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STABLE CARBON AND SULFUR ISOTOPES AS RECORDS
OF THE EARLY BIOSPHERE

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The abundance ratios of the stable isotopes of light elements such as carbon and sulfur can differ between various naturally-occurring chemical compounds. If coexisting compounds have achieved mutual chemical and isotopic equilibrium, then the relative isotopic compositions of these compounds can record the conditions (e.g., temperature) at which equilibrium was last maintained. If coexisting chemical compounds indeed formed simultaneously but had not achieved mutual equilibrium, then their relative isotopic compositions often reflect the conditions and mechanisms associated with the kinetically-controlled reactions responsible for their production. In the context of Mars, the stable isotopic compositions of various minerals (and organic compounds?) might record not only the earlier environmental conditions of that planet, but also whether or not the chemistry of life ever occurred there.

Two major geochemical reservoirs occur in Earth's crust, both for carbon (carbonates and reduced organic carbon) and sulfur (sulfates and sulfides). In rocks formed in low-temperature sedimentary environments, the oxidized forms of these elements (the carbonates and sulfates) tend to be enriched in the isotope having larger mass (^{13}C , ^{34}S), relative to the reduced forms (organics and sulfides). In sediments where the organics and sulfides were formed by biological processes, these isotopic contrasts have been caused by the processes of biological CO_2 fixation and dissimilatory sulfate reduction. Because these isotopic patterns are pervasive in sedimentary rocks, and, in addition, they persist through geologic time despite frequent thermal alteration of their host rocks, these patterns have become important indicators of the antiquity of life on Earth.

Such isotopic contrasts between oxidized and reduced forms of carbon and sulfur are permitted by thermodynamics at ambient temperatures. Thus they do not necessarily require the intervention of life. However, nonbiological chemical reactions associated with the production of organic matter and the reduction of sulfate are extremely slow at ambient temperatures. Thus the ubiquitous synthesis of organics and sulfides under ambient conditions illustrates life's profound role as a chemical catalyst that has altered the chemistry of Earth's crust.

For carbon, the isotopic "signature" of biological CO_2 fixation is the remarkably consistent two to four percent depletion in the $^{13}\text{C}/^{12}\text{C}$ value of organic matter, relative to carbonate, in sedimentary rocks. This isotopic contrast is, in most cases, due to the activity of the enzyme ribulose biphosphate carboxylase, which incorporates the CO_2 into a sugar molecule. The persistence of this isotopic contrast in rocks ranging from the Recent to more than 3.5 billion years ago might very well testify to the extreme age of this key enzyme.

For sulfur, the isotopic signature of bacterial sulfate reduction is the presence in sediments of sulfide which has a wide range of $^{34}\text{S}/^{32}\text{S}$ values that are generally lower than the corresponding values of coeval sulfates. This isotopic signal is relatively clearly expressed in rocks as old as 2.3 billion years. The interpretation of the older rock record is controversial, and might indicate that sulfate reducing bacteria arose between 2 and 3 billion years ago.

The biological isotopic signatures for carbon and sulfur differ in that the carbon signal is typified by a clearly biomodal isotopic contrast between the carbonates and organics, whereas the sulfur "biogenic" signal is the wide range of $^{34}\text{S}/^{32}\text{S}$ values formed at low temperature, most frequently

in sediments. These patterns reflect the properties of the specific environments and organisms that formed them, and, as such, allow us to interpret them as biological signatures.

Because the stable isotopes of carbon and sulfur can reflect their chemistry, they will be useful probes of the Martian surface. Will they show that carbon and sulfur have been reacting at ambient temperatures due to some consistent, life-like process? Perhaps we will be able to measure the average isotopic compositions of carbon and sulfur in the Martian crust (e.g., measured perhaps by analyses of igneous rocks). Can an isotopic contrast between these average values and composite values for carbonates or sulfates be used to infer the presence of other more reduced, carbon and sulfur reservoirs, even at sites where no reduced species are found?