Isotope Ratio Patterns

Patterns of isotopic abundances within and between molecules can serve as ‘fingerprints’ of biological activity – hence isotopic biosignatures. Several biologically important elements (e.g., H, C, N, S, O) have two or more stable isotopes. Multiple isotopes of an element differ in the number of their neutrons. Differences in the nuclear masses of isotopes have minimal effects upon the electron orbitals of atoms and molecules, but they do alter the vibrational energy states of polyatomic molecules. Chemical bonds having heavier isotopes have lower vibrational energy states than those with lighter isotopes; accordingly, bonds between lighter isotopes are somewhat weaker than bonds having a heavier isotope. Molecules having bonds with higher force constants exhibit greater differences in zero-point energies between the molecules’ lighter and heavier isotopes. Therefore, compounds having bonds with higher force constants tend to acquire greater abundances of heavier isotopes.

Physiochemical and biological processes transport and transform the biologically important elements between their planetary rock, water, and atmospheric reservoirs, and can create patterns of isotopic abundances (isotopic ratio patterns) in their abiotic and biotic products. These patterns are recorded in biomass, water bodies and rocks. Interpreting isotope patterns in the geologic rock record helps us interpret our biosphere’s history.

Fractionation at equilibrium. Coexisting molecules can achieve mutual chemical and isotopic equilibrium when the forward and backward reactions between them occur at equal rates. Among molecules at chemical equilibrium, molecules having bonds with greater force constants will exhibit greater abundances of heavier isotopes. Differences in isotopic abundances between equilibrated molecules generally decrease at higher temperatures. Where isotopic differences between equilibrated molecules can be achieved due purely to chemical and physical phenomena, they do not necessarily require biological processes and therefore are not definitive biosignatures. But in some circumstances, enzymatic processes can achieve equilibrium between molecules under conditions where equilibration would otherwise be extremely slow in the absence of life. In those cases, evidence of isotopic equilibrium could constitute a definitive biosignature. Examples of these are given in subsequent sections.

Kinetic isotope fractionation. A kinetically controlled reaction can arise under conditions when its rate is at least somewhat inhibited and the rate from reactant to product is greater than the rate of the reverse reaction. In this case, a reactant equilibrates with a higher energy (less stable) ‘reaction intermediate’ species that ultimately leads to the product. Because the reacting bonds in the ‘reaction intermediate’ are typically weaker (they have lower force constants) than the bonds in the reactant, the ‘reaction intermediate’ becomes enriched in lighter isotopes, relative to the reactant. Also, for a reactant having lighter isotopes, the differences between its vibrational energy states and the states of the ‘reaction intermediate’ are smaller than the corresponding differences for a reactant having heavier isotopes. This also favors the ‘reaction intermediate’ to become enriched in lighter isotopes relative to the reactant. Thus, the ultimate reaction product is enriched in lighter isotopes relative to the reactant.

Enzymes can alter reaction pathways and rates of reactions in ways that create biosignatures.

The capacity of an enzyme to modulate the rate of a biochemical reaction arises from the molecular structure of its ‘reaction intermediate’ and the environment within the enzyme’s reaction center. These attributes create the isotopic fractionation expressed in the overall reaction. Differences in the reaction mechanisms employed by biological versus nonbiological processes can create differences in the isotopic compositions of their respective products. Such differences can form the basis for distinguishing between isotopic patterns of biosignatures versus patterns that arise from nonbiological processes.

Isotopic ratios expressed in ‘del’ notation. In the natural sciences, the stable isotopic composition of a sample is typically expressed as the ratio of the abundance of the heavier isotope over that of the lighter isotope, relative to a standard. Carbon isotopic abundances are represented as follows:

$?^{13}C_{VPDB} = (({}^{13}C/{}^{12}C)_{sample}/({}^{13}C/{}^{12}C)_{VPDB} - 1)1000,$

where $?^{13}C_{VPDB}$ is the difference in permil (parts per thousand) between a sample and the carbon isotopic standard (the Vienna Pee Dee Belemnite carbonate -VPDB).

Sulfur isotopic abundances are represented as follows:

$?^{34}S_{VCDT} = (({}^{34}S/{}^{32}S)_{sample}/({}^{34}S/{}^{32}S)_{VCDT} - 1)1000,$

where $?^{34}S_{VCDT}$ is the difference in permil (parts per thousand) between a sample and the sulfur isotopic standard (Vienna Cañon Diablo Troilite - VCDT)