

Molecular isotopic structures: Advances, opportunities and hurdles

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There has been dramatic progress in the analysis of molecular isotopic structures by mass spectrometry, NMR, and IR-spectroscopy, enabling several new sub-disciplines: the biogeochemistry of N₂O; clumped isotope thermometry of CO₂, carbonate, O₂ and methane; food-product forensics. Other observations suggest many additional areas of future application. We will review this field, focusing on strengths and weaknesses of known methods, emerging analytical capabilities and anticipated fields of application.

Clumped isotope thermometry of small molecules (CO₂, CH₄, etc.) arguably constitutes the largest and fastest growing sub-discipline of stable isotope geochemistry involving intramolecular isotope effects. An important question is whether this field can be applied to large molecules. Theoretical models predict that 'clumping' of heavy isotopes in large molecules should resemble better-known effects in small molecules. It is less clear how they will be observed at useful precision. One simple solution is to extract portions of large molecules and convert them into easily-analyzed small compounds; we will explain a recent effort to do this for the study of C-H bonds in moieties from refractory organics. A more general solution must involve an analytical technique that can observe clumped isotope effects in large, intact molecules. NMR techniques may eventually provide a powerful approach to this problem, but must achieve sensitivities and precisions well beyond published measurements. IR spectroscopy is likely to be restricted to small compounds simply because of the vibrational complexity and low volatility of larger molecules. We will present measurements of n-hexane and other compounds that illustrate how this problem may be resolved through mass spectrometric analysis of molecular fragment ions.

The best-established use of position specific isotope effects examines the difference in ¹⁵N/¹⁴N between α and β sites in N₂O (by mass spectrometry or IR spectroscopy). NMR study of ¹³C and D distributions in sugars, alkanes and other compounds suggest many more tools of this kind are possible. Application of NMR to geochemical problems is limited by large sample sizes (100's of mg). We will present mass spectrometric methods for making such measurements on amino acids, alkanes and moieties of larger organic compounds. These techniques demand careful study of source chemistry and are challenging to standardize, but provide a means of precise site-specific measurement of μ m and smaller samples.