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ScienceDirect
Quaternary Geochronology 3 (2008) 328–341
QUATERNARY GEOCHRONOLOGY
www.elsevier.com/locate/quageo

Research Paper

Identifying outliers and assessing the accuracy of amino acid racemization measurements for geochronology: II. Data screening

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Received 27 November 2007; received in revised form 8 April 2008; accepted 11 April 2008

Abstract

Amino acid racemization (AAR) is a cost-effective method for dating the large numbers of specimens required for time-averaging studies. Because the aim of time-averaging studies is to determine the structure of the age distribution, any data screening must be done cautiously and systematically. Methods to quantitatively assess the quality of AAR data and to identify aberrant specimens are underdeveloped. Here we examine a variety of screening criteria for identifying outliers and determining the suitability of specimens for numerical dating including: high serine concentrations (modern contamination), covariance of aspartic acid (Asp) and glutamic acid (Glu) concentrations (diagenetic influences), replication of measurements (specimen heterogeneity), and the relation between Asp and Glu D/L values (internal consistency). This study is based on AAR analyses of 481 late Holocene shells of four molluscan taxa (*Ethalia*, *Natica*, *Tellina*, and *Turbo*) collected from shallow sediment cores from the central Great Barrier Reef. Different outliers are flagged by the different screening criteria, and 6% of specimens were found to be unsuitable for time-averaging analyses based on screening the raw AAR data. We recommend a hybrid approach for identifying outliers and specimens for numerical dating.

Keywords: Mollusca; Amino acid geochronology; Holocene; Carbonate sediments; Time-averaging; Great Barrier Reef; Amino acid racemization

1. Introduction

Age determination is of paramount importance in a wide variety of paleontological and geological studies, and amino acid racemization (AAR) geochronology is increasingly used for studies involving a large number of ages. AAR is particularly suited to time-averaging studies because it is cost-effective and of sufficient resolution (e.g., Kowalewski et al., 2000; Carroll et al., 2003; Kidwell et al., 2005; Kosnik et al., 2007). Interpreting AAR data for time-averaging studies is challenging because any data screening will influence the inferred age-population distribution of a collection, which itself is the primary interest. Previous analyses of uncertainties involved in AAR geochronology have focused either on inter-shell variability, which does not apply to specimen-specific studies, or on analytical precision, which is relatively easy to determine but underestimates realistic uncertainties. These uncertainties result from the poorly understood effects of non-temporal variability related to individual shell or environmental factors (including thermal), and preferential leaching or contamination of amino acids. A fundamental goal of AAR, as for other geochronological methods, is to better understand the source of non-temporal variability. Investigating amino acid datasets for signatures of non-temporal variability can lead to a better understanding of the underlying processes as well as to developing criteria to objectively recognize specimens that are not suited for the technique.

In part I of this two-part study, we examined age calibration curve options and the consistency of ages inferred using two different amino acids, aspartic acid (Asp) and glutamic acid (Glu). Here, in part II, we explore a series of screening methods suitable for use with raw

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doi:10.1016/j.quageo.2008.04.001

(e.g., before calibration curves are made) AAR data in AAR time-averaging studies. Rigorous evaluation of AAR data and thoughtful selection of specimens for numerical dating substantially improve the resulting calibration curves and inferred ages. Because D/L values vary within and between shells of a collection, it is important to establish reasonable goals and expectations for the method, while maximizing the accuracy of each step in the dating process. The goal is to demonstrate objective and reproducible criteria based on mechanistic hypotheses for identifying and rejecting outliers, and for selecting specimens for numerical dating. We focus on the AAR data from within individual shells to flag specimens with poorly resolved AAR. This study is based on our extensive suite of AAR data from four molluscan taxa from late Holocene (i.e., ~live to ~5000 years) sediment of the Great Barrier Reef, Australia.

2. Study site and sample description

Rib Reef is typical of the mid-shelf central Great Barrier Reef (18.479°S; 146.869°E). Specimens of four molluscan taxa were collected from lagoonal sediments in ~7 m of water using a diver-operated suction sampler. AAR analyses were performed for 126 *Ethalia*, 121 *Natica*, 507 *Tellina*, and 230 *Turbo* subsamples from 60, 57, 250, and 114 specimens, respectively. Kosnik et al. (2008) present the sample site, specimen selection, and analytical methods in detail. AAR data are presented in supplemental online material.

3. AAR screening criteria

3.1. Serine abundance

Previous AAR studies have used various screening criteria, but the most commonly cited is an over-abundance of serine (Ser). Because Ser decomposes rapidly, excessive amounts indicate contamination by modern amino acids. Setting a universal cutoff for the level that constitutes "excessive" is not possible because Ser is preserved to some extent in relatively young shells. To account for the expected reduction of Ser with time, its abundance can be compared with other amino acids. For example, Kaufman (2006) compared the concentration of L-Ser to that of L-aspartic acid ([L-Ser]/[L-Asp]) and used a value of 0.8 as a cutoff for foraminifera tests with Asp D/L < 0.55. At higher Asp D/L values, amino acid concentrations decrease, so an [L-Ser]/[L-Asp] value of 1.2 was used as a cutoff.

3.2. Total abundance of amino acids

D/L values from shells that contain low concentrations of amino acids are associated with large uncertainties. Old shells or shells subjected to strong leaching or decomposition contain too few amino acids to analyze accurately. For these specimens, background issues, whether post-depositional addition of amino acids or laboratory limitations, become overwhelming. For example, the concentration of amino acids in marine bioclastic eolianite decreases with stratigraphic age in Plio-Pleistocene beds of Western Australia, and the D/L values from the lower part of the stratigraphic sequence were rejected because they were based on low amino acid content (Hearty and O'Leary, 2008).

3.3. Covariance between different amino acid fractions

Although not examined in this paper, previous studies have used the covariance between different fractions of amino acids from the same shell as a means of assessing the internal consistency of the results and therefore, the integrity of the diagenetic system. Most commonly, the total hydrolysable amino acid population is compared with the free amino acid population of the same amino acid (e.g., Miller and Brigham-Grette, 1989). Other subpopulations including the intracrystalline (Sykes et al., 1995; Penkman et al., 2007, 2008), and high-molecular-weight fractions of amino acids (Kaufman and Miller, 1995; Kaufman and Sejrup, 1995) have been analyzed and compared to evaluate the integrity of specimens for AAR geochronology. These fractions are necessarily analyzed from different, albeit adjacent subsamples of the same shell, and therefore might be subject to intra-shell variabilities.

3.4. Covariance between concentration and D/L values of different amino acids

Each amino acid is influenced differently by environmental factors that control hydrolysis, leaching, and other processes that affect the rate of racemization. Under ideal conditions, the concentration and extent of racemization of different amino acids will covary according to a predictable function. Analyses by gas or by reverse-phase liquid chromatography yield D/L values for multiple amino acids. Each amino acid has a different rate of racemization, and results can be compared to assess their internal consistency. For example, the covariance between D/L values in Glu and Asp was used to identify individual specimens that fell off the trend established by the other molluscan shells (Laabs and Kaufman, 2003), ostracode valves (Kaufman, 2003), and foraminifera tests (Kaufman, 2006).

3.5. Outlier D/L values

Specimens that yield D/L values falling outside the 2σ range of the group are often excluded from calculations of the group mean. These studies typically aim to resolve the central tendency of a collection of shells to assign a single best age. The shells with unusually high D/L values are potentially reworked into the younger population. Specimens with unusually low D/L values are often ascribed to