



Molecular fossils and the late rise of oxygenic photosynthesis

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Biomarkers are the molecular fossils of natural products such as lipids and pigments. They can yield a wealth of information about early microbial ecosystems and are particularly valuable when preserved in > 1 billion-year old (Ga) sedimentary rocks where conventional fossils are often lacking. Therefore, in 1999, the detection of traces of biomarkers in 2.5 to 2.7 Ga shales from Western Australia (Brocks et al. 1999, Summons et al. 1999) was celebrated as a breakthrough. The discovery, which was later confirmed by several independent studies, led to far reaching conclusions about the early evolution of oxygenic photosynthesis (Summons et al. 1999) and ancestral eukaryotes (Brocks et al. 1999). However, here we present new data based on the carbon isotopic composition of solidified hydrocarbons (Rasmussen et al. 2008) and the spatial distribution of liquid hydrocarbons within the original 2.5 and 2.7 Ga shales (Brocks 2011) that demonstrate that the molecules must have entered the rocks much later in Earth's history and therefore provide no information about the Archean (>2.5 Ga) biosphere or environment.

The elimination of the Archean biomarker data has immense implications for our understanding of Earth's early biosphere. 2-Methylhopanes have been interpreted as evidence for the existence of cyanobacteria at 2.7 Ga, about ~300 million years before the atmosphere became mildly oxygenated in the Great Oxidation Event (GOE; between 2.45 and 2.32 Ga). Now, the oldest direct fossil evidence for cyanobacteria reverts back to 2.15 Ga, and the most ancient robust sign for oxygenic photosynthesis becomes the GOE itself. Moreover, the presence of steranes has been interpreted as evidence for the existence of ancestral eukaryotes at 2.7 Ga. However, without the steranes, the oldest fossil evidence for the domain falls into the range ~1.78-1.68 Ga. Recognition that the biomarkers from Archean rocks are not of Archean age renders permissive hypotheses about a late evolution of oxygenic photosynthesis, and an anoxygenic phototrophic origin of the vast deposits of Archean banded iron formation.

Brocks et al. (1999) *Science* 285, 1033-1036.

Brocks (2011) *Geochim. Cosmochim. Acta*, 75, 3196-3213.

Rasmussen et al. (2008) *Nature* 455, 1101-1104.

Summons et al. (1999) *Nature* 400, 554-557.