

Tapping the Late Archean Molecular Fossil Record: New Evidence for Fossil Syngenicity and Ecological Implications

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Resolving the biogeochemical changes stemming from the onset of oxygenic photosynthesis is critical to understanding events that culminated in the oxygenation of the global atmosphere at ~2.3 Ga. Published carbon-isotope, sulfur-isotope, and molecular-fossil records suggest oxygenic photosynthesis was extant and that a microbial methane cycle was established by 2.7 Ga. Notably, these records do not reveal the ecological trends expected of incipient and/or shallow marine oxygenation. Moreover, the evidence for syngenetic relationships between molecular fossils and host rocks, and the proposed 2.7 Ga constancy of oxygen-dependent biosynthetic pathways, have both been queried. In order to test the syngenicity of late Archean molecular fossils, we systematically evaluated our kerogen-carbon isotopic ($\delta^{13}\text{C}_{\text{kerogen}}$) and extractable molecular fossil data for samples representing diverse depositional environments acquired from three Hamersley Basin drill cores.

Our analyses reveal that ratios of redox-sensitive molecular-fossils strongly correlate to each other and/or to $\delta^{13}\text{C}_{\text{kerogen}}$ values (-57 to -28‰ range). Furthermore, they show significant relationships with dolomite abundance and to sedimentologically-defined depositional facies. The observation of patterns of extractable hydrocarbons with strong correlations to the lithological and isotopic features of host rocks provides strong support for a syngenetic relationship. Molecular fossils provide evidence for the existence of aerobic methanotrophy in the late Archean biosphere, but, surprisingly, their abundances are anti-correlated with the extreme ^{13}C -depletion that has been a notable characteristic of the kerogen isotopic record in this time period. Evidently, processes commonly proposed to explain extreme ^{13}C -depletion in the late Archean kerogens, for example aerobic recycling of methane, are more complex than previously thought. Most importantly, molecular fossil-carbon isotope-depositional facies patterns and trends within these

patterns reflect ecological diversification most likely due to increasing marine oxidation, which led to atmospheric oxygenation >400 Ma later.