Discussion paper to supplement SEGSA2024 Wehmiller et al. Poster:

AAR and 14C data from NCVC08 and NCVC09, FRYING PAN SHOALS, CAPE FEAR AREA OF NORTH CAROLINA

John Wehmiller

U Delaware jwehm@udel.edu

May 18, 2024

This is a "work in progress" to present and discuss AAR data from two cores taken as part of the BOEM 2015 SE ASAP Program from the Frying Pan Shoals- Cape Fear area, SE North Carolina. Data for additional cores from the Onslow Bay region (also part of the BOEM project) are cited where relevant. Information presented here provides background for the poster presentation, in order to provide some context for optional interpretations of 14C and AAR data.

The maps below are from our ArcGIS Online database, each progressively zooming in on the area of cores NCVC08 and NCVC09. The 2015 BOEM cores are discussed in Conery et al. (2021). https://www.tandfonline.com/doi/full/10.1080/1064119X.2021.1967531

Data discussed here are from NCVC08, NCVC09, and NCVC31, NCVC32 and NCVC34. 08 and 09 are south of Cape Fear; 31, 32 and 34 are in northern Onslow Bay. Other cores from the 2015 BOEM project have AAR data, and numerous other analyses have been conducted at U Delaware on samples from cores and grab samples along the nearshore of Onslow Bay. York and Wehmiller (1992) summarize data from some of the sub-barrier cores (Duke Univ) from Bogue, Shackleford, and Core Banks.

The NCVC08 AND NCVC09 cores were taken at water depths of approximately 13 m; the NCVC31, 32, and 34 cores were taken at approximately 19 m depth.







Core CFNC-53 is one of a series of ACOE cores taken in the late 1970's (Meisburger). Samples from these cores were obtained by USGS colleagues and passed on to UD for AAR analysis in the early 1990's.

Relevant data and figures are discussed in the following sections.



This is the first of a series of plots of D/L Aspartic or D/L Alanine vs D/L Glutamic. These three amino acids are the most abundant in Mulinia and most clearly resolved instrumentally. The co-variance of one D/L vs. another is a useful criterion for assessing the integrity of the results. Plots like these were used extensively in our Mid-Atlantic AAR paper (Wehmiller et al., 2021: Quaternary Geochronology). D/L values increase non-linearly with increasing sample age.

Graph #1 shows the D/L Asp and D/L Ala vs D/L Glu in Mulinia from NCVC08. All data are shown so that one gets a sense for the scatter observed when multiple samples from the same depth are analyzed. Two broad clusters are seen, "01" and "02". The "01" samples are from ~10 to 12' downcore; the "02" samples are from ~17' downcore. However, there is evidence of age mixing, as one group 2 sample is found in the depth interval of the group 1 samples. The simplest interpretation of these results is that there are two ages represented, but it is quite likely that a significant age is represented by each of the two groups. The range of values within the two groups can be interpreted as representing real age differences within each group or diagenetic artifacts that yield a "typical" scatter for samples that are the same age. These two options must be weighed against other stratigraphic or sedimentological evidence. Note that Ala and Asp have similar D/L values for Group 1, but that these D/L values are distinctly different for the "older" group 2. Ala seems to be more useful for resolving apparent age differences. Graphs that follow will use Ala vs. Glu data only.

Note added June 6 2024: Data for Mulinia samples from cores taken by Duke Univ in the 1970's (York and Wehmiller, 1992) supplement this work. New analyses from selected cores from Bogue, Shackleford, Core and Portsmouth Banks are in progress. Data from Shackleford and Bogue at depths ~25m bsl fall into the group of higher D/L values seen in Figure 1, above.



This figure shows Mulinia D/L Alanine in NCVC08 AND NCVC09 plotted vs. D/L Glutamic. The range of Ala and Glu in NCVC08 & NCVC09 (the group of lower D/L values) is similar in both cores, implying a similar age or age range for the units sampled in these two cores. The NCVC09 samples are from ~14' to 18' downcore.

A very similar range of D/L values is observed in Mulinia from the Meisburger cores (CFNC53 and others) when compared with the NCVC08 and NCVC09 Group 1 results. NCVC08 and NCVC09 are located on opposite flanks of the Frying Pan Shoals, suggesting (perhaps) that there is a "continuous" unit represented by the Group 1 AAR results. The concordance of results from CFNC53 and NCVC08 is reassuring, given that the sampling dates for these two cores are separated by nearly 40 years.

This figure provides additional context for the two groups of D/L values. Here Mulinia data from NCVC32 and NCVC34 are plotted, along with the results for NCVC08 and NCVC09. The results are labelled "32 Ala" for the results from NCVC32 and "34 Ala 1" and "34 Ala 2" for the two clusters of results from NCVC34 (another group, labelled "34 Ala 3", overlaps with 34 Ala 2. Both NCVC08 and NCVC34 contain samples that cluster within Groups 1 or 2, further supporting the "reality" of these aminozones as regionally important units, whether or not the samples are in place. The 34 Ala 1 group is found at ~1.0 to 1.5' downcore; the overlapping 34 Ala 2 and Ala 3 groups are found at multiple depths from ~4' to 18' down core. As above, the range of D/L values within each of the groups can represent real age differences and/or diagenetic effects on the observed values. Also included in this plot are three points (solid triangles) for samples with paired 14C/AAR results. The 14C results are discussed further in relation to graph 4.



This figure is used to address the question of the age of the samples represented by AAR group 1 as seen in graphs #1 and #2.

During the 2015 ASAP BOEM program, there was a systematic effort to obtain at least one 14C date for each of the cores. In most cases, several 14C results were obtained for each core. Examples of these results are found in Conery et al. (2021) and Long et al. (2021). In many cases, it was possible to obtain both 14C and AAR results from the SAME shell, thereby eliminating any ambiguities related to shells of different ages being found in the same core sample interval. The data presented here are for those shells with these PAIRED analyses (combined 14C and AAR). In addition to results from NCVC 08, 09, 32, and 34, results for paired analyses from other cores in the immediate area are included to supplement the interpretation of these paired results. For comparison with Graphs 1-3, the data for Group 1 of NCVC08 are also plotted. Results are identified with the core number (32, 08, etc) and then the 14C age in ka.

The range of observed 14C results is between ~33 ka and ~49 ka, but there is no general systematic trend of increasing D/L value with increasing 14C age. However, two 14C results from NCVC08 ARE consistent with the observed D/L values, showing increases in D/L values for samples with ~33 ka and ~42 ka 14C ages, respectively. These samples were found in stratigraphic superposition, so the 14C and AAR results appear internally consistent. Taken at face value, these results imply that the AAR Group 1 results in NCVC08 represent an age between ~35 and ~45 ka, within MIS 3.

An alternative approach to the assignment of ages for the samples plotted here will be discussed in relation to Graph #7. *That alternative approach interprets ALL the 14C ages plotted in Graph #4 as minimum ages, instead indicating that the shells with AAR Groups 1 and 2 are all late and middle Pleistocene, respectively.* The issue of 14C "finite" ages between ~30 and ~50 ka on shell carbonate has been debated for decades, as trace amounts of carbonate exchange (with modern or young carbon) can result in incorrectly young 14C results. Given the sea-level history of the past ~75ka, and the present water depth of the cores (~20m) the shells with these finite 14C ages would have been subaerially exposed during the last glacial maximum, thereby susceptible to a variety of weathering or diagenetic processes that could have led to low-level carbonate contamination.



Graph #5 Age mixing – evidence from 14C results on shell material in NCVC08, 09, 32, 34.

Numerous examples of apparent age mixing within the BOEM cores can be cited. AAR and 14C results can be used for this discussion, reminding us that it cannot be assumed that samples from these cores are in place. This figure shows the 14C results for NCVC08, 09, 32, and 34, plotted vs. depth in core. As noted above, the samples in question have almost definitely been subaerially exposed during the last glacial maximum, so there is a high probability that shells have been transported during regressions/transgressions related to late Pleistocene sea-level history. A particularly graphic example of age mixing is seen in the results for NCVC34, where two "greater than" 14C ages are found at core depths stratigraphically above a 43ka 14C result. Additionally, the NCVC09 14C ages between ~30 and ~43 ka are not in stratigraphic order, suggesting either age mixing or that these results reflect sample alteration. Other analyses that we have conducted on grab samples from Onslow Bay (and on beach samples from the region) further demonstrate the frequency of "old" shells at the sediment-water interface.



Graph #6: Age mixing – evidence from AAR data from shell material in NCVC08, 09, 32, 34. Here we plot D/L Glu values in multiple taxa (Mulinia, Spisula, and Mercenaria) vs. depth in core. Prior work (Wehmiller et al., 2021) indicates that D/L Glu values in these three taxa, if the same age, are similar (within ~10%) so this plot can be used as a qualitative indicator of at least three apparent clusters of D/L values - ~0.25, ~0.45, and ~ 0.63 (the latter including an "old" Spisula sample found at ~0.3m in NCVCC34. As before, we note that the scatter within each of these groups can be caused by real age differences or a combination of diagenetic, age-mixing, or even thermal factors. As noted above, NCVC08 has both the 0.25 and 0.45 groups, with evidence of the 0.45 group mixed into the 0.25 group at ~10.5'.



Graph #7 Plot of D/L Glu in Mulinia from onshore and offshore sites, Delaware to Georgia. This figure is an extension of the work presented in <u>Wehmiller et al. (2021)</u>. It is based on the principle that D/L values will increase with decreasing latitude for samples of "equal" age. Offshore data from DE-NC-SC-GA are shown as green solid circles. Onshore sites (many from subsurface sections in NC) are shown as triangles or squares. The dashed lines represent an "envelope" of D/L values interpreted to represent MIS 5. These lines were presented in our 2021 paper based on data from sites between NC (~35.5N) and DE (~39N). They are projected here to southern latitudes and "capture" data from two MIS 5 calibration sites, Berkeley Pit (SC) and Jones Pit (GA), both having yielded MIS5a coral U-series results (Wehmiller et al., 2004). The BOEM core results from GA, SC, and NC plot either within a Holocene group (identified with ~7 to 8 ka 14C data) or just below the lower line for the "MIS 5 envelope". It is possible that these offshore results (with 14C ages between ~33 and ~44 ka) plot below this envelope because of contrasting temperature histories (offshore vs. onshore) or because the samples are truly in the ~40 ka age range. One notable result, however, is for the NCVC34 43ka sample, which has a D/L value equivalent to a nearby onshore site (CIVC2, which has an [unpublished] U-series coral age of ~95 ka).

Our 2021 paper used a modeling approach to estimate age <u>differences</u> for samples with differing D/L values. For example, the two D/L clusters from NCVC08 are roughly 0.24 and 0.45. Using Figure 12 of our 2021 paper as a template, this difference in D/L values represents approximately a 5x age difference. If the lower D/L group is "assigned" an age of 40ka, then the higher D/L group would be estimated to be ~200 ka; corresponding pairs of age estimates of 80 and 400 ka, respectively, result. This latter pair of age estimates is consistent with modeling results from NE NC (35.5-36N) and limited Sr-isotope calibrations of "mid-Pleistocene shells) from central NC (Wehmiller et al., 2012; 2021). Furthermore, the range of results for OBX17 (a core at Cape Hatteras) is interpreted to represent the entire Pleistocene (Culver et al., 2011; 2016), providing further perspective on the temporal range represented by the observed D/L values.

The information presented in Graph #7 does not rule out the possibility that some (or all) of the 14C ages on the GA-SC-NC BOEM shells are correct, but it places those results in the broad context of AAR data from the entire mid- and southeastern Atlantic coastal plain. Issues of contrasting temperature histories, age mixing, and diagenetic alteration all affect the interpretation of AAR (and 14C) results, so additional "experiments" on specific shells can or should be conducted where possible. One Mercenaria shell (thought to be MIS 5 based on AAR) from our mid-Atlantic study yielded a range of 14C ages between ~40 and ~46 ka when serial fractions were analyzed separately (sample JW2017-306) (Table 2a, Wehmiller et al. 2021), demonstrating the apparent 14C "noise" within shells that are actually too old to be reliably dated by 14C.



SELECTED REFERENCES

Ian Conery, John P. Walsh, David Mallinson & David R. Corbett (2021): Marine Geology and Sand Resources of the Southern North Carolina Inner Shelf, Marine Georesources & Geotechnology, DOI: 10.1080/1064119X.2021.1967531

Culver, S.J., Farrell, K.M., Mallinson, D.J., Horton, B.P., Willard, D.A., Thieler, E.R., Riggs, S.R., Snyder, S.W., Wehmiller, J.F., Bernhardt, C.E., Hillier, C., 2008. Micropaleontologic record of late Pliocene and quaternary paleoenvironments in the northern Albemarle Embayment, North Carolina, U.S.A. Palaeogeogr. Palaeoclimatol. Palaeoecol. 264, 54–77.

Culver, S.J., Farrell, K.M., Mallinson, D.J., Willard, D.A., Horton, B.P., Riggs, S.R., Thieler, E.R., Wehmiller, J.F., Parham, P., Snyder, S.W., Hillier, C., 2011. Micropaleontologic record of quaternary paleoenvironments in the central Albemarle Embayment, North Carolina, U.S.A. Palaeogeogr. Palaeoclimatol. Palaeoecol. 305, 227–249.

Culver, S.J., Farrell, K.M., Mallinson, D.J., Willard, D.A., Horton, B.P., Riggs, S.R., Thieler, E.R., Wehmiller, J.F., Parham, P., Moore, J. P., Snyder, S.W., Hillier, C., 2016. Micropaleontologic record of Pliocene and Quaternary paleoenvironments in the southern Albemarle Embayment, North Carolina, U.S.A. Palaeogeogr. Palaeoclimatol. Palaeoecol. 457, 360-379.

Long, J.H.; Hanebuth, T.J.J.; Alexander, C.R., and Wehmiller, J.F., 2021. Depositional environments and stratigraphy of Quaternary paleochannel systems offshore of the Georgia Bight, southeastern U.S.A. Journal of Coastal Research, 37(5), 883–905. Coconut Creek (Florida), ISSN 0749-0208.

Wehmiller, J.F., Simmons, K.R., Cheng, H., Edwards, R.L., Martin-McNaughton, J., York, L.L., Krantz, D.E., Shen, C.-C., 2004. Uranium-series coral ages from the US Atlantic Coastal Plain: the "80 ka problem" revisited. Quaternary International 120, 3-14.

Wehmiller, J.F., Thieler, E.R., Miller, D., Pellerito, V., Bakeman Keeney, V., Riggs, S.R., Culver, S., Mallinson, D., Farrell, K.M., York, L.L., Pierson, J., Parham, P.R., 2010. Aminostratigraphy of surface and subsurface Quaternary sediments, North Carolina coastal plain, USA, Quaternary Geochronology 5, 459-492. doi:10.1016/j.quageo.2009.10.005.

Wehmiller, J. F., Harris, W. B., Boutin, B. S., Farrell, K. M. F., 2012. Calibration of amino acid racemization (AAR) kinetics in United States mid-Atlantic Coastal Plain Quaternary mollusks using 87Sr/86Sr analyses: Evaluation of kinetic models and estimation of regional Late Pleistocene temperature history. Quaternary Geochronology 7, 21-36.

Wehmiller, J. F., York, L. L., Pellerito, V., Thieler, E. R., 2015. Racemization-inferred age distribution of mollusks in the US Atlantic margin coastal system. Geological Society of America Annual Meeting, Baltimore. Available at: https://gsa.confex.com/gsa/2015AM/webprogram/Paper263915.html

Wehmiller, J. F., Brothers. L., Foster, D. S. Ramsey, K. W., 2019a. Southern Delmarva barrier island beaches: linking offshore and onshore units using racemization geochronology to infer sediment sources during shoreline migration. Paper 13-5, Geological Society of America, SE Sectional meeting, Charleston SC. https://gsa.confex.com/gsa/2019SE/webprogram/Paper326646.html

Wehmiller, J. F. Ramsey, K. W., Howard, S., Mattheus, C. R., Harris, M. S., Luciano, K., 2019b. New perspectives on US Atlantic coastal plain aminostratigraphy gleaned from extensive analyses of shell specimens from inner continental shelf vibracores. Paper 39-1, Geological Society of America, SE Sectional Meeting, Charleston SC. https://gsa.confex.com/gsa/2019SE/webprogram/Paper326300.html Wehmiller, J.F., Brothers, L.L., Ramsey, K.W., Foster, D.S., Mattheus, C.R., Hein, C.J., Shawler, J.L., 2021. Molluscan aminostratigraphy of the US Mid-Atlantic Quaternary coastal system: Implications for onshore-offshore correlation, paleochannel and barrier island evolution, and local late Quaternary sea-level history. Quat. Geochronol. 66. <u>https://doi.org/10.1016/j.quageo.2021.101177</u>

https://www.sciencedirect.com/science/article/pii/S1871101421000285

York, L. L., Wehmiller, J. F., 1992. Aminostratigraphic results from Cape Lookout, N.C. and their relation to the preserved Quaternary marine record of SE North Carolina. Sedimentary Geology 80, 279-291.

York, L. L., Wehmiller, J. F., Cronin, T. M., Ager, T. A., 1989. Stetson Pit, Dare County, North Carolina: an integrated chronologic, faunal, and floral record of subsurface coastal Quaternary sediments. Palaeogeography, Palaeoclimatology, Palaeoecology 72, 115-132.