, ca. 20 ka. CLIMAP Project Members (1981) sea-surface temperature estimates indicated that tropical oceans, including the Gulf of Mexico, were only ≈ 1 – 2 °C cooler during the last glacial maximum. Conflicts between CLIMAP results and the terrestrial paleoclimate record were soon noted (Rind and Peteet, 1985). Furthermore, several recent studies conclude that glacial maximum continental and sea-surface paleotemperatures in the tropics and subtropics were perhaps 5–8 °C lower than Holocene values (e.g., Anderson and Webb, 1994; Guilderson et al., 1994; Stute et al., 1995a, 1995b; Thompson et al., 1995).

Amino acid paleotemperature estimates of significant last glacial maximum cooling in the lower Mississippi Valley are consistent with claims of relatively low temperatures as inferred

from several other paleoclimate proxies. Through their study of paleovegetation zonation, Woodcock and Wells (1990) suggested that full glacial summer temperatures were 5–6 °C lower than present for the Gulf coastal region of the United States. Seasonal temperature reconstructions based on pollen data for 18 ka suggest a cooling of perhaps 4–6 °C in July and as much as 12–16 °C in January for the Gulf coast and Mississippi embayment (Webb et al., 1993). Work by Jasper and Gagosian (1989) in the northern Gulf of Mexico suggested that the surface temperature during the last glacial maximum was 8 °C lower than Holocene temperatures, based on laboratory temperature calibration of a ratio of long chain unsaturated alkenones (UK37) in a Deep Sea Drilling Project core. It may therefore be concluded that the 7–13 °C temperature reduction estimated here for the lower Mississippi Valley during the last glacial maximum is in general agreement with paleoclimatic inferences suggested by several other types of proxy climate data.

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the improvement of the manuscript.

APPENDIX 1. KEY TO RADIOCARBON DATING FACILITIES AND PREPARATION PROCEDURES

Ages reported by the National Science Foundation Accelerator Facility, University of Arizona (AA), are corrected for isotopic fractionation, assuming 0‰ ^{13}C for these shell samples. Additional preparation details are not specified.

Samples submitted to Geochron Laboratories Division, Krueger Enterprises, Inc. (GX), were prepared according to their standard procedures. Shells were cleaned thoroughly in an ultrasonic cleaner. They were then leached lightly with dilute HCl to remove additional surficial material which may have been altered and to be sure only fresh carbonate material was used. The cleaned shells were then hydrolyzed with HCl, under vacuum, and the CO_2 was recovered for analysis.

Reported ages are ^{13}C corrected, and the dates are based on the Libby half-life (5570 yr) for ^{14}C , referenced to the year A.D. 1950. Errors stated are $\pm 1\sigma$ as judged by the analytical data alone. The modern standard used is 95% of the activity of National Bureau of Standards (NBS) oxalic acid.

Illinois State Geological Survey (ISGS) samples are prepared similarly. The outer 10% of shell material is leached with dilute HCl, and CO_2 is collected from the remaining 90% for analysis. Ages reported are calculated on the basis of the Libby half-life (5570 yr) for ^{14}C and are corrected for isotopic fractionation, normalized to -25‰ ^{13}C . NBS oxalic acid is used as the reference standard. Errors reported are $\pm 1\sigma$, and ages are referenced to the year A.D. 1950.

APPENDIX 2. THERMOLUMINESCENCE ANALYSIS—SAMPLE PREPARATION AND MEASUREMENT PROCEDURES

Thermoluminescence analyses were performed by Steve Forman, formerly at INSTAAR Thermoluminescence Laboratory (ITL), University of Colorado, Boulder. Procedures are as reported by S. Forman (written commun.).

Prior to analysis, the carbonate and organic fractions were removed from the samples. These samples required extending soaking in HCl to completely remove dolomite. The 4–11 μm silicate fraction was isolated for TL analysis. Prior to glowing, all samples were preheated for 16 h at 150 °C in order to remove the anomalous fading component of the TL signal. Equivalent doses were determined by the total bleach method with growth curve data fitted by a saturating exponential function. The reduction in the natural TL signal after 16 h of sunlight exposure defines the resid-

TABLE A1. TL DOSE RATE DATA FOR PEORIA LOESS SAMPLES

Lab number	Bulk alpha count rate (ks/cm ²)	Th (ppm)	U (ppm)	U/S*	K (%)	H ₂ O (%)	α value [†]	DR [§] (Gy/ka)
ITL-100	0.29 ± 0.02	2.9 ± 0.5	1.6 ± 0.1	0.96	1.41 ± 0.02	10 ± 3	0.050 ± 0.005	2.43
ITL-101	0.57 ± 0.01	7.7 ± 1.0	2.5 ± 0.3	1.00	1.46 ± 0.02	10 ± 3	0.080 ± 0.005	3.51
ITL-104	0.54 ± 0.01	5.2 ± 0.6	3.0 ± 0.2	0.97	1.38 ± 0.02	10 ± 3	0.040 ± 0.005	2.91
ITL-105	0.39 ± 0.01	4.2 ± 0.5	2.0 ± 0.2	0.97	1.45 ± 0.02	10 ± 3	0.18 ± 0.03	3.69
ITL-106	0.43 ± 0.01	5.2 ± 0.8	2.1 ± 0.2	0.96	1.55 ± 0.02	10 ± 3	0.12 ± 0.01	3.53

Note: Th and U calculated from bulk alpha count rate, assuming secular equilibrium. All errors are one sigma. See text for explanation of variables.

*U/S is sealed versus unsealed bulk alpha count ratio. Ratios of >0.95 indicate little or no radon loss.

[†]The measured alpha efficiency factor as defined by Aitken and Bowman (1975).

[§]DR = Dose rate, which includes a contribution from cosmic rays of 0.14 ± 0.01 Gy/ka.

ual level. Extended anomalous fading tests were performed over 30 days, and none of the samples exhibited any fading within analytical resolution of 5%.

The dose rate (Table A1) for all samples was calculated from the U, Th, and K contents of the sediment. U and Th contents were determined by thick source alpha counting. The %K was measured by atomic absorption spectrophotometry. A moisture content of 10% ± 3% was assumed for all samples.

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