On the history and future of natural isotopic signals in biomarkers

John M. Hayes

National Ocean Sciences Accelerator Mass Spectrometry Facility and Department of Geology and Geophysics, Woods Hole Oceanographic Institution, USA
(current address: 1862 Tacoma Ave., Berkeley, CA 94707)

The development of compound-specific isotopic science, which now spans multiple disciplines, has a three-part foundation: problem-oriented motivation, theoretical analysis, and technical developments. Organic geochemists wanted to know not only the structures but also the origins and histories of the molecules they found in sediments. The work of Craig, Epstein, and Galimov pointed strongly to the value of isotopic evidence. Straightforward statistical calculations showed that sample sizes should be small, just enough to produce mere billions of ions. Analysis of the performance of isotopic mass spectrometers showed efficiencies of 0.001 ion/molecule and near-noiseless operation of signal-processing systems. Nanomole samples should have been more than large enough! Actual requirements were nevertheless grotesquely large because inlet systems were so inefficient. The direct connection of isotopic mass spectrometers to micro-scale combustion reactors fed by gas chromatographs was doubly significant. It solved the inlet-system problem and it immediately unified organic-chemical techniques with isotopic measurements. It worked in spite of the wide variations in ion current (characteristic of chromatographic peaks) apparently because the large background of carrier gas buffered the electrostatic properties of the ion source. Substitution of pyrolysis for combustion added H and O to C and N as analyzable elements. For C, N, and O, sample requirements closely approach theoretical minima and, when competing gases are absent, precision can extend to per meg levels. What next for isotopic biogeochemistry and related fields? Some goals are clear: a return to intramolecular studies, expansion to carbon-14, and a union with molecular biology paralleling that already achieved with organic chemistry. The first may depend on NMR more than mass spectrometry or it may be facilitated by post-column reactor technology like that introduced by Dias, Freeman, and Franks. The second already has strong scientific and instrumental pioneers. So many people see the benefits and possibilities of gene-specific isotopic techniques that this conference seems practically guaranteed to bring new results in that field. As long as the scientific benefits expand, so will the measurements.