AMINOSTRATIGRAPHY OF THE PLIO-PLEISTOCENE OF FLORIDA

by

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of the requirements for the degree of
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INTRODUCTION

During the Mesozoic and Cenozoic Eras, shallow marine waters and a tropical climate regime dominated the Florida Platform, resulting in the production of carbonate sediments. As sea level fluctuated during the Pliocene and Pleistocene epochs, the geomorphology of Florida was shaped and modified as carbonate and siliciclastic sediments were deposited, reworked and eroded. Evidence of sea level fluctuations is recorded in terraces and low-lying sedimentary deposits. Biostratigraphic and topographic studies have interpreted features such as upland terraces as relict shorelines (Scott 1992; MacNeil 1950). Despite numerous attempts to date and correlate Pleistocene deposits in Florida, the numerical ages of these sediments is poorly constrained. Consequently, further analysis is required for an understanding of the timing of sea level change during the Pleistocene.

Dating methods such as ^{14}C, Uranium decay series, magnetostratigraphy and biostratigraphy have been employed for years with little success in attempt to unravel the chronology of Florida's Pleistocene history (Jones 1992). However, these methods have limitations or may not be applicable to older carbonate materials found in Florida. Amino acid geochronology offers an alternative method when other techniques are inconclusive, inapplicable or otherwise have failed. Amino acid geochronology is based on the sterochemical inversion, or racemization, of isomeric forms of amino acids.

Aminostratigraphy is the development of a stratigraphic framework based on assemblages of amino acid racemization data collected from marine and freshwater mollusks (Wehmiller 1993).

The prime objective of this study is to establish the aminostratigraphy for the Plio-Pleistocene of the Gulf Coast of Florida by measuring amino acid isomers ratios (D/L ratios) in carbonate fossils. Furthermore, amino acid D/L ratios measured in samples collected from northern and southern localities will be compared to evaluate the effect of latitudinal thermal gradient on racemization. Independent numerical age estimates will be determined by TIMS U-series method performed on corals obtained from the same stratigraphic units as mollusks sampled in this study.

Specific research objectives include:

1. Establish aminostratigraphic ages (mean amino acid D/L ratios) for the Pinecrest Beds, Caloosahatchee, Bermont and Ft. Thompson Formations along the Gulf Coast of Florida.
2. Evaluate the thermal gradient effect on racemization rates.
3. Determine the suitability of different bivalve genera for aminostratigraphic analysis.
4. Address the effects of environmental factors, such as mixing and leaching, that have influenced amino acid racemization data.

Results of this study will help to unravel the geochronology of the Plio-Pliestocene sediments of the Gulf Coast of Florida and will expand the understanding of the aminostratigraphy of the Atlantic Coastal Plain.

AMINO ACID GEOCHRONOLOGY

Amino acid geochronology is a biochemical dating technique used to establish relative age estimates of fossil shells (Wehmiller 2000). Proteins present in all living organisms are made of amino acids that have a specific chemical configuration. These amino acids exist in two isomeric forms that are mirror images of each other (stereoisomers). The L-isomer (laevorotatory) and D-isomer (dextrorotatory) forms characterize isomeric configuration. Initially, amino acids are produced in the L-isomer form during the growth of any organism. However, as amino acids are isolated from living tissue and incorporated into layers of the carbonate shell matrix, they slowly invert to the D-isomer form (Miller and Brigham-Grette 1989).

When an amino acid has one central carbon atom, the conversion to the D-isomer is called racemization. However, when two central carbon atoms exist in the amino acid, inversion occurs around the alpha carbon, and the process is called epimerization (Wehmiller 1993). Racemization and epimerization are illustrated in figure 1. Amino acids addressed in this study that exhibit racemization include aspartic acid, glutamic acid, valine and phenylalanine. Isoleucine, which epimerizes to its D-isomer form alloisoleucine, has been measured extensively in previous investigations

(Wehmiller and Belknap 1982, Wehmiller et al., 1992, Wehmiller et al.,1995, Wehmiller and York 2001, York et al., 2000). Unfortunately, due to inconsistent resolution using reversed phase liquid chromatography, these amino acids pair was not considered in this study.

With increasing time after formation of the carbonate shell matrix, the amount of D-isomer increases with respect to the L-isomer until a D/L equilibrium value of 1.0 is reached for racemization and 1.3 in the epimerization process (Miller and Brigham-Grette1989). Hence, the ratio of D/L isomers is a function of time and can be used as a relative dating technique and, when independently calibrated, can yield numerical age estimates.

Factors that influence racemization include temperature, water availability, pH, metal ions and intermolecular structure (Smith and Evans 1978). However, due to the buffering capacity of the carbonate shell, most of these factors become insignificant while temperature is the dominate factor affecting racemization. Temperature and rate of racemization have a direct relationship resulting in an increased rate of racemization with increased temperatures (Miller and Hare 1978). For example, two specimens of the same age, but from different latitudes, e.g. Alaska and Florida, will reveal different D/L ratios due to different thermal histories (Miller & Brigham-Grette 1989; Wehmiller & Miller 2000). Even within the latitudinal span of the Florida Peninsula, mean annual temperature differences between the north and south may have a measurable influence on D/L ratios across the study area. Because racemization rates are influenced by

these factors, there is no universally applicable upper age limit for this method (Wehmiller & Miller 2000).

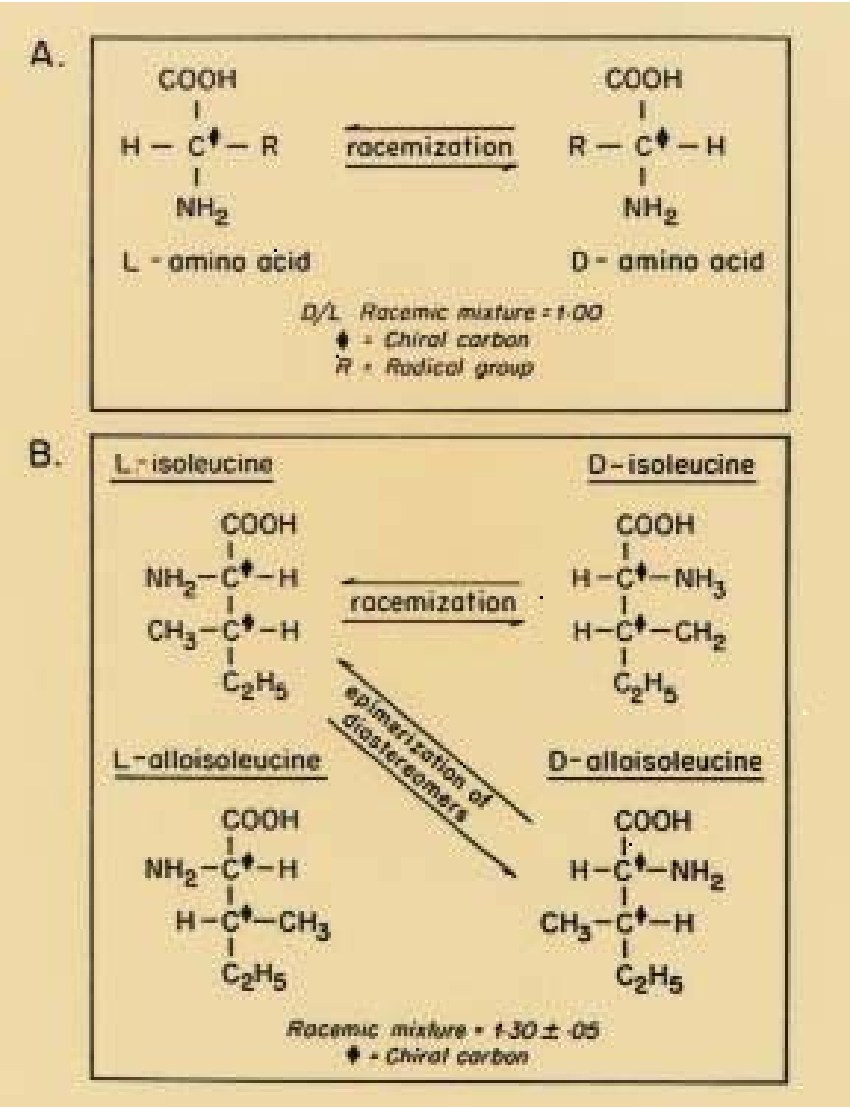


Figure 1. Amino acid racemization. (A) racemization around a chiral carbon (B) epimerization around the alpha carbon (Miller and Brigham-Grette 1989)

The location of an amino acid within the protein chain can also affect the rate of racemization. Amino acids found in the internal structure of the protein and those that

are free from the protein chain racemize slowly compared to amino acids located at the terminal ends of the protein chain, which racemize rapidly (Miller and Brigham-Grette 1989). Furthermore, different amino acid do not exhibit the same rate of racemization, nor do mollusks of different genera. This is due to differences in molecular and protein structures between mollusk genera and chemical configuration of amino acid molecules (Lajoie et al., 1980; Wehmiller & Miller 2000). Additionally, the rate of racemization is not linear. Racemization is initially rapid followed by a sharp decrease in the racemization rate (Wehmiller & Hare 1971).

As mentioned above, amino acid geochronology is a relative dating technique. In order for this method to be numerically calibrated, a numerical dating method, such as Uranium decay series (U-series), should be employed to establish a numerical age estimate.

U-SERIES

Uranium decay series (U-series) refers to the isotopic dating technique that establishes the numerical age of an organism based on the ratio of Thorium (^{230}Th) to Uranium (^{238}U) isotopes (Ku 2000). During growth of a carbonate organism, radioisotopes of Uranium are taken up from seawater and incorporated into the carbonate structure of mollusk shells and coral skeletons. Because the carbonate structure is assumed to act as a closed system, any ^{230}Thorium detected in the carbonate structure is the product of ^{238}Uranium decay. Initially, the amount of thorium in the carbonate or coral structure is essentially zero; however, as uranium decays, the

amount of thorium increases over time. Thus, the ratio of $^{230}Th/^{238}U$ is a function of time and is the basis for this branch of U-series dating (Ku 2000).

The stratigraphic units sampled in this study exceed the time range of other methods such as radiocarbon dating, having with a half-life of 5,730 years (Trumbore 2000). Uranium, on the other hand, has a half-life of 4.5 B.y. and is therefore suitable for this study. U-series dating can be applied to both mollusks and corals. However, corals are better suited for this method as they offer a closed-system, whereas mollusks do not offer a closed-system required for this method. TIMS U-series refers to thermal ionization mass spectrometry method used to measure uranium in carbonate samples for this study. The TIMS method offers a higher degree of measurement precision and uses a smaller sample size (Edwards 1987).

GEOLOGIC SETTING

Geologic History

What we know today as peninsular Florida is a gently sloping feature with an average elevation of 30 meters. Peninsular Florida represents approximately one-half of the Florida Platform while the remaining half is submerged beneath the Gulf of Mexico (Schmidt 1997). The Florida Platform is a thick accumulation of carbonate and siliciclastic sediments deposited over tens of millions of years as a consequence of sea level fluctuation, weathering, erosion and reworking (Scott 1992, Schmidt 1997, Scott 1997). Beneath the carbonate platform lies Florida basement rock correlated with

Paleozoic Gondwana through continental, paleontologic, lithologic and isotopic analysis (Smith and Lord 1997).

In southern and central Florida, carbonate sedimentation was dominant during the mid-Mesozoic. By the early Cenozoic, carbonate sedimentation, with sporadic but minor inputs of siliclastic material, was dominant over the entire platform (Scott 1992). Major siliciclastic deposition was blocked during that time due to the presence of the Suwannee Straits. The Suwannee Straits was a trough-like feature in northern Florida that essentially isolated the Florida Platform from siliclastic sediment sources to the north. However, by the late Paleogene, the Suwannee Straits were inundated with sediment due to increased sediment erosion and transport from the Appalachian Mountains. Eventually, the Suwannee Straits filled in with sediment and the Florida Platform was no longer isolated from siliciclastic sediments to the north thereby increasing siliciclastic deposition on the Florida Platform. Sea level fluctuated during that time as well, resulting in erosion and reworking of sediments (Scott 1997).

Throughout the Pliocene and Pleistocene, sea level fluctuated as much as 140 m below present to at least 20 m above present sea level. During this time siliciclastic material was the dominant sediment deposited. Although, in low-lying regions covered by marine waters, carbonate sediments accumulated as well. Pleistocene sea level fluctuations are recorded as disconformities, and transitions between marine and freshwater environments. Transitions between these environments are evident by biotic changes in the stratigraphic record (Scott 1997).

As illustrated above, sediments in Florida have accumulated for millions of years. However, assigning a specific age to stratigraphic units in Florida has proven to be quite challenging. The principal method of stratigraphic classification in Florida is based on biostratigraphy. Unfortunately, this method is thwart with problems as described in the subsequent section.

Florida Stratigraphy

Generally speaking, Florida is covered with a thin veneer of Pleistocene sands, limestone and mud. However, the extact age and relationships of these units is poorly understood mainly due to stratigraphic classification issues surronding these units (Dubar 1974). According to the North American Stratigraphic Code, stratigraphic classification is based on detailed lithologic description, termed lithostratigraphy. However, as there are few lithologic differences between stratigraphic units in Florida, geologists have relied on biostratigraphic description when naming units (Lyons 1991). Unfortunately, biostratigraphic correlation in Florida is problematic as it is hindered by limited and discontinuous exposures, rapid facies changes and contradictions in biostratigraphy (Jones 1997). Moreover, this method describes the faunal relationships between various beds rather than the ages of the beds, caution should therefore be taken when classifying units based solely on biostratigraphic characteristics (Lyons 1991). The factors described above can lead to incorrect identification and correlations of Plio-Pleistocene deposits in Florida. Amino acid geochronology offers an independent means by which existing biostratigraphy can be compared and tested.

Stratigraphic units addressed in this study include the Pinecrest Beds, Caloosahatchee, Bermont, and the Ft. Thompson Formations. A generalized schematic of accepted ages for these units is illustrated in figure 2 and the locations were these units were sampled is illustrated in figure 3. Detailed description of these units is in the subsequent section.

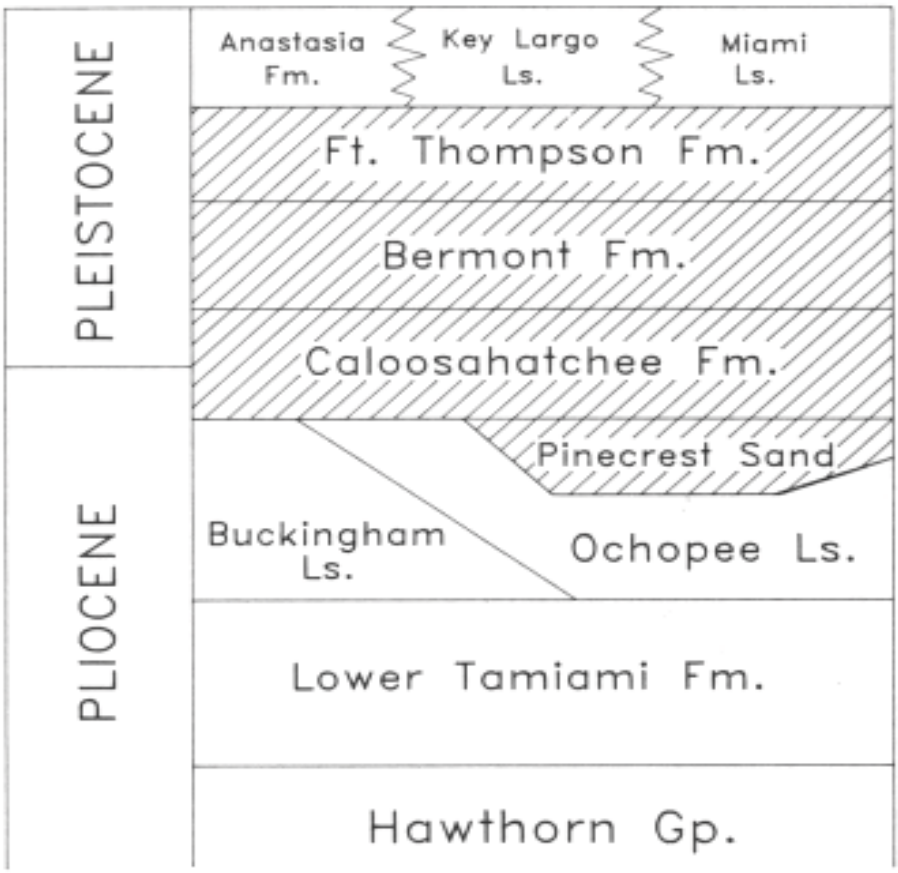


Figure 2. Florida stratigraphic hierarchy. Defined Plio-Pleistocene stratigraphic units in Florida. Cross-hatched units are composed of fossiliferous sands, limestone and clay (Allmon 1992)

Pinecrest Beds

Olsson (1964) described the Pinecrest Beds as a sandy-barren or highly fossiliferous unit located around the 40 mile bend along the Tamiami Trial in the western Dade County that extends into Collier County. The Pinecrest name was taken from an old settlement on Everglades Road in Dade County (Olsen 1964). In Sarasota, the Pinecrest Beds were exposed during excavation at the Macasphalt Pit Mine, which were later described by Petuch (1982) (Figure 3). Assigning an age to the Pinecrest Beds has proven to be quite challenging. Olsen proposed that the Pinecrest is younger than the Tamiami Formation and older than the Caloosahatchee Formation (Lyons 1991). Despite this accepted view, controversies remain as to the exact relationship of the Pinescrest with the Tamiami and the Caloosahatchee Formations (Lyons 1991, Jones 1997). What's more, biostratigraphic analysis conducted on the Pinecrest Beds revealed that unit 1 may correlate with the Caloosahatchee Fromation, units 2-9 represent the Pliocene while units 10 and 11 correlate with the Tamiami Formation (Petuch 1982).

Overall, the Pinecrest is represented by the gastropod genera *Latirus, Turritella, Cancellaria, and Siphocypraea* (Lyons 1991). In this study, only beds 2 and 3 were sampled at Quality Aggregates in Sarasota, Florida.

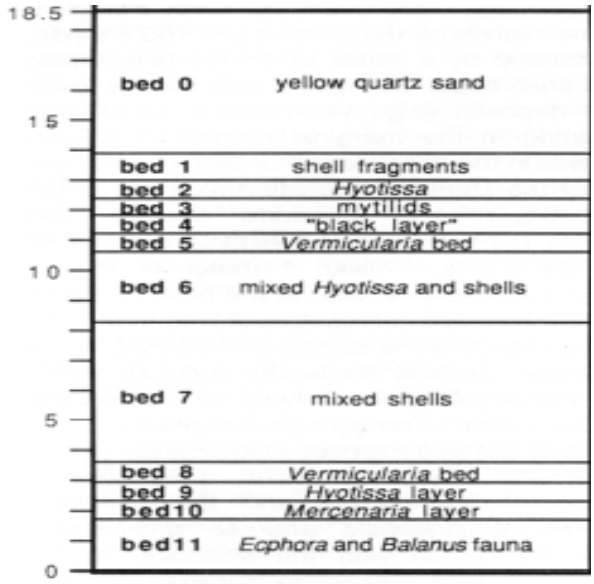


Figure 3. The Pinecrest Beds. Nomenclature described by Petuch (1982) for the Pinecrest Beds exposed at the Macasphalt Mine in Sarasota, Fl. Modified from Petuch (1982).

Caloosahatchee Formation

The Caloosahatchee Formation was first identified by Heilprin in 1887 as the lower shell beds exposed along the Caloosahatchee River. Heilprin believed that this unit was Pliocene in age and originally named it the Floridan. However, Dall later designated this same unit as the Caloosahatchee Formation. This name (Caloosahatchee) has subsequently been accepted as representing this unit (Dubar 1958). Generally speaking, the Calooshatchee is a fossiliferous quartz sand unit with variable amounts of carbonate interbedded with sand and shells (Scott 1992). Exposed units are usually white to cream in color. Most layers are highly fossiliferous. However, some sands are actually barren (Dubar 1958).

The exact age of the Caloosahatchee Formation is debatable. However, the base of this formation is estimated to be Pliocene, while the upper half of the formation

is most likely early Pleistocene (Lyons 1991). Furthermore, this formation separates the Tamiami Formation from the Ft. Thompson Formation (Olsson 1964). DuBar listed 66 gastropod species as characteristic of the Caloosahatchee. A few of the representative molluska include *Siphocypraea problematica, Liochlamys bulbosa, Typhis floridanus* and *Hystrivasum horridum* (Lyons 1991).

Bermont Formation

What we know today as the Bermont Formation was initially described by Vokes as the Glades Formation and later as Unit A by Ollson. Dubar later dubbed this unit as the Ft. Thompson Formation. The Bermont Formation was designated as a fossiliferous marine sands found along the upper portion of Shell Creek in the Bermont Quadrangle of Charlotte County (Lyons 1991). This formation represents a distinct biostratigraphic zone separating the Caloosahatchee Formation from the Ft. Thompson Formation (Jones 1997). The general structure can be described unconsolidated gray sand with abundant and well fossils. This unit extends from southern Desoto and Highlands Counties into Palm Beach and Martin Counties and possibly into the Everglades. The age of the Bermont is thought to be early to mid Pleistocene (Dubar 1974). A few representative gastropod taxa for this formation include *Fasciolaria okeechobensis, Fusinus watermani, Melongena bispinosa, Strombus mayacensi and Vasum floridanum,* which are not present in the Caloosahatchee Formation (Lyons 1991).

Ft. Thompson Formation

The Ft. Thompson was designated by Sellards in 1919 as fresh-water, brackish-water, marine marls and limestone along the Caloosahatchee River (Lyons 1991). This unit lays unconformably over the Bermont Formation. Furthermore, Dubar divided the Ft. Thompson into two subunits or members. The Coffee Mill Hammock represents the upper member while the Okaloakoochee member represents the lower unit .

The lithology of the Ft. Thompson Formation can be described as fossilerous siliciclastics with interbedded carbonate sediments (Scott 1997). Nearly all molluskan species of this formation are extant. However, extinct gastropods found in this unit include *Pyrazisinus scalatus* and *Turritella subannulata.* The age of the Ft. Thompson has been debated extensively and is suggested to be as old as early-to-mid Pleistocene (Lyons 1991).

A few of the representive gastropods for the The Ft. Thompson include *Anachis avara, Bulla occidentalis, Ceithium musarum* (Dubar 1974).

PREVIOUS WORK

Previous attempts to unravel the Plio-Pleistocene stratigraphy for the Gulf coast of Florida utilized techniques such as bio- and lithostratigraphy, magnetostratigraphy, strontium and uranium isotope analysis and aminostratigraphy. Biostratigraphy, by far, has been the most extensively used tool in this endeavor with the majority of analysis occurring at the Caloosa Shell Inc. (formerly Leisey Shell Inc.) in Ruskin and in Quality Aggregates in Sarasota.

Biostratigraphic analysis performed on sediments collected during initial excavations at Leisey Shell Pits indicated that the upper shell bed correlated with the Ft. Thompson Formation while the lower shell bed and bone bed correlated with the Bermont Formation. However, subsequent investigations at this site proved to be problematic as key index taxa were absent, therefore, hindering age confirmations at this location (Portell 1992). Alternatively, magnetostratigrapic analysis suggested that the Leisey Shell Pit lies within the Matuyama magnetochron. Strontium isotope analysis revealed that the lower bed correlates with the late Pliocene to early Pleistocene in age while the upper bed correlates with the early to middle Pleistocene in age (Jones 1992).

Biostratigraphic analysis conducted on the Pinecrest Beds in Sarasota revealed that this unit is composed of 11 complex units or beds. Units 2-9 represents the Pliocene while units 10 and 11 correlate with the Tamiami Formation (Lyons 1992). Nonetheless, precise stratigraphic correlation of these units has been hindered due to rare or absent microfossil content. Yet again, magnetostratigraphy and strontium isotopic analysis were utilized to establish a numerical age estimate for this unit.

Magnetostratigraphy revealed that the Pinecrest beds are reversed polarity and therefore lie within the Matuyama magnetochron. Strontium isotope analysis indicated that beds 2-4 are 2.0 to 2.5 million years old, whereas units 5-11 are slightly older at 2.5-3.5 million years old (Jones 1992).

In southern Florida, uranium-series (u-series) analysis dating has been carried out on fossil coral fragments obtained from the Ft. Thompson, Bermont, and Caloosahathee Formations (Muhs 1992). Unfortunately, though, samples analyzed by Muhs (1992) showed that no corals acted as a closed system with regard to uranium and its daughter products Therefore, only approximate ages were obtained from this study. Based on these u-series results, the Caloosahatchee Formation is greater than 400,000 years old. The Bermont Formation gave an isotopic age of about 230,000-360,000 years, and the Ft. Thompson Formation revealed an isotopic age of approximately 144,000 years (Muhs 1992).

Aminostratigraphy has been extensively conducted along the Atlantic Coastal Plain (ACP) (Figure 4) from Delaware to Florida, albeit, with the majority of analysis taking place in New Jersey, Maryland, Delaware, Virginia, and in North and South Carolina (Karrow 1996, Wehmiller and Belknap 1982 Wehmiller and Belknap 1982, Wehmiller et al., 1992, Wehmiller et al.,1987, Wehmiller and York 2001, York et al., 2000). In these studies, aminostratigraphic results were used to established stratigraphic ages, areas of erosion or nondeposition, mixing and transport, thermal histories and stratigtraphic correlation. However, as illustrated in Figure 4, the aminostratigraphy of Florida is limited and incomplete.

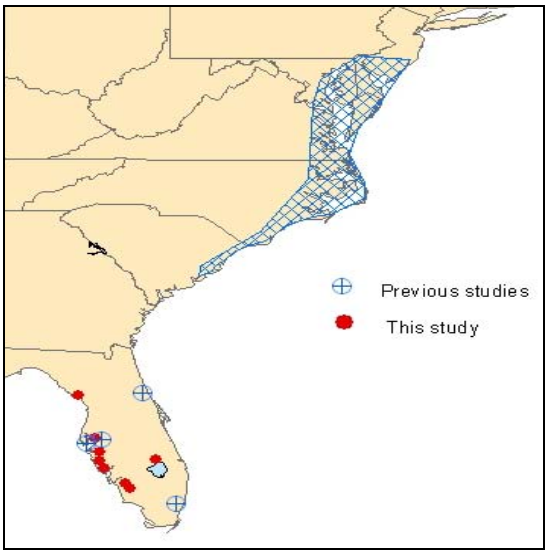


Figure 4 Atlantic Coast Plain (ACP).
Previous aminostratigraphic studies conducted along the ACP (Karrow 1996,Wehmiller and Belknap 1982, Wehmiller et al., 1992, Wehmiller et al.,1995, Wehmiller and York 2001, York et al., 2000) depicted as crosshatched areas compared to aminostratigraphic analysis done in this study illustracted as red areas.

In Florida, previous aminostratigraphic analyses have been performed on mollusks from Fernandina Beach, Pinellas County, Miami Ruskin and Caloosa Shell Inc in. Results from Fernandina Beach showed two distinct aminozones that may be indicative of transport and mixing. Unfortunately, though, a true aminostratigraphic age was not established at this site as there were limited analyses conducted on these specimens (Wehmiller et al., 1993). In Pinellas County, City of Oldsmar, mollusk specimens collected at two locations from an urban excavation site were identified as belonging to the Ft. Thompson Formation. Aminostratigraphic analysis revealed two aminozones at these sites. Site 1 gave an amino age of 250 ka while site two revealed an amino age of 120-210 ka. These age differences were interpreted as representing an unconformity that was not clearly visible (Karrow 1996). Wehmiller (1988) used amino

acid racemization results from Miami (Mitterer 1975) in an attempt to establish a latitudinal trend in racemizations rates along the ACP. Furthermore, in southern and central Florida amino acid results revealed three aminozones with the youngest correlating with marine isotope stage (MIS) 5e (Wehmiller et al., 1988)

At the Leisey Pit in Ruskin, amino acid D/L values were compared to strontium isotope data. In that study, amino acid racemization results indicated a much younger age for these units than did strontium isotopes. These findings however, pointed to diagenetic processes that may affect each of these dating methods (York et al., 2000).

As discussed above, numerous aminostratigraphic analyses have been performed along the northern region of the ACP. However, very few studies have been conducted along the Gulf Coast of Florida. Moreover, the few studies that have been done in Florida where focused on either establishing a latitudinal trend in racemization, or used to compare methods (i.e. strontium isotopes) to amino acid racemization, or to establish the stratigraphy at only one excavation site. Nor have these studies attempted to resolve the broader stratigraphic relationships between formational units in Florida. Clearly, a more comprehensive aminostratigraphic framework of Florida is needed.

The goal of this study is to extend the aminostratigraphy for the ACP to the Gulf Coast of Florida. This will be achieved by comparing amino acid D/L ratios obtained in this study with results from previous studies conducted along the ACP. Furthermore, results from this study will be compared site by site in an attempt to establish a comprehensive understanding for the Plio-Pleistocen of Florida.

METHODS

Field Sampling

Localities in which the Pinecrest Beds, Calooshatchee, Bermont and Ft. Thompson Formations were previously identified and described were targeted for sampling in this study. Attempts were made to sample each of these units from several sites across a wide latitudinal gradient. Sampling sites were identified and selected with the assistance of Roger Portell, Florida Museum of Natural History (FLMNH).

Sites assumed to be undisturbed and approximately Pleistocene in age were selected for sampling (Figure 4). Bivalve genera *Chione* and *Mercenaria* (Figure 5) were selected for sampling due to the hardiness of the shell and wide temporal and spatial distribution of these genera. All samples were collected from below surface level and from fresh or mechanically cleaned exposures to avoid increased racemization due to surface heating or contamination from over-washed samples. Bulk sediments were collected and placed into a plastic bag, labeled according to location and date, and taken to the laboratory for preparation.

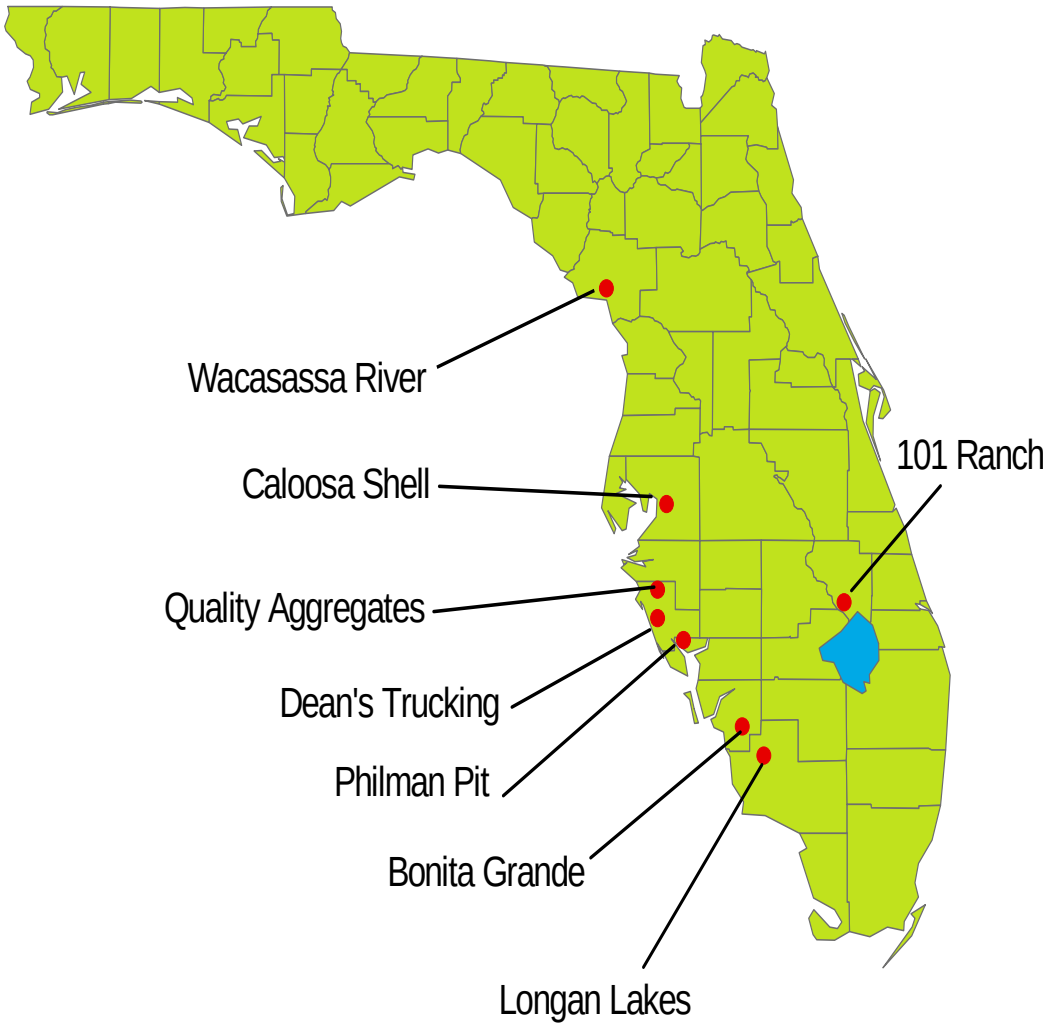


Figure 5. Site location map. Site formation designation are as follows.
Wacasassa River = Caloosahatchee Formation
Caloosa Shell = Bermont and Ft. Thompson Formations
Quality Aggregates= Pinecrest Beds
Dean's Trucking = Ft. Thompson Formation
Philman Pit = Ft. Thompson Formation
Bonita Grande = Caloosahatchee Formation
Longan Lakes = Bermont Formation
101 Ranch = Caloosahatchee and Bermont Formations

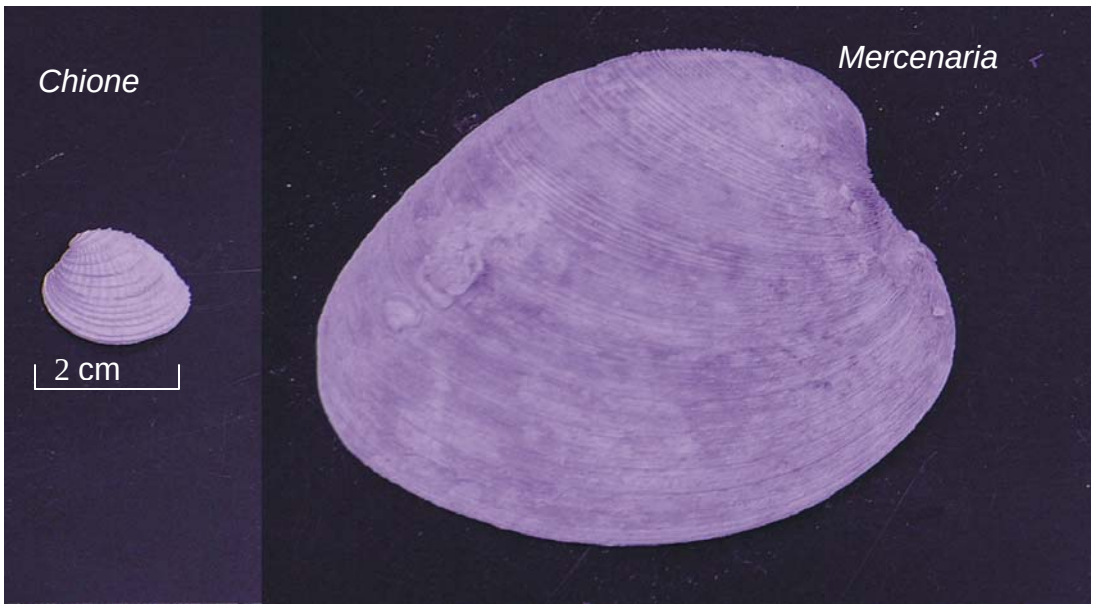


Figure 6. Genera *Chione* and *Mercenaria*
Selected genera for aminostratigraphic analysis. Both genera have large temporal and spatial distributions

SITE DESCRIPTION

Wacasassa River

The Wacasassa River site is located in Levy Co. (29°17.629 N. latitude and 82° 43.84 W. longitude). Sediments along the Wacasassa River were sampled at two locations (sites 1 and 2). Site 1 samples were collected about two miles upstreat along the river, below water level from a fossiliferous layer within a sand-filled karst feature at the top of exposed Eocene limestone. Due to the presence of *Konis adversa*, this site was assumed to be part of the Caloosahatchee Formation (R. Portell pers. conv. 2001). Site 2 was sampled from a fossiliferous sand layer overlying the karstified limestone bedrock approximately 1 mile south of site 1. Shell abundance was less than site 1 with a different depositional environment indicated by brackish water-fauna. Site 2 was

initially proposed to be a different facies of the same stratigraphic unit sampled at site 1 (R. Portell, pers. conv. 2001).

Caloosa Shell Pit

Caloosa Shell Corp in located in Ruskin, FL (27 ^{o} 41'47.8" N. latitude and 83^{o}29'14.5" W. longitude). Mining for road and construction fill began in 1980 at an adjacent site under the name Leisey Shell Pit. Eventually that operation was sold and renamed Caloosa Shell Corperation. Previous excavations revealed two highly fossiliferous shell beds and one bone bed. The bone bed, along with a sandy unit, separates the upper and lower shell beds. The upper shell bed unconformably overlies the lower shell bed in areas where the sandy unit or bone bed has pinched out. Samples analyzed in this study were collected from the upper and lower shell beds (Figure 7).

The upper bed is densely fossiliferous with a sand matrix. Dominant mollusk genera are *Chione*, *Mercenaria* and *Anadara.* Well-preserved articulated mollusks and in situ specimens are found here along with many broken specimens. The upper bed has been identified as belonging to the Ft. Thompson Formation (Portell et al. 1992, Jones 1993). The intermediate bed between the upper and lower beds is a light-colored, sandy layer showing heavy bioturbation. The lower bed is not as homogenous as the upper bed and is largely composed of shell hash. This bed has been assigned to the Bermont Formation (Portell et al. 1992, Jones 1993).

Figure 7. Caloosa Shell Inc.

Quality Aggregates

Quality Aggregates quarries are located in Sarasota, FL (27^{o}22'22.3" N. latitude and 82^{o}23'9.6" W. longitude). Phase 9 of the quarry excavation exposed fossiliferous sediments that were identified as beds 2 and 3 of the Pinecrest Formation (R. Portell pers. conv. 2001). *Mercenaria* is the dominant genus, with few *Chione* present in these beds. Coral fragments and oyster shells are also present in this exposure. Bed 2 showed evidence of $CaCO_3$ recrystallization into a dense pavement. The base of bed 3 was a prominent oyster bed. The matrix of both beds is a sandy to muddy consistency.

101 Ranch

101 Ranch is located in Okeechobee, FL (27°31'31.5' N. latitude and 80°58'8.6" W. longitude). This site has exposures of the Caloosahatchee and Bermont Formations (R. Portell, pers.conv. 2001). Samples were collected from the middle of the Bermont Formation, which was highly fossiliferous with evidence of parasitic shell worms. Although the fauna is similar to that expected from the Bermont Fm., this exposure may actually be younger than the Bermont (Portell, pers. conv. 2001).

Dean's Trucking Pit

Dean's Trucking Pit is located in Venice, (SW ¼, Section 22, T38s, R19E of the Laurel Qudarangle) in Sarasota County, Fl. Specimens from this site were donated by Roger Portell of the FLMNH for analysis in this study. Fossilifeous sediments exposed at this site correlate biostratigraphically with the Ft. Thompson Formation (R. Portell, pers.conv. 2001).

Philman Pit

Philman Pit is located in Grove City, Englewood, FL (26°54'44.9" N. latitude and 82°18'28.9" W. longitude). Sediments exposed at this site are believed to be part of the Ft. Thompson Formation. However, in some places of this exposure, the top of the Tamiami Formation may be exposed (R. Portell pers. conv. 2001). The exposed outcrop is fossiliferous and shows evidence of calcite nodules and precipitation of $CaCO_3$ contained in a sandy matrix.

Bonita Grande

Bonita Grande is located in Lee County, FL (26°21.48 N. latitude and 81°44.18 W. longitude). This site was sampled twice (site 1 and 2). Site 1 was sampled from a spoil pile with both fresh and saltwater taxa. Due to the presence of *Stenophysaa*, these sediments are assumed to be part of the Caloosahatchee Formation (R. Portell, pers. conv. 2001). Site 2 samples were taken from an exposure located below a thick cemented carbonate overburden. This site is also correlate with the Caloosahatchee Formation (R. Portell, pers. conv. 2001).

Longan lakes

Longan Lakes Quarry is located Collier County, FL. (in the NE ¼, Section 25, R27E, T47S). This exposure had low diversity and was dominated by *Chione.* Due to the gastropod fauna, this site is assumed to be part of the Bermont Formation (R. Portell pers. conv. 2001).

LABORATORY PROCEDURES

In the laboratory, bulk sediments were sieved, and *Chione* and *Mercenaria* were selected for analysis. Selected specimens were assigned a USF Amino Acid Geochronology (FAL) number and cataloged. Large *Mercenaria* shell valves were sliced perpendicular to growth lines using a water-cooled tile saw. *Chione* shells were broken into smaller fragments using a hammer. Fragments from the umbo (hinge) region weighing approximately 5 to 100 mg were selected for analysis. These

fragments were repeatedly rinsed with pure water and placed into an ultrasonic cleaner for 5 to 10 minutes. Once the specimens were clean, they were then placed under a fume hood for drying. When dry, the samples were reweighed and 20% of their mass was removed in a 2 N HCl leach to ensure no external contamination remained. After leaching was complete, the samples were rinsed 4 times with purified water and dried overnight under a fume hood. The dry samples were reweighed, placed into vials and dissolved in 7 N HCl. Vials were then flushed with N_2 to prevent oxidation and placed in an oven at 110^0 C for 22 hours to induce hydrolysis. Hydrolyzed samples were placed into an evaporator under N_2 to remove the remaining HCl. Following evaporation, the amino acid residues were rehydrated with purified water adjusted to pH 2 and injected onto a HP1100 reverse phase liquid chromatograph for analysis of L and D isomers of amino acids.

Sample Analysis

All samples were prepared and analyzed at the University of South Florida Amino Acid Geochronology Laboratory in the Geology department in Tampa, Florida. D/L ratios of approximately 10 amino acids can be measured using the HP1100 reverse phase liquid chromatograph following the methods of Kaufman and Manley (1998). In this system, amino acids are placed onto a liquid phase and passed into a fine-grained stationary bed at high pressure. Each amino acid moves through the stationary column at different rates, which is a function of the chemical properties of individual amino acids. Concentrations of individual amino acid isomers are determined through

fluorescence detection (Kaufman and Manley 1998). The relative peak heights plotted on the chromatogram (Figure 5) represents amino acid concentrations. D/L ratios are obtained by dividing the peak heights of the D isomer and L isomer forms for each amino acid. Although the HP1100 reverse phase liquid chromatograph can potentially resolve more than 10 amino acid D and L isomers, only four representative D/L pairs were selected for comparison. Selected amino acids include aspartic acid, glutamic acid, valine and phenylalanine. Isoleucine was originally selected for analysis; however, due to inconsistent chromatographic resolution, isoleucine was rejected for analysis in this study.

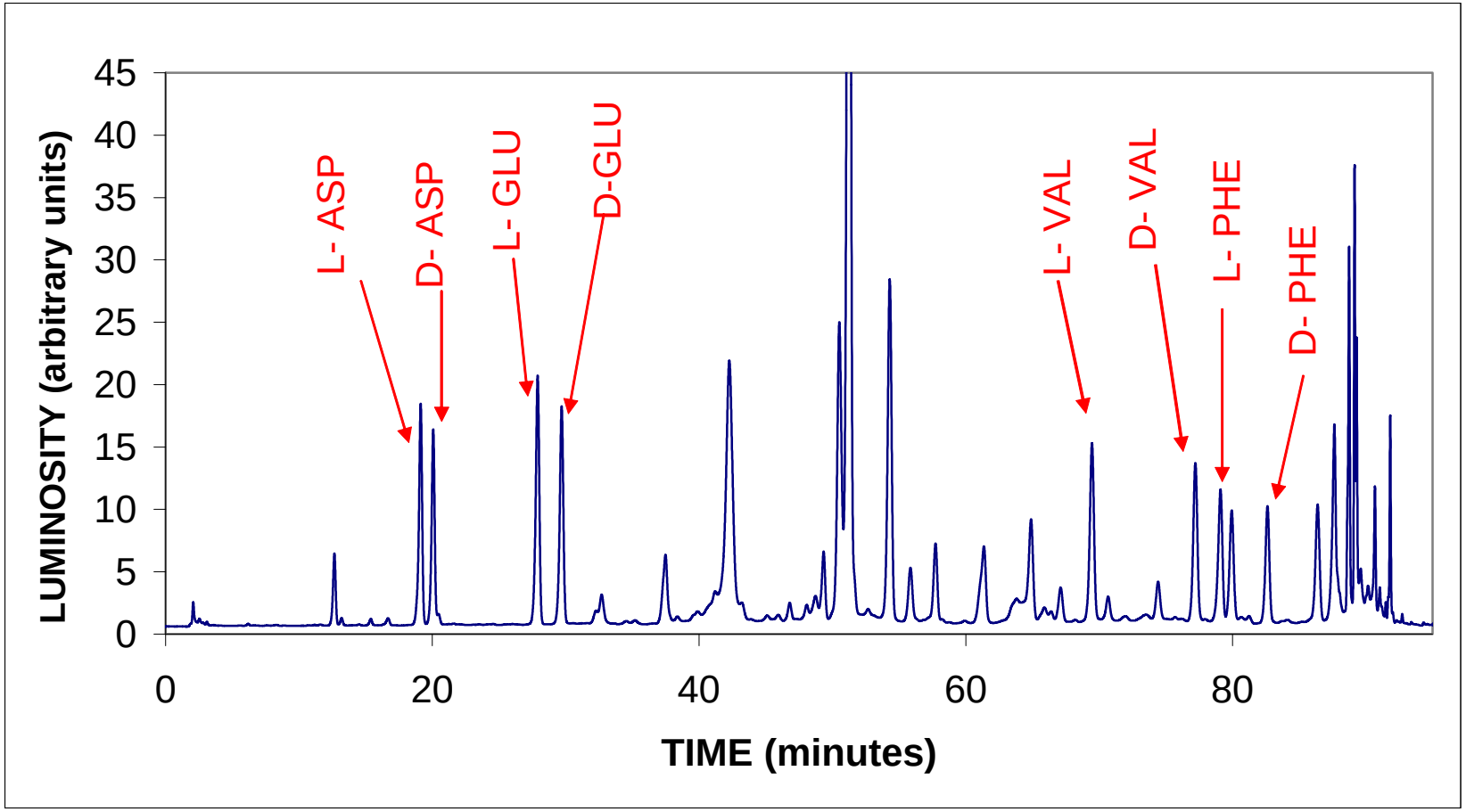


Figure 8. HPLC Chromatogram.
Chromatogram showing amino acid concentrations by measuring luminosity.
Amino acid isomer configuration are depicted as laevorotatory (L) or dextrorotary (D).
Selected amino acids analysed in this study include aspartic acid (ASP), glutamic acid (GLU), valine (VAL) and phenylalanine (PHE).

Hydrolysis Experiment

As part of the preparation process, samples were subjected to hydrolysis by heating samples in an oven for 22 hours at 110^{o}C. Hydrolysis is the breaking of peptide bonds, releasing free amino acids from the bound peptide chain (Mitterer 1993). Hydrolysis is required in order that bound amino acids are released from the peptide chain thus making them available for individual analysis. Unfortunately, subjecting the samples to heat can induce further racemization (Kaufman & Manley 1998). To assess the optimal time for hydrolysis without inducing excessive racemization, 40 samples taken from a modern articulated *Mercenaria* were used in a heating experiment. In this experiment, two dissolved shell samples, from each one *Mercenaria* valve, were prepared as described above and placed in an oven and heated to 110^{0}C. Two pieces (one per valve) were removed from the oven at two-hour intervals starting at two and ending at 40 hours. Amino acid D/L ratios where then measured and plotted in figures six and seven. In theory, this experiment should show the trend of racemization in relation to time of hydrolysis (heating). Prior to hydrolysis, free (unbound in peptide chain) D/L ratios are low. Following hydrolysis, free amino acids concentrations increase (Mitterer 1993). The optimal time for hydrolysis is achieved when D/L ratios reach a stable plateau. Induced racemization is observed when, after the plateau is reached, D/L ratios start to increase again indicating that the rate of racemization is greater than the rate of hydrolysis (Kaufman & Manley 1998).

Genera Study

Although only *Chione* and *Mercenaira* were selected for analysis in this study, many other mollusk genera are available for analysis. To assess the suitability of other genera for aminostratigraphy, four genera (*Anadara, Anadontia, Dosinia, and Trachycardium)*, in addition to *Chione* and *Mercenaria*, were collected from the upper shell bed at the Caloosa Pits and analyzed in the methods outlined above. The suitability of these genera for aminostratigraphy was assessed by calculating mean D/L value, standard deviation (Figure 8) and coefficient of variation (CV) (Figure 9) for each amino acid in each genera. These values were then compared to *Chione* and *Mercenaria* D/L values that were collected from the same stratigraphic unit.

RESULTS

Two hundred eighty three samples were analyzed in this study. Of the 283 samples, 40 were used to determine the optimal time of hydrolysis, and 43 were used to assess the suitability of different genera for aminostratigraphy. The remaining 200 were used to establish the aminostratigraphy for the Pleistocene of Florida based on samples collected from the Pinecrest Beds, Caloosahatchee, Bermont and Ft. Thompson Formations at eight localities throughout Florida.

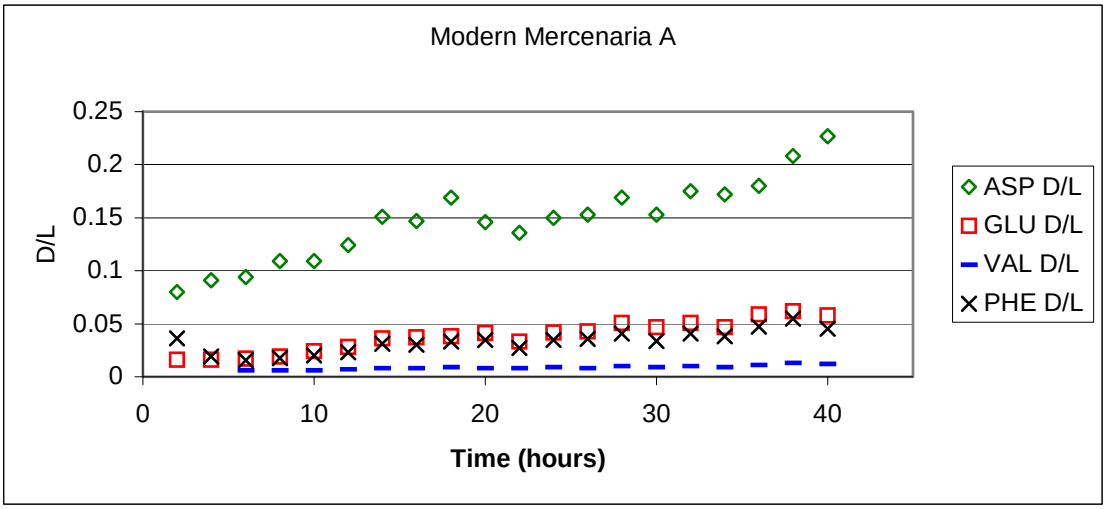
Mollusk genera *Chione,* and *Mercenaria* (Figure 4) where selected for analysis in this study. However, during field sampling, it was discovered that *Mercenaria* was not present at all field sites, whereas *Chione*, which was ubiquitous. Therefore, *Chione* may be a better representative for the Pleistocene of Florida than *Mercenaria*.

As previously mentioned, racemization rates of individual amino acids are variable and vary between mollusk genera as well (Kaufman & Manley 1998, Wehmiller & Miller 2000). To address this issue, each amino acid and mollusk genus will be discussed separately.

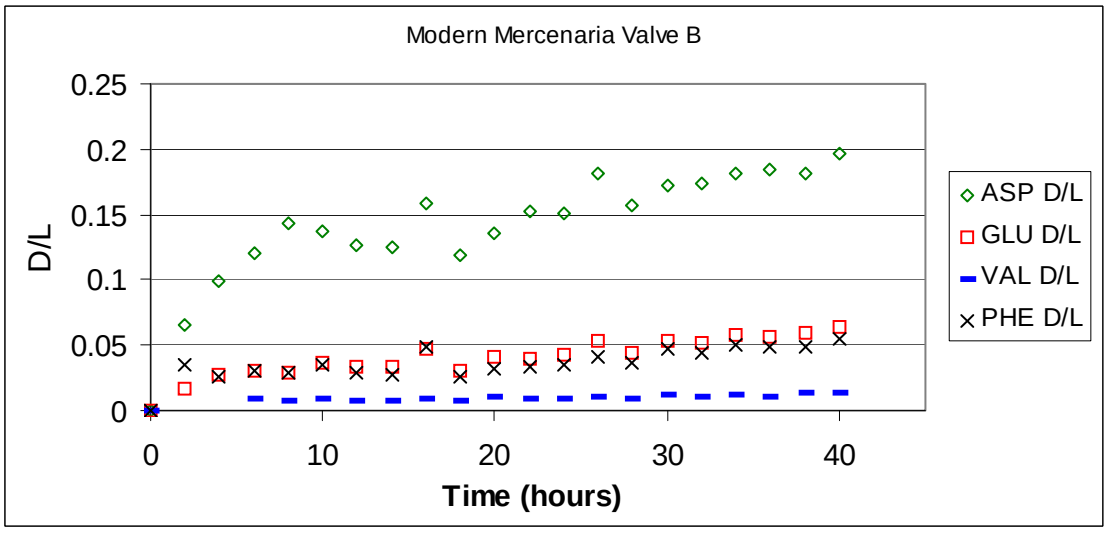
Hydrolysis Experiment

The optimal time for hydrolysis is illustrated in Figures 6 and 7. Valve A from a modern articulated *Mercenaria* is represented in figure 6a, and valve B is represented in figure 6b. Since valves A and B are from the same modern articulated Mercenaria, the D/L ratios should be essentially identical between the two valves. Amino acids measured in this study include aspartic acid, glutamic acid, valine and phenylalanine.

However, as illustrated in Figure 6, aspartic acid racemizes rapidly and has the highest degree of variability. Valine, on the other hand, is the slowest to racemize and has the least amount of variability. Because of this quality, valine was exclusively selected to evaluate the optimal time of hydrolysis (Figure 7).



(a)



(b)

Figure 9. Optimal time for hydrolsys.
Extent of racemization (Y axis) in relation to time of hydrolysis (x axis).
Graph A represents valve A and graph B represents valve B.
Amino acid abbreviations are: ASP = aspartic acid, GLU = glutamic acid, VAL = valine, PHE = phenylalanine

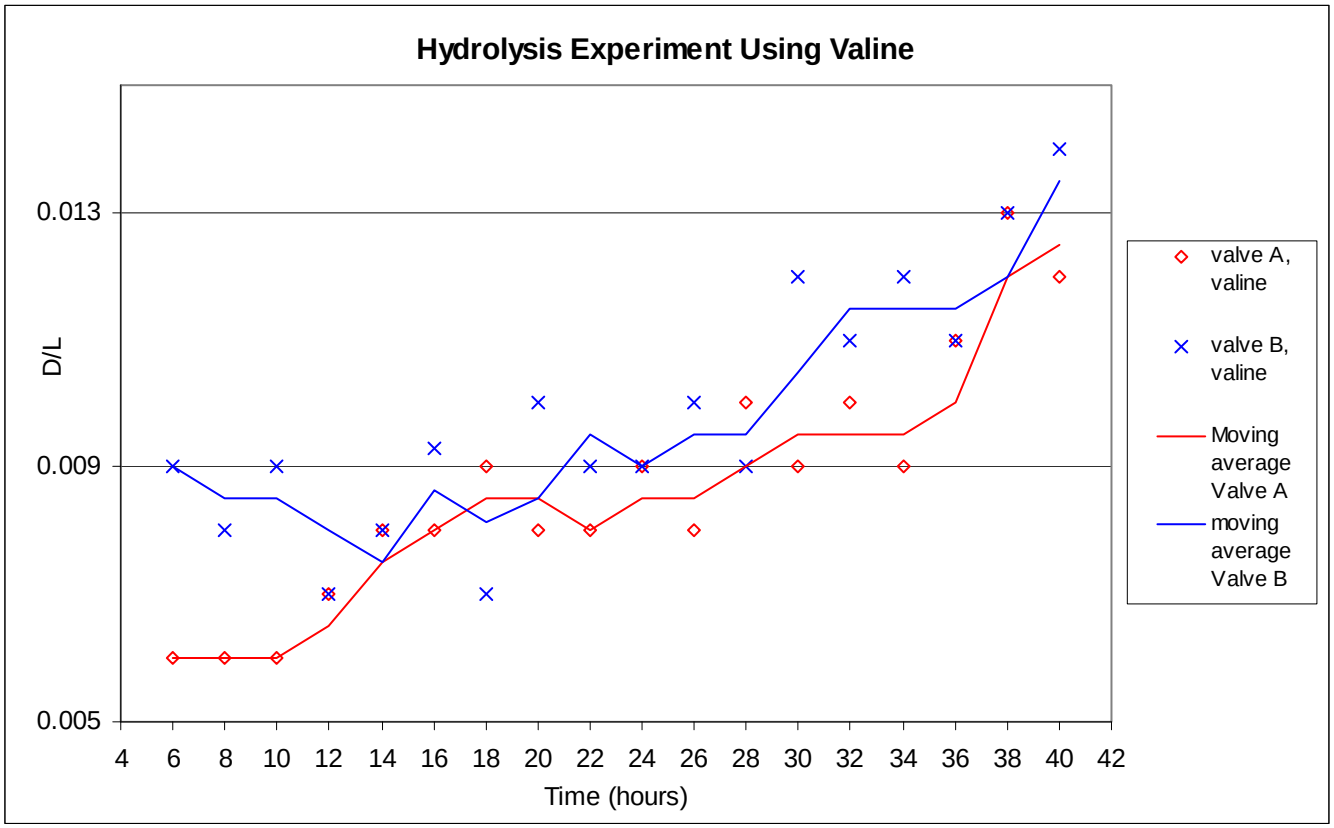


Figure 10. Optimal time for hydrolsys using valine
Extent of racemization (Y axis) in relation to time of hydrolysis (x axis) for the amino acid valine. Moving average added to illustrate the trend in rate of racemization.

While an attempt was made to collect all samples solely from the umbo region, sampling from across the whole shell could not be avoided. Racemization rates across the shell matrix can vary by as much as 30% (Goodfriend et al, 1997) which may account for the scatter seen in Figures 6 and 7.

Optimal time for hydrolysis ranges from 15 to 25 hours as demonstrated by the initial plateau in D/L ratios (figure 7). D/L ratios start to increase after 25 hours

indicating the time at which the rate of racemization is greater than the rate of hydrolysis. Furthermore, it is necessary for relatively old samples, such as mollusks utilized in this study, to be hydrolyzed longer compared to younger samples that hydrolyze in just a few hours. This is because older specimens are less vulnerable to heating and resistant peptides require longer heat exposure for hydrolization (Kaufman and Manley 1998). A hydrolysis time of 22 hours was selected based on this study and applied to all sample used in this aminostragraphic investigation.

Genera Study

Results of racemization analysis of four genera (*Anadara, Anodontia, Dosinia, Trachycardium*) collected from the upper shell bed at Caloosa Shell Inc. is illustrated in Figures 11 and 12. The mean D/L ratios and standard deviation are plotted in figure 11, while the coefficient of variation (CV) is plotted in figure 12. To establish the suitability of these genera for aminostratigraphy, these statistical data were compared to those of *Chione* and *Mercenaria*. All specimens were collected from the same unit. It is therefore assumed that all genera sampled experienced the same thermal, taphonomic, and burial history.

Trachycardium has the highest degree of variability, as measured by coefficient of variation, whereas *Anadara* has the lowest variability. Surprisingly though, *Chione* has a relatively high degree of variability compared to that of Anadara (figures 11 and 12). Consequently, if genus *Anadara* is as ubiquitous as *Chione*, *Anadara* may then be suitable genus for use in aminostratigraphy.

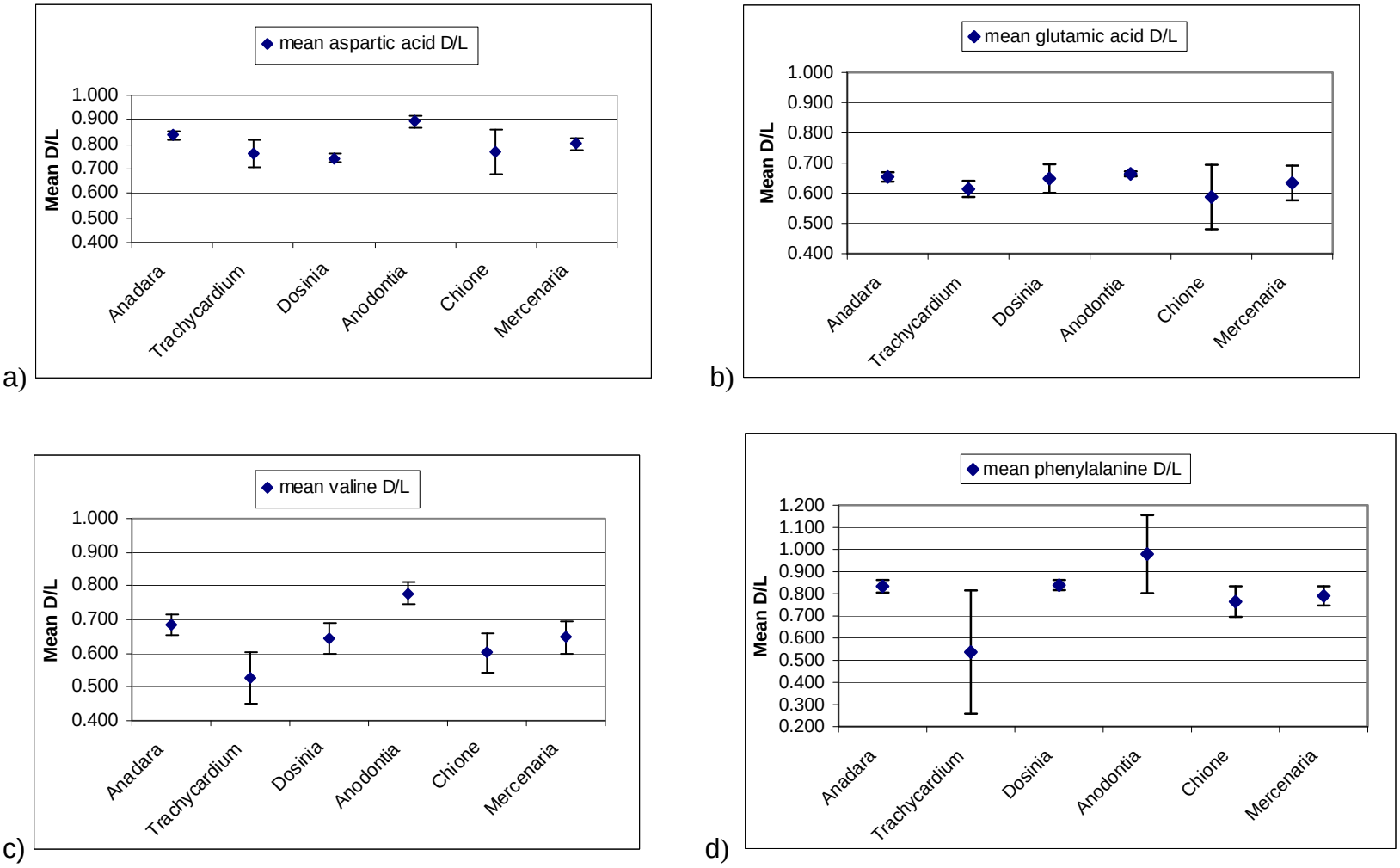


Figure 11 Mean D/L ratios and standard deviation for amino acids measured in gerera *Anadara, Anodontia, Dosinia, Trachycardium Chione* and *Mercenaria*. All samples were collected from the upper bed at Caloosa Shell Inc.

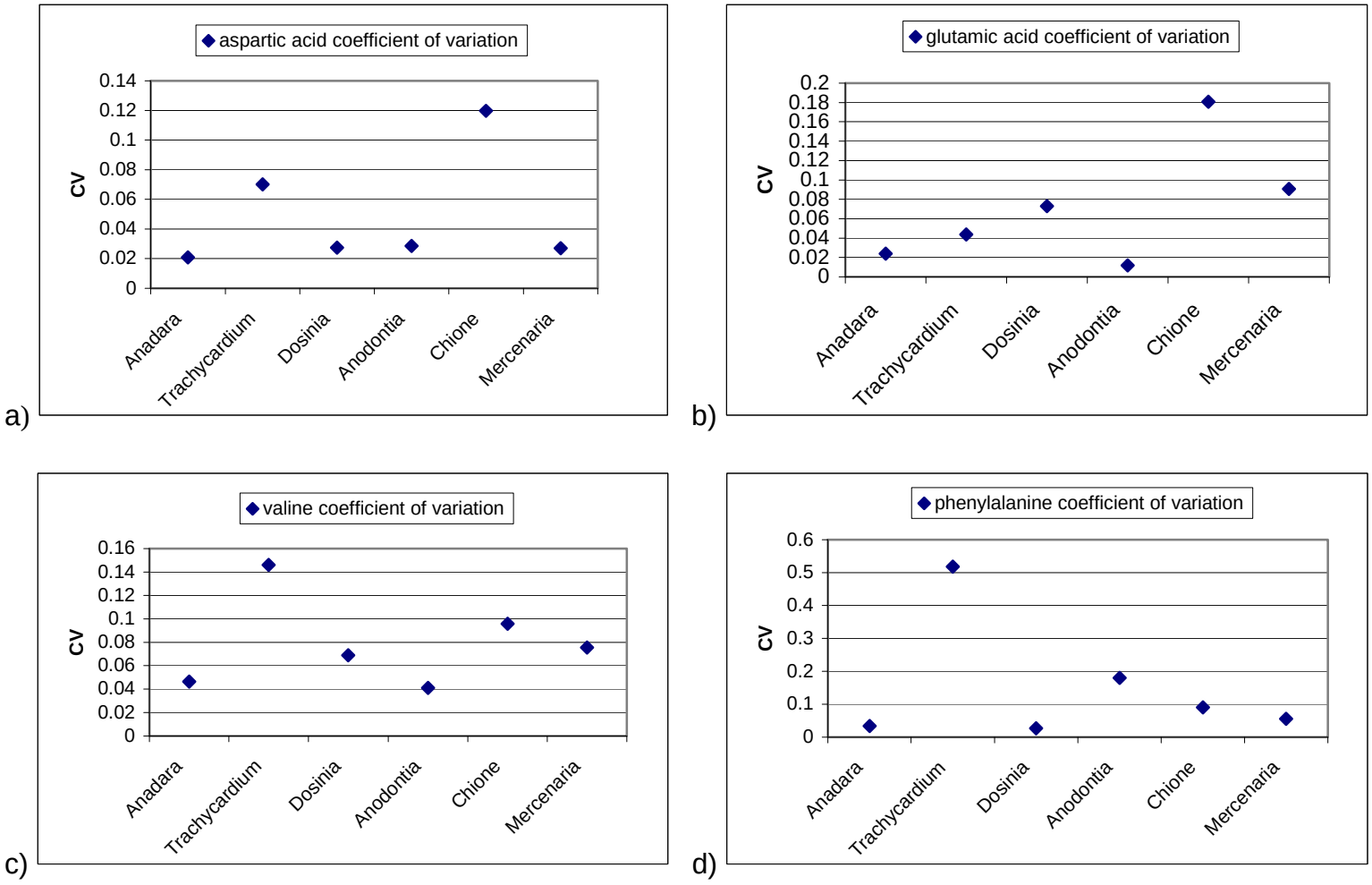


Figure 12 Coefficient of variation (CV) (calculated as standard deviation/mean) for genera *Anadara, Anodontia, Dosinia, Trachycardium Chione* and *Mercenaria*. All samples were collected from the upper shell bed at Caloosa Shell Inc.

Furthermore, aspartic acid again appears to have reached equilibrium while phenylalanine appears to have the highest variability. Hence, glutamic acid and valine appear to be the best suited amino acid for analysis in this study.

U-Series Dating

U-Series dating was performed courtesy of Dr. Larry Edwards from the University of Minnesota.

The error is 2σ error.

Sample Number	^{238}U (ppb)	^{232}Th (ppt)	$\delta^{234}U^*$ (measured)	$^{230}Th/^{238}U$ (activity)	^{230}Th Age (years) (uncorrected)	^{230}Th Age (years) (corrected)	$\delta^{234}U$ Initial** (corrected)
010105-1 (I)	3137 ± 4	25340 ± 94	92.0 ± 1.3	0.6438 ± 0.0030	95600 ± 740	**95400 ± 750**	120.6 ± 1.7
010105-1 (II)	3484 ± 5	33630 ± 120	90.8 ± 1.4	0.6371 ± 0.0030	94230 ± 730	**93980 ± 740**	118.5 ± 1.9
020223-1 (I)	2573 ± 3	19560 ± 72	102.9 ± 1.3	0.7521 ± 0.0035	121760 ± 1050	**121570 ± 1050**	145.2 ± 1.9
020223-1 (II)	2703 ± 3	23540 ± 110	102.0 ± 1.4	0.7486 ± 0.0042	120960 ± 1260	**120740 ± 1260**	143.6 ± 2.0
010105-2 (I)	3914 ± 5	68200 ± 330	85.8 ± 1.3	1.0658 ± 0.0062	341200 ± 13200	**340800 ± 13200**	225 ± 9
010105-2 (II)	4075 ± 6	79150 ± 460	86.4 ± 1.5	1.0871 ± 0.0076	392700 ± 26000	**392200 ± 26000**	262 ± 20

$\lambda_{230} = 9.1577 \times 10^{-6}\ y^{-1}$, $\lambda_{234} = 2.8263 \times 10^{-6}\ y^{-1}$, $\lambda_{238} = 1.55125 \times 0^{-10}\ y^{-1}$. $*\delta^{234}U = ([^{234}U/^{238}U]_{activity} - 1)x1000$. ** $\delta^{234}U_{initial}$ was calculated based on ^{230}Th age (T), i.e., $\delta^{234}U_{initial} = \delta^{234}U_{measured} \times e^{\lambda 234 x T}$. Corrected ^{230}Th ages assume the initial $^{230}Th/^{232}Th$ atomic ratio of $4.4 \pm 2.2 \times 10^{-6}$. Those are the values for a material at secular equilibrium, with the crustal $^{232}Th/^{238}U$ value of 3.8. The errors are arbitrarily assumed to be 50%. I and II are different fragments of the same sample.

Three coral samples were analyzed with two tests per sample. All three coral fragments were obtained from Caloosa Shell Pit. One fragment was collected from the lower bed belonging to the Bermont Formation, and two fragments were collected from the upper bed belonging to the Ft. Thompson FormationTable 1. ^{230}Th Dating Results (from L. Edwards, pers comm.)

Isotopic ages for each sample are shown in table 1. Sample number 010105 -1 = upper Ft. Thompson Formation, 020223 -1 = lower Ft. Thompson Formation and 010105 -2 = Bermont Formation.

Of the three samples analyzed, two appear to be altered possibly resulting in erroneous age estimates (Edwards, pers comm. 2002). Consequently, only the pristine sample, sample 020223, can be considered for age determination with confidence. Sample 020223 (pristine sample) from the lower Ft. Thompson Formation has an average isotopic age of 121,155 ± 1,155 years. Based on the oxygen isotope curve of Shelckleton (1969) the lower Ft. Thompson Formation correlates with oxygen isotope state (OIS) 5e.

Additionally, if the isotopic ages for samples 010105 -1 and 010105 -2 are correct, then the upper Ft. Thompson Formation correlates with OIS 5c and the Bermont Formation correlates with OIS 9. However, as mentioned above, these samples (010105 -1 and 010105 -2) may be altered resulting in questionable age estimates. To address this issue, further Protactinium (^{231}Pa) analysis would determine if the ^{230}Th age estimates are either too high or low (L. Edwards, pers. comm. 2002).

Aminostratigraphy of Florida

Two hundred samples from eight sites (figure 3) were analyzed to establish the aminostratigraphy of Florida. Using box-whisker plots, D/L distribution for aspartic acid, glutamic acid, valine and phenylalanine are plotted for genera *Chione* and *Mercenaria.* Genus *Chione* results are shown in figures 13, 14, 15, and in table 2 while *Mercenaria* results are shown in figures 16, 17, 18 and in table 4. The box-whisker plots (figures 13 and 16) represent 50% of the D/L ratio distribution; the median value is illustrated as a horizontal line in the box diagram, and 1.5 times the interquartile range of D/L values are represented as (T) bars that extend beyond the box diagrams. Outliers are illustrated as (+).

Additional statistical analyses calculated on these data include mean D/L value, standard deviation, and the coefficient of variation (C.V), which is calculated as standard deviation/mean. The C.V. (figures 15 and 18) is measured as percent variability and may be an indication of the reliability of selected amino acids and genera, and may also indicate whether other environmental factors are influencing the results. “N” represents the number of samples analyzed. Mean D/L ratios (figures 14 and 17) were used to determine the relative ages of samples.

Results are plotted from left to right, corresponding to the north-south latitudinal gradient of sites (Figure 3). This was done to illustrate the expected increase in racemization associated with thermal effects of cooler to warmer climate regimes (Wehmiller and Belknap 1982).

Although four amino acids (aspartic acid, glutamic acid, valine and phenylalanine) were selected for analysis in this study, only two of the four amino acids (glutamic acid and valine) will be used aminostratigraphic age interpretation (figures 14 and 17) and environmental factors (figures 15 and 18) in this study. Selection of these amino acids is because aspartic acid is known to racemize rapidly resulting in poor resolution for older samples such as the ones used in this study and phenylalanine was not selected due to excess scatter and inability to resolve for age differences between young and old formations. Both phenomena described above are evident in figures 13 and 16.

As demonstrated in figures 13, 14, 16, and 17, there are two distinct aminozones evident in this data. Two sites, Wacasassaa River site 2 and the upper Caloosa Shell bed, belong to a younger aminozone while all other sites (Wacasassaa River site 1, lower Caloosa Shell bed, Quality Aggregates, 101 Ranch, Dean's Trucking, Philman Pit, Bonita Grande, and Longan Lakes) belong to an older aminozone.

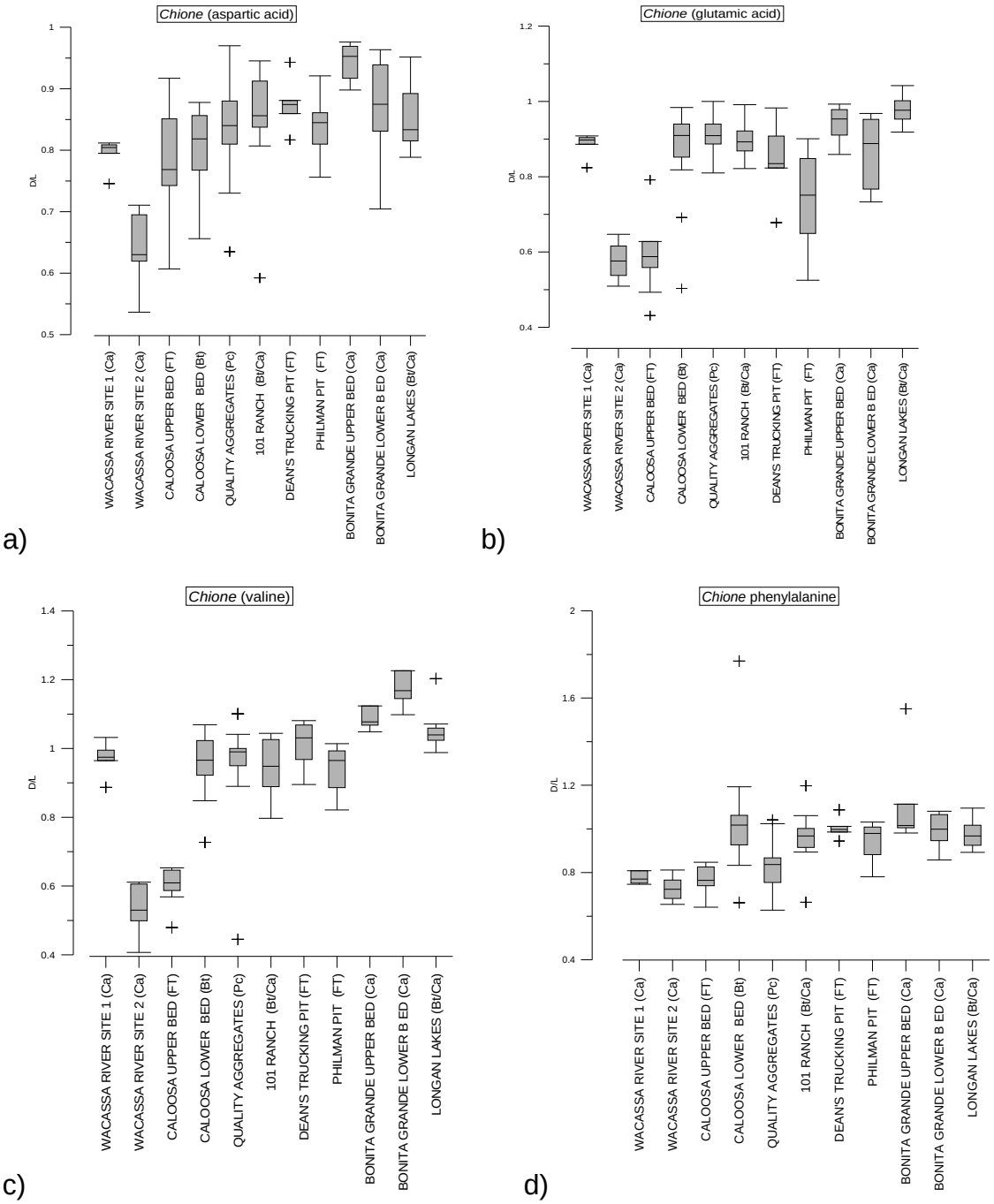


Figure 13. *Chione* box whisker plots.
These plots illustrate D/L distribution for amino acids D/L ratios measured in genus *Chione.* Abbreviations next to site names indicate stratigraphic unit (formation). Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest. See text for explanation Of box-wisker plots

Table 2. *Chione* D/L ratio statistics.
Stastical information such as mean D/L ratio, standard deviation (sd), number analyzed (n) and coefficient of variation (cv) calculated for each amino acid analyzed in genus *Chione.* Amino acids are abbreviated as ASP = aspartic acid, GLU = glutamic acid, VAL = valine, PHE = phenylalanine. Formations at all site locations are abbreviated as Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

Amino acid	ASP	ASP	ASP	ASP	GLU	GLU	GLU	GLU	VAL	VAL	VAL	VAL	PHE	PHE	PHE	PHE
Site locations	mean D/L	sd	n	cv	mean D/L	sd	n	cv	mean D/L	sd	n	cv	mean D/L	sd	n	cv
WACASASSA RIVER SITE 1 (Ca)	0.79	0.03	5	0.03	0.89	0.04	5	0.04	0.97	0.05	5	0.06	0.77	0.03	4	0.04
WACASASSA RIVER SITE 2 (Ca)	0.64	0.07	5	0.11	0.58	0.06	5	0.10	0.53	0.08	5	0.16	0.73	0.06	5	0.09
CALOOSA UPPER BED (FT)	0.77	0.09	8	0.12	0.59	0.11	8	0.18	0.60	0.06	8	0.10	0.76	0.07	8	0.09
CALOOSA LOWER BED (Bt)	0.81	0.06	25	0.07	0.88	0.10	25	0.12	0.96	0.08	24	0.09	1.01	0.19	25	0.19
QUALITY AGGREGATES (Pc)	0.84	0.07	31	0.08	0.91	0.05	26	0.05	0.97	0.12	26	0.12	0.83	0.10	25	0.13
101 RANCH (Bt/Ca)	0.86	0.09	14	0.10	0.89	0.04	15	0.05	0.95	0.09	14	0.09	0.96	0.11	14	0.12
DEAN'S TRUCKING PIT (FT)	0.87	0.05	5	0.05	0.84	0.11	5	0.13	1.01	0.08	5	0.08	1.00	0.05	5	0.05
PHILMAN PIT (FT)	0.84	0.05	9	0.06	0.75	0.12	9	0.17	0.95	0.07	9	0.07	0.95	0.08	9	0.09
BONITA GRANDE UPPER BED (Ca)	0.94	0.03	5	0.04	0.94	0.06	5	0.06	1.08	0.03	4	0.03	1.11	0.24	5	0.22
BONITA GRANDE LOWER B ED (Ca)	0.86	0.10	5	0.12	0.87	0.11	5	0.13	1.17	0.06	4	0.05	0.99	0.09	5	0.09
LONGAN LAKES (Bt/Ca)	0.85	0.05	10	0.06	0.98	0.04	10	0.04	1.05	0.06	9	0.06	0.98	0.07	10	0.07

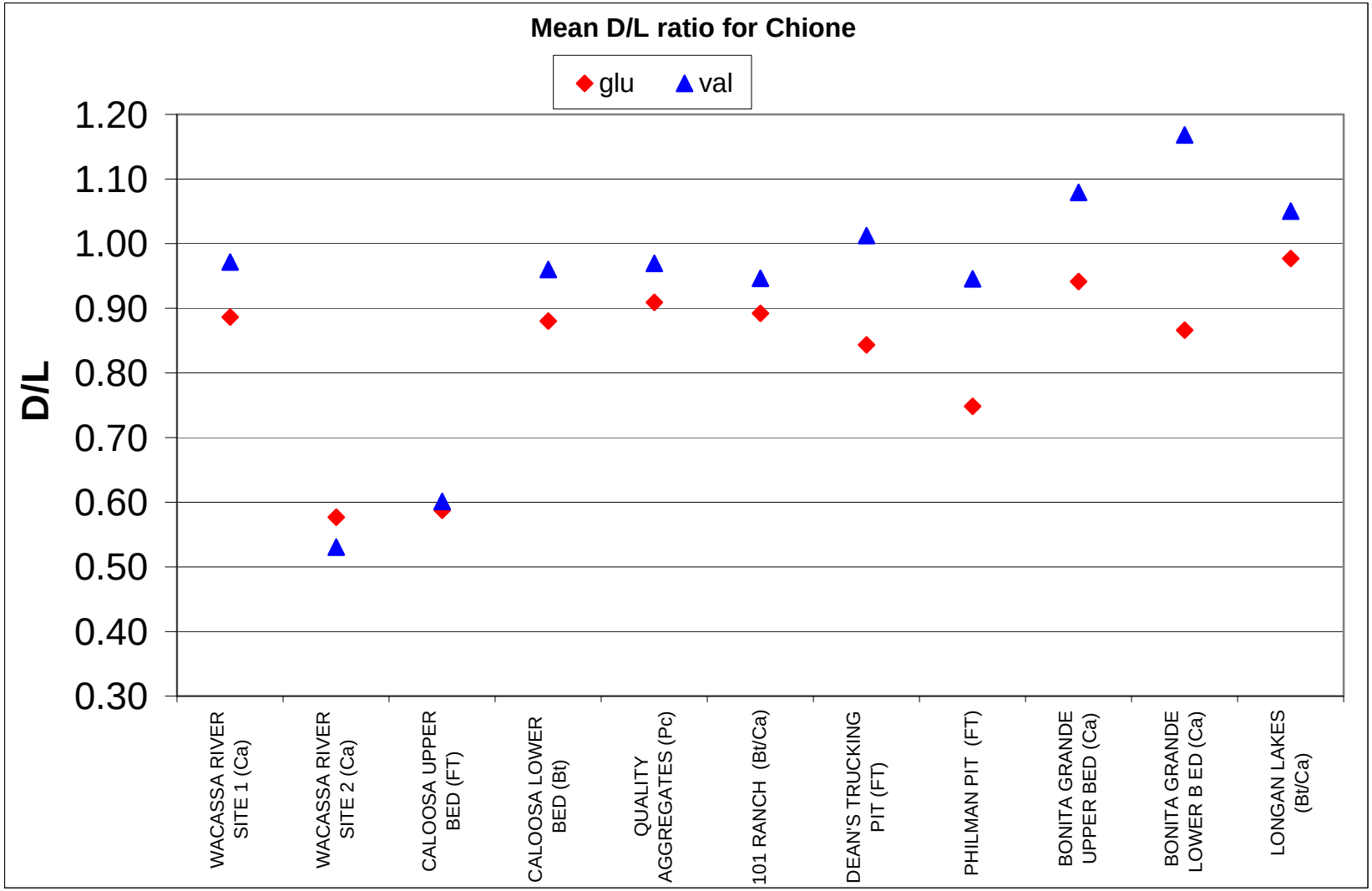


Figure 14. Mean D/L ratios for genus *Chione.* Mean D/L ratio used to establish the aminostratigraphic age of site locations. Amino acids are abbreviated as Glu = glutamic acid, VAL = valine, Formations are abbreviated as: Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

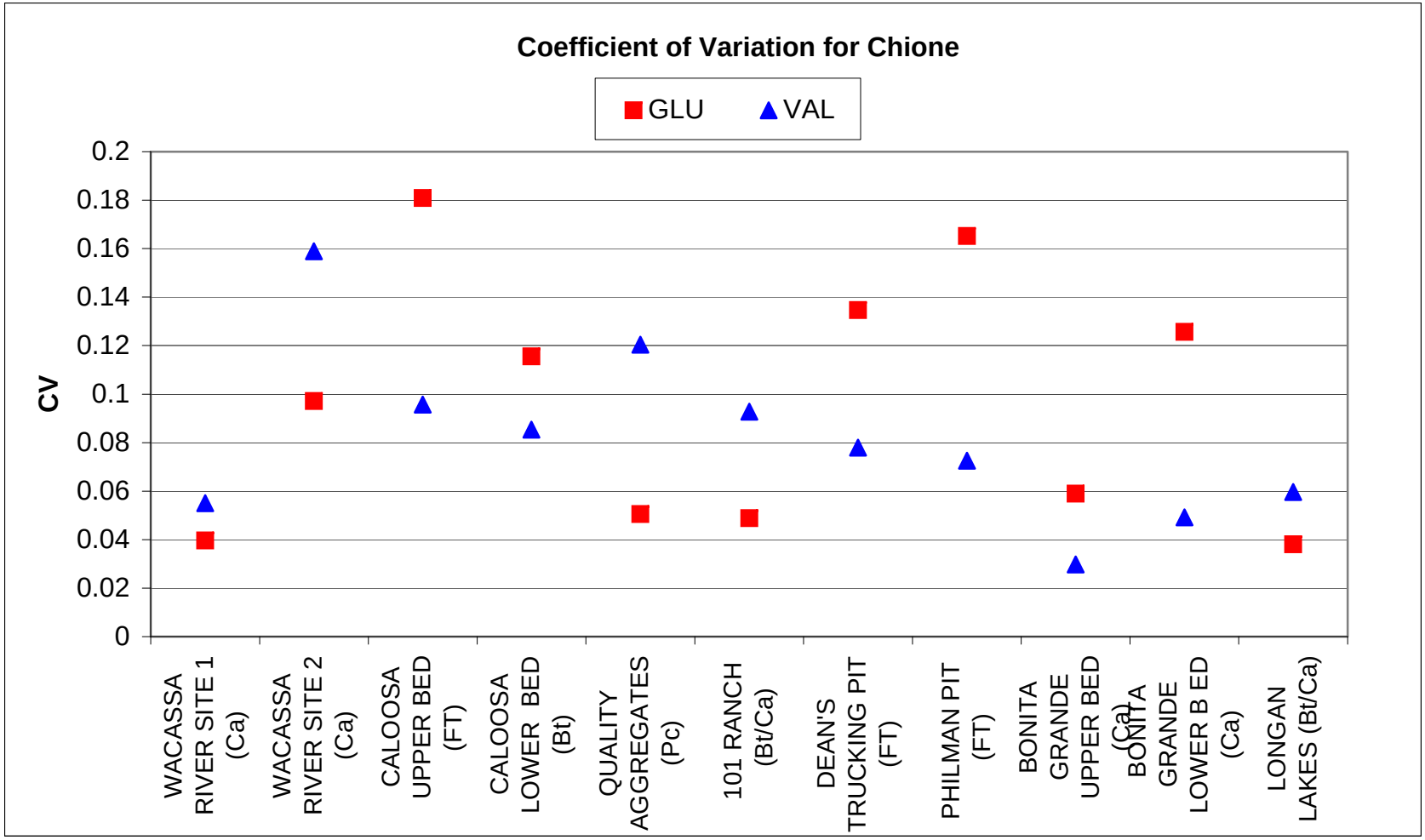


Figure 15. Coefficient of variation (cv) for genus *Chione.* CV is used to establish environmental factors such as leaching or mixing. Amino acids are abbreviated as Glu = glutamic acid, VAL = valine, Formations are abbreviated as: Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

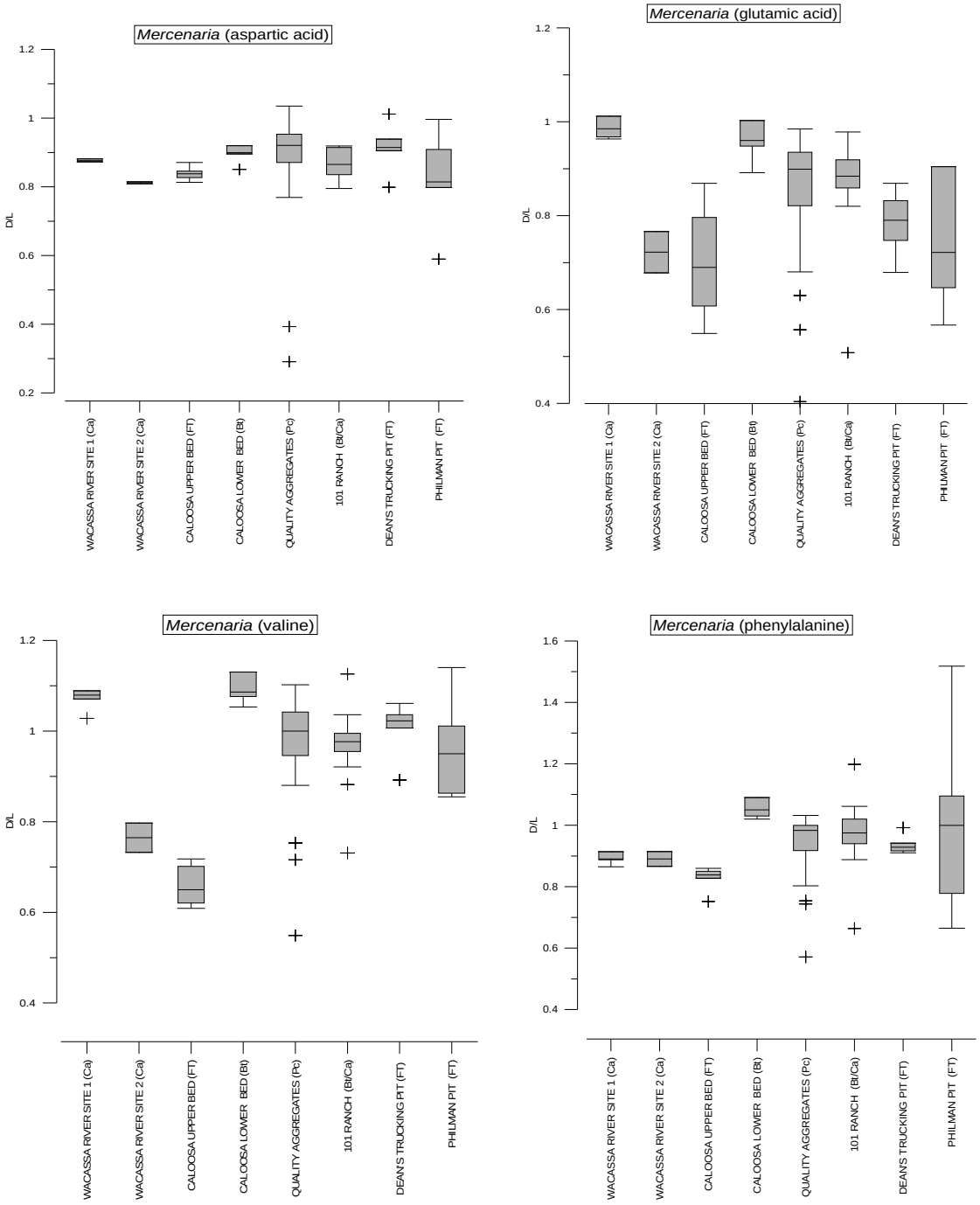


Figure 16. *Mercenaria* box whisker plots.
These plots illustrate D/L distribution for amino acids D/L ratios measured in genus *Mercenaria.* Abbreviations next to site names indicate stratigraphic unit (formation). Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

Table 3. *Mercenaria* D/L ratio statistics.
Stastical information such as mean D/L ratio, standard deviation (sd), number analyzed (n) and coefficient of variation (cv) calculated for each amino acid analyzed in genus *Mercenaria.* Amino acids are abbreviated as ASP = aspartic acid, GLU = glutamic acid, VAL = valine, PHE = phenylalanine. Formations at all site locations are abbreviated as Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

Amino acid	ASP	ASP	ASP	ASP	GLU	GLU	GLU	GLU	VAL	VAL	VAL	VAL	PHE	PHE	PHE	PHE
	mean D/L	sd	n	cv	mean D/L	sd	n	cv	mean D/L	sd	n	cv	mean D/L	sd	n	cv
WACASASSA RIVER SITE 1 (Ca)	0.876	0.004	4	0.005	0.985	0.023	4	0.024	1.071	0.029	4	0.027	0.89	0.02	4	0.023
WACASASSA RIVER SITE 2 (Ca)	0.812	0.004	2	0.005	0.722	0.062	2	0.086	0.765	0.046	2	0.06	0.89	0.034	2	0.038
CALOOSA UPPER BED (FT)	0.839	0.022	5	0.026	0.611	0.057	5	0.094	0.658	0.049	5	0.074	0.828	0.044	5	0.053
CALOOSA LOWER BED (Bt)	0.896	0.031	4	0.035	0.96	0.052	4	0.054	1.086	0.032	4	0.03	1.05	0.032	4	0.03
QUALITY AGGREGATES (Pc)	0.879	0.174	25	0.197	0.849	0.13	30	0.153	0.972	0.121	30	0.124	0.939	0.106	29	0.112
101 RANCH (Bt/Ca)	0.867	0.041	15	0.048	0.869	0.112	14	0.129	0.967	0.084	15	0.087	0.971	0.113	15	0.117
DEAN'S TRUCKING PIT (FT)	0.914	0.077	5	0.084	0.785	0.074	5	0.095	1.007	0.066	5	0.066	0.936	0.033	5	0.036
PHILMAN PIT (FT)	0.82	0.152	5	0.185	0.722	0.147	4	0.204	0.961	0.118	5	0.123	1.009	0.331	5	0.328

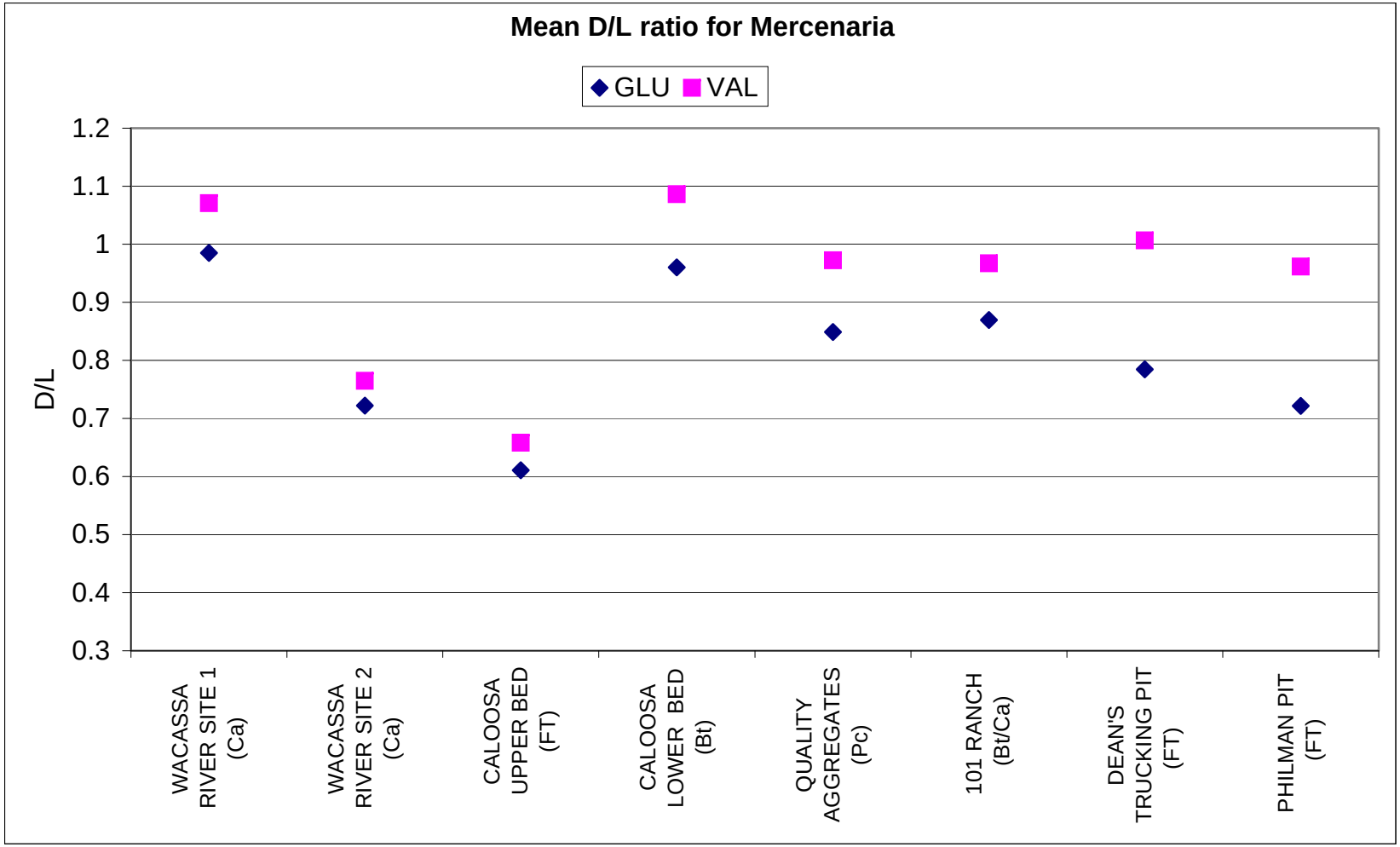


Figure 17. Mean D/L ratios for genus *Mercenaria.* Mean D/L ratio used to establish the aminostratigraphic age of Site locations. Amino acidsare abbreviated as Glu = glutamic acid, VAL = valine, Formations are abbreviated as: Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

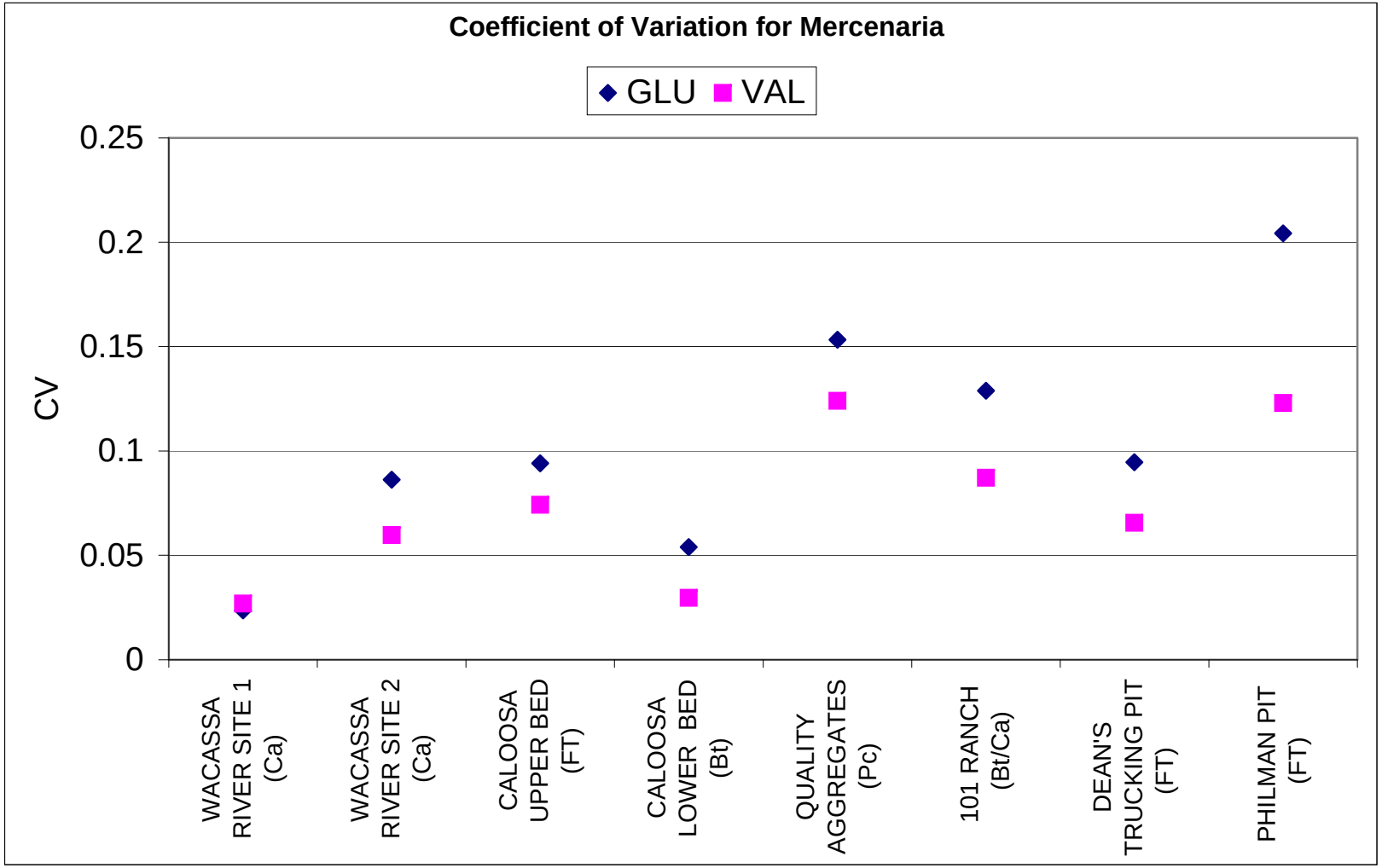


Figure 18. Coefficient of variation (cv) for genus *Mercenaria.* CV is used to establish environmental factors such as leaching or mixing. Amino acids are abbreviated as Glu = glutamic acid, VAL = valine, Formations are abbreviated as: Ca = Caloosahatchee, FT= Ft. Thompson, BT= Bermont, Pc = Pincrest

DISCUSSION

The objective of this study is to establish the aminostratigraphy of Florida by measuring amino acid D/L ratio analyzed in carbonate fossils in an attempt to unravel the Plio-Pleistocene of Florida. Prior stratigraphic analysis and classification in Florida has proven problematic as it is based on biostratigraphy rather than lithostratigraphy. Aminostratigraphy, on the other hand, offers an alternative or supplemental dating method to other techniques that have been plagued with problems. In this study, the relative ages of stratigraphic units are established from the mean D/L ratio of amino acids, and the numerical ages are determined by calibration with U-series age estimates. Likewise, environmental factors or conditions can be assessed by measuring the coefficient of variation (cv) of amino acid D/L ratios for each sample site.

Aminostratigraphy of Florida

The aminostratigraphy of the Plio-Pleistocene of Florida is illustrated in figures 13-18 and in tables 2-4 and as mentioned previously only the amino acid D/L ratios from glutamic acid and valine will be used aminostratigraphic interpretation in this study. Selection of these amino acids is based on the fact that aspartic acid is known to racemize rapidly resulting in poor resolution for older samples, such as the ones used in this study, and phenylalanine was not selected due to excess scatter and inability to resolve for age differences between young and old formations. Both phenomena described above are evident in figures 13 and 16.

The mean D/L ratios for glutamic acid and valine for genera *Chione* are illustrated in figure 14 and for genera *Mercenaria* in figure 17. Two distinct aminozones are apparent in these figures. Wacasassa River site two and the upper Caloosa Shell bed belong the younger aminozone while all other sites (Wacasassa River site 1, lower Caloosa Shell bed, Quality Aggregates, 101 Ranch, Dean's Truck Pit, Philman Pit, Bonita Grande and Longin Lakes) correlate with an older aminozone. Originally, Wacasassa River sites one and two were though to be part of the Caloosahatchee Formation (R. Portell pers. comm. 2002). The Caloosahatchee Formation is thought to be late Pliocene to early Pleistocene in age (Lyons 1991). Nevertheless, as demonstrated from this data, Wacasassa River sites one and two are of two different ages. Since Wacasassa River site 1 aminostratigraphically correlates with the upper shell bed at Caloosa Shell Inc., which has been biostratigraphically assigned to the Ft. Thompson Formation, Waccasass River site 1 may actually be part of the Ft. Thompson Formation.

Moreover, as previously mentioned, Dean's Trucking Pit and the Philman Pit were correlated with the Ft. Thompson Formation based on fossil content. Yet, as demonstrated in figures 13 and 16, these sites are much older than previously assumed. Based on these data, Dean's Trucking Pit and Philman Pit may actually belong to the Caloosahatchee or Bermont Formations. Younger fossil specimens collected during sampling at these locations may be the result of mixing in these units.

The oldest unit analyzed in this study is the Pinecrest Beds, which was sampled at Quality Aggregates in Sarasota. Accordingly, this unit should have the highest D/L. Nonetheless, the Pinecrest Beds essentially has the same D/L ratio as units assigned to the Caloosahatchee and Bermont Formations (figures 14 and 17), which are assumed to be younger than the Pinecrest. As addressed above, the age of the Pinecrest bed is poorly understood. In fact, the Pinecrest Beds has been identified as one of the unit members that encompasses the Tamiami Formaion (Scott 1992). On the other hand, as described by Petuch (1982) bed one of the Pinecrest may correlate with the Caloosahatchee Fromation, beds 2-9 represent the Pliocene while units 10 and 11 correlate with the Tamiami Formation. Clearly, the age of the Pinecrest is not well constrained.

Based on results from this investigation, beds two and three (units that were sampled in this study) of the Pinecrest Beds may correlate with the Caloosahatchee Formation according to amino acid D/L ratios. However, caution should be taken with this interpretation, as amino acid racemization may not be able to resolve for older specimens sampled in warm Florida climates. As described previously, temperature is the most significant factor that influences amino acid racemization. Amino acid D/L ratios reach equilibrium rapidly in these environments therefore inhibiting resolution of older samples like those of the Pinecrest Beds, Caloosahatchee and Bermont Formations (Miller & Brigham-Grette 1989; Wehmiller & Miller 2000). Therefore, further analysis is required to accurately assign an age to beds two and three of the Pinecrest.

Chione amino acid D/L ratios from the Philman Pit (figures 14 and 17) suggest that this unit also belongs to the older aminozone. Moreover, it appears that this site is the youngest of all unit correlated with this older aminozone. Accordingly, the Philman Pit may represent the early-middle Pleistocene.

Conversely, the upper and lower units at Bonita Grande appear to be the oldest of all units sampled in this study (figure 14). Unfortunately, though, the genus *Mercenaria* was not present at Bonita Grande and therefore cannot be compared with *Chione* D/L ratios for age estimate purposes. Nonetheless, Bonita Grande may correlate with the late Pliocene to early Pleistocene.

The upper and lower beds at Caloosa Shell Inc. have been extensively studied and are well defined based on biostratigraphic, isotopic and magnetostratigraphic analyses (Jones 1992, Muhs 1992, Portell 1992). As a result, coral samples from these units were selected for U-series analysis in an attempt to establish a numerical age estimates in this study. U-series dating performed on corals collected from the lower half of the upper bed (FT. Thompson Formation) at Caloosa Shell Inc. revealed an average isotopic age of 121,265 ± 1155 corresponding to marine isotope stage (MIS) 5e the last interglacial period. (L. Edwards pers. comm. 2002). As a result of the U-series calibration, the mean amino acid D/L ratios from the Ft. Thompson Formation can be used in establishing numeric amionstratigraphic ages. Accordingly, the last interglacial period for the central region of the Gulf Coast of Florida are represented by the mean D/L ratios for genera *Chione* for 0.59 (glutamic acid) and 0.60 (valine) and for genera Mercenaria 0.61 (glutamic acid) and 0.69

(valine). Alternatively, it can be hypothesized that higher D/L ratios (older specimens) may correlate with MIS 7, 9 or 11.

Another characteristic addressed in this study was variability measured as coefficient of variation (CV), calculated as standard deviation/mean. The CV for genus *Chione* is illustrated in figure 15 and *Mercenaria* CV is illustrated in figure 18. Variation was compared among all sample sites and used to hypothesize as to taphonomic processes such as leaching and contamination that may be occurring in these environments.

Leaching is defined as diffusion of amino acids out of the shell matrix. Mixing is defined as the incorporation of older amino acids into the matrix of younger shells, and visa versa for older shells (Mitterer 1993). Accordingly, sites that have experienced significant leaching or contamination may not be well suited for aminostratigraphic analysis. Leaching and contamination are hypothesized to be represented by a higher degree of variation (CV) measured in this study.

At first glance, it is apparent in figures 15 and 18 that variation among amino acids (glutamic acid and valine) has an inconsistent trend in genus *Chione* compared to *Mercenaria.* This characteristic may therefore be an indication of vulnerability to leaching potential between these genera, and hence could aid in the selection of mollusks genera for aminostratigraphic analysis. Due to this characteristic, only genus Mercenaria (figure 18) will be used to address leaching and contamination.

As illustrated in figure 18, Wacassasa River site 1 has the lowest degree of variability, whereas Philman Pit and Quality Aggregates had the highest degree of variability. Based on this quality, Philman Pit and Quality Aggregates may have experienced more mixing of young and old mollusks and leaching of amino acids out of fossil shell matrices. Accordingly, the high degree of variability needs to be considered when assigning an aminostratigraphic age to Philman Pit and Quality Aggregates. On the other hand, aminostratigraphic age estimates at Wacasassa River site 1 can be regarded with confidence due to low variability. Overall, further analyses are required required to accurately assess historic environmental factors that may affect amino acid racemization at these sites.

In the broader sense of the aminostratigraphy of the Atlantic Coastal Plain, mollusks sampled at Wacasassa River site 1 and the upper bed at Caloosa Shell Inc represent MIS 5e correlating with Mitterer's (1974, 1975) aminozone Va sampled in southern and central Florida. The older aminozone recongnized in this study may also correspond with Mitterer's Vb, Vc and Vd aminozones.

SUMMARY AND CONCLUSIONS

The prime objective of this study is to establish the aminostratigraphy for the Plio-Pleistocene of the Gulf Coast of Florida by measuring amino acid isomers ratios (D/L ratios) in carbonate fossils. Specific goals include:

1. Establish aminostratigraphic ages (mean amino acid D/L ratios) for the Pinecrest Beds, Caloosahatchee, Bermont and Ft. Thompson Formations along the Gulf Coast of Florida.
2. Evaluate the thermal gradient effect on racemization rates.
3. Determine the suitability of different bivalve genera for aminostratigraphic analysis.
4. Address the effects of environmental factors, such as mixing and leaching, that have influenced amino acid racemization data.

SUMMARY OF FINDINGS

- Selected amino acids analyzed in this study include aspartic acid, glutamic acid, valine and phenylalanine. Despite the availability of four amino acids for analysis, only two were selected for aminostratigraphic interpretation. Rapid racemization in aspartic acid obscures D/L resolution making this amino acid unsuitable as a stratigraphic tool in warmer climates. A significant degree of scatter observed in phenylalanine ratios resulted in questionable D/L ratios. Accordingly, only glutamic acid and valine are the most appropriate amino acids for this study.

- The optimal time for hydrolysis was assessed by subjecting 40 samples, taken from a modern articulated *Mercenaria*, to heating at 110^{o}C. Two samples, one from each valve, were removed from the oven at two-hour intervals starting at two and ending at 40 hours. The results of this experiment showed that the optimal time for hydrolysis without inducing extensive racemization is from 15 to 25 hours.
- Although only *Chione* and *Mercenaria* were utilized in this study, other genera are available for analysis as well. Four genera (*Anadara, Anadontia, Dosinia,* and *Trachycardium,)* were collected from the upper Caloosa Shell beds and analyzed for D/L ratios. Based on comparison of variation between genera Anadara, appears to have the smallest degree of variation, whereas *Trachycardium* had the highest amount of variation. Consequently, Anadara may be suitable for aminostratigraphic analysis in the future.
- Mean D/L values from the "u-series calibrated" Upper Caloosa Shell bed can be assigned to MIS 5e. Accordingly, glutamic acid mean D/L ratio of 0.59 (*Chione*) and 0.61 (*Mercenaria*) and valine mean D/L value of 0.60 (*Chione*) and 0.69 (*Mercenaria*) obtained from the calibrated upper Caloosa shell bed (Ft. Thompson Formation) represent MIS 5e in central Florida.
- Amino acid racemization (AAR) data revealed two distinct aminozones. The younger aminozone includes the Ft. Thompson Formation and the

older aminozone includes the Pinecrest Beds, Caloosahatchee and the Bermont Formations.

- AAR was not able to resolve for age differences between older units such as the Pinecrest Beds, Caloosahatchee and the Bermont Formations. Alternatively, one may question whether these units are distinct separate divisions, or if they represent one stratigraphic unit. Based on amino acid D/L ratios, the later hypothesis can be supported.
- AAR data suggests that Wacasassa River site 2 is significantly younger than site 1. Previously, Wacasassa Rivers sites 1 and 2 were thought to belong to the Caloosahatchee Formation. Based on D/L ratios, Wacasassa River site 2 correlates with the younger aminozone and possibly the Ft. Thompson Formation.
- AAR data also suggests that Dean's Trucking and 101 Ranch sites, previously thought to belong to the Ft. Thompson Formation, belong to the older aminozone corresponding to the Caloosahatchee or Bermont Foramtions.

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Appendices

Appendix I: Hydroloysis Experiment results
Florida amino lab (FAL) number, time in over (hours)
Amino acid D/L ratio ASP= aspartic acid, GLU=glutamic acid
VAL=valine, PHE=phenylalanine

FAL	HOURS	ASP D/L	GLU D/L	VAL D/L	PHE D/L
0590 FH1	**2**	0.066	0.017	0	0.0357
0634FH1	**2**	0.08	0.016	0	0.0363
0590 GH1	**4**	0.099	0.028	0	0.026
0634 GH1	**4**	0.091	0.016	0	0.0189
0590HH1	**6**	0.121	0.03	0.009	0.03
0634 HH1	**6**	0.094	0.017	0.006	0.0156
0590 IH1	**8**	0.144	0.029	0.008	0.0293
06343 IH1	**8**	0.109	0.019	0.006	0.0178
0590JH1	**10**	0.137	0.037	0.009	0.0352
0634 JH1	**10**	0.109	0.024	0.006	0.02
0590 KH1	**12**	0.127	0.033	0.007	0.0284
0634 KH1	**12**	0.124	0.028	0.007	0.0233
0590 LH1	**14**	0.125	0.033	0.008	0.0276
0634 LH1	**14**	0.151	0.036	0.008	0.0312
0590 MH1	**16**	0.159	0.048	0.0093	0.0485
0634 MH1	**16**	0.147	0.037	0.008	0.0304
0590 nh1	**18**	0.119	0.031	0.007	0.0263
0634NH1	**18**	0.169	0.038	0.009	0.0332
0590 ah1	**20**	0.136	0.041	0.01	0.0327
0634 ah1	**20**	0.146	0.041	0.008	0.0349
0590 bh1	**22**	0.152	0.04	0.009	0.033
0634 BH1	**22**	0.136	0.033	0.008	0.027
0590 ch1	**24**	0.151	0.042	0.009	0.0353
0634 ch1	**24**	0.15	0.042	0.009	0.0347
0590 dh1	**26**	0.182	0.053	0.01	0.0416
0634 dh1	**26**	0.153	0.043	0.008	0.0355
0590 eh1	**28**	0.157	0.044	0.009	0.0361
0634 eh1	**28**	0.169	0.051	0.01	0.0409
0590oh2	**30**	0.172	0.054	0.012	0.0469
0634 oh1	**30**	0.153	0.047	0.009	0.0338
0590 ph2	**32**	0.174	0.052	0.011	0.0435
0634ph1	**32**	0.175	0.051	0.01	0.0405
0590qh2	**34**	0.181	0.058	0.012	0.05
0634qh1	**34**	0.172	0.047	0.009	0.03811
0590rh2	**36**	0.185	0.057	0.011	0.0483
0634rh1	**36**	0.18	0.059	0.011	0.0475
0590sh2	**38**	0.181	0.0599	0.013	0.0491
0634sh1	**38**	0.208	0.062	0.013	0.0547
0590 th2	**40**	0.197	0.064	0.014	0.0556
0643th1	**40**	0.227	0.058	0.012	0.0453

Appendix II: Genera experiment results

Florida amino lab (FAL) number, molluska genera (genera)
Amino acid D/L ratio ASP= aspartic acid, GLU=glutamic acid
VAL=valine, PHE=phenylalanine

FAL	genera	ASP D/L	GLU D/L	VAL D/L	PHE D/L
0845H1	anadara	0.8167	0.6368	0.6594	0.8105
0846H1	anadara	0.8308	0.6769	0.6848	0.8651
0847H1	anadara	0.8322	0.6528	0.7362	0.8459
0848H1	anadara	0.8581	0.6598	0.6889	0.8476
0849H1	anadara	0.8546	0.6434	0.6577	0.7969
0867H1	trackycardium	0.7590	0.5804	0.5334	0.2382
0867H1	trackycardium	0.7179	0.5902	0.4927	0.2400
0867H2	trackycardium	0.7179	0.5902	0.4927	0.2400
0868H1	trackycardium	0.8641	0.6501	0.6655	0.4200
0868H2	trackycardium	0.7169	0.6512	0.6048	0.8172
0869H1	trackycardium	0.7544	0.6121	0.5160	0.8393
0869H2	trackycardium	0.8214	0.6213	0.4797	0.7803
0870H2	trackycardium	0.7523	0.6173	0.4208	0.7169
0874H1	dosinia	0.7452	0.6545	0.6561	0.8410
0874H2	dosinia	0.7300	0.6497	0.6200	0.8026
0875H1	dosinia	0.7424	0.6276	0.6162	0.8689
0876H1	dosinia	0.7547	0.6163	0.6339	0.8407
0877H1	dosinia	0.7204	0.6072	0.6066	0.8534
0878H1	dosinia	0.7790	0.7381	0.7268	0.8266
0879H1	anadontia	0.9237	0.6844	0.8775	1.0570
0880H1	anadontia	0.9034	0.6912	0.7701	0.9480
0881H1	anadontia	0.7879	0.5741	0.6848	0.9785
0882H1	anadontia	0.9561	0.7063	0.7779	0.9303

Appendix III: *Chione* D/L ratios

Site location, Florida amino lab (FAL) number, Amino acid D/L ratio ASP= aspartic acid, GLU=glutamic acid, VAL=valine, PHE=phenylalanine

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
wacasasa river	0809H	0.8056	0.8996	0.9646	0.8086
site 1	0810h	0.7456	0.8239	0.8871	0.746
	0811h	0.8033	0.9038	0.9779	0.7749
	0812h	0.8117	0.8952	1.032	0.7512
	0813h	0.8087	0.9083	0.9952	0.7207
wacassa river	0840h	0.6195	0.5751		0.6543
site 2	0841h	0.6231	0.5093	0.529	0.8118
	0842h	0.7105	0.6471	0.407	0.6811
	0843h	0.5365	0.5376	0.611	0.7657
	0844h	0.695	0.6159	0.499	1.079
login lake	0818H	0.8922	1.0019	0.606	0.9682
	0819H	0.7886	0.9531	1.041	1.0957
	0820H	0.8152	0.9985	1.203	0.8926
	0821H	0.827	0.955	1.025	0.9253
	0822H	0.789	0.951	1.038	0.9641
	0823H	0.8193	0.9184	0.988	1.0167
	0824H	0.9515	1.0419	1.059	0.9761
	0825H	0.8969	1.016	1.071	0.9197
	0826H	0.8334	0.9553	1.004	0.9566
	0827H	0.8518	0.9774	1.024	0.9035
101 RANCH	0601AH	0.8477	0.8716		0.9677
	0601BH	0.8158	0.8803	0.9317	0.915
	0601CH	0.8468	0.8958	0.943	0.8937
	0602AH	0.9125	0.8951	0.97	0.9419
	0602BH	0.8837	0.9216	0.948	0.9755
	0602CH	0.8979	0.9424	1.026	1.0021
	0603BH	0.8882	0.9915	1.026	0.965
	0603CH	0.8387	0.8378	0.815	0.9828
	0607AH	0.807	0.8499	0.811	
	0607BH	0.5922	0.8755	1.044	1.0614
	0607CH	0.9453	0.8686	1.0329	1.198
	0608AH	0.9284	0.8973	0.8891	0.9759

Appendix III Continued

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
101 RANCH	0608BH	0.9438	0.8216	1.031	1.0201
	0608CH	0.8375	0.893	0.9809	0.8245
	0496AH	0.7482	0.6227	0.6529	0.8471
CALOOSA UPPER	0496BH	0.7426	0.7917	0.6428	0.7778
BED	0497AH	0.7936	0.6001	0.5684	0.8259
	0497BH	0.6069	0.6279	0.625	
	0759AH	0.8489	0.9172	1.069	1.07
	0760AH	0.8778	0.9401	1.066	1.02
	0761AH	0.8204	0.9078	1.053	1.09
	0762AH	0.8757	0.9641	1.048	1.06
	0763AH	0.8436	0.9369	0.9613	1.0423
	0673AH	0.7185	0.4312	0.4794	0.6414
	0674AH	0.7703	0.5588	0.5868	0.7493
	0675AH	0.851	0.493	0.609	0.7109
	0676AH	0.917	0.575	0.646	0.7395
	0764AH	0.86	0.9271	1.02	1.0621
CALOOSA LOWER	0765AH	0.693	0.503	0.848	0.882
BED	0766AH	0.8189	0.9339	1.009	1.034
	0767AH	0.8563	0.9112	0.9223	1.0048
	0464AH2	0.818	0.914		0.8487
	0464BH2	0.8622	0.9652	0.945	1.0518
	0465AH1	0.7254	0.8521	0.984	0.9771
	0465AH2	0.7668	0.8646	0.919	1.0457
	0466AH2	0.767	0.832	0.852	0.833
	0466BH2	0.8079	0.8648	0.889	0.927
	0467AH1	0.7736	0.8223	0.86	0.6617
	0467BH1	0.8585	0.8183	0.933	1.1111
	0468AH2	0.8733	0.9607	0.974	1.1935
	0468BH1	0.845	0.9839	1.031	1.095
	0469AH1	0.7676	0.8664	0.985	0.9808
	0469BH1	0.7831	0.8428	0.966	0.9639
	0470AH2	0.656	0.6917	0.727	0.8496
	0470BH2	0.851	0.9601	0.962	1.7697
	0471AH1	0.764	0.882	0.988	0.8615
	0471BH1	0.803	0.943	1.023	0.9374

Appendix III continued

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
DEAN TRUCKING	0785H	0.881	0.678	0.968	1.0874
	0786H	0.8595	0.9825	0.895	0.9909
	0787H	0.874	0.908	1.081	0.9863
	0788H	0.8169	0.8258	1.049	0.9446
	0789H	0.943	0.823	1.068	1.0119
BONITA GRANDE	0800h	0.9389	0.9103	1.2258	1.0057
LOWER BED	0801H	0.7044	0.733	1.0984	0.8579
	0802h	0.9636	0.9524	1.1452	0.9464
	0803H	0.8312	0.9682	1.2028	1.0659
	0804H	0.885	0.767	1.048	1.0812
BONITA GRANDE	0795h	0.9171	0.9107	1.0676	1.0236
UPPER BED	0796H	0.969	0.859	1.099	1.0073
	0797h	0.9611	0.9931	1.0771	1.5506
	0798h	0.9759	0.9781	1.1239	0.9814
	0799H	0.8979	0.9657	1.0484	1.0052
PHILMAN PIT #1	0770H	0.81	0.649	0.886	
	0771H	0.769	0.525	0.821	0.8823
	0772H	0.854	0.754	1.014	0.7806
	0773H	0.861	0.739	0.944	0.9873
	0775H	0.7561	0.6493	0.876	0.9779
PHILMAN PIT #2	0776H	0.921	0.787	1.006	0.8746
	0777H	0.8748	0.9009	0.993	1.0316
	0778H	0.8593	0.8816	0.986	0.9805
	0779H	0.8159	0.8483	0.984	1.0212
	0539 ah1	0.83		1	0.7982
	0539 BH1	0.81	0.93	1	0.8617
	0539 CH1	0.78	0.91	0.95	0.7613
	0539 DH1	0.79	0.81	0.98	
QA SARASOTA	0540 ah1	0.83	0.86	0.97	0.8635
	0540 BH1	0.84	0.89	0.95	0.7548
	0540 CH1	0.8	0.9	1.03	0.8479
	0540 DH1	0.79	0.9	0.99	0.7394
	0541 AH1	0.73	0.9	0.89	0.8463
	0541 BH1	0.84	0.82	1	0.9396
	0541 CH1	0.82	1	1.02	0.8674
	0541dh1	0.775	0.951	0.92	0.7841
	0542 aH1	0.867	0.887	1.028	0.9426
	0542bh1		0.867		

Appendix III continued

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
	0542ch1	0.863		0.998	0.8202
QA SARASOTA	0542dH1	0.83	0.912	0.97	0.6967
	0543 AH1	0.88	0.85	0.99	0.9127
	0543BH1	0.922	0.94	1.101	1.0415
	0543CH1	0.869	0.989	0.968	0.7257
	0543DH1	0.891	0.887	0.445	0.7359
	0544ah1	0.872	0.965	1.041	1.0243
	0544bh1	0.89	0.961	1.1	0.6277
	0544ch1	0.97	0.94	1	0.8669
	0544dh1	0.81	0.93	0.95	0.8279
	0545AH1	0.842	0.93	0.991	0.8546
	0545bh1	0.82	0.907	0.95	0.6486
	0545ch1	0.84	0.89	0.97	0.9085
	0545dh1	0.86	0.91	0.97	0.9149
	0546ah1	0.93	0.95	1	0.9997
	0546bh1	0.635	0.63	0.88	0.8465
	0546CH1	0.949	0.938	1.038	0.9835
	0546DH1	0.958	0.916	0.972	1.0269

Appendix IV: *Mercenaria* D/L ratios
Site location, Florida amino lab (FAL) number, Amino acid D/L ratio ASP= aspartic acid, GLU=glutamic acid, VAL=valine, PHE=phenylalanine

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
wacasasa river	0814h	0.8769	1.0119	1.0887	0.8877
site 1	0815h	0.8721	0.9678	1.0792	0.8647
	0816h	0.8817	0.9973	1.0869	0.8953
	0817h	0.8737	0.9634	1.028	0.9139
wacassa river	0838h	0.8092	0.6781	0.7324	0.866
site 2	0839h	0.8149	0.7662	0.797	0.9144
101 RANCH	0599AH	0.8488	0.884	0.972	0.9926
	0599BH	0.9147	0.878	0.979	0.9585
	0599CH	0.8622	0.894	0.994	0.9818
	0600AH	0.8357	0.898	0.9741	0.9401
	0600BH	0.8712	0.82	0.987	0.9742
	0600CH	0.9172	0.941	0.921	0.8878
	0604AH	0.863	0.919	1.008	0.8908
	0604BH	0.848	0.948	0.995	0.9727
	0604CH	0.81	0.859	1.036	1.0574
	0605AH	0.826		0.882	0.9828
	0605BH	0.873	0.5081	0.7309	0.6639
	0605CH	0.795	0.8817	0.955	1.0614
	0606AH	0.919	0.9782	1.1258	1.198
	0606BH	0.909	0.9168	0.959	0.9759
	0606CH	0.919	0.8464	0.9878	1.0201
CALOOSA	0667AH	0.8369	0.6425	0.7013	0.8503
UPPER BED	0668AH	0.871	0.549	0.609	0.7519
	0669AH	0.8458	0.6076	0.6204	0.8599
	0670AH	0.8132	0.5648	0.6418	0.8457
	0671AH	0.827	0.6899	0.7178	0.8307
CALOOSA LOWER	0754AH	0.8995	0.9482	1.076	1.03
BED	0755AH	0.9136	0.9976	1.086	1.02
	0756AH	0.8507	0.8916	1.13	1.09
	0758AH	0.9198	1.0026	1.053	1.06

Appendix IV continued

LOCATION	FAL	ASP D/L	GLU D/L	VAL D/L	PHE D/L
DEAN TRUCKING	0790H	0.7987	0.7473	1.061	0.9166
	0791H	0.905	0.679	0.892	0.9102
	0792H	0.939	0.8319	1.021	0.9418
	0793H	1.012	0.869	1.036	0.9921
	0794H	0.915	0.796	1.024	0.9208
PHILMAN PIT #2	0780H	0.798	0.567	0.855	0.7784
	0781H	0.5898	0.6464	0.863	0.6648
	0782H	0.9088	0.9042	1.14	0.9897
	0783H	0.8084	0.7696	0.938	1.0953
	0784H	0.9962	0.725	1.011	1.5178
QA SARASOTA	0547AH1	0.972	0.935	1.102	0.9783
	0547BH1	0.822	0.839	0.968	0.9501
	0547CH1	0.949	0.911	1.042	1.0078
	0547DH1	0.953	0.942	1.038	0.9467
	0548AH1	0.945	0.886	0.946	1.0286
	0548BH1	0.908	0.936	0.967	0.983
	0548CH1	0.291	0.404	0.549	0.5713
	0548DH1	0.915	0.899	1.052	0.9504
	0549AH1	0.769	0.68	0.716	0.7542
	0549BH1	0.903	0.851	0.957	1.0036
	0549CH1				
	0549DH1	0.863	0.815	0.905	0.9178
	0550AH1	0.85	0.831	1.008	0.9039
	0550BH1	0.918	0.778	0.942	0.9956
	0550CH1	0.871	0.821	0.894	0.8684
	0550DH1	0.89	0.753	0.967	0.8028
	0551AH1	1	0.944	1.072	0.9963
	0551BH1	0.971	0.922	1.041	0.9929
	0551CH1	1.029	0.904	1.068	1.0318
	0551DH1	0.943	0.919	1.02	0.9987
	0552AH1	1.035	0.927	1.079	1.0064
	0552BH1	0.996	0.946	1.072	0.9978
	0552CH1	0.935	0.985	1.095	0.9521
	0552DH1	0.393	0.557	0.753	0.7437
	0553AH1	0.923	0.85	1.023	1.0034
	0553BH1	0.939	0.891	1.035	0.9894