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Reference: Ltr, Brocoum to Bell, dtd 4/24/95

In our letter dated April 24, 1995, we enclosed a package of references cited in DOE's responses to NRC's comments on the subject topical report, "Evaluation of the Potentially Adverse Condition 'Evidence for Extreme Erosion During the Quaternary Period' at Yucca Mountain, Nevada."

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Aminostratigraphic Relations and Age of Quaternary Deposits, Northern Española Basin, New Mexico SCP: N/A

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Amino acid ratios of gastropods provide a useful basis for correlation and approximate dating of middle to late Quaternary fluvial deposits from the northern Española basin, New Mexico. Sparsely fossiliferous slackwater deposits in the Rio Chama–Rio Grande floodplain were buried episodically by piedmont alluvium during periods of climatic change as the axial river system cut down 120 m during the past 620,000 yr. Alloisoleucine/isoleucine (alle/Ile) ratios in the total hydrolysate and free fraction of amino acids in *Succinea* and *Vallonia* are strongly correlated with elevation. Ratios in *Succinea* range from 0.01 to 0.79 in the total hydrolysate and from 0.00 to 1.15 in the free fraction for deposits that range in age from modern to ≥620,000 yr old. Amino acid ratios are tightly clustered for deposits that contain the 620,000-yr-old Lava Creek B tephra layer, demonstrating their utility for correlation and providing a calibration point for a local dating curve. Two ^{14}C ages from younger deposits and limiting ages for erosion surfaces that lie above gastropod-bearing units tend to support the validity of much of the curve. Combining the dating curve with the geologic constraints suggests that aggradation events, separated by episodes of net incision, occurred at about 620,000, 310,000 ± 70,000, 170,000 ± 40,000, 95,000 ± 15,000 yr ago, after 19,000 yr ago, and during two minor periods between 80,000 and 25,000 yr ago. ©1993 University of Washington.

INTRODUCTION

The northern Española basin, New Mexico (Fig. 1), exposes an extensive sequence of early through late Quaternary fluvial sediment deposited on strath surfaces by the axial river and tributary arroyos. The ages of erosion surfaces that cut the fluvial deposits are known approximately (Dethier *et al.*, 1988), but until recently we had not identified datable material in the fluvial deposits. Detailed mapping showed that fine-grained facies of the axial channel deposits contain fossil gastropods and include the 1.5-myr-old Guaje Pumice Bed at several localities and the 620,000-yr-old Lava Creek B tephra at 25 exposures. Studies of aminostratigraphy in the southwestern United States have focused on lacustrine deposits where fossils are relatively abundant and where fossiliferous units were buried by sediment or water soon after deposition, buffering short-term temperature fluctuations (McCoy, 1987a). In contrast, fluvial deposits in arid and semiarid environments are sparsely fossiliferous, preservation of deposits is incomplete, and rapid burial may be relatively uncommon. Shells in this environment might be exposed to seasonally and diurnally high surface temperatures. In the northern Española basin, however, piedmont alluvium from arroyos buried axial channel deposits repeatedly during Quaternary time, preserving gastropods that lived on the floodplain of the Rio Chama and Rio Grande. These fossiliferous deposits are exposed from near the elevation of the modern Rio Chama to more than 130 m above it and offer an unusual opportunity to apply aminostratigraphic methods to fluvial deposits.

This study is an outgrowth of investigations by Dethier *et al.* (1988) on the influence of uplift and climate change on the geomorphic evolution of the northern Española basin during Quaternary time. These investigations concentrated on ages of erosion surfaces that cut across Quaternary deposits and on the incision history that could be inferred from the pattern of these ages. Detailed mapping of deposits beneath these surfaces in a 500-km^2 area demonstrated that sparsely fossiliferous silty sand is present at numerous stratigraphic levels and that the Lava Creek B tephra forms a relatively widespread layer 104 to 114 m above the modern axial drainage. This paper reports results of amino acid analyses of gastropods from deposits that represent at least six cycles of aggradation during general incision of the Española basin in middle and late Quaternary time. We correlate deposits using amino acid data and elevation; age estimates are derived using ^{14}C ages, the age of Lava Creek B tephra, and minimum ages for erosion surfaces.

The epimerization of isoleucine in fossil mollusc shells of a single genus, expressed as the ratio of D-alloisoleu-

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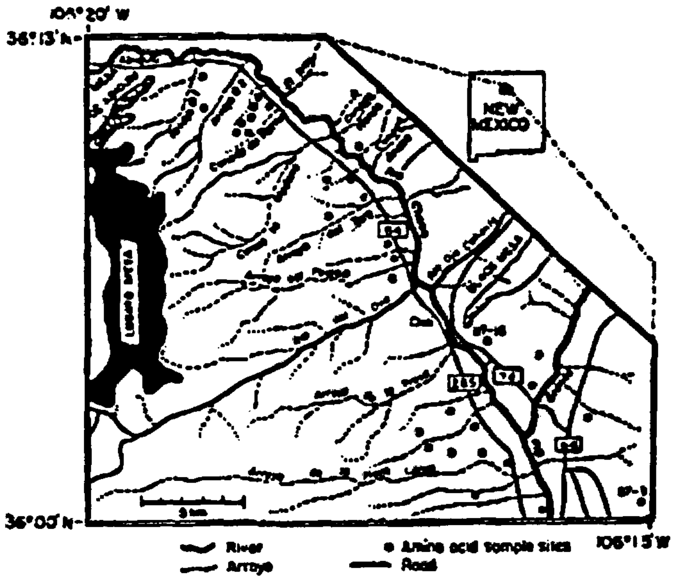

FIG. 1. Map showing selected drainages, sample sites, and location of the northern Española basin.

cine to L-isoleucine (alle/Ile), depends on time and temperature (Schroeder and Bada, 1976; Wehmiller, 1984). The extent of isoleucine epimerization should provide a basis for correlating deposits of similar age and temperature history (Wehmiller, 1984). Where epimerization kinetics and the absolute age of a deposit are known, the effective temperature since deposition can be estimated. Within a limited geographic region, alle/Ile ratios can be used to estimate relative shell ages. However, local temperature gradients and shallow (<3 m) depths of burial may produce significant alle/Ile variations in fossils from deposits of the same age.

The magnitude and pattern of Quaternary climate change is not well established in the nonglaciated parts of northern New Mexico and southern Colorado. Temperature estimates from previous studies (Rogers *et al.*, 1985; Bachhuber, 1989) serve as a guide to climate change during pluvial/interpluvial transitions in the mid and late Quaternary, but are not sufficiently precise to use in calculations of epimerization rates. Data presented by Spaulding *et al.* (1983), COHMAP Project Members (1988), and Spaulding and Graumlich (1986) suggest that summer monsoonal precipitation became reestablished as climate warmed in the latest Pleistocene and early Holocene, producing increased summer precipitation and decreased winter precipitation in the southwestern United States. Regional palynologic studies suggest that the change from glacial to interglacial conditions occurred about 14,000 yr B.P. and that early Holocene climate was relatively cool and moist (Hall, 1985). Studies of Holocene soil development in southern New Mexico indicate that the middle Holocene was warmer and dry (Gile *et al.*, 1981). Temperature during the past 12,000 yr, however, probably did not deviate more than about 1.5°C from present. The present mean annual temperature is 9.0°C at Los Alamos (2260 m), about 13°C at Española (1735 m), and probably between 11° and 12°C in most of the study area.

METHODS

Field

We collected shell samples from fresh exposures along arroyo walls, at the heads of gullies, in roadcuts, and, in one case, in the floodplain of the Rio Grande. Shells were hand-picked from fine-grained deposits exposed at these locations. We generally sampled stratigraphic units more than 3.5 m below the top of any overlying soil or unconformity in order to minimize the influence of seasonal temperature fluctuations that can cause an increase in the effective diagenetic temperature, EDT (Wehmiller, 1977), also called the effective Quaternary temperature (Wehmiller, 1982). At sites 88-14 and 88-49 (Appendix 1), however, gastropods were collected from deposits that had been buried by 1.3 to 2.0 of alluvium. We assumed that *in situ* samples collected at gully heads were exposed at or near the surface by erosion during the past 100 yr, but in some cases shell-bearing exposures may have been near the surface for longer periods of Holocene time. We concentrated on analyzing shells of the genus *Succinea*, which are relatively large and widespread in the Quaternary deposits of the northern Española basin. We also analyzed gastropods from the genus *Vallonia* at 22 sites. *Vallonia* species, although widespread locally, are generally small and have been reported infrequently in the literature.

Laboratory

Approximately 100 ± 50 mg of shell (generally 3–5 individual shells) were selected for each preparation. Each sample was cleaned ultrasonically and air dried at room temperature. The sample was dissolved and hydrolyzed in 6 *N* HCl under a nitrogen atmosphere at 110°C for 22 hr. It was then dried under vacuum and rehydrated with a solution of 1.25×10^{-5} *M* norleucine at pH 2. The total acid hydrolysate was analyzed to determine the concentrations of all detectable amino acids in the sample: the naturally free amino acids plus the formerly peptide-bound amino acids. When we had sufficient sample, another 100 mg of shell were dissolved in 6 *N* HCl in the proportion of 1 ml HCl per 50 mg shell (McCoy, 1987a). The solution was dried in a vacuum desiccator and rehydrated with a solution of 1.25×10^{-5} *M* norleucine at pH 2. The sample was then analyzed to determine the concentrations of free (i.e., non-peptide-bound) amino acids. Samples were analyzed on a cation-exchange, liquid chromatograph (Benson and Hare, 1975). Many samples had sufficient shell material for preparation and analysis of several subsamples, which allowed us to estimate analytical precision (Appendix 1).

The ratio of alloisoleucine to isoleucine was calculated from both peak heights and peak areas in both the free fraction and the total hydrolysate of each sample. Peak-height ratios were found to be more consistent than peak–area ratios (McCoy, 1987a), perhaps because of errors in the integration of areas for small alle peaks. Only peak–height ratios are given in this paper.

Certain ratios are also useful indicators of sample contamination. For example, threonine and serine generally exist in approximately the same proportion in many mollusk shells. Serine, however, is much more abundant than threonine on human skin. Analyses with anomalously high serine/threonine ratios were considered to have been contaminated during preparation or injection and were not used in this study. Additional details of laboratory techniques can be found in McCoy (1987a,b).

RESULTS

Amino acid ratios in gastropods from 44 sites, in deposits ranging in age from >620,000 yr to modern, indicate that this technique can be used for correlation of Pleistocene fluvial deposits. Deposits lie from 130 to 15 m above channels of the modern Rio Chama and Rio Grande and are buried by sequences of piedmont alluvium that are truncated by erosion surfaces. Based on deposit elevation, we can distinguish 11 groups of fluvial sequences including the Lava Creek B deposits. Amino-acid ratios are available for 8 of these groups and are discussed below (Table 1).

Amino acid (alle/Ile) ratios in the hydrolysate and free fractions from gastropods in the Española basin are highly correlated and increase with increasing deposit age (Fig. 2). Ratios in *Succinea* range from 0.01 to 0.79 in the total hydrolysate and from 0.00 to 1.15 in the free fraction (Fig. 2; Appendix 1). for deposits that range from modern to >620,000 yr old. Ratios in the hydrolysate of *Vallonia* are similar, but slightly lower (Appendix 1). The alle/Ile ratios in the total hydrolysate and the free fraction of *Succinea* are highly correlated (Fig. 2). We use primarily hydrolysate values from *Succinea* in this discussion because those data are more complete.

Because the Rio Chama–Rio Grande system has been cutting down throughout middle and late Pleistocene time, elevation of deposits above the present river provides a primary basis for correlation, assuming that local gradients have remained relatively constant during the past 700,000 yr. Elevation above grade and alle/Ile values in the total hydrolysate are highly correlated (Fig. 3). All fluvial deposits 30 m above grade, for instance, should have similar ratios in *Succinea*, assuming that shell was buried at least 3.5 m below the surface soon after deposition.

TABLE 1

Amino Acid Ratios for *Succinea* from Quaternary Deposits Grouped by Altitude, Española Basin, New Mexico

Altitude above grade (m)	Sample number (age 10^3 yr)	Amino acid ratio (hydrolysate) Range	Amino acid ratio (hydrolysate) Mean
244	(3200)	[a]	[a]
232 ± 9	(1500)	[a]	[a]
172	?	[a]	[a]
123 ± 3	86-11a, 87-46(L), 88-35	0.63–0.79	0.68 ± 0.07
110 ± 9	83-5, 88-23, 89-14, 89-25 90-1, 90-6	0.69–0.72	0.70 ± 0.01
92 ± 8	88-5, 88-16a	0.53–0.70	[b]
75 ± 8	87-23(L), 87-3V, 89-17, 89-30,[c] 89-32, 89-34	0.41–0.63	0.46 ± 0.03
59 ± 7	86-13V, 87-5, 87-41(N), 88-51	0.31–0.34	0.32 ± 0.02
42 ± 8	85-132	0.20–0.25	[b]
24 ± 9	87-16, 88-14,[c] 88-49,[c] 89-47, 89-40, 89-58	0.15–0.33	0.23 ± 0.08
<14	87-11 (modern)	0.013	[b]

[a] No gastropods were collected.
[b] No mean calculated; number of analyses <8.
[c] Not used for mean calculations.

Uncertainty in correlating deposits using elevation and alle/Ile ratios, however, arises from four sources: (1) analytical uncertainty; (2) uncertainty about deposit elevation; (3) geologic uncertainty, particularly in assessing the burial history of individual sites and the possibility of shell reworking; and (4) the variable temperature history experienced by the youngest Quaternary deposits. Analytical errors are likely to be small (±5–10%) except for the lowest alle/Ile ratios. We know deposit elevation within 6 m and locally within 3 m where we have control

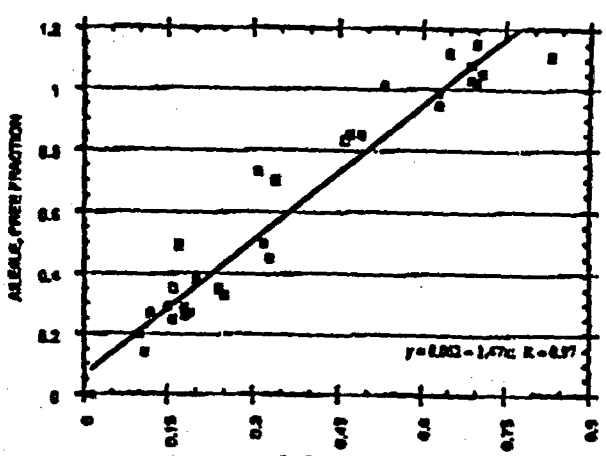

FIG. 2. Scatterplot of relation between alle/Ile ratios in the total hydrolysate and free fraction of gastropods from the Española basin, New Mexico. Data from *Succinea* (filled squares; $N = 29$) and *Vallonia* (open squares; $N = 2$). Line fitted to *Succinea* data.

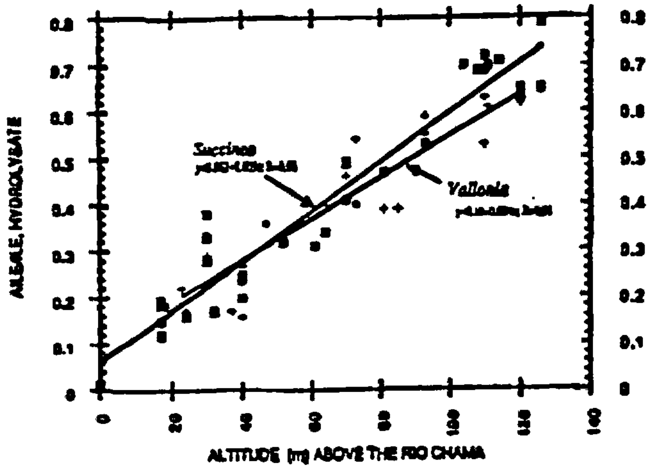

FIG. 3. Relationship between deposit elevation, in meters, and alle/Ile ratios measured in the total hydrolysate of *Succinea* (filled squares) and *Vallonia* (crosses).

from a benchmark. Variation in the elevation of the gravel surface across the modern floodplain is about 3 m. Motion on faults can also displace deposits that originally were at the same elevation. More significantly, episodes of incision from one stable base level to another may produce deposits separated by only 9 to 15 m vertically, but differing in age by 20,000 to 40,000 yr. Erosion and deposition of overlying deposits may impose a complex thermal history on sediments that appear to have been deeply buried since deposition. These effects complicate correlation of units separated by tens of kilometers, but our data show that correlation using alle/Ile ratios is a useful technique in the Española basin.

The Lava Creek B tephra layer, which crops out at two dozen sites in the study area, provides field constraints on our measurements. Outcrops of nearly pure tephra are probably isochronous and comparable in age to the 620,000 yr date assigned to the Lava Creek B tephra layer by Sarna-Wojcicki *et al.* (1987). The elevation of the upper surface of the gravel associated with the tephra is 110 ± 5 m (N = 20) above the present Rio Chama (Table 2). We use Δx m in this discussion to indicate the difference between deposit elevation and the elevation of the present Rio Chama. Elevations range from Δ110 m in the south, to Δ117 m in the central part of the area, to Δ102 m near Mesa de Abiquiu, in the northwest corner of Figure 1. Most of this variation arises from uncertainty in projecting remnants of paleochannels several kilometers to the modern river. Amino acid ratios in *Succinea* average 0.70 ± 0.01 (hydrolysate) and 1.07 ± 0.05 (free) at sites where gastropods are interbedded with the tephra; *Vallonia* ratios are slightly lower in the total hydrolysate (0.60 ± 0.05; Table 2). Three deposits that are about 10 m higher than the Lava Creek B tephra have similar amino acid ratios, suggesting that they are not significantly older (Table 2).

TABLE 2

Amino Acid Ratios from Sites Associated with the Lava Creek B Tephra Layer, Española Basin, New Mexico

Sample	Genera	Amino acid ratios: Free	Amino acid ratios: Hydrolysate	Elevation above Rio Chama (m)
83-5 (AGL-504)	*Succinea*	1.08	0.69 ± 0.03	108
89-14 (AGL-1332)	*Succinea*	1.03	0.69 ± 0.02	110
89-25 (AGL-1360)	*Succinea*	1.15	0.70	111
89-23 (AGL-1340)[a]	*Succinea*	1.05 ± 0.06	0.71 ± 0.05	114
90-1 (AGL-1508)	*Succinea*	—	0.72 ± 0.01	110
90-6 (AGL-1510)	*Succinea*	1.02 ± 0.04	0.71 ± 0.01	104
89-14 (AGL-1402)	*Vallonia*	—	0.53	110
89-25 (AGL-1404)	*Vallonia*	—	0.61	111
88-39 (AGL-1401)	*Vallonia*	0.95 ± 0.02	—	114
90-1 (AGL-1509)	*Vallonia*	—	0.63 ± 0.01	110
86-11a (AGL-1395)[b]	*Vallonia*	—	0.62	120
86-11a (AGL-506)[b]	*Succinea*	1.12	0.65 ± 0.02	120
86-11a (AGL-1396)[b]	*Gyraulus*	—	0.66	120
87-46(L) (AGL-576)[b]	*Succinea*	0.99 ± 0.08	0.63 ± 0.04	119
88-35 (AGL-955)[b]	*Succinea*	—	0.79	126
88-35 (AGL-1341)[b]	*Succinea*	—	0.65 ± 0.01	126

[a] Two other collections from location 88-23 (AGL-954, AGL-1083) give similar values for the free fraction (1.03 ± 0.02 and 1.11 ± 0.01, respectively) but anomalously high values for the hydrolysate fraction (0.93 ± 0.04 and 0.83 ± 0.07, respectively).

[b] Sites about 10 m higher (and thus slightly older) than the Lava Creek B tephra.

DISCUSSION

Age of Deposits

Our data generally constrain the relationship between alle/Ile in the total hydrolysate of *Succinea* shells and the age of deposits for the Española basin. Alle/Ile ratios in *Succinea* and *Vallonia* do not reach equilibrium in 620,000 yr. Interpretation of the relationship in terms of reaction kinetics is complicated by the fact that the EDT experienced by the shells has changed over time, especially over the last 20,000 or 30,000 yr. Holocene and latest Pleistocene shells have experienced an EDT dominated by the relatively warm Holocene environment. The EDT of older shells would have been less dominated by warm interglaciations (Wehmiller, 1982; Appendix 1). When considering intervals of 10^5 yr or so, there likely is not much difference in EDTs. For example, there is probably little difference in the EDT between samples that are 400,000 yr old and those that are 600,000 yr old, but samples from this region that are 12,000 yr old would be expected to have a significantly (perhaps several degrees) higher EDT than those of much older samples.

The curve plotted in Figure 4 is a fit of a parabolic kinetic curve to the 620,000-yr-old samples having an average alle/Ile ratio of 0.70 in the total hydrolysate and to the nearly modern sample having an alle/Ile ratio of

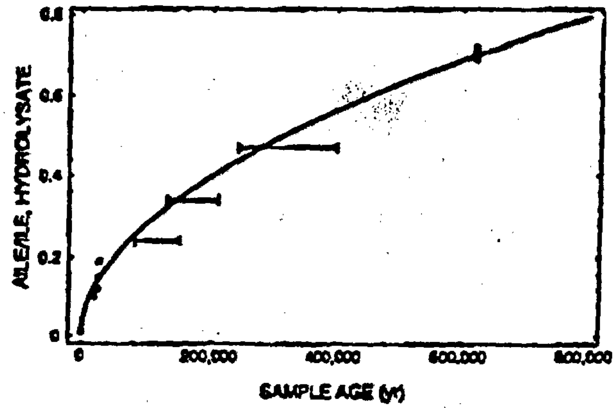

FIG. 4. Relationship between alle/Ile ratios in the total hydrolysate from *Succinea* and deposit age. Curve was fitted using data from the Española basin. Error bars show age uncertainty listed in Table 3. The envelope shows the age (and uncertainty) of deposits that would be predicted for a measured alle/Ile ratio in this region. The bold line is drawn through alle/Ile ratios predicted for shells of various ages by a linear kinetic model, using the Lava Creek B ratios as a fixed point.

0.013. Fitting of alle/Ile ratios as a linear function of the square root of sample age was suggested by Mitterer and Kriausakul (1989) and has been used by Kaufman (1992). Their data show that such a function generally does not provide a very close fit at the extremes, i.e., for alle/Ile ratios less than about 0.20 or greater than about 1.0. Nonetheless, most of the samples of unknown age in this study have alle/Ile ratios falling within the range for which Mitterer and Kriausakul (1989) have shown that the fit can be excellent.

The epimerization data tend to support the age constraints provided by the field data of Dethier *et al.* (1988) (Table 3). The fitted curve (Fig. 4) favors the younger ends of the age ranges provided by the geologic constraints, as indicated by the error bars. The confidence limits for the fitted curve are not known for this data set, but are generally less than about 25% (in terms of sample age) in the fits to data given in Mitterer and Kriausakul (1989). Combining an estimated 25% uncertainty in the fitted curve, an approximate 8% uncertainty in the mean alle/Ile values, and the geologic constraints, we estimate the times of aggradation as 95,000 ± 15,000, 170,000 ± 40,000, and 310,000 ± 70,000 yr ago.

The radiometric dates that we report (Table 3) help to establish a chronology of late Wisconsinan events in the Española basin. Both ^{14}C analyses were performed on a crushed and acid-leached composite of 10 to 20 shells. The older ^{14}C date (25,800 ± 200 yr B.P.; TO-1755), however, is best interpreted as a minimum age because some of the alle/Ile ratios for this unit are high relative to those associated with the 19,000-yr age.

The older ^{14}C date demonstrates that the Rio Chama flowed at an elevation about 16 m higher than at present ≥26,000 yr B.P., and local stratigraphic relations show that a short period of alluvial fan aggradation occurred

TABLE 3
Age Control for Gastropod-Bearing Deposits, Northern Española Basin, New Mexico

Sample	Amino-acid ratio in *Succinea*: Free	Hydrolysate	Age (10^3 yr)	Method
87-11	0.0	0.013	0	Shell in active floodplain
87-9	0.14	0.10	19.0 ± 0.15	AMS ^{14}C age determined on *Succinea* shells (TO-1474)
87-16	0.28	0.17	25.8 ± 0.2	AMS ^{14}C age determined on *Succinea* shells (TO-1755)
85-132	0.35	0.24	>80; <150	Approximate age of erosion surface (Q_4) that truncates deposit (Dethier *et al.*, 1988)
87-41(N)	0.70	0.34	>130; <210	Age estimated for Q_3 surface (Dethier *et al.*, 1988), which truncates deposit
87-23(L)	0.85	0.47	>240; <400	Age estimated for younger Q_2 surface (Dethier *et al.*, 1988; Gonzales and Dethier, 1991), which truncates deposit
88-23	1.05	0.70	620	Age of Lava Creek B tephra that forms matrix for sample

subsequently. Gastropods collected at site 87-9 lived in and were buried by sand dunes and loess east of Española about 19,000 yr ago, probably when the braid plain of the Rio Grande was considerably wider than it is at present (Love *et al.*, 1987). The radiometric age also permits us to assign an age of late Wisconsinan to the upper part of the Española Formation (Galusha and Blick, 1971).

The alle/Ile ratios of the radiocarbon-dated shells plot close to the fitted line. However, the fit may be somewhat fortuitous in that those samples probably experienced a somewhat higher EDT than the older samples because of the significant influence of the warm Holocene on latest Pleistocene samples. In addition, the samples plotted at 26,000 yr B.P. could be older and may have experienced unusually high EDTs because of relatively shallow burial. The amino acid data of Mitterer and Kriausakul (1989) having aIle/Ile ratios less than 0.2 generally plot below or to the right of the fitted parabolic curve.

Fluvial deposits exposed along arroyos south of Abiquiu (Fig. 1) illustrate both the possibilities and uncertainty inherent in the use of aIle/Ile ratios for correlation. The deposits record repeated episodes of downcutting by the Rio Chama and burial by alluvial fan deposits during the past 620,000 yr. We sampled six sequences exposed south of Arroyo 2 (Figs. 1 and 5), where exposures of the two highest gravels are extensive and nearly continuous. At several nearby locations (for instance, 88-16a; Appendix 1) we also mapped a gravel intermediate in elevation between the two highest gravels of Figure 5. Ratios at the sites associated with the Lava Creek B tephra (89-25, 89-14) are typical of those that we have measured elsewhere in the Española basin (Table 2). Samples 89-17, 89-34, and 89-30 (Appendix 1) were collected from above an extensive gravel that is exposed about 75 m above the modern Rio Chama near Abiquiu. Ratios from 89-30 are "too high" compared to samples from the other two sites and to other sites at this elevation (Table 1). Field evidence indicates that 89-30 was buried soon after deposition by more than 5 m of alluvial fan deposits. Thus, if a high EDT produced the anomalously high aIle/Ile ratios at 89-30, it was due to slope aspect (south) and colluvial cover that thinned before the Holocene, rather than original depth of burial.

Site 89-32 is about 3 m lower than 89-34, but its amino-acid ratio is not significantly different, assuming that *Succinea* and *Vallonia* have similar aIle/Ile ratios in this age range. Ratios at the lower elevation sites (Fig. 5) demonstrate a progressive decrease. Gastropods at sites nearest the Rio Chama probably were deposited during late Wisconsinan time. Their elevation (Δ20 m) and amino acid ratios are similar to those of shells collected at 87-16, which gave a ^{14}C age of 25,800 ± 200 yr B.P. (TO-1755). Location 89-47, at about Δ30.5 m, gives aIle/Ile ratios that suggest it may be considerably older than sites only 10 m lower.

aIle/Ile ratios determined at some of the lower elevation sites in the Española basin, such as 89-47, are variable and difficult to interpret. Hydrolysate aIle/Ile ratios range from about 0.17 to 0.33 for sites that range from Δ22 to Δ40 m (Table 1). Site 89-58 (Δ24 m), gives aIle/Ile ratios of about 0.16, similar to those at 87-16 (Δ16 m), whereas 89-47 (Δ30 m) and 87-1 (Δ30 m) have ratios over 0.30, and 87-2 and 85-132, at elevations from Δ32 to Δ40 m, gave values between 0.17 and 0.25. We had no a priori reason to suspect shallow burial at these sites.

The aIle/Ile data imply that deposits at Δ30 m are somewhat older than those about 8 m higher. Geologically this would correspond to aggradation of the axial channel by about 8 m, followed by rapid incision of about 20 m, without removal of the older deposit. This is geologically plausible, particularly if the locus of arroyo incision shifted away from previous areas of deposition and if aggradation occurred during a warm period when rates of epimerization were rapid. Alternatively, ratios from deposits at Δ30 m may be too high due to anomalously high EDTs or reworking. In this case the data could suggest that incision from Δ40 m to Δ15 m occurred in a relatively short period of time. We believe that we can rule out analytical error, but our data are not sufficient to decide between these other possibilities.

Record of Incision

Because of age uncertainty and uncertainty in aIle/Ile ratios, the age curve (Fig. 4) should be used only as a guide. We do not have aIle/Ile data for early Quaternary deposits near the Rio Chama because we have not found gastropods in fluvial units older than about 650,000 yr. Our aIle/Ile ratios and age control for deposits containing the Lava Creek B tephra are excellent. Deposits younger

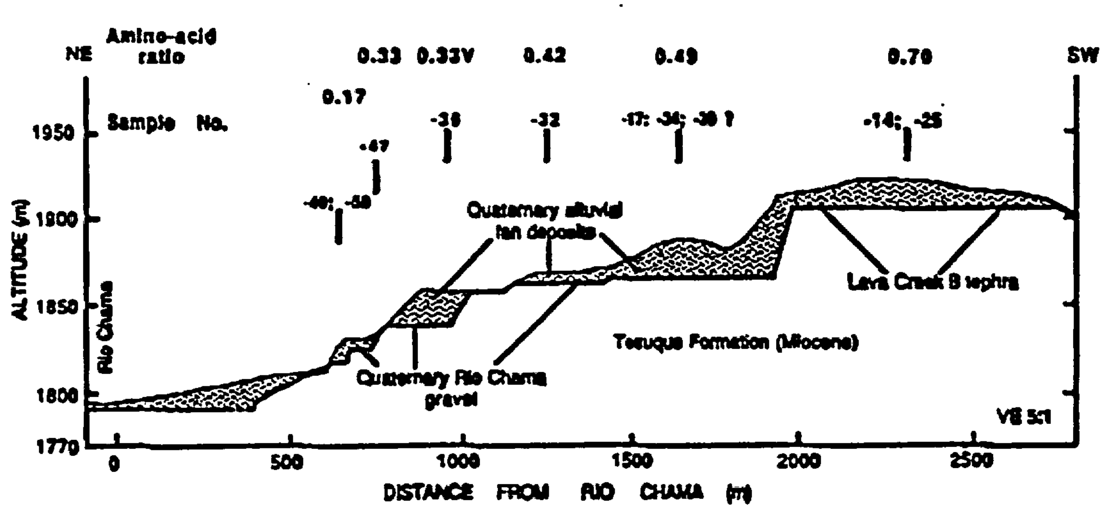

FIG. 5. Cross-section south of Arroyo 2, SE of Abiquiu, New Mexico (Fig. 1), showing amino acid ratios from gastropods at sample sites in the Quaternary deposits.

than 620,000 yr are better preserved, but age control, except for the ^{14}C ages, is only approximate. The data, however, allow us to make reasonable estimates about the timing of incision and aggradation in the Española basin. Arroyo aggradation followed deposition of the Lava Creek B tephra 620,000 yr ago. Aggradation events, separated by episodes of net incision, also occurred about 310,000 ± 70,000, 170,000 ± 40,000, 95,000 ± 15,000 yr ago, after 19,000 yr ago, and following several periods of minor incision between 80,000 and 25,000 yr ago. Aggradational events are also recorded soon after 1.5 myr and before 620,000 yr ago; we have not found unequivocal evidence for a significant aggradational event between 620,000 and about 310,000 yr ago. The data suggest that major intervals of aggradation have occurred about once in 100,000 yr since about 300,000 yr ago. The record of the past 100,000 yr indicates that less significant cycles of aggradation and incision probably occurred with a periodicity of 10,000 to 40,000 yr, but were less likely to be preserved in the geologic record. The ages and position of the latest Pleistocene deposits suggest that the Rio Chama–Rio Grande system incised ca. 16 m between ≥26,000 and 19,000 yr ago and that construction of the modern alluvial fans began some time after 19,000 yr B.P.

The amino acid ratios, age relationships, and elevation of deposits (Fig. 3) reflect general incision by the Rio Chama system over at least the past 620,000 yr. Incision rates during that time have averaged 18 cm/1000 yr. Our data suggest, however, that most incision occurred rapidly during episodes of relatively short duration. For instance, if the Rio Chama has been cutting down at a constant rate since deposition of sample 87-16 at 25,800 yr B.P., the incision rate would be about 64 cm/1000 yr, or somewhat less if the date is regarded as a minimum. Geologic considerations, however, suggest that most of that incision occurred between 26,000 and 19,000 yr ago, giving a rate of about 240 cm/1000 yr. Surface and subsurface data from the Española area presented by Love *et al.* (1987) suggest that since the latest Pleistocene, the braid plain of the Rio Grande has changed to a meander belt and narrowed significantly as alluvial fans prograded from both sides of the valley. Aggradation by the axial stream has apparently been minimal during that time. This evidence suggests that rapid incision occurs during periods that correspond to glacial maxima, that arroyo aggradation and alluvial fan expansion occur during transitional climates, and that base level is relatively constant during periods of "stable" climate, whether warm or cool.

APPENDIX 1

Locations and Amino Acid Ratios for Gastropod Samples from the Española Basin, New Mexico

Sample	Location	Altitude[a] of sample above Rio Chama (m)	Geomorphic surface[b] that overlies deposit	Amino-acid ratios[c] alle/Ile	
				Free	Hydrolysate
87-11 (AGL-573)	36°0.58′N;106°4.36′W	0	Floodplain	nd(2)	0.013 ± 0.0(2)
87-9a (AGL-572)	36°0.52′N;106°1.73′W	—	Española Fm.	0.14 ± 0.02(3)	0.11 ± 0.03(3)
87-9b (AGL-717)	36°0.52′N;106°1.73′W	—	Española Fm.	0.20	0.10 ± 0.01(2)
87-9V[d] (AGL-1397)	36°0.52′N;106°1.73′W	—	Española Fm.	na	0.10
87-16 (AGL-574)	36°5.00′N;106°6.91′W	17	Q_5	0.27	0.12
87-16 (AGL-948)	36°5.00′N;106°6.91′W	17	Q_5	0.27 ± 0.06(2)	0.19 ± 0.04(2)
87-16 (AGL-1339)	36°5.00′N;106°6.91′W	17	Q_5	na	0.15 ± 0.03(4)
87-16a (AGL-1502)	36°5.00′N;106°6.91′W	17	Q_5	0.26 ± 0.0	0.18 ± 0.02
87-16b (AGL-1503)	36°5.00′N;106°6.91′W	17	Q_5	0.29 ± 0.02	0.15 ± 0.02
89-40(O) (AGL-1330)	36°12.24′N;106°14.80′W	18	Q_5?	0.29 ± 0.01	0.18 ± 0.01
88-14 (AGL-951)	36°8.23′N;106°10.30′W	23	Q_5?	na	0.33 ± 0.02(2)
88-14V (AGL-952)	36°8.23′N;106°10.30′W	23	Q_5?	na	0.22
89-58(O) (AGL-1331)	36°12.80′N;106°16.44′W	24	Q_5?	0.25 ± 0.04	0.16 ± 0.01
89-58V (AGL-1410)	36°12.80′N;106°16.44′W	24	Q_5?	na	0.17
88-49 (AGL-956)	36°9.05′N;106°10.59′W	26	Q_5?	na	0.25
87-1 (AGL-568)	36°2.95′N;106°3.09′W	30		na	0.28 ± 0.02(3)
89-47 (AGL-1362)	36°12.61′N;106°15.22′W	30	Q?	0.45 ± 0.01	0.33 ± 0.07
89-47V (AGL-1409)	36°12.61′N;106°15.22′W	30	Q_4?	na	0.33
89-47G (AGL-1408)	36°12.61′N;106°15.22′W	30	Q_4?	na	0.24
89-47b (AGL-1506)	36°12.61′N;106°15.22′W	30	Q_4?	na	0.38
89-47bV (AGL-1507)	36°12.61′N;106°15.22′W	30	Q_4?	na	0.29
87-2 (AGL-569)	36°3.93′N;106°5.13′W	32	Q_4	0.49 ± 0.01(2)	0.17 ± 0.01(2)
88-55V (AGL-959)	36°10.87′N;106°11.00′W	37		na	0.17
85-132 (AGL-505)	36°1.50′N;106°5.51′W	40	Q_4	0.38 ± 0.02(3)	0.20 ± 0.01(3)
85-132 (AGL-1393)	36°1.50′N;106°5.51′W	40	Q_4	0.33 ± 0.02(2)	0.25 ± 0.01(2)
85-132a (AGL-1500)	36°1.50′N;106°5.51′W	40	Q_4	0.35 ± 0.01(3)	0.24 ± 0.01

APPENDIX 1—*Continued*

Sample	Location	Altitude[a] of sample above Rio Chama (m)	Geomorphic surface[b] that overlies deposit	Amino-acid ratios[c] alle/Ile	
				Free	Hydrolysate
85-132V (AGL-1394)	36°1.50′N;106°5.51′W	40	Q_4	0.35	0.16
85-132aV (AGL-1501)	36°1.50′N;106°5.51′W	40	Q_4	na	0.27
89-36aV (AGL-1407)	36°12.54′N;106°15.22′W	47	Q_4	na	0.36
88-51 (AGL-957)	36°11.40′N;106°10.87′W	52		0.50 ± 0.03(2)	0.32 ± 0.01(3)
88-51G (AGL-958)	36°11.40′N;106°10.87′W	52		na	0.36 ± 0.0(2)
87-5 (AGL-571)	36°1.64′N;106°6.02′W	61	Q_3/Q_4	0.73 ± 0.02(2)	0.31 ± 0.03(2)
87-41(N) (AGL-577)	36°0.73′N;106°0.12′W	64	Q_3	0.70 ± 0.01(2)	0.34 ± 0.02(2)
86-13G (AGL-515A)	36°2.94′N;106°7.12′W	64	Q_3	na	0.33
86-13P (AGL-509A)	36°2.94′N;106°7.12′W	64	Q_3	na	0.36
86-13V (AGL-947)	36°2.94′N;106°7.12′W	64	Q_3	na	0.40
89-17 (AGL-1333)	36°12.40′N;106°16.49′W	70	Q_3?	0.85 ± 0.03	0.49 ± 0.03
89-17V (AGL-1403)	36°12.40′N;106°16.49′W	70	Q_3?	0.83	0.46
89-32 (AGL-1361)	36°12.29′N;106°15.29′W	70	Q_3?	na	0.41
89-30 (AGL-1334)	36°11.91′N;106°15.19′W	73	Q_3?	0.95 ± 0.02	0.63 ± 0.01
89-30V (AGL-1405)	36°11.91′N;106°15.19′W	73	Q_3?	na	0.54
89-34V (AGL-1406)	36°12.07′N;106°18.38′W	73	Q_3?	na	0.40
87-3V (AGL-570)	36°4.35′N;106°5.13′W	81	Q_3	na	0.39 ± 0.05(2)
87-23(L) (AGL-575)	36°2.18′N;106°7.06′W	81	Q_3	0.85 ± 0.04(2)	0.47
88-5V (AGL-950)	36°6.50′N;106°10.07′W	85		na	0.39 ± 0.01(2)
88-5 (AGL-949)	36°6.50′N;106°10.07′W	88		na	0.70 ± 0.01(2)
88-16aV (AGL-953)	36°8.41′N;106°10.50′W	93		na	0.59 ± 0.01
88-16a (AGL-1398)	36°8.41′N;106°10.50′W	93		1.01	0.53 ± 0.02(2)
88-16aV (AGL-1399)	36°8.41′N;106°10.50′W	93		na	0.55 ± 0.02(2)
90-6 (AGL-1510)	36°11.55′N;106°16.44′W	104	Q_2?	1.02 ± 0.04	0.70 ± 0.01
83-5 (AGL-504)	36°3.20′N;106°7.93′W	108	Q_2	1.08	0.69 ± 0.03(3)
89-14 (AGL-1332)	36°12.11′N;106°16.19′W	110	Q_2?	103 ± 0.04	0.69 ± 0.02
89-14V (AGL-1402)	36°12.11′N;106°16.19′W	110	Q_2?	na	0.53
90-1 (AGL-1508)	36°9.33′N;106°11.65′W	110	Q_2?	na	0.72 ± 0.0
90-1V (AGL-1509)	36°9.33′N;106°11.65′W	110	Q_2?	na	0.63 ± 0.01
89-25 (AGL-1360)	36°11.51′N;106°15.31′W	111	Q_2?	1.15	0.70
89-25V (AGL-1404)	36°11.51′N;106°15.31′W	111	Q_2?	na	0.61
88-23 (AGL-954)	36°8.66′N;106°11.69′W	114	Q_2?	1.03 ± 0.02(2)	0.93 ± 0.04(3)
88-23C (AGL-1083)	36°8.66′N;106°11.69′W	114	Q_2?	1.11 ± 0.01(4)	0.83 ± 0.07(2)
88-23 (AGL-1340)	36°8.66′N;106°11.69′W	114	Q_2?	1.05 ± 0.06(3)	0.71 ± 0.05
88-39V (AGL-1401)	36°9.69′N;106°11.60′W	114	Q_2?	0.95 ± 0.02(2)	na
87-46(L) (AGL-576)	36°2.72′N;106°7.92′W	120	Q_2	0.99 ± 0.08(2)	0.63 ± 0.04(2)
86-11a (AGL-506)	36°2.67′N;106°7.77′W	120	Q_2	1.12(1)	0.65 ± 0.02(2)
86-11aV (AGL-1395)	36°2.67′N;106°7.77′W	120	Q_2	na	0.62
86-11aG (AGL-1396)	36°2.67′N;106°7.77′W	120	Q_2	na	0.66
88-35 (AGL-955)	36°9.40′N;106°12.43′W	126	Q_2?	na	0.79
88-35 (AGL-1341)	36°9.40′N;106°12.43′W	126	Q_2?	na	0.65 ± 0.01

[a] Projected to the Rio Chama.
[b] See Dethier *et al.* (1988). Blank where unknown.
[c] nd, None detected; na, not analyzed. The number of separately prepared and analyzed subsamples is given in parentheses when $n > 1$.
[d] Samples without designation are *Succinea*; V, *Vallonia*; G, *Gyraulus*; C, *Catonella*; P, *Pupilla*.

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LETTER TO THE EDITOR

Comment on "Evidence Suggesting That Methods of Rock-Varnish Cation-Ratio Dating Are neither Comparable nor Consistently Reliable," by P. R. Bierman and A. R. Gillespie

In their recent paper on cation-ratio dating of rock varnish, Bierman and Gillespie (1994) describe how they collected and analyzed rock varnish from late Holocene chert artifacts, surface clasts, and from chert bedrock at a prehistoric quarry site they believed to be "older." No independent age verification was available, however, for any of the samples at this archeological site. They used both of the published techniques of varnish cation-ratio dating (Dorn, 1983; Harrington and Whitney, 1987) and the analytical results failed to produce lower cation ratios for samples believed by the authors to be older. Primarily on the basis of these results the authors seek to discredit cation-ratio dating as a useful chronometer. We believe that this is an example of "throwing the baby (cation-ratio dating) out with the bath water (a poorly conceived and executed study)." Additionally, we believe they have inappropriately generalized their results far beyond their specific study area by use of justifications such as "the varnish is chemically similar to other varnishes in the Southwest"; they have also drawn conclusions from weak inferences (e.g., "the results are not inconsistent with" their interpretations).

Several misconceptions and inappropriate conclusions about cation-ratio dating and specifically about *in situ* varnish analyses are presented in this study. We believe the investigators are incorrect in their assumptions or interpretations of the following points: (1) the suitability of chert as a varnish substrate; (2) the suitability for varnish cation-ratio dating of all clasts from a geomorphic surface; (3) the accuracy of SEM analytical procedures in *in situ* varnish analyses; (4) the suitability of evaluating only a three-element cation-ratio curve that does not include barium; and (5) the role of substrate inclusion in *in situ* varnish analyses. We address each point below.

1. Bierman and Gillespie assume chert is a representative and acceptable substrate on which to study varnish development and preservation.

No study on rock varnish has stated that all rock types varnish equally; neither has any study maintained that any rock type can be used for cation-ratio dating. Bierman and Gillespie (1994) took the approach that *every rock is a good rock* for surface dating, and nothing could be farther from the truth. We tested clasts on alluvial surfaces along Las Vegas Wash and in the North Las Vegas Valley to determine which rock types are better receptors for varnish development and which rock surfaces are the most stable, accreting varnish over long time periods. Chert clasts were common on these alluvial surfaces but proved to be inappropriate substrates for maximum varnish development. Although chert clasts possessed significant surface irregularities, commonly vertical-edged steps on the rock face, they lacked the surface microdepressions that are inherent on fine-grained sandstones or volcanic rocks. The varied development of rock varnish on surface clasts of an alluvial surface is shown in Figure 1, where varnish on different rock types ranges from nonexistent to well developed. If we were to attempt to determine the age of this surface, we would select only the clasts with well-developed varnish (which here are volcanic rocks and sandstones), not the poorly varnished (here the metaquartzites and chert) clasts.

Bierman and Gillespie (1994) assumed that varnish accumulates in the same manner on very young chert artifacts and on bedrock exposures composed of chert as it does on proven substrates such as fine-grained welded tuffs, basalts, and well-cemented fine-grained quartz sandstones. Indeed, this study confirms our own testing of the suitability of different rock types as hosts for varnish development: chert is an unsuitable rock type for cation ratio dating.

2. The authors assume that all clasts from a geomorphic surface record the same exposure history, and thus any subset of these clasts will yield consistent cation-ratio data.

Dethier and others (1988) demonstrated that piedmont and alluvial fan surfaces possess varied exposure histories, and rock varnish sampled across these surfaces is likewise variable in its age and degree of development. Because surfaces contain both young and fully mature subareas or clast populations, surface clasts, even on a surface of a single age, can present highly variable varnish histories. An appreciation of the evolution of alluvial surfaces led to the development of our sampling protocol, based on the assumption that the clasts most closely representing the exposure age of a surface are those with the

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FIG. 1. Clasts of multiple rock types on an alluvial fan surface in Death Valley, California. Clasts A and B are metaquartzite or chert clasts with smooth surfaces and poorly developed rock varnish coatings. Clasts C and D are argillites with surface micro-roughness and well developed varnish coatings. Clasts E and F are clasts that are being actively weathered and possess unstable surfaces for varnish development. Other rock types on this surface record intermediate levels of varnish patination.

most developed (oldest) varnish (Harrington and Whitney, 1987; Whitney and Harrington, 1993). To maximize the probability of selecting the oldest clasts on a surface we originally collected ~20 clasts from a deposit or surface and then culled them to the best 8 to 10 clasts, based on the macroscopic quality of each varnish coat (Whitney and Harrington, 1993). This sample selection procedure reduces the analytic variability in varnish cation ratios for an individual deposit. Failure to follow a sampling strategy that assembles only the oldest varnished clasts on a geomorphic surface will combine the variation in varnish age of the collected clasts and the variation in rock varnish chemistry inherent in any group of varnished clasts. Analyses will then overstate the inconsistency in varnish chemistry and rock varnish age for the surface being analyzed.

Sampling considerations are critical in cation ratio dating of rock varnish. Detailed sampling strategies are an equally important component in the application of nearly all dating methods. K–Ar and Ar–Ar dating protocols, for example, exclude rocks that are vesicular, or weathered, or possess carbonate deposits in vesicles or along fractures, in addition to other imperfections. Collecting appropriate samples demands careful evaluation of many more candidates than those few ultimately selected for the dating application.

3. Bierman and Gillespie contend that *in situ* varnish measurements in which elemental concentrations are derived by comparison to standards produce results of high analytical accuracy.

The elemental abundances published by Bierman and Gillespie (1994) may not be accurate because the analytic program that was used compares data from rough, porous varnish surfaces to elemental concentrations for dense polished standards. Such analyses will commonly be inaccurate, and thus, the cation ratios calculated from these data will also be inaccurate, which may mask any trend in cation ratios that occurs within their analyzed varnish.

In situ varnish analyses on surfaces that possess appreciable micro-roughness (surface irregularity) are problematic in that irregularities on the analyzed surface produce scattering of the electron beam, resulting in either a greater or a lesser beam return than that produced when analyzing a polished surface. Additionally, (1) variable X-ray path lengths owing to topography of the rough samples will lead to different absorption-fluorescence interaction volumes in the unknown and standard; and (2) porosity and microstratigraphy in the *in situ* samples but not in the standards leads to complex X-ray scattering, different effective mass absorption coefficients, and an asymmetric volume of excitation in the unknowns. If the analytic program compares the X-ray beam return affected by surface scattering to the beam return from a polished standard, the resulting concentrations will be inaccurate—sometimes more and sometimes less than the real concentration in the sample, depending on whether the beam scattering and the variable X-ray paths focus more X-rays at the detector or disperse them so that fewer reach the detector. If one uses such data to calculate a cation ratio, the resulting ratio will also be inaccurate, commonly differing from the true ratio by a greater degree than the inaccuracies in individual elemental concentrations.

In contrast, the scanning electron microscope (SEM) varnish analyses of Harrington and Whitney (1987), as well as those in Whitney and Harrington (1993), used a software program called SSQ (standardless semiquantitative) that uses elemental peak intensities (by integrating the area under the peak) to calculate elemental concentrations. The cation ratios they calculate are the ratios of these peak intensities. Because the cation ratio is a ratio determined from fluorescent emissions in a narrow energy range ($KK\alpha$ = 3.31 keV; $CaK\alpha$ = 3.69 keV; $TiK\alpha$ = 4.51 keV; $BaL\alpha$ = 4.47 keV), the effect of X-ray beam scattering and variable X-ray path lengths is similar for all the ratioed elements. Most importantly, as noted in our methodology paper (Harrington and Whitney, 1987), the concentration of individual elements may not be very accurate; however, the ratio among elements is accurate.

4. Bierman and Gillespie examined trends only in a three-element [(K+Ca)/Ti] cation ratio, although all earlier cation-ratio dating curves were calibrated using four-element ratios that included barium.

We believe it is inappropriate to compare three-element cation ratios derived with software programs that deconvolute peak overlaps and do not include Ba with earlier data generated by programs that do not deconvolute peak overlaps and therefore do incorporate Ba into the cation ratio calculated. We find it puzzling, especially in light of the acceptance by Bierman and Gillespie (1991) of the inclusion of Ba in earlier calibrated cation ratio curves, that they made no attempt to evaluate the role of barium in their present varnish study.

Harrington and others (1989) noted the presence of Ba in rock varnishes from Nevada and commented on the mismeasurement of part of this Ba as Ti in all earlier analyses of rock varnish that were made using analytical software (such as the SSQ program) that did not perform deconvolution of elemental peak overlaps. Harrington and others (1991) further noted that if elemental peaks were not deconvoluted, about a third of the Ba would be included as Ti. Thus, the cation ratio used to calibrate the cation ratio curves of Harrington and Whitney (1987), and Dethier and others (1988) is (Ca+K)/Ti+~1/3Ba) instead of (Ca+K)/Ti as originally published.

Bierman and Gillespie (1991) also recognized that all earlier calibrated rock varnish curves include Ba as a component in the calculated cation ratios, and they cite the work of Bard (1979), who suggested that the only element in varnish to exhibit a trend with varnish age was Ba. Harrington and others (1991) and Bierman and Gillespie (1991) further suggest that the included Ba may contribute to the observed decrease in cation ratios with increasing rock varnish age.

The inability of Bierman and Gillespie to obtain a trend in the three-element cation ratio does not preclude the possibility of a trend in the cation ratio if Ba is included. In fact, their study suggests that Ba may be a significant, if not major, contributor to the decrease in cation ratios with varnish age.

5. Bierman and Gillespie contend that the trend of decreasing cation ratios with increasing varnish age is produced by the reduced incorporation of rock substrate into the varnish analyses.

Bierman and Gillespie (1994) and Reneau and Raymond (1991) suggest that the trend of decreasing cation ratios with increasing varnish age may be an artifact of incorporation of rock substrate in the varnish analysis. According to Reneau and Raymond, greater amounts of substrate are incorporated into analysis of young, thin varnishes and result in higher cation ratios; lower cation ratios then result from analyses of older, thicker varnishes which incorporate lesser amounts of substrate.

The analytic procedure of Harrington and Whitney (1987) does not support this hypothesis. In this procedure, an *in situ* varnish analysis was run at 15 keV and then at greater energy in 5 keV increments, which deepen the beam penetration in association with the larger volume analyzed, until the maximum Mn concentration was reached (Mn is only a trace or minor constituent in the rock substrates commonly used in varnish studies). The calculated cation ratio selected as representative of a particular analytic site was the lowest that occurred at or before the peak Mn concentration was reached.

If incorporation of substrate into the volume of material being analyzed played a role in producing a decreasing trend in cation ratios from older varnishes, then each increase in the energy level (e.g., from 15 to 20 keV) during analysis, resulting in greater depth penetration of the electron beam, should also result in a greater volume of substrate being included in the analysis, with an attendant decrease in Mn concentration. By using the maximum Mn concentration as the cutoff point for cation ratio selection, we preclude the inclusion of greater quantities of substrate as energy levels are increased. Therefore, substrate inclusion is not a major determinant of calculated cation ratios.

DISCUSSION

We believe that most cherts and other siliceous rock types that exhibit very smooth surfaces are poor candidates for varnish cation-ratio dating. The variety of rock varnish preserved on Death Valley alluvial fans clearly shows that cation-ratio analyses on different rock types would yield radically different results. We do not discard the technique because some rock types are poor hosts for, or do not preserve, rock varnish. Indeed, we urge extreme caution in sampling. Several different rock types on geomorphic surfaces of different ages should be tested before selecting samples for cation ratio analysis.

Varnish cation-ratio dating is a calibrated technique. Nearly all published studies that report varnish cation ratios used as a dating tool have first demonstrated that cation ratios do decrease with increasing age of the exposed surface. These reported cation-ratio dates depend on varnish cation-ratio curves that are tied to samples dated by other chronometric techniques. Before any rock type is used for varnish cation-ratio dating, investigators must first demonstrate, not assume, that varnish cation ratios change with time on the host rock, especially if that rock type is one that has not previously been used in varnish cation ratio studies. Without independent age assignments for cation ratios determined on clasts from an exposed surface, the usefulness of the technique for a particular region and specific rock type is severely limited.

The systematics of varnish chemistry are still poorly understood. On the basis of our SEM studies, we believe that the explanation of changing cation ratios owing to substrate inclusion is incorrect. The presence of barium, as discussed by Bard (1979), Harrington *et al.* (1991), and Bierman and Gillespie (1991), appears to influence the decrease of cation ratios with varnish age and thickness. The exclusion of barium from cation ratios calculated by Bierman and Gillespie (1994) for the KER-140 site seriously limits the applicability of their results and may, in part, explain the lack of cation-ratio trends in their data.

We urge a careful evaluation of the role of barium in producing the decreasing trend of cation ratios with varnish age that is documented in a number of studies (Harrington and Whitney, 1987, and Dethier *et al.*, 1988). Further, we hope that these evaluations will examine varnish on substrates commonly used in the calibration of rock varnish dating curves. Additionally, we hope that the cation ratios used will include barium, as in previous studies that found a decreasing trend in cation ratios with increasing varnish age.

CONCLUSIONS

The study of site KER-140 has demonstrated that varnish cation-ratio dating is not a reliable method for dating young chert artifacts. Although Bierman and Gillespie may have demonstrated that rock varnish cation-ratio dating is inappropriate for determining the age of late Holocene chert artifacts, we believe the generalization of these results to assert that all cation-ratio dating is unreliable is not warranted by the data presented in their study.

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