Quaternary Geochronology 16 (2013) 50–61

Contents lists available at SciVerse ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

Research paper

Amino acid racemization in mono-specific foraminifera from Quaternary deep-sea sediments

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ARTICLE INFO

Article history:
Received 28 November 2011
Received in revised form
12 June 2012
Accepted 27 July 2012
Available online 17 August 2012

Keywords:
Amino acid racemization
Foraminifera
Quaternary geochronology
Marine sediment

ABSTRACT

The deep-sea environment is among the most stable on Earth, making it well suited for amino acid geochronology. Foraminifera with calcareous tests are distributed across the World Ocean and are often recovered in sufficient abundance from sediment cores to derive robust mean amino acid D/L values of multiple replicates from each stratigraphic level. The extent of racemization (D/L) can be compared with independent age control, which in most cases is based on correlation with global marine oxygen-isotope stages and radiocarbon ages from the same stratigraphic levels. In this study, we report the results of amino acid racemization analysis of multiple foraminifera species from well-dated sediment cores taken from the Pacific, Atlantic, and Arctic oceans. The composite of results analyzed to date (179 samples, each composed of an average of 8.6 subsamples = 1531 analyses) show that D/L values generally increase systematically down core, and are similar for samples of comparable ages from different deep-sea sites. Previously published equations that relate D/L values of aspartic and glutamic acids to post-depositional temperature and sample age for *Pulleniatina obliquiloculata* generally conform to the D/L trends for species analyzed in this study. Laboratory heating experiments were used to quantify the difference in the rate of racemization between *P. obliquiloculata* and other taxa. For example, aspartic acid in *P. obliquiloculata* racemizes an average of 12–16% faster than in the common high-latitude species, *Neogloboquadrina pachyderma* (s). Apparently, the unexpectedly high D/L values previously reported for *N. pachyderma* (s) older than 35 ka from the Arctic Ocean cannot be attributed to taxonomic effects.

1. Introduction

Among the wide range of applications of amino acid geochronology, the technique seems especially well suited for dating marine sediments using foraminifera. Foraminifera inhabit most of the World Ocean and they contain high concentrations of amino acids that are well retained by their carbonate test. The relatively stable thermal environment of deep-sea sites minimizes the often-complicating effect of variable temperature on the long-term rate of racemization. Using foraminifera also takes advantage of improved analytical procedures (Kaufman and Manley, 1998) that enable subsamples in the sub-milligram range to be analyzed. Preparing samples composed of fewer tests is less time-consuming than picking larger samples, and it can improve the accuracy of the results because the best-preserved individuals can be selected.

Some of the earliest research on amino acid geochronology focused on deep-sea sediment, including the rate of racemization in foraminifera (Wehmiller and Hare, 1971; Bada and Schroeder,

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http://dx.doi.org/10.1016/j.quageo.2012.07.006

1972; King and Hare, 1972; Kvenvolden et al., 1973; Schroeder and Bada, 1977; Bada et al., 1978; Bada and Man, 1980; King, 1980; Belknap and Doyle, 1986; Stathopolos et al., 1987; Robbins and Brew, 1990). These studies took advantage of the long-term stability of deep-sea settings to investigate the diagenesis (including racemization) of amino acids over geologic time. The extent of amino acid racemization in fossil foraminifera has also been used to estimate the ages of Quaternary marine sediment (Müller, 1984; Sejrup et al., 1982; Macko and Aksu, 1986; Sejrup and Haugen, 1992; Knudsen and Sejrup, 1993; Murray-Wallace and Belperio, 1994; Harada et al., 1996), and in a few cases, to reconstruct paleotemperature histories (Bada and Man, 1980; Lehman et al., 1988; Johnson et al., 1990).

Previous analyses in the Amino Acid Geochronology Laboratory (AAGL) at Northern Arizona University focused on the low-latitude planktonic foraminiferal species, *Pulleniatina obliquiloculata*. This taxon is large enough to analyze single individuals (~0.1 mg). A suite of well-dated sediment cores from the Queensland Trough, Australia, was used to assess the utility and limitations of amino acid geochronology in this taxon (Hearty et al., 2004). Laboratory experiments were used to quantify the temperature sensitivity of amino acid racemization in *P. obliquiloculata*, and to develop an equation for relating time and temperature to the extent of racemization (Kaufman, 2006). More recent work in the AAGL has focused on the common high-latitude planktonic species, *Neogloboquadrina pachyderma* (s). The rate of racemization in *N. pachyderma* was tentatively calibrated to about 150 ka in the Arctic Ocean (Kaufman et al., 2008) based on previously studied biostratigraphic and lithostratigraphic markers.

Two general approaches can be used to convert the extent of amino acid racemization to a numeric time scale: In the first approach, the effects of time and temperature on the extent of racemization are determined in modern shells subjected to high-temperature laboratory experiments (e.g., Kaufman, 2006). This relation, together with a model of racemization kinetics, is used to calculate the age of a sample if its temperature history is known. A more secure approach that does not require assumptions about temperature history is to calibrate the rate of racemization by analyzing securely dated samples of a particular taxon from a region where temperature histories are uniform (e.g., Hearty et al., 2004). The calibrated reaction rate is then used to date samples of the same taxon of unknown age from the same environment. Once calibrated, amino acid geochronology can be more cost effective than other dating methods.

In this study, we analyze 114 samples from sites in the Pacific, Atlantic, and Arctic oceans, and combine these with previously published results on 65 additional samples to better constrain the rate of racemization across a range of marine depositional environments. We analyze multiple species of foraminifera to assess the differences in the rates of racemization, and supplement this with analyses of laboratory-heated specimens. We restrict our analysis to mono-specific samples from marine sediment cores whose ages are well known based on other methods, including ^{14}C dating and marine oxygen-isotope stratigraphy. The results of amino acid analysis of all 1531 subsamples included in this study are contained in a digital Appendix that is available through the publisher's website, and archived at the World Data Center for Paleoclimatology (ftp://ftp.ncdc.noaa.gov/paleo/aar.html).

2. Methods — Analytical

Foraminifera samples were received by the AAGL in bulk or sieved sediment, or as individual specimens picked by the submitter. Sediment samples were sieved and collections of mono-specific foraminifera tests were cleaned by light sonication in a bath sonicator and immersion in 1 mL of 3% H_2O_2 for 2 h. Foraminifera from Site 1056 (Fig. 1) were pre-treated both by sonicating and not sonicating. Because the intra-sample variability was lower for the non-sonicated tests (Billups et al., 2010), we report only those results. All tests were rinsed with deionized H_2O, and air-dried under a filtered-air hood. The best-preserved, most-thoroughly cleaned, whole tests were then picked and divided into

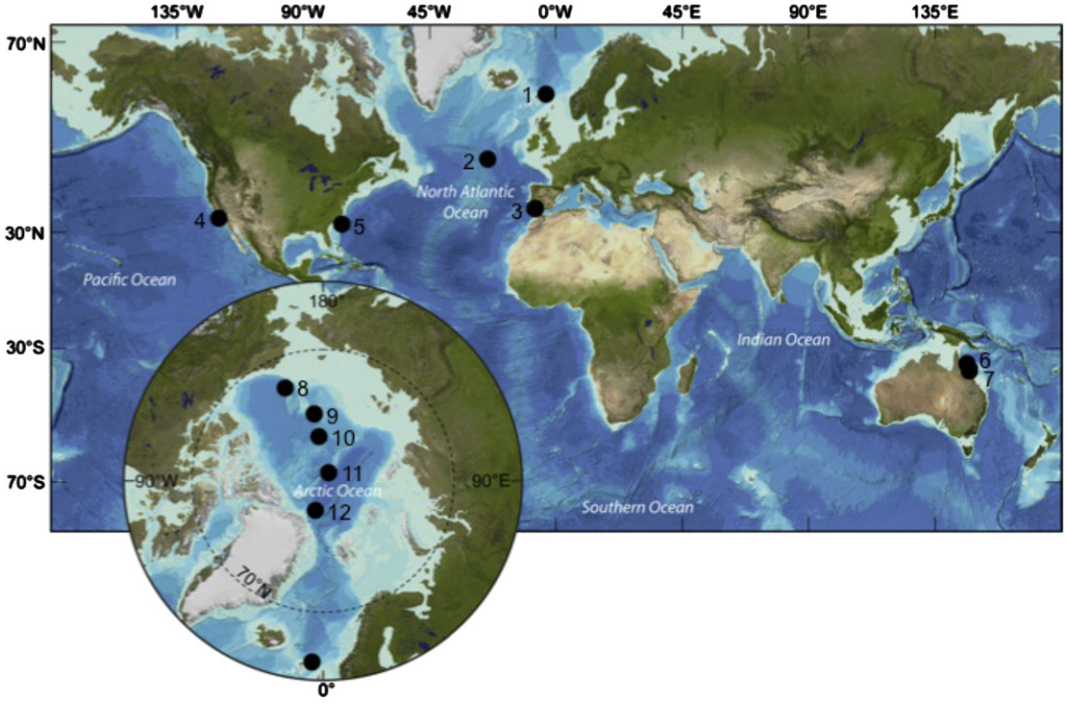

Fig. 1. Location of cores sampled for foraminifera analyzed in this study. Details listed in Table 1.