AMINO ACID RACEMIZATION

Dating Methods in Quaternary Systems
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Within the last twenty-five years, the study of amino acid racemization as a relative dating technique has attracted a great deal of attention by geologists and the like. This technique is based on the process of fossilization, thus permitting the natural hydrolysis and breakdown of proteins "into lower molecular weight polypeptides and free amino acids" (Wehmiller 1986, p. 139). Based on the analysis of these organic samples, this method accesses the relative and absolute ages of associated inorganic geologic deposits.

The basic principles of the technique rely on the molecular structure of an amino acid. Amino acids are actually molecular subunits of proteins. All of the amino acids frequently found in proteins are composed of a carboxyl group (-COOH), an amino group (-NH2), a hydrocarbon group (-R), and a hydrogen atom, which all commonly link to a central carbon atom. When each of these separate amino acids are contained within a living organism they take the form of a levo-stereoisomer (L-configuration). At the time of death of the organism, these L-configured amino acids interconvert to the D-configuration or dextro-stereoisomers. This process of the L-configuration producing a mirror image of itself is hereby known as racemization. Racemization occurs with increasing time and temperature after the organism dies, thereby producing a D/L ratio that eventually reaches equilibrium (~1.0). Racemization rates vary among each individual amino acid. Depending upon which amino acid is being analyzed and the corresponding climatic condition, a D/L ratio can be obtained to represent a segment of time. For example, at lower latitudes D/L ratios of specific amino acids are a great deal higher compared to the D/L ratios at higher latitudes, therefore different ratios can represent the same time span.

The calculation of these D/L ratios are obtained by the use of a gas or liquid chromatographers. Once the ratios are obtained, there are two methods used to calculate absolute ages, these being the calibrated and the uncalibrated methods. Otherwise these ratios are more accurately used for correlation and relative dating techniques.

There is an abundance of limitations associated with the application of amino acid racemization as a dating technique. First and foremost is the temperature dependance of this reaction. To obtain an absolute date the temperature history of the sample needs to be clearly understood within +/-2 C. If this is not the case the date could be thrown off +/-50%. On the other hand, for correlation studies such as aminostratigraphy or geochronology, a thorough understanding of the thermal histories of each of the analyzed samples is extremely relevant. Not only are temperature and age limiting factors, but also the variability of each individual amino acid D/L ratio. The D/L ratios are matrix dependant, thereby producing a separate rate in bones, wood, corals, mollusks and foraminifera. These rates have also been found to be genus dependant in mollusks. In addition, the D/L ratios differ according to anatomical parts of specimens being considered as samples must be derived from the same anatomical part of each specimen. Sample contamination also poses as a limitation to this method. Although it does not require a very large sample (5-10mg) to undergo amino acid analysis, it is important that this sample be highly preserved. Sufficient preservation of a sample requires that it has not undergone recent thermal activity and especially that it has not had a reintroduction of younger amino acids. This reintroduction of younger amino acids may appear as a result of leaching or by the appearance of bacteria or fungus on the sample. Careful sampling stratedies need to be incorporated into this procedure. Finally, PH, oxidation-reduction factors, and moisture content, are considered to influence the ability to obtain an accurate D/L ratio. The latter factors appear to affect bone and wood moreso than mollusks.

Because there are so many variables involved with the actual racemization process, it would appear obvious that there are many methodological problems associated with the use of this technique as a dating method. Due to the insufficient amount of paleoclimatilogical evidence needed to accurately obtain the mean annual temperature of the sample, temperature appears to be a major problem, particularly in environments of high climatic variability when compared to a cave

or deep ocean. Even in the areas of low climatic variability, the climate still fluctuates more than +/-2 C.

Other problems lie within the laboratory preparation of the samples. Although the gas and liquid chromatographic analyses yield a good count of the separate amino acids, they pose as limitations on the ratio calculations. The limitations are as follows:

1) The liquid chromatographer requires a very small sample, is faster, cheaper, and more sensitive to the measures of the amino acids, yet it only reveals one amino acid count at a time.

2) The gas chromatographer takes longer, is more expensive and is not as sensitive to each individual amino acid, yet it has the ability to reveal the counts of up to eight individual amino acids, thus allowing for an internal check on the sample. John F. Wehmiller, in his 1984a paper, noted: "Interlaboratory comparison of gas chromatographic methods has revealed a range of uncertainty between about 5% and 15% for different amino acids." (Kvenvolden, 1980) Thus yhe idea that some of the basic problems lie within the laboratory preparation is reaffirmed. This is also compounded by sampling problems that occur in the field. Before the amino acids arrive at the laboratory, they have to be selected from the "best preserved" field samples. The ambiguity falls within this definition of what is best preserved. The typical criteria that Wehmiller uses is luster, porosity, and texture. These criteria are usually done visually or by x-ray and microscope methods. This approach is too subjective and needs to be more systematic. A more objective approach needs to be adopted.

Much work has been done using amino acid racemization as a correlation/relative dating technique and also as an absolute dating method in Quaternary studies. Here the focus is on Reiner Protsch's work, which involves an extensive amount of amino acid analyses on the skeletal remains of fossil hominids. Protsch wanted to use amino acid dating as a cross check to his "radio-carbon dates of bone samples older than 30,000 years." Because the bone samples used were from a cave, he felt that the temperature variability could be controlled. Because this technique requires such a

small sample size, the hominid bone did not have to be destroyed in order to obtain a date. Protsch used the radio-carbon dating as the control for the upper stratigraphic levels and then extrapolated into the lower levels where the radio-carbon dates would be out of range. By comparing the amino acid dates from the controlled upper stratigraphic levels, he was able to obtain amino acid dates for the lower levels.

Protsch had two major problems with this application of amino acid dating. The first one, of course, was his lack of ability to obtain a feasible mean annual temperature over a period of 60,000 years. He felt that the anomalies in the amino acid dates were limited to the period from 10,000 years to 60,000 years. This was a time of extreme climatic variability. Yet he goes on to say that evidence from microbotanical samples indicated that the climate was similar to present day climatic conditions.

Protsch also noted that the presence of fire poses a real problem when using amino acid dating techniques on fossil hominid bones. If a sample came in contact with fire the D/L ratios would be much higher. Therefore, sampling strategies would need to inspect for the presence of burning.

Protsch also used the amino acid ratios and the radio-carbon dates to obtain a mean annual temperature of 26.5+/-.3 C for the year of 39,000 before present. The present day temperature is 28 C. Protsch states that "If a sample is dated by radiocarbon and the aspartic-acid corrected for temperature based on the radiocarbon date, aspartic-acid dates based on this same temperature could be computed for samples which do not have enough collagen left and are also out of the range of radiocarbon." Because the temperature difference is less than two degrees, this applicability of the dating technique might be possible. It seems highly unlikely that all the variables are sufficiently understood. Therefore, I don't feel that the use of the amino acid dating for a cross check is necessarily a valid one. Yet more work in this area of cross checking dating techniques appears to have a lot of applicability for further understanding of the various new experimental dating techniques.

It appears necessary to try and understand the variables involved, that is, how much they affect the system and how can they be controlled. It seems highly unlikely to find an environment that is conducive to control for all of these variables. Therefore to acquire an accurate absolute date appears impossible. Yet, as reflected by the work Wehmiller has done with geochronology along the Atlantic and Pacific coasts using fossil mollusks on marine terraces, and that done by N.W. Rutter and R.J. Crawford in the Northern Yukon, applying the ratios of amino acids from wood samples to better understand regional aminostratigraphy, it is apparent that using amino acids for correlation, aminostratigraphic, and paleotemperature has been extremely useful.