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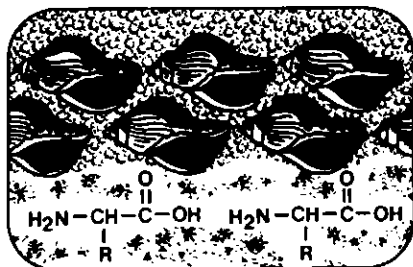
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Conference Reports



Amino Acid Geochronology: Applications to Late Cenozoic Geology

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As a part of the Geological Society of America Annual Meeting in New Orleans, October 17, 1982, a symposium on amino acid racemization geochronology was held (GSA Abstracts with Programs 1982, p. 389-390). During the session, thirty people from amino acid laboratories in Canada and the USA detailed their theoretical concerns in the morning session and reported on specific results in the afternoon session.

The format of this symposium differed from the norm in that each speaker was allowed only five minutes in which to present the crux of his or her work. The last hour of the day was allocated for a general discussion during which several problems were addressed by the group. Although the format was an improvement over the normal 15 to 20 minute lecture format, it could perhaps have been improved by allowing each speaker a bit more time. Although not as many talks could have been included, lengthening the symposium could have resulted in just as many talks with more time for discussion both individually and as a group.

G.H. Miller, University of Colorado, opened the symposium with a short histori-

cal perspective of amino acid analysis and dating. J. Wehmiller, University of Delaware, then presented the results of the interlaboratory calibrations. Consisting of three different samples of powdered mollusc shell, these standards were analyzed by most of the amino acid laboratories. Results from the different laboratories were widely scattered, even for the sample which had already been desalted. Wehmiller felt that much of the scatter was method dependent and recommended that all future publications of results from shells include as well that particular laboratory's result for the shell standards.

In soils and paleosols from the Front Ranges, S.L. Forman, J.K. Brigham, and G.H. Miller, all with the University of Colorado, discovered that amino acid concentration profiles in the A horizons were similar, while levels in the B horizons decreased with depth, except where expandable clays preferentially adsorbed and concentrated amino acids.

In their studies of nonmarine ostracodes from cores of Lakes Bonnyville and Lahontan, W.D. McCoy, University of Massachusetts, and R.M. Forester, U.S. Geological Survey, showed that ostracodes from the tops of some cores had experienced higher temperatures which resulted in abnormally high alloisoleucine/isoleucine ratios. Otherwise, the ratios uniformly increased with depth in the core.

R. Cunningham, Exxon, and W.C. Burnett, Florida State University, reported that amino acids constituted less than 10% of the organic matter in phosphate nodules from the Peru/Chile shelf. In the nodules, which were dated from 7 to >350 Ka by uranium series dating, amino acid ratios increased regularly with age. While aspartic acid and glutamic acid were concentrated in the nodules, threonine and serine were depleted with respect to the surrounding shelf sediment. The authors felt that the amino acids had probably been incorporated into the nodules by adsorption, a process which has remained unchanged for at least 300 Ka. B.J. Katz, E.H. Man, and G.C.A. Harrison, University of Miami, found that alloisoleucine/isoleucine

ratios in DSDP Core 148 significantly deviated from the theoretical projected ratio pattern for the core. This deviation could be attributed to several factors, including increased heat flow, elevated bottom water temperatures, complex bottom water temperature history, reworking, slumping, or contamination.

W.A. Bonner, Stanford University, and R.H. Lemmon, University of California Berkeley, reported on the amino acid ratios found in the Murchison meteorite, a carbonaceous chondrite. In addition, they found that serine decomposed rapidly when mixed with the powdered meteorite. Leucine underwent similar decomposition and racemization when mixed with several mineral powders.

M.H. Engel and P.E. Hare, Carnegie Institute, demonstrated that amino acids in the presence of sugars decompose when heated to form melanoidin polymers in which racemization proceeded more slowly than in pure amino acids. R.A. Scheinfeld, University of Delaware, found a low molecular weight organic molecule in the matrix of fossil *Mercenaria* which binds calcium and, possibly, magnesium and strontium. A result of the decomposition of a preexisting molecule, this compound may play an important role in fossilization. Its composition is unknown at present, but it may be a peptide or a sugar.

In comparing the kinetics of amino acid racemization in modern and fossil molluscs, E.M. Keenan and J. Wehmiller, University of Delaware, found that the high molecular weight fraction racemized very slowly, while the free amino acids racemized very quickly. Pyrolyzed modern shells exhibited different kinetics for all fractions compared with the kinetics of the fossil shells.

J.L. Bada, S. Steinberg, M.S. Ho, and K. Rittenberg, Scripps Institute, examined rates of epimerization in the products of amino acid diagenesis. Kinetics for isoleucine are not first order reversible either in these diketopiperazines or the fossil molluscs. In comparing the degrees and rates of epimerization in di- and tri-peptide chains and free amino acids, R.M. Mitterer, University of Texas, found that for COOH-

terminal isoleucine, the rate of epimerization was faster than in the free amino acid fraction, but the NH_2 -terminal isoleucine proved to be faster than either. Although the rate of epimerization in the tripeptides was significantly faster than that in the dipeptides, the rate in the diketopiperazine was faster than that in either.

J.T. Andrews, University of Colorado, and D.C. and K. Davies, University College of Wales, used ratios of various amino acids to determine the taxa of unidentifiable mollusc fragments in tills. When subjected to the same analysis, known fossils were correctly identified. This could prove a powerful technique for identifying taxa in the future. Using Arrhenius equations determined for several molluscan genera associated with Clovis sites, G.H. Miller, W.D. McCoy, and A.R. Nelson, Denver Federal Centre, found that temperature predictions determined for the sites were not significantly different from the temperatures defined by sucrose probes at depths greater than 2 m. However, because samples obtained from depths of less than 1 m showed greatly increased rates of racemization, all samples for correlation or dating should be collected from depths greater than 2 m.

P.E. Hare and C.V. Haynes, University of Arizona, discovered that the rates of aspartic acid racemization in bone collagen were significantly lower than those in denatured collagen gel. At temperatures greater than 15°C, denaturation of the collagen was the rate-limiting step, but at higher temperatures the aspartic acid racemization was rapid but appeared to have first order reversible kinetics. P.J. Ennis, P.E. Hare, and R.E. Taylor, all with the University of California Riverside, demonstrated a method for separating aspartic acid enantiomers from bone in order to improve detection precision. Using this method, several controversial Paleoindian skeletons from California were redated. Temperature and groundwater percolation were thought to be crucial in determining these dates.

In the afternoon session, presentations centred on specific results utilizing amino acid analyses, including several papers which concerned the Pleistocene stratigraphy of the southern U.S. Atlantic coastal plain. D.F. Belknap, University of South Florida, and J. Wehmiller showed that the amino acid stratigraphy on the coastal plain was consistent for any one site, but extremely difficult to correlate from site to site. Furthermore, where it was possible to correlate with amino acid ratios, correlations are at variance with those determined from uranium series dates on corals. If the dates are correct, then the temperature gradients have been nonuniform with latitude along the coast. In a summary of the lithostratigraphy for the coast, J.P. Owens,

U.S. Geological Survey, reported that six terraces ranging in age from 30 Ka to 1.5 Ma had been recognized. Because terrace distribution appears to be partially controlled by tectonics, elevation alone cannot be used to correlate the terraces. B.J. Szabo, U.S. Geological Survey, reported that the uranium series ages for the corals along the coast fell into four age groups at approximately 80, 200, 460, and 700 Ka, but because detritus in the samples proved problematic, errors for the ages were large. J.N. Rosholt and B.J. Szabo, U.S. Geological Survey, used uranium trend (not uranium series) dating of sediment on the terraces to determine that these were deposited at approximately 75, 200, 400, and 700 Ka, dates which agree well with the uranium series coral dates. J.C. Liddicoat, Lamont-Doherty Institute, D.F. Belknap, and J. Wehmiller showed that paleomagnetic analyses agreed with leucine ages for the sediment from the coastal plain, although in some samples secondary magnetization complicated the correlation. L. McCartan, U.S. Geological Survey, discussed possible explanations for the disagreement of the amino acid ages with the lithostratigraphy and the uranium series dates. During past glacial maxima, a high temperature gradient would have existed in the central part of the study area near South Carolina. This may have fluctuated north or south with the stadial/interstadial shifts, as well as with the glacial/interglacial shifts. Problems with the amino acid ratios may result also from catalysis, bacterial contamination, groundwater effects, or radioactively induced racemization.

Reporting on similar amino acid studies of the British Pleistocene stratigraphy, D.Q. Bowen, D.C. Davies, K. Heddon-Davies, S. Hughes, all with University College of Wales, discovered that amino acid analysis appears to correlate marine units well, and may accurately date the nonmarine units. As a result, three raised beaches dating from isotope stage 5e have been correlated along portions of the south coast. Several of the till units show multiple faunae, either because of multiple glaciations in the area, or mixed source areas for the glaciers. Because it was often difficult to be certain that samples had been reworked or mixed, H.P. Sejrup, Bergen Universitet, K. Rokoengen, Continental Shelf Institute, and G.H. Miller obtained only preliminary dates by using amino acid stratigraphy of molluscs for correlation of the late Quaternary sediment on the continental shelf of Norway.

P.A. Smith, U.S. Geological Survey, and J.K. Brigham found that sealevel fluctuations for samples collected in water depths less than 15 m in the Beaufort Sea had suffered complex temperature histories.

The Flaxman Formation is now correlated with isotope stage 5, and is therefore post-Pelikian. J.S. Vincent, Canadian Geological Survey, N.W. Rutter, University of Alberta, and G.H. Miller showed that sediments from Banks Island exhibited three glaciations, based on amino acid analysis of wood and shells. Amino acid ratios were used to correlate widely-spaced units in the Arctic.

G.L. Kennedy, U.S. Geological Survey, found that Pacific Coast terrace faunae exhibited different amino acid ratios depending upon the species' ecological and temperature preferences. As a result, terraces could be correlated based on both their faunal assemblages and amino acid ratios. N.W. Rutter and R.J. Crawford, University of Alberta, analyzed many wood samples from the Arctic, where long periods of permafrost slow the rate of racemization. Correlations have been possible at sites separated by 1000 km for units assumed to be as old as Sangamon. Very old samples, however, showed anomalously little racemization, possibly due to leaching.

D. Blount, K.A. Kvenvolden, both of the U.S. Geological Survey, and D.A. Warnke, California State University, examined ratios of leucine, proline, aspartic acid, and glutamic acid for Quaternary molluscs and wood from the Puget Lowlands. Plots of D/L glutamic acid versus D/L leucine showed good age resolution for the molluscs, but were less definitive for the wood. Based upon these plots, it was possible to correlate the units in some of the sites. D.J. Easterbrook, Western Washington University, and N.W. Rutter used wood and shell amino acid ratios to correlate Quaternary sediment in the Puget Lowlands. Shells proved useful in discriminating between and correlating three glaciomarine units, while wood proved useful in correlating interglacial deposits.

Discussion at the end of the day focussed on several topics. After a long session about the sources of variation in the interlaboratory calibration results, it was generally agreed that all ratios reported henceforth would include a report on the interlaboratory standard as well. The problem was raised of splitting free and combined amino acid fractions in the analysis, a common practice in many laboratories. In samples which have not been hydrolyzed, peptides, especially those of high molecular weight, will adhere to the glassware. Therefore, rather than decanting a subsample from the dissolved shell prior to hydrolysis in order to analyze for the free amino acid component, a separate piece of shell should be dissolved for free amino acid analysis to prevent fractionation of the amino acid and peptide chains. Also, the sample should not be transferred to other

glassware between the solution of the shell and its hydrolization. This indicates that many analyses reported up to now may have discrepancies if free amino acid splits were removed from the shell solution prior to hydrolization.

The problem of increased rates of racemization as a result of the presence of radioactive elements raised an interesting problem, especially with respect to bone. Increased racemization results either from the increased energy available from α decay, which provides the necessary activation energy for the racemization reaction, or from radioactive damage to the protein chains, which results in more amino acids located in terminal peptide chain positions where they racemize more quickly. As bone ages, it tends to concentrate uranium in the organic matrix. Gradually increasing amounts of uranium in the bone could result in accelerating rates of racemization. Because the rate of increase of uranium could not easily be mathematically modelled, the rate of racemization used in calculating dates also would be extremely difficult to model.

After several questions had been raised regarding wood analysis, N.W. Rutter reported that kinetics for wood were being studied at the University of Alberta. Correlations at present seem to offer no problem for pre-Illinoian samples from the Arctic, but work is still in the preliminary stages, and much more remains to be done.

Symposia such as this one are extremely helpful for those involved in amino acid analysis, and should occur more frequently. Let's hope we won't have to wait another four years for the next one.