

**PROCEEDINGS OF THE  
EIGHTH SYMPOSIUM  
ON THE GEOLOGY  
OF THE BAHAMAS AND  
OTHER CARBONATE REGIONS**

Edited by  
James L. Carew

Production Editors  
Daniel R. Suchy  
Nicole G. Suchy

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**Front Cover:** View to the SSE on White Cay in Grahams Harbour off the north coast of San Salvador, Bahamas. At this spectacularly scenic site one can see that marine erosion has removed the entire windward portion of these early Holocene eolianites (North Point Member, with an alocchem age of ~5000 radiocarbon years B.P.) that were deposited when sea level was at least 2 meters below its present position.

**Back Cover:** Stephen Jay Gould, keynote speaker for this symposium, holds a *Cerion rodregoi* at the Chicago Herald Tribune's 1891 monument to the landfall of Christopher Columbus, which is located on the windward coast of Crab Cay on the eastern side of San Salvador Island, Bahamas. The monument consists of an obelisk constructed from local limestone which houses a carved rock sphere depicting the globe with the continents. The inscription carved in a marble slab, reads: "On this spot, Christopher Columbus first set foot upon the soil of the New World."

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# PRECISION OF AMINO ACID EPIMERIZATION ANALYSES OF FOSSIL TERRESTRIAL LAND SNAIL *CERION*, WITH IMPLICATIONS FOR AMINOSTRATIGRAPHY OF LATE QUATERNARY EOLIANITES AT SAN SALVADOR ISLAND, BAHAMAS

June E. Mirecki and James L. Carew  
Department of Geology  
University of Charleston  
Charleston, SC 29424

## ABSTRACT

Amino acid epimerization (allo-Isoleucine/Isoleucine; or AILE/ILE) values of hydrolyzed protein from fossil mollusc shell carbonate have been used by several researchers to attempt to correlate strata of similar age and temperature history, and to distinguish those strata deposited during successive Quaternary glacial-interglacial cycles on San Salvador Island, Bahamas. The results of these investigations are contradictory regarding: 1) analytical reproducibility of AILE/ILE values from *Cerion* fossil shells, and 2) chronostratigraphic interpretations of AILE/ILE values from *Cerion* fossils preserved in carbonate eolianite deposits. Amino acid AILE/ILE values obtained in 1992 (all whole shell *Cerion*, N = 19; Mirecki et al., 1993) are supplemented by new analyses (all adult apertural lip of *Cerion*; N = 38) to test the following hypotheses: 1) that use of only the adult apertural lip of adult *Cerion* (compared to whole shell) for amino acid analysis will enhance analytical precision of fossil data sets, 2) that AILE/ILE values from the apertural lip of the mollusc fossils have sufficient precision to enable aminostratigraphic correlation among outcrops of similar age on San Salvador, and 3) that AILE/ILE values that define each aminozone have the precision to distinguish units deposited during substages of oxygen isotope Stage 5.

## INTRODUCTION

San Salvador Island, Bahamas (Figure 1) is a tectonically stable, slowly isostatically subsiding carbonate bank, as interpreted from geomorphic and geologic evidence (Carew and Mylroie, 1995a, b). The surficial geology of

this island, and most Bahamian islands, consists largely of terrestrial eolianite deposits. At several places on San Salvador, outcrops consist of upper and lower cross-bedded units intercalated with a weakly developed soil (protosol), and capped by a terra rossa paleosol (Figure 2). Fossil terrestrial land snails (*Cerion*) often are preserved within the upper unit and paleosol, and the protosol. Amino acid AILE/ILE values obtained from *Cerion* fossils were used by several researchers to correlate outcrops representing a single glacial-interglacial cycle on San Salvador, and elsewhere in the Bahamas (e. g., Carew and Mylroie, 1995 a, c; Hearty et al., 1993). If AILE/ILE values are calibrated by an independent radiometric dating method, fossil-bearing sequences characterized by increasing AILE/ILE values in stratigraphic superposition can be interpreted in the context of numerical age (e. g., Wehmiller et al., 1988; 1992; Mirecki and Miller, 1994; Mirecki et al., 1995, Oches and McCoy, 1995). Unfortunately, a consensus has not been reached among researchers regarding the utility of amino acid methods at the San Salvador exposures despite (or possibly because of) the use of different amino acid laboratories and sample matrices (e. g., Mirecki et al., 1993; Hearty and Kindler, 1993, 1994; Carew and Mylroie, 1995 a, c). This conflict results, in part, from the lack of consensus on criteria for the evaluation of amino acid data. Criteria for the evaluation of our amino acid data sets are defined based on field, sample, and instrumental features. An analysis of instrumental precision of fossil mollusc and standard powder analyses was determined for the period 1990 through 1995. Once the level of precision of our amino acid data set is established, the utility of aminostratigraphic methods in fossil-bearing Quaternary

# SAN SALVADOR, THE BAHAMAS

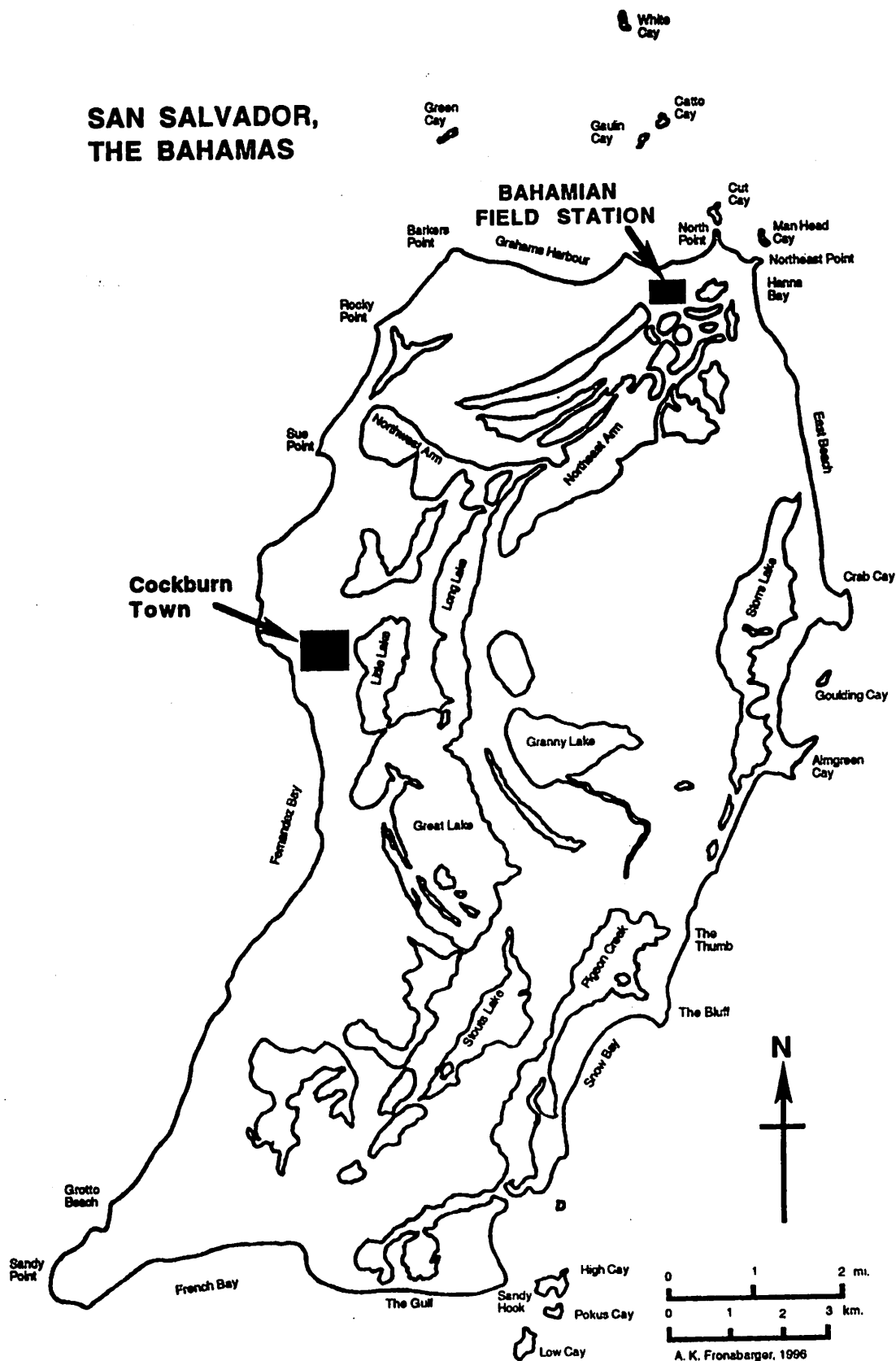


Figure 1. Map of San Salvador Island, Bahamas showing the locations of sites mentioned in the text.

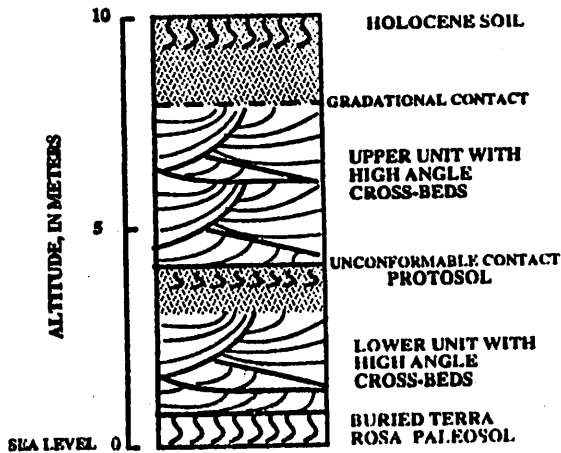


Figure 2. Composite generalized section of a depositional sequence observed in outcrops at Man Head Cay, Crab Cay, Almgreen Cay, The Bluff; and seen in part at The Gulf.

eolianites on San Salvador are evaluated.

#### CRITERIA FOR EVALUATION OF AMINO ACID AILE/ILE VALUES

Physical stratigraphic, sample, and instrumental criteria serve as guidelines for the evaluation of AILE/ILE values, and these have been defined by several researchers (Table 1; Murray-Wallace and Kimber, 1987; Miller and Brigham-Grette, 1989; Walker, 1992; Wehmiller, 1993). Precision of AILE/ILE data can be evaluated qualitatively in the context of field setting and fossil sample quality; for example, spurious AILE/ILE could conceivably be eliminated from the data set if reworking of the shell is indicated, or if those fossil molluscs are poorly preserved. Quantitative estimates of precision are used routinely by most amino acid laboratories, to define variation in AILE/ILE values obtained over a few years time. Instrumental criteria described in Table 1 are used by JEM at her laboratories at the University of Memphis (1989-1994) at the University of Charleston (1994-present).

##### Field Precision

To enable correlation and fine temporal resolution of AILE/ILE values from terrestrial deposits, mollusc fossils must be contemporaneous with enclosing sediment, and without reworking. Detection of reworked

*Cerion* specimens is difficult because the mollusc species present today are, especially on San Salvador, identical to species present during the late Pleistocene (Clench, 1957; Gould and Woodruff, 1978; Gould, this volume). Fossil gastropods can be reworked by wind, wave, and tidal action, or transported and reburied by hermit crabs (Walker, 1992). Physical processes related to soil formation in carbonate parent material, including dissolution and bioturbation in soil horizons A through C, may result in rearrangement of fossils and degradation of the temporal resolution of AILE/ILE values.

Correlation of eolianite deposits on San Salvador usually requires recognition of a suite of characteristics held in common by some eolianite outcrops (Figure 2). Eolianite deposits on San Salvador represent episodes of dune activity and soil formation laterally adjacent to marine deposition. The specific outcrops discussed in the aminostratigraphic correlation section of this work (Man Head Cay, Crab Cay, Almgreen Cay, The Bluff, and The Gulf) are correlated on the basis of similar geomorphic and lithostratigraphic characteristics, and similar position relative to modern sea level. Although eolianite sequences may be incomplete at some outcrops, we assume that these eolianites, which outcrop at or near (usually within 5 m) present sea level, were deposited during oxygen isotope stage 5. Faulting or differential uplift has not affected the altitude of the late Quaternary shoreline at San Salvador. These outcrops are interpreted as having been deposited during regression at the end of oxygen isotope substage 5e (~119 ka) by Carew and Mylroie (1995a), or as the result of deposition during oxygen isotope substage 5a (~85 ka) by Hearty and Kindler (1993). *Cerion* fossils have been found throughout these eolianite sequences, but the majority are found in the protosol and near the top of the eolianite sedimentary package. All shells used in our analyses were collected from within the matrix, and appeared pristine; that is, they exhibited no signs of reworking or contamination (e. g., algal or cyano-bacterial infestation).

##### Sample Precision

To improve the precision of fossil

TABLE 1. Criteria for the evaluation of amino acid AILE/ILE values.

CRITERIA FOR ACCEPTANCE OF AMINO ACID DATA		
PRECISION	PROBLEM	
PHYSICAL STRATIGRAPHIC	Is the sample reworked?	Sequence shows increasing AILE/ILE with increasing stratigraphic age, consistent with the laws of superposition. Trend in AILE/ILE values is shown by several molluscan genera.
		Fossils show characteristics of in-situ burial: articulated valves, presence of a hinge ligament or operculum; absence of sedimentary structures indicating wind and wave action; absence of abrasion, pitting, breakage of fossil specimen.
SAMPLE	Has the fossil been heated during burial?	Samples collected at the surface show the same AILE/ILE value as buried (1 m) samples (otherwise, avoid surficial samples).
	Is the fossil representative of an aminozone?	Low (<15%) coefficient of variation of AILE/ILE values obtained from at least 3 separate specimens of from a mollusc genus from a single stratigraphic unit.
	Are the fossils from a single mollusc genus?	Low (<15%) coefficient of variation of AILE/ILE values obtained from at least 3 separate specimens of a mollusc genus from a single stratigraphic unit.
INSTRUMENTAL	Is the same portion of the fossil used for analysis?	Low (<15%) coefficient of variation of AILE/ILE values obtained from the same morphologic portion of the shell from at least 3 separate specimens.
	Are multiple chromatograms from a single sample reproducible?	Low (<5%) coefficient of variation of AILE/ILE values obtained from multiple HPLC chromatograms of ILC standard powders run on a single day with each batch of fossil shells.
	Are Allo-Isoleucine and Isoleucine peaks well-resolved?	Peak area/height ratios (on chromatogram output) less than 0.8 for Allo-Isoleucine, Isoleucine and Leucine. All peaks resolved to baseline.
	Are AILE/ILE values calculated from peak area and peak height reproducible?	AILE/ILE values calculated from peak area and peak height values on a single chromatogram usually differ. AILE/ILE peak height values usually are greater than AILE/ILE peak area values, but there should be a linear relationship between peak area and peak height values from a single chromatogram, over a wide range of AILE/ILE values.

analyses, we changed our sampling procedure between the 1992 and 1995 data sets. In the 1992 data set, approximately half of a *Cerion* shell, extending from the apex to the base of the columella was used (Figure 3). Each mollusc sample was cleaned mechanically, inside and out, with a dremel tool to remove carbonate encrustation and the outer prismatic layer of the shell. Samples were then chemically cleaned in a sequence of dilute (2M) hydrochloric acid, deionized water, 7M ammonium hydroxide, and deionized water. It has been shown that consistent sampling of a single morphologic region of a shell will lead to greater precision of AILE/ILE values (Brigham, 1983). So, for our 1995 data set, only the adult apertural lip of each *Cerion* fossil was used (Figure 3). Each subsample was ultrasonicated, then rinsed twice in the acid and base solution sequence. Lab gloves were worn during the entire cleaning procedure. Because apertural lip sample masses were small (less than 40 mg), all hydrolyses were performed in ultraclean (nitric acid wash, deionized water rinse, 250° C for 24 hr) 2 ml conical, screw-top glass vials. Replicate HPLC (high pressure liquid chromatography) analyses were conducted by manual injection of 50 µL sample volumes. Routine sample preparation and HPLC analytical methods are described in Mirecki (1990).

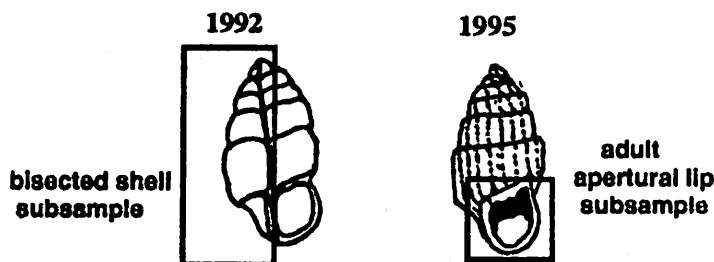


Figure 3. Illustration showing sampling method for *Cerion* mollusc fossils. In the 1992 data set, approximately one-half of a cleaned specimen was prepared; in the 1995 data set, only the adult apertural lip was prepared for amino acid analysis.

To determine whether a data set lacks, or maintains, high sample precision requires a population of data that is large enough to attempt statistical testing. Previous work of Mirecki (1990) analyzed AILE/ILE values

from as many as 30 separate mollusc fossils to define an aminozone within a single lithologic unit. At present, no one has attempted to define a single aminozone on San Salvador, or elsewhere in the Bahamas, using a large (N=30, where N = number of fossils) sample population. However, the combined 1992 and 1995 data set (Table 2) shows the greatest number of fossil sample analyses for any Bahamian site published thus far. Each fossil mollusc was analyzed at least twice (n=2, where n= number of chromatograms) by HPLC to calculate the mean sample AILE/ILE value. The mean AILE/ILE value that defines a lithologic unit (or aminozone) is compiled from all sample mean AILE/ILE values. Mean AILE/ILE values from a single lithologic unit are defined using data from 2 to 8 separate molluscs. Analytical data presented here (Table 2) were obtained from *Cerion* collected from 10 Pleistocene (Stage 5) outcrop sites (N = 39), 6 of which are characterized by 3 or more fossil individuals; and 4 Holocene/Modern sites (N = 11), for a total of 50 separate *Cerion* sample preparations.

#### Instrumental Precision

Confirmation of instrumental precision is perhaps the most readily quantified variable of amino acid analyses, especially when standard mollusc powders (Wehmiller, 1984) having a known AILE/ILE value are run consistently with fossil mollusc samples. The ILC-B standard powder has been run by HPLC along with fossil mollusc samples in all work performed by the analyst (JEM) since 1986, and these data are published with their respective fossil analyses so that anyone can check the reproducibility of our amino acid analyses over time (Mirecki, 1990; Mirecki and Miller, 1994; Mirecki et al., 1995; Karrow et al., 1997). Unfortunately, no standards data have been published by Hearty and colleagues for any of these Bahamian data (e. g., Hearty and Kindler, 1993, 1994, 1995; Hearty et al., 1993; Kindler and Hearty, 1995), so it is not possible to assess the precision of their analyses. AILE/ILE values from ILC-B total hydrolyzate powder analyses run between 1990 and 1995 have been compiled to estimate the degree of precision that can be expected during routine HPLC operation. These data

**TABLE 2.** Summary of mean amino acid epimerization (Allo-Isoleucine/Isoleucine, AILE/ILE) values in total hydrolyzate samples from *Cerion*, San Salvador, Bahamas. Amino acid values are listed as Mean +/- Standard Deviation (n), where n=number of chromatograms for each *Cerion* sample. Each lab number represents a single mollusc specimen from which several runs (chromatograms) were made. Analyses run in 1992 used the whole shell (minus outer prismatic layer); analyses run in 1995 were from only the adult apertural lip of the *Cerion* specimen.

Lab No.	Run Date	Aile/Ile peak area	Aile/Ile peak height	Locality
<b>AILE/ILE values from <i>Cerion</i> collected from Stage 5 sites identified in the text</b>				
92013	1/92	0.32 +/- 0.04 (2)	0.36 +/- 0.00 (2)	Gulf (upper)
92026	4/92	0.61 +/- 0.03 (2)	0.74 +/- 0.04 (2)	Gulf (upper)
92040	4/92	0.41 +/- 0.03 (3)	0.46 +/- 0.06 (2)	Gulf (upper)
95007	2/95	0.75 +/- 0.01 (2)	0.79 +/- 0.03 (2)	Gulf (upper)
95008	2/95	0.48 +/- 0.05 (6)	0.53 +/- 0.07 (6)	Gulf (upper)
95018	3/95	0.50 +/- 0.03 (4)	0.57 +/- 0.02 (4)	Gulf (upper)
95020	3/95	0.49 +/- 0.05 (3)	0.57 +/- 0.07 (3)	Gulf (upper)
95029	6/95	0.30 +/- 0.01 (3)	0.35 +/- 0.02 (3)	Gulf (upper)
95021	3/95	0.17 +/- 0.01 (4)	0.21 +/- 0.03 (4)	Gulf (protosol)
95034	6/95	0.56 +/- 0.01 (3)	0.67 +/- 0.01 (3)	Crab Cay (upper)
95035	6/95	0.09 +/- 0.00 (3)	no data <sup>1</sup>	Crab Cay (upper)
95043	6/95	0.88 +/- 0.04 (3)	0.86 +/- 0.04 (3)	Crab Cay (upper)
92029	4/92	0.93 +/- 0.01 (2)	1.00 +/- 0.00 (2)	Crab Cay (protosol)
92041	4/92	0.67 +/- 0.05 (2)	0.73 +/- 0.05 (2)	Crab Cay (protosol)
92030	4/92	0.63 +/- 0.00 (2)	0.69 +/- 0.01 (2)	Man Head (protosol)
95016	3/95	0.44 +/- 0.02 (3)	0.52 +/- 0.01 (3)	Man Head (protosol)
95026	6/95	0.54 +/- 0.03 (3)	0.55 +/- 0.02 (3)	Man Head (protosol)
95030	6/95	0.53 +/- 0.00 (3)	0.63 +/- 0.03 (3)	Man Head (protosol)
95032	6/95	0.57 +/- 0.03 (3)	0.67 +/- 0.02 (3)	Man Head (protosol)
95039	6/95	0.55 +/- 0.02 (3)	0.60 +/- 0.02 (3)	Man Head (protosol)
92028	4/92	0.65 +/- 0.01 (2)	0.68 +/- 0.04 (2)	Almgreen (protosol)
95017	3/95	0.11 +/- 0.02 (2)	0.10 (1)	Almgreen (protosol)
92027	4/92	0.61 +/- 0.03 (2)	0.74 +/- 0.04 (2)	Bluff (protosol)
95015	3/95	0.36 +/- 0.02 (2)	0.43 +/- 0.05 (3)	Bluff (protosol)
<b>AILE/ILE values from <i>Cerion</i> collected from other Stage 5 sites</b>				
92031	4/92	0.64 +/- 0.02 (2)	0.74 +/- 0.00 (2)	Watlings Quarry
95009	2/95	0.55 +/- 0.04 (2)	0.60 +/- 0.05 (4)	Watlings Quarry
95013	3/95	0.46 +/- 0.01 (2)	0.44 +/- 0.06 (3)	Watlings Quarry
95019	3/95	0.41 +/- 0.02 (3)	0.49 +/- 0.04 (3)	Watlings Quarry
95027	6/95	0.55 +/- 0.02 (3)	0.61 +/- 0.02 (3)	Watlings Quarry
95028	6/95	0.55 +/- 0.02 (3)	0.61 +/- 0.02 (3)	Watlings Quarry
92011	1/92	0.50 +/- 0.05 (3)	0.62 +/- 0.06 (3)	Altar Rd. Cut
95044	6/95	0.36 +/- 0.03 (3)	0.39 +/- 0.01 (3)	Altar Rd. Cut
95045	6/95	0.46 +/- 0.01 (3)	0.52 +/- 0.00 (3)	Altar Rd. Cut
95046	6/95	0.31 +/- 0.01 (3)	0.36 +/- 0.01 (3)	Altar Rd. Cut
95047	6/95	0.50 +/- 0.02 (3)	0.56 +/- 0.02 (3)	Altar Rd. Cut



TABLE 2, continued

Lab No.	Run Date	Alle/Ile peak area	Alle/Ile peak height	Locality
92025	4/92	0.45 +/- 0.01 (2)	0.50 +/- 0.00 (2)	Sandy Point
95031	6/95	0.26 +/- 0.02 (3)	0.24 +/- 0.01 (3)	Sandy Point
95033	6/95	0.47 +/- 0.01 (3)	0.56 +/- 0.02 (3)	Sandy Point
95038	6/95	0.63 +/- 0.01 (3)	0.69 +/- 0.04 (3)	Sandy Point
<b>AILE/ILE values from <i>Cerion</i> collected from Modern and Holocene sites</b>				
95010	2/95	0.04 +/- 0.00 (2)	0.04 +/- 0.00 (3)	Bluff (Modern)
95040	6/95	0.02 +/- 0.01 (2)	0.03 +/- 0.00 (2)	Bluff (Modern)
95006	2/95	0.03 +/- 0.00 (2)	0.04 +/- 0.00 (2)	Pigeon Creek (Modern)
95042	6/95	0.02 +/- 0.00 (2)	0.03 +/- 0.01 (2)	Pigeon Creek (Modern)
95001	2/95	--- <sup>2</sup>	0.05 +/- 0.01 (4)	North Point (Holocene)
95004	2/95	0.08 +/- 0.01 (3)	0.11 +/- 0.01 (3)	North Point (Holocene)
95041	6/95	0.09 +/- 0.02 (2)	0.11 +/- 0.02 (2)	North Point (Holocene)
92033	4/92	0.06 +/- 0.01 (2)	0.09 +/- 0.01 (2)	North Point (Holocene)
95002	2/95	0.06 +/- 0.01 (2)	0.08 +/- 0.01 (3)	East Beach (Holocene)
95005	2/95	0.06 +/- 0.00 (2)	0.07 +/- 0.01 (2)	East Beach (Holocene)
95014	2/95	0.08 +/- 0.01 (2)	0.09 +/- 0.01 (2)	East Beach (Holocene)

<sup>1</sup>Alle/Ile peak height values are not reported because isoleucine peaks were off scale.

<sup>2</sup>Alle peak too small to integrate.

were run primarily by JEM at the University of Memphis and the University of Charleston, but also include analyses by students. Because ILC-B standard samples are run as a diagnostic to determine chromatographic resolution during daily operation, AILE/ILE values from some samples are extreme and probably result from less-than-acceptable column performance. Therefore, this compilation of standard data represents a "worst case" estimate of precision, taken over 5 years of laboratory operation. The %CV for AILE/ILE values calculated from peak area measurements of ILC-B standard analyses is 10.0%. The %CV for AILE/ILE values calculated from peak height measurements of ILC-B standard analyses is 12.9% (Figure 4). Thus, an analyst should expect a minimum level of precision ranging from 10 -15 % about the mean sample AILE/ILE value, if that sample was run during an extended period of analysis. Replicate analyses of the ILC-B standard accompanying the 1992 and 1995 San Salvador analyses show %CV from 9-18 %. Poorer

precision usually occurs with the analysis of young (modern or Holocene) samples that have low allo-isoleucine concentrations, because it is difficult to integrate a small peak (Meyer, 1995a). Daily instrumental precision is somewhat better, and can be estimated by calculating the %CV in AILE/ILE values from a single sample that was run several times during a day. Typically, daily %CVs are low (2-5%) using AILE/ILE values calculated from peak area and peak height.

#### Comparison of AILE/ILE Values Calculated Using Peak Area and Peak Height Measurements

Amino acid laboratories do not use the same method to calculate AILE/ILE value from a chromatogram. Although AILE/ILE values from a single laboratory may show a high degree of internal consistency, it is difficult to compare data among laboratories because of the following factors: 1) differences in HPLC analytical methodology

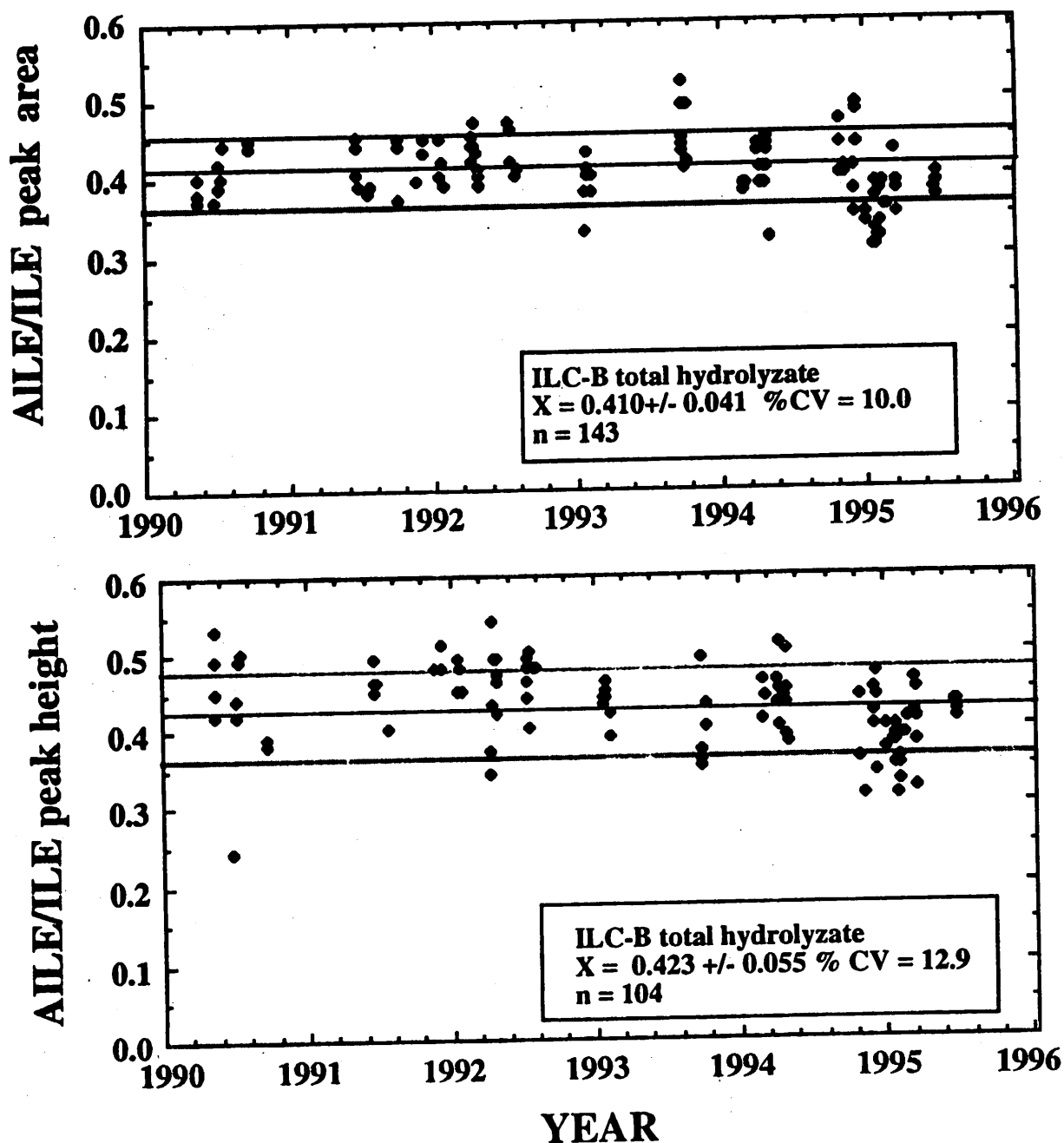


Figure 4. AILE/ILE values calculated using peak area (top) and peak height (bottom) measurements from HPLC analysis of the ILC-B standard (Wehmiller, 1984), run at the University of Memphis (1989-1994) and the University of Charleston (1994-present).

(Wehmiller, 1984), 2) differences in peak integration method (Meyer, 1995a, b), and 3) calculation of AILE/ILE from peak area versus peak height output from an integrator. Data comparison is especially difficult if fossil AILE/ILE values are not reported relative to a widely available standard sample (such as the common use of the Pee Dee belemnite standard

for standardizing stable oxygen and carbon isotope data).

Standardization of amino acid analytical and interpretation methods among practicing laboratories is a distant goal. However, to facilitate comparison of data produced in the University of Charleston laboratory with those of other laboratories,

AILE/ILE values are reported as calculated using both peak area integrator output and peak height measurements. Chromatographic peak areas are integrated using an HP3396A integrator. Peak area integration is calculated using the "valley-to-valley" method, rather than using the vertical drop method, although differences in integration method should result only when peaks are not resolved to baseline. Greatest reproducibility results when allo-isoleucine, isoleucine, and leucine peaks are resolved to baseline. Peak heights are measured from a baseline drawn from valley tick-marks on the chromatogram. A sample chromatogram is shown in Figure 5.

#### EVALUATION OF AMINO ACID AILE/ILE VALUES FROM FOSSIL *CERION*

Amino acid data from the 1992 (Mirecki et al., 1993) and 1995 San Salvador data sets are tabulated (Table 2) and interpreted to test the following hypotheses: 1) that use of the apertural lip of *Cerion* (compared to whole shell) for amino acid analysis will enhance precision of the analyses, 2) that amino acid analyses from the apertural lip portions of mollusc specimens have sufficient precision to enable aminostratigraphic correlation among outcrops on San Salvador; and 3) the precision of these amino acid analyses is capable of resolving units deposited during substages of oxygen isotope Stage 5.

#### Precision of Apertural Lip Samples

Comparison of mean AILE/ILE values from 1992 (N=3 mollusc samples; Table 2) with 1995 (N=5) data sets from a single site (The Gulf) showed no improvement in analytical precision with the use of the apertural lip for analysis. However, %CVs were large (25-35 % for both 1992 and 1995 data sets), which suggests that factors other than sample precision are responsible for AILE/ILE variation. Despite the apparently pristine outward appearance, undetected poor sample integrity, leaching, and reworking may contribute to the high %CVs at The Gulf and other sites. Because previous work (Brigham, 1983) indicates greater precision of AILE/ILE

values when a subsample of mollusc shell is used consistently, we agree with Hearty and Kindler (1994) that use of only the *Cerion* apertural lip for analyses is preferable. However, use of the apertural lip in the 1995 San Salvador data set did not improve the precision of AILE/ILE values for the aminozone analyzed.

#### Aminostratigraphic Correlation of Specific Outcrops Near Sea Level

Aminostratigraphy is the method of correlation among outcrops of similar age and temperature history, based on the similarity of AILE/ILE values. At San Salvador, the feasibility of aminostratigraphic methods is tested using AILE/ILE values from five sites on the eastern and southeastern coast: Man Head Cay, Crab Cay, Almgreen Cay, The Bluff, and The Gulf. These outcrops show similar geologic and geomorphic characteristics suggesting that they represent deposition during a single glacial-interglacial cycle. Because fossil AILE/ILE values are most numerous from the protosol facies, and because those deposits probably represent a short interval of time (see discussion in Carew and Mylroie, 1995a), only those values will be considered for the hypothesis test.

Fossil *Cerion* preserved in the protosol at each outcrop showed the following mean AILE/ILE peak area values (N = number of molluscs analyzed): Man Head Cay, 0.54+/-0.06 (%CV=10.3, N=6); Crab Cay, 0.80+/-0.18 (%CV=23, N=2); Almgreen Cay with 2 molluscs showing widely differing AILE/ILE values (0.11, 0.65); The Bluff with 2 molluscs showing widely differing AILE/ILE values (0.36, 0.61); The Gulf, with a single mollusc AILE/ILE value of 0.17. AILE/ILE peak height values show similarly large %CVs. Variation in AILE/ILE peak-area and peak-height values measured in individuals collected from the protosol (%CV ranges from 10 to >23%) exceed variation of mollusc shell powder ILC-B during the period 1990-1995 (10-13%). Therefore, the large variation in AILE/ILE values of San Salvador *Cerion* fossils analyzed by JEM cannot be attributed to instrumental factors or lab technique, as alleged in Hearty and Kindler (1994). Other factors, including reworking

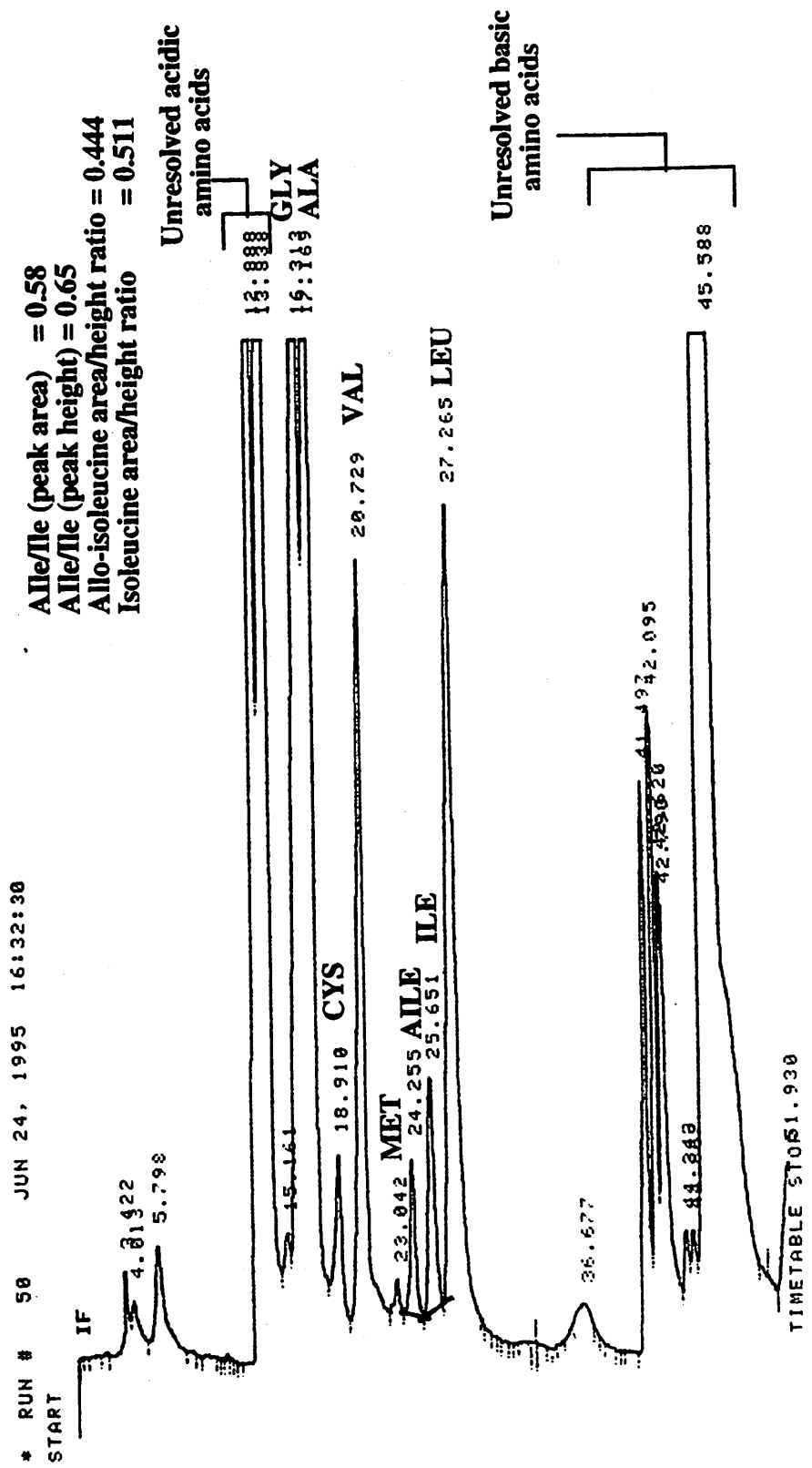


Figure 5. Typical HPLC chromatogram from Cerion total hydrolyzate 95032 (fossil sample SS95T-27; protocol, Man Head Cay). Resolved amino acid peaks are labeled: CYS - cysteine; VAL - valine; MET - methionine; AILE - alloisoleucine; ILE - isoleucine; LEU - leucine. The number at each peak is the retention time. This chromatogram was obtained on a HP3396A integrator using the valley-to-valley integration method, and was not enhanced or edited after scanning.

and diagenesis on the microstructural scale must be considered as the causes of variation in this large amino acid data set. Furthermore, previous statements of high precision of the San Salvador amino acid data should be tempered by the fact that in those studies only a few molluscs were analyzed from each outcrop (16 fossils from 5 outcrops, each fossil analyzed 1 or 3 times; Kindler and Harty, 1994). The large %CV of AILE/ILE values presented here for most sites (Table 2) precludes specific aminostratigraphic correlation among different Pleistocene outcrops on San Salvador.

Holocene and modern *Cerion* molluscs were also analyzed to compare with AILE/ILE values with fossils. Modern specimens collected from the land surface should show AILE/ILE values that reflect epimerization resulting from surficial heating. Typically, modern AILE/ILE values generally are <0.03. Modern specimens collected from The Bluff and Pigeon Creek localities show these typical AILE/ILE values (Table 2). Holocene subfossil molluscs should begin to show the effects of diagenetic hydrolysis and epimerization, marked by increased allo-isoleucine concentrations and AILE/ILE values. *Cerion* collected from Holocene protosols at the North Point and East Beach localities, do show slightly higher AILE/ILE values than those of Modern *Cerion* (Table 2). Thus, it is possible to distinguish between Pleistocene, Holocene subfossil, and modern *Cerion* individuals using AILE/ILE values, which may be important in support of other paleontologic investigations (e. g., Goodfriend and Gould, 1996).

## CONCLUSIONS

Amino acid AILE/ILE values were measured in a large (N=50) number of individual fossils outcropping in eolianite deposits at San Salvador to test the hypotheses: 1) that use of the apertural lip of *Cerion* (compared to whole shell) for amino acid analysis will enhance precision of the analyses; 2) that amino acid analyses from the apertural lip portions of mollusc specimens have sufficient precision to enable aminostratigraphic correlation among Pleistocene outcrops on San Salvador; and 3)

the precision of these amino acid analyses are capable of resolving units deposited during different substages of oxygen isotope Stage 5.

Use of the apertural lip of *Cerion* specimens did not increase the precision of AILE/ILE values, as tested using fossil molluscs analyzed in 1992 (whole shell) versus 1995 (apertural lip) from specimens collected at The Gulf locality. However, previous work indicates that uniform sampling of any mollusc fossil will eliminate variation due to intrashell differences in amino acid content. Therefore, apertural lip samples are the preferred subsamples for use in amino acid analyses.

AILE/ILE peak area and peak height values from fossils collected at 5 similar outcrops at or near sea level show high %CVs (10 to >23%). The precision of fossil analyses is lower than that of the ILC-B mollusc powder standard (%CV 10-13%) run by JEM from 1990 through 1995, which indicates that instrumental factors are not the dominant source of AILE/ILE value variation. The precision shown by the San Salvador fossil data is not sufficient for aminostratigraphic correlation. It is likely that reworking and fossil diagenesis on the microstructural scale are, at least in part, responsible for the lack of analytical precision. We are studying this possibility, but as yet these effects have not been characterized in fossil *Cerion*.

Until it can be shown that fossil *Cerion* from within a single lithologic unit can yield AILE/ILE values of sufficient precision (%CV<20, similar to that of ILC powders) for a large number of samples, it is not possible to apply these data for aminostratigraphic correlation among units from a single glacial-interglacial cycle, much less to discriminate units deposited within oxygen isotope stage 5.

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