Isotope Ratio Patterns

Reactions between chemical species can create patterns in the relative abundances of their stable isotopes that reflect the reaction mechanisms and environmental conditions involved. Isotopes of an element differ in the number of neutrons and therefore in their masses. Because chemical bonds having heavier isotopes have lower vibrational energy states than those with lighter isotopes, bonds having a heavier isotope are stronger (they have larger force constants) than bonds having only lighter isotopes. Molecules with stronger bonds exhibit greater differences in zero-point energies between the molecules' lighter and heavier isotopes. Compounds having stronger bonds tend to maintain relatively greater abundances of heavier isotopes (e.g., see http://www.soest.hawaii.edu/krubin/GG325/textbook/Chapter09.pdf).

Equilibrium fractionation. Coexisting molecules can achieve mutual chemical and isotopic equilibrium when the forward and backward reactions between them have equal rates, allowing the isotopes to achieve equilibrium distributions among molecules. At chemical equilibrium, molecules having stronger bonds will exhibit greater abundances of heavier isotopes. Differences in isotopic abundances between equilibrated molecules generally decrease at higher temperatures. When isotopic differences between equilibrated molecules can be achieved solely by chemical and physical phenomena, they do not necessarily require biological processes and are not definitive biosignatures. In some cases, enzymatic processes can approach isotopic equilibrium between molecules under conditions where equilibration would otherwise be extremely slow without life (e.g., Kolodny, 1983; Colman 2005), thus evidence of isotopic equilibrium might indicate biological activity.

Kinetic isotope fractionation. A kinetically controlled reaction can arise when its rate is at least somewhat inhibited and the rate from reactant to product is greater than the rate of the reverse reaction. A reactant can still equilibrate with a higher energy (less stable) 'transition state' species that ultimately leads to the product. Because the reacting bonds in the 'transition state' are typically weaker than the reactant's bonds, the 'transition state' becomes relatively enriched in lighter isotopes. Thus, the product of a kinetically-controlled reaction is typically enriched in lighter isotopes relative to the reactant.

Enzymes can alter reaction kinetics and isotopic discrimination and create distinctive isotopic patterns in biomolecules (e.g., Hayes, 2001). An enzyme's isotopic discrimination is determined by the molecular structure of its substrate's 'transition state' and the environment within the enzyme's reaction center. Differences in reaction mechanisms employed by biological versus nonbiological processes can form the basis for distinguishing between isotopic patterns from biotic versus abiotic sources. For example, the biosynthesis of straight-chain lipids involves isotopic discrimination during the formation of 2-carbon subunits that are then linked, creating alternating different $^{13}C/^{12}C$ values along the lipid's C backbone (e.g., Monson, 1982). Isotopic differences between groups of biogenic amino acids reflect each group's biosynthetic pathway and these pathways are highly prevalent in life (e.g., Scott, 2006).

Mass-independent isotopic fractionation. Elements having multiple (>2) stable isotopes can exhibit isotopic patterns that reflect reaction mechanisms and pathways. For example, compounds associated with dissimilatory sulfate reduction, elemental S disproportionation and sulfite disproportionation exhibit patterns of multiple isotopes that can discriminate between these different metabolic processes (Johnston 2005). Different isotopic patterns in mid-ocean ridge hydrothermal deposits indicate abiotic processes (McDermott 2015).

Clumped isotopic patterns. Abundance patterns among four rare isotopologues of methane ($^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$ and $^{12}CH_2D_2$) can indicate their sources. For example, methane produced by methylotrophic methanogens is more depleted in clumped isotopologues ($^{13}CH_3D$ and $^{12}CH_2D_2$) than methane from hydrogenotrophic methanogens (Shuai 2021). These patterns differ from those among methane isotopologues at equilibrium at ambient environmental temperatures.

Parallel observations of associated environments, processes, and geochemical reservoirs are essential (e.g., Des Marais, 2001; Lloyd, 2020). Physicochemical and biological processes transport and transform biologically important elements between their crustal, marine, and atmospheric reservoirs. These processes collectively contribute to the isotopic patterns observed in their abiotic and biotic products. Interpretations of isotope patterns in the geologic record help to decipher our biosphere's history. Investigating isotopic patterns also promotes an interdisciplinary approach toward determining environmental contexts for interpreting biosignatures (e.g., Chan, 2019).