

The importance of metabolism for lipid D/H ratios

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Recent work on factors controlling hydrogen-isotopic fractionations in lipids has yielded two rather surprising observations. The first is that the net D/H fractionation between growth water and synthesized lipids ($\epsilon_{w/l}$) can change substantially as a function of environmental salinity. Experiments with halotolerant cyanobacteria reveal that this effect can reach ~55‰ over a range of salinities from 2-10‰, without any significant corresponding change in lipid abundance. Whereas similar responses in *E. coli* were attributed to the accumulation of respiration-derived water inside the cell, cyanobacteria are photoautotrophs and so a different mechanism must be at work. We suggest that proton pumping related to maintenance of osmotic gradients may be the relevant process. Perhaps more importantly, the results demonstrate that individual cells (and by inference cellular compartments) are able to maintain internal pools of water that are far from isotopic equilibrium with external water. Similar effects thus might exist in multicellular organisms.

The second observation is that $\epsilon_{w/l}$ in bacteria varies quite strongly, over a ~400‰ range, depending on the mode of metabolism being employed. In general, aerobic heterotrophy yields D-enriched lipids (-100 to +200‰), photoautotrophy yields intermediate values (-150 to -250‰), and chemoautotrophy yields the most highly D-depleted lipids (-200 to -400‰). The most likely causes of such variations are isotope effects occurring during the reduction of NADP⁺ to NADPH, which is used for lipid biosynthesis. While the effect has thus far only been demonstrated in bacteria, there are hints that similar processes are relevant to multicellular organisms, including higher plants. δD of plant leaf waxes is inversely correlated with growth rate, consistent with increasing δD values during times of increased reliance on heterotrophic recycling.

Taken together, these new findings suggest that the H-isotopic composition of lipids is strongly dependent on dynamic metabolic processes, and not a static lipid biosynthetic pathway. Conceptual models analogous to carbon (you are what you eat) are likely to be inappropriate here, and we should think of hydrogen isotopes as being recorders of metabolic processes, not growth substrates.

Of modern lakes and ancient oceans: Trace metals and their isotopes in an anoxic African rift lake

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Lake Tanganyika in the African rift valley is one of the largest anoxic bodies of water on the Earth today. In contrast to the Black Sea—a marine marginal basin that is often cited as a modern analog for the earliest oceans—Lake Tanganyika is a freshwater lake with very low dissolved sulfate (~35 μM), sulfide (~30 μM) and iron (~250 nM) concentrations; these properties make this lake an ideal analog for the ocean at the Archean/Proterozoic transition, when hydrothermal iron input were waning but atmospheric oxygen was low and sulfate was still largely absent in the ocean.

We have assembled an extensive data set of organic carbon contents, sulfur speciation, major and trace element abundances, and iron and molybdenum isotope compositions to investigate transition metal isotope variations under sulfur limited, anoxic conditions. In a sedimentary record spanning 18 ky we have observed systematic variations that occur synchronous in many of the parameters analyzed. These variations are thought to be related to regional changes in climate, and particularly in variable rainfall patterns. The continental delivery of macronutrients, sulfate and trace elements is changing the reservoir size of these components in the lake, as well as affecting the lake's ecology. By combining novel isotope systems with established proxies of redox conditions and biological activity we are able to explore the relative importance of isotope fractionation mechanism, mass balance relationships and environmental changes in governing isotope variations in the sedimentary isotope record.