Archean Sterol Biomarkers Do Not Prove Oxygenic Photosynthesis

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As of 2004, at least 473 biochemical reactions were known in which molecular O_2 was a substrate (*1*). Hence, one way to constrain the history of oxygen is to look for biomarkers preserved in sediments that are the product of oxygen-dependent reactions. For organic biomarkers to provide a good constraint on paleo-oxygen levels it is also important to verify that the fundamental chemistry involved requires oxygen, precluding any possibility of anaerobic mechanisms.

Of particular importance as potential constraints on the history of oxygen are the degradation products of polycyclic isoprenoids, particularly hopanols and sterols, which preserve enough of their structural information to identify the biochemical pathways through which they formed. These have been the primary focus of a series of papers (e.g., (*2*)). Although although we now know the hopanols can be produced anaerobically, it is still an open question for sterols.

In yeast, the modern biosynthetic pathway to ergosterol is a long chain of biochemical reactions that use three O_2-dependent enzymes. Although squalene can be cyclized without oxygen, to convert lanosterol to ergosterol, enzymes use oxgyen to remove three methyl groups, two on C4 and one on C14. Because of the inertness of the C-H bond in hydrocarbons, it is often assumed that oxygen must be involved in the activation, rearrangement, and metabolism of molecules like these. For demethylation, oxygen is used to introduce hydroxyl groups by replacing one of the carbon-bound hydrogens, after which other enzymes can proceed through a series of steps including dehydrogenation and eventual decarboxylation. However, this C-H extraction is done anaerobically in methane oxidizing bacteria.

Recent discoveries in the biochemistry of anaerobic sulfate reducing bacteria demonstrate that all chemical reactions for sterol synthesis can be done by special enzymes using Fe-S clusters (radical SAM reactions) as well others utilizing Mo and Ni cofactors; none of the fundamental chemistry demands oxygen. As most of these enzymes are poisoned by molecular oxygen, natural selection would have favored strongly their replacement by aerotolerant or O_2-utilizing forms, as noted by (*1*) and (*3*). Hence, fossil sterol derivatives might have been produced through ancestseral anaerobic anabolic processes.

References

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