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GEOCHEMICAL APPLICATIONS OF THE AMINO ACID RACEMIZATION REACTION

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A method of dating based on the chemical racemization of amino acids has been developed in the last fifteen years. It is a promising new technique for dating fossil materials of biological origin. Only a few grams (3-7) of the sample are required for racemization analysis.

The applicability of this method ranges to the Pleistocene and, in some cases, it may eventually be useful throughout the Pliocene, the actual range being dependent upon the general temperature of the region where the sample is collected.

This method is based on the fact that in living organisms, amino acids exist almost entirely in a structural configuration called the L-isomer, which, following the death of the organism, undergoes a structural rearrangement reaction called racemization. Over long periods of geological time, racemization converts the L-isomers to D-isomers and the reaction continues until equal quantities of both isomers are present.

Most amino acids have only one center of asymmetry, but some, such as isoleucine, have two. In the case of isoleucine, the structural rearrangement (in this case called epimerization) produces another amino acid called D-alloisoleucine. L-isoleucine (ile) and D-alloisoleucine (alle) are directly separable on an amino acid analyzer.

Given that racemization is a chemical reaction, it is inherently temperature-sensitive. Thus, there are two major variables which affect the extent of racemization in a fossil: time and temperature. The increase in D/L or alle/ile ratios can be used to obtain a measure of the time that has elapsed since the organism died.

Important applications of the amino acid racemization reaction have been implemented in archeology, anthropology, paleontology, and geochronology. Most of the research has been conducted on fossil bones, teeth, and shells. In archeology, for example, the paper entitled "Direct aspartic acid racemization dating..." (see BELLUOMINI, 1981) describes the first application of this new technique based on the racemization of amino acids contained in collagen, that is, aspartic acid, in order to date some specimens of human and big-mammal faunal bones from archeological sites in central and southern Italy.

In paleontology, the isoleucine epimerization reaction has been used to date tooth enamel from dwarf elephants in samples collected in the Sicilian caves of Spinagallo and Puntali (BELLUOMINI & BADA , 1985) and from several Pleistocene formations in the Rome area (BELLUOMINI, BRANCA, DELITALA, MALATESTA & ZARLENGA, 1986). The ages obtained for the dwarf elephant samples from the Spinagallo Cave - *Elephas (Palaeoloxodon) falconeri* - are considerably older than those of the more robust dwarf species - *Elephas (Palaeoloxodon) mnaidriensis* - from the Puntali Cave. These dates suggest that more than one invasion of continental species apparently produced varying stages of dwarfism.

As regards the second paper, the isoleucine epimerization dates represent the first age determinations made directly on the fossil material from the Rome deposits.

In geochronology, the extent of amino acid racemization in *Glycymeris*, *Arca*, and *Astralium* shells has been analyzed in order to estimate the ages of numerous raised marine terraces in the regions of Sardinia (WANET, LEONE, OZER & ULZEGA, 1982; BELLUOMINI, BRANCA, DELITALA, PECORINI & SPANO, 1986), Calabria (BELLUOMINI, BRANCA, DELITALA, GLIOZZI & RUGGIERI, in press), Latium (BARTOLINI, BOSI, BELLUOMINI & DELITALA, 1984) and Apulia (HEARTY & DAI PRA, 1985). The ages of marine deposits demonstrate tectonic activity in the Mediterranean basin and suggest the need for a reassessment of geomorphic correlations. More specifically, amino acid dating is a useful method for estimating the ages of marine deposits that are a few hundred thousand years old.

In conclusion, the racemization reaction method has been used as a paleothermometer to estimate the average temperature to which samples of independently known ages have been exposed since their deposition (BELLUOMINI & DELITALA, 1983; BELLUOMINI, BRANCA, DELITALA, GLIOZZI & RUGGIERI, in press) and to investigate the distribution and geochemical significance of amino acids in clays of Pleistocene age (BELLUOMINI, BRANCA, CALDERONI & SCHNITZER, 1986).

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