Narrative for Wehmiller et al., SE GSA 2019 Poster April 5, 2019

BOEM ASAP CORES Amino acid Racemization results and discussion

INTRODUCTION

The goal of this project is to demonstrate utility of AAR for the interpretation of stratigraphy and geochronology of shelf cores; the dating method requires calibration with independent (isotopic or radiometric) dates. AAR itself produces "age estimates" rather than "numerical dates" but can be more quantitative in selected areas. The NC Albemarle Embayment study is a good example (Wehmiller et al., 2010).

Selected cores for which the most data are available are the focus of most of this discussion. Other cores with fewer results or with complex interpretations (likely because of shell alteration and/or age mixing) are discussed in a separate section. Data for cores from Delaware to Georgia are reported. Data are reported for samples from onshore sites, several of which are independently calibrated with U-series coral ages (Skidaway Island, GA; Berkeley Pit, SC; East Lake Pit and Stetson Pit, NC; Gomez Pit, VA).

Because the interpretation of AAR results depends on the genus analyzed (different genera racemize at different rates), comparisons between cores and within single cores must focus on individual genera. If multiple genera are present in a core or region and all data for these multiple genera are internally consistent, the stratigraphic interpretations are reinforced. Inconsistencies in results can usually be explained by either age mixing or sample alteration.

References to prior AAR study of regions within the broad study area are listed at the end of this text.

For the purposes of the on-line poster on the GSA web site, the poster is divided into three panels. Panel 1 contains introductory material text from the poster; panel 2 contains data and graphs for the southeastern region (GA, SC, and NC); panel 3 contains data from the mid-Atlantic (DE, MD, VA) and a discussion of different approaches to age estimation. Funding for this project has been provided by the Bureau of Ocean Energy Management (BOEM) through the Delaware and South Carolina Geological Surveys.

POSTER PANEL FOR SC AND GA (panel 2)

Sub-panel A: The results for SC24 and SC22 demonstrate many of the principles of AAR. These results are plotted in a "spider diagram" that shows the D/L values for multiple amino acids identified along the x-axis. The most abundant amino acids in the samples are aspartic, glutamic, alanine, and valine (asp, glu, ala, val); phenylalanine, isoleucine, and leucine (phe, ileu, leu) are less abundant and often yield more scattered results, so they are considered less useful for stratigraphic purposes. Increasing D/L values (y-axis) indicate increasing age. The amino acid serine (Ser) behaves differently from the other amino acids, with decreasing D/L values with sample age (reference). The SC24 plot shows that the Holocene samples in this core have consistently lower D/L values than the Pleistocene samples in the core (serine excepted). These results are based on multiple analyses at each core interval, and the AAR results are consistent with both stratigraphy and 14C results, the latter in some cases obtained on the SAME shell as the AAR results (defined as paired analyses).

The similarity of the D/L values for most of the amino acids in SC22 and SC24 (Pleistocene) indicate that, based on AAR, these two cores have sampled the same Pleistocene unit.

Sub-panel B: Results for GAVA11 and the onshore calibration site at Skidaway Island, GA. The latter has an MIS 5a U-series coral age (Wehmiller et al., 2004). This plot shows that there is an overlapping range of D/L values for the four Mulinia samples from each site, hence the simplest interpretation is that they all represent the same aminozone with an age of ~ MIS 5a. However, the scatter of the results shows that the VC11 results cluster at slightly lower (~10%) values than those for the Skidaway site, but that there is one sample from each site that falls within the majority of results for the other. This observation can be explained as "typical inter-sample variation" caused by diagenetic factors, or by possible age mixing. The general conclusion, however, is that GAVC11 samples are MIS 5a in age, perhaps younger by a few thousand years. The temperature difference between the onshore and offshore samples may also be a factor in this age interpretation. This difference is addressed in discussions that follow.

Sub-panel C: This "spider diagram" plot compares results for GAVC6 and GAVC11 with the Skidaway Island site. SCVC24 results are also shown. The Skidaway results are shown with a 10% error bar to demonstrate that the GA6 and GA11 results fall within this range (with the exception of serine). The SCVC24 results plot slightly below those for the GA cores, perhaps because of an age difference (younger) or because of slight temperature differences between the environments of the GA and SC cores. The simplest interpretation of the GA-SC results shown in panels A, B, and C is that the Pleistocene aminozone seen in these cores represents an age of MIS 5a, perhaps broadly defined as between ~70 and 100 ka.

Results for SCVC01, 14, and 18 are also available. SCVC01 is entirely Holocene; 14 and 18 show evidence of two Pleistocene aminozones, with apparent age mixing. Further study is warranted.

Sub-panel D: The 14C ages in SC24, plotted vs. depth, show that a Pleistocene sample has been reworked into the Holocene section. This reworked sample was first identified in the AAR results, then confirmed with 14C. The Pleistocene section of SC24 shows a cluster of "finite" 14C ages in the 40ka range; the apparent reproducibility of these results, combined with the AAR data, is suggestive of a "real" MIS 3 age, but ages in this range must always be considered minimum ages in the absence of other evidence. See "Age estimation" panel, below, for further discussion.

POSTER PANEL FOR NC (panel 2)

Sub-panel A: The Mulinia "spider diagram" shows that nearby cores NC08 and NC09 have an aminozone that clusters very tightly for multiple amino acids. These results duplicate results obtained for samples from CFNC53, one of several ACOE cores taken over 30 years ago and analyzed by Linda York (1990 PhD, University of Delaware). CFNC53 was taken very near NC08, hence the comparison with the newer NC08 and NC09 affirms the integrity of the AAR results for this region. The lower D/L value cluster from NC08 and NC09 appears to be a late Pleistocene aminozone, as the 14C results for samples from this depth and aminozone all fall in the range of 30 to 43 ka (see below). A single Mulinia sample from NC01 also falls in this same aminozone.

Core, depth (ft)	14C age, yrs
NC VC08 3.16'	33230
NC VC08 10.48'	42130
NC VC09 4.73'	1500
NC VC09 9.57'	7670
NC VC09 14.23'-14.40'	42630
NC VC09 16.23'	35100
NC VC09 17.15'	30020

A second aminozone in NC08, stratigraphically lower, has significantly higher D/L values. The reproducibility of the two NC08 aminozones and stratigraphic consistency is an important test of the integrity of the results for this core. The D/L values for the older (higher D/L values) aminozone in NC08 are comparable to results seen in mid-Pleistocene samples from the Albemarle Embayment (Wehmiller et al., 2010). Hence it appears that there is a significant hiatus in NC08, with a regionally significant late Pleistocene unit over an older, mid-Pleistocene unit (a unit that is found in other cores in the region – see below).

Sub-panel B: This figure shows the co-varying relation between alanine, aspartic, and glutamic D/L values in NCVC cores 31, 32, and 34. The older aminozone seen in NCVC09 is evident in NCVC34 (labeled as part of the "P2" group in sub-panel B). The results for cores 31 and 32 cluster around D/L values that are about 15% to 20% higher than those seen in the younger aminozone in NC08. The cluster for cores 31 and 32 is labeled P1, and these values appear to represent an age somewhat older than the youngest Pleistocene aminozone seen in NC08 and NC09, but not as old as the aminozone seen in the deepest part of NC08. P1 also is evident in VC34 – see sub-panel C for discussion.

Sub-panel C: This graph shows the distribution of D/L values in NCVC34 vs. depth in the core, for Mulinia results only. Mercenaria data (not shown) from this core are consistent with these observations. The P1 and P2 clusters for alanine are delineated with the two rectangles; alanine is the amino acid with the "best" resolving power for age differences in these samples, but other amino acid results are consistent with this conclusion. The depth distribution of D/L values in VC34 can be interpreted in several ways, but the preferred interpretation is that the P2 aminozone is seen throughout the core, in place below 1.8 meters and reworked in the shallowest (~0.4 m) samples. The P1 aminozone, seen only at ~1.4 m, represents the "true age" of this shallower unit, with (as noted above), P2 samples reworked into the younger unit represented by P1. This interpretation is consistent with the lithology of the core in this depth interval.

The alternative explanation for the VC34 results could be that the entire core is represented by ONLY the P2 aminozone and that the P1 results in this core represent altered (lower D/L values) samples. However, the overall precision of the P1 results in multiple cores argues against this option.

PANEL FOR THE DELMARVA REGION (panel 3)

The cores reviewed here include three out of a series originally reported by Toscano et al. (1989) and York (1990). Several of these cores were re-sampled for the present study, and paired analyses of shells by both AAR and 14C conducted. The interpretations of Toscano et al. (1989) have not changed with the newer results, but the number of analyses is now much larger lending further support to the original interpretations. The analyses of these Maryland shelf cores were conducted in a preliminary phase of the BOEM project in order to establish a link between the pending [newer] analyses and the original work by Toscano et al. (1989).

27-1520: these results show the trend of D/L vs. depth for multiple amino acids, thereby demonstrating the apparent variability for multiple amino acids in samples that are interpreted as belonging within the same aminozone. The original work of Toscano et al. for this core suggested that there was one aminozone throughout the core, and the newer data confirm this conclusion.

18-1248: the original data for this core implied that there were two aminozones, and the newer results confirm this observation. Results from depths to ~ 4 m indicate a single aminozone; an aminozone with ~ 40 to 50% higher D/L values is found at ~ 6 m.

27-1520, 18-1230, and 18-1248: this plot shows the mean value for 27-1520 compared with all the data for 18-1230 and 18-1248. The latter two cores have results that overlap with 27-1520 and both then have two older aminozones found stratigraphically lower in each core. The deeper aminozones in 1230 and 1248 appear to be different, but both are clearly indicative of a unit that is older than the one found in 27-1520. Toscano et al., designated the older and younger units (aminozones) as Q1 and Q2, and the seismic line that crosses the location of 18-1230 shows these two units. We conclude that the seismic- and amino-stratigraphy are internally consistent, providing a good test of the AAR method.

Seismic lines for 18-1230 and 27-1520 are from USGS collaborators.

There are no 14C data for these three cores, and limited 14C data from nearby cores exist. Nevertheless, for Mulinia from the region with 14C results, the D/L values around alanine of ~ 0.40 are definitely Pleistocene, having yielded finite 14C ages in the range of 30 ka.

VA2016-16-01 and VA2016-16-02: this plot shows the covarying aspartic, glutamic, and alanine D/L values for two BOEM cores VA2016-01 and -02. These cores are from nearby (<2 km) sites offshore of Metompkin Island, VA. Initial analyses from these cores showed a wide range; additional analyses clustered more tightly, but all analyses are shown in the figure. The spread of results is quite large, but the cluster of lowest D/L alanine values falls slightly above the cluster of alanine D/L values for 27-1520 and 18-1248 (lower cluster). This relation is not seen for aspartic and glutamic. Are the alanine values the better ones to rely upon for identifying an age distinction, or are aspartic and glutamic the better ones to use? In this case, it appears that aspartic and glutamic may be the more useful, identifying a "single aminozone" that is found in 27-1520, 18-1230, 18-1248 and the two VA2016 cores. Nevertheless, the broad spread of D/L values in the two VA2016 cores is interpreted to represent mixing of a wide range of sample ages.

Two cores on the Maryland shelf, 18-1230 and 18-1248, sampled two major stratigraphic units, Q1 and Q2. Data for 18-1230 and the associated seismic line are shown in this poster. Q1 and Q2 were originally defined by Toscano et al. (1989); the use of these terms has been continued by Brothers et al.

(USGS). Q1 is interpreted to represent a unit that pre-dates the Eastville Paleovalley, hence it is likely MIS 7 or MIS 9. Q2 is a regionally extensive unit that is found throughout the mid-Atlantic shelf. AAR results clearly resolve these two units, and Q2 is interpreted to represent all or part of MIS 5.

THREE APPROACHES TO AGE ESTIMATION (panel 3)

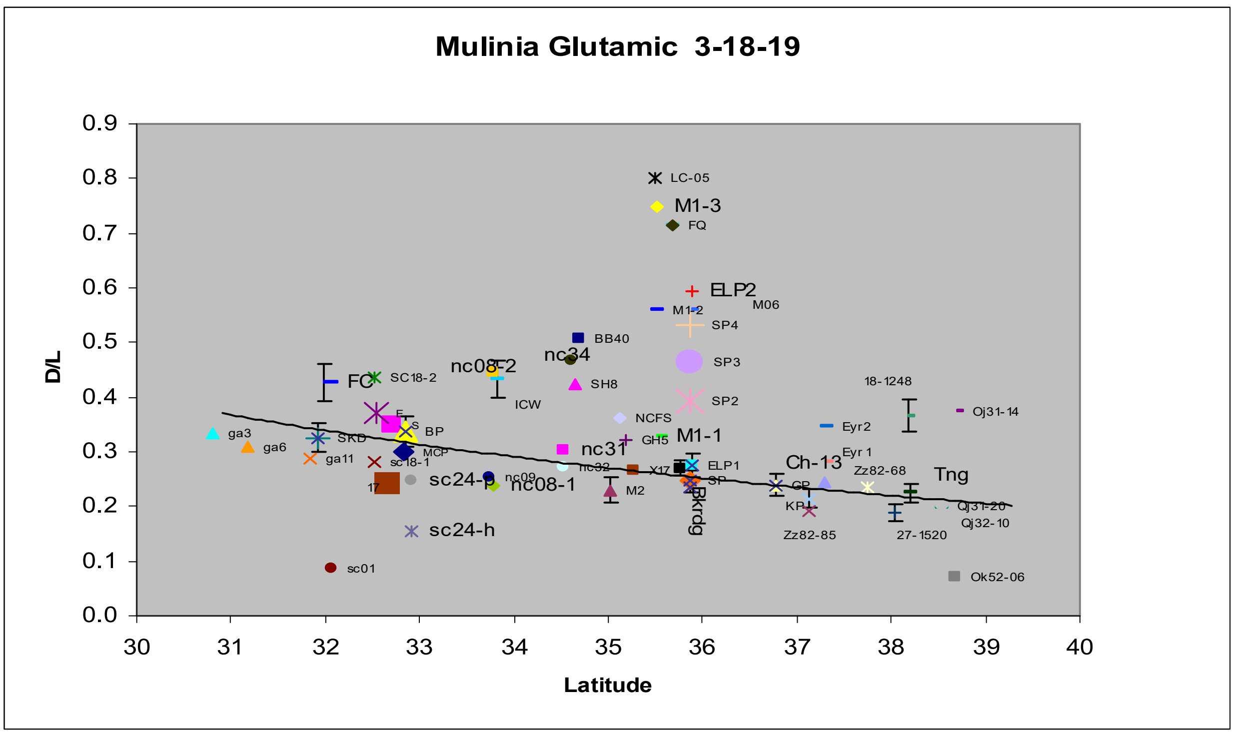
Sub-panel A: This is a histogram plot of the 14C results (all shell samples) from the BOEM mid- and southeast Atlantic projects. The results are separated by genus. With the exception of two Astarte and two Mercenaria samples, no results were reported as being greater than the lab detection limit. The main point to take from this figure is that, if no other chronological data were available for the BOEM core samples, one would conclude that there is a unit on the shelf that clusters in the 35-45 ka age range. Broadly speaking, this unit is found at elevations of ~ -10 to -20 meters. AAR data for most, if not all, the shells that fall in this finite 14C age range actually indicate that the shells are older, usually in the MIS 5a (~80 ka) range but occasionally older. Therefore, the issue of low-level contamination of “old” shells with “young” carbon must be addressed. This is a common issue in the field of 14C dating of shell carbonate (see Busschers et al., 2014).

Sub-panel B: An underlying principle of racemization is that D/L values for samples of the same age will increase with increasing temperature or decreasing latitude. This figure demonstrates this principle using summary data for the P1 aminozone as recognized in the mid- and southeast Atlantic regions. We show mean values for aspartic and glutamic the offshore and onshore Mulinia samples from each region. The onshore samples are all considered to be MIS 5a in age. In both cases, the D/L values from the offshore samples plot slightly below those for the onshore samples. This offset between the results can be explained by one of two options: 1) the offshore samples are the same age as the onshore samples, with the lower D/L offshore values being explained by slight differences in effective temperatures for the offshore (cooler) samples; 2) the offshore samples are slightly younger than the onshore MIS 5a samples, and there is no difference between the effective temperatures for the onshore and offshore samples. The trends for aspartic and glutamic are generally consistent, although the aspartic results identify a smaller separation between the trends for onshore and offshore results. As this figure is a summary only, we include also a graph for glutamic D/L values vs. latitude (in Mulinia) in the Appendix (below).

Sub-panel C: The concept of proportional time applied to the estimation of age differences for selected aminozones. This figure is based on laboratory kinetic experiments reported by Kaufman (2006). It shows the covarying relation of aspartic and glutamic D/L values in foraminifera samples heated at 110^o for periods of 2, 4, 8, 16, 32, 64 …. out to 499 days. The figure shows that the two mid-Atlantic aminozones P1 and P2 plot at positions equivalent to ~ 8 and ~32 days; the two southeast Atlantic zones plot at roughly 32 and 64 “equivalent” days, respectively. These observations suggest age differences only, but if an age is assigned to any observed value, a corresponding age can be assigned to the other. For the mid-Atlantic results, P2 represents Q1 of Toscano et al. (1989), thought to represent either MIS 7 or MIS 9 based on stratigraphic relations (USGS interpretation). If Q1 = MIS 9 (assume ~300 ka), then Q2, is approximately 75 ka (MIS 5a). For the southeast region, the age difference between P1 and P2 is at least a factor of 2 to 2.5; if P1 is MIS 5, P2 is likely MIS 9, which is consistent with how the P2 results (southeast) compare with results from the Albemarle Embayment results (Wehmiller et al., 2010).

This proportional time approach was used by Wehmiller et al. (2010) to estimate age differences from D/L values observed in multiple cores from the Albemarle Embayment. This prior study reported extensive analyses from multiple cores, many of which sampled the complete Quaternary section within the Albemarle Embayment. It is a qualitative approach to estimation of ages that must be tested by results that are independently calibrated. Because the relative rate of aspartic racemization appears to "slow" as the D/L values increase, aspartic loses some ability to resolve age differences (compared with glutamic) as the D/L values increase.

Appendix: D/L glutamic vs. latitude, Mulinia, GA to MD; line connects onshore MIS 5a calibration sites; increasing D/L values indicate increasing age. D/L values around 0.7 represent early Pleistocene; values around 0.4 to 0.6 at 36N represent middle Pleistocene. Values below 0.15 represent Holocene.



SE GSA 2019 WEHMILLER ET AL POSTER REFERENCES

Wehmiller website: http://www.ceoe.udel.edu/our-people/profiles/jwehm

Busschers et al. 2014 *Radiocarbon*

Harris 2000 University of Delaware PhD

Toscano et al. 1989 Md Geol Survey RI 50:
http://www.mgs.md.gov/publications/report_pages/RI_50.html

Wehmiller et al. 1992 *Quaternary Research*

Wehmiller et al. 2010 *Quaternary Geochronology*

Wehmiller et al. 2012 *Quaternary Geochronology*

Wehmiller 2013 *Quaternary Geochronology*

Wehmiller and Pellerito 2015 *GeoResJournal*:
https://www.sciencedirect.com/science/article/pii/S2214242815000170

Wehmiller et al. 2015 GSA Baltimore poster with extensive list of references:
https://gsa.confex.com/gsa/2015AM/webprogram/Paper263915.html

Wehmiller et al., 2019 SE GSA Presentation: southern Delmarva Island beaches:
https://gsa.confex.com/gsa/2019SE/webprogram/Paper326646.html

York and Wehmiller 1992 *Sedimentary Geology*

Online maps:
https://www.arcgis.com/home/webmap/viewer.html?webmap=49c4b9d1312c433b9ca461fab7fce8b5

USGS DelMarVa project: http://woodshole.er.usgs.gov/project-pages/delmarva/

http://www.ceoe.udel.edu/our-people/profiles/jwehm