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Establishing the temperature sensitivity of amino acid racemization rates in planktic foraminifera

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Traditionally, AAR is a geochronological tool that provides ages for fossils based on the degree of protein diagenesis (e.g., Walker, 2005). Upon the death of the organism, L-amino acids invert to D-amino acids leading to an increase in D/L ratios of amino acids that comprise organic residues in fossil material with time. The method works best in thermally stable environments so that D/L ratios reflect time and not temperature variations of the post depositional environment. On the other hand, in well-dated samples racemization rates have been used to deduce post depositional temperature histories in terrestrial and marine settings (Miller et al., 1997; Kaufman, 2006; Hearty et al., 2004). The original goals of this research project were to use amino acid racemization (D/L ratios) in three planktic foraminiferal species from sites located along two Atlantic Ocean depth transects (~2000-4800 m water depth) to establish the temperature sensitivity of this proxy. One of the sites will then provide preliminary depositional temperature data since the glacial period, ~ 20 ka.

Work accomplished thus far focuses on the depth transect in the northwestern Atlantic Ocean. We are testing methods by pretreating samples with bleach. This removes contaminants and isolates the intra-crystalline fraction of amino acids, which is less prone to environmental influences for a better approximation of a closed system (Penkman et al., 2008). We investigate the effect of this pretreatment method on the D/L ratios in three species of planktic foraminifera (*Pulleniatina obliquiloculata, Globorotalia tumida, Globorotalia truncatulinoides*) from late Holocene (~4-5 ka) deep sea sediments of similar environmental setting (Ocean Drilling Program Sites 1056, 1059, and 1062). And, we apply the method test to down-core intervals from Site 1056 (and nearby core KNR140-37PC, Hagen and Keigwin, 2002).

To date, the majority of the late Holocene and three of the five the down-cores intervals (10.5 ka, 51.5 ka, and 400 ka) have been analyzed at the state-of-the art Amino Acid Geochronology Laboratory at Northern Arizona University. Here I provide a brief description of these first results from aspartic acid D/L ratios, details will be shown at the 2018 Fall meeting of the AGU (Watson et al., 2018). We find that bleaching does not reduce the rate at which subsamples (n = 6-10 for each method) from the same sample of foraminiferal tests (n = 22 paired bleached/unbleached samples) have to be rejected based on previously established screening criteria such as not conforming to a curve-liner trend when plotted against glutamic acid D/L ratios. In the late Holocene samples, bleaching tends to reduce the variability in D/L values within the subsamples from a particular group by about 2%, and it shifts the mean of the D/L ratios (Figure 1). In about half of the analyzed samples, bleaching reduces species offsets. In down-core samples, on the other hand, bleaching does not have an effect on subsample variability or mean D/L ratios (Figure 2). Furthermore, in the down-core data set species offsets are relatively constant whether or not the sample is bleached. This suggests that it may be possible to make species corrections to *Pulleniatina*, for which the racemization rate constant has been determined in laboratory (Kaufman et al., 2006) and field (Hearty et al., 2004) studies. We conclude that while bleaching may reduce intra-specific differences in D/L values, it does not offer an overall advantage over the method that does not include this extra step.

This PRF grant has made a positive impact on my career as a professor as well as the post-graduate education of the student who is using this project as the focus of her Master's Thesis. In particular, the study allows me to investigate a long standing paleoceanographic research question (paleothermometry) with a potentially new proxy based on organic biochemistry, an area that is not within my realm of expertise. This new direction has resulted in collaborative work with Dr. Kaufman that will extend beyond the grant period. The graduate student directly benefited from visiting the AAR laboratory of Dr. Kaufman and learning the skills necessary for processing samples in the context of testing chemical methods and the down-core application. The student plans to continue her education with a PhD, and these skills will serve her well for further geochemical studies that involve method testing and processing of foraminiferal samples for trace metal studies, for example. She is the lead author on the presentation of results at the upcoming Fall 2018 AGU meeting.

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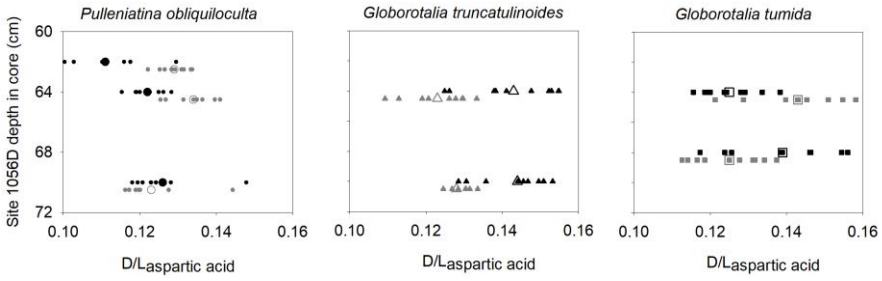

Figure 1. Comparison of subsample (small symbols) and mean (large symbols) D/L ratios of aspartic acid in bleached (grey) samples versus unbleached samples (black) for three late Holocene planktic foraminiferal species. The figure shows an example from three core intervals from Ocean Drilling Program Site 1056.

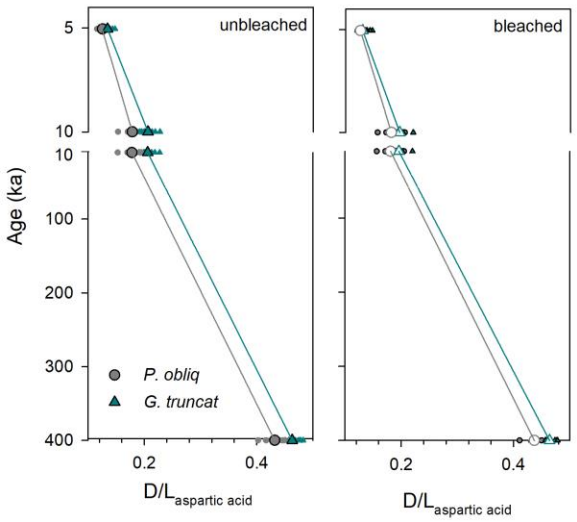

Figure 2. Comparison of down-core changes in mean (large symbols) and subsample (small symbols) D/L ratios of aspartic acid in two planktic foraminiferal species for unbleached (left panel) and bleached (right panel) samples. The down-core D/L ratios of *Pulleniatina obliquiloculata* (grey cicles) and *Globorotalia truncatulinoides* (blue-green triangles) appear to be offset by a relatively constant amount regardless of unbleached (solid symbols) or bleached (open symbols).