

Archean hydrocarbon biomarkers: Archean or not?

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Understanding the origin of oxygenic photosynthesis relative to the Great Oxygenation Event (GOE) is one of the key goals in geobiology today. Archean organic biomarkers provide evidence for oxygenic photosynthesis and eukaryotes predating the GOE [e.g. 1, 2]. However, these results have been challenged and remain controversial [e.g. 3]. Resolving the controversy about the syngeneity of these compounds with their Archean host rock will clarify our understanding of the antiquity of oxygenesis and aerobiosis.

Samples were collected from three diamond drill holes in the Australian Pilbara according to unprecedented protocols during the 2012 Agouon Institute Drilling Program (AIDP). Molecular spikes, tracer experiments, negative controls, and replicate analyses of duplicate samples by multiple independent laboratories were used to constrain results.

To date, a total of seven “biomarker target” samples have been analysed from the AIDP-2 core near Ripon Hills, which intersected the Carawine and Jeerinah Formations, and the AIDP-3 core between Tom Price and Karratha, which intersected the Marra Mamba and Jeerinah Formations. Alkanes, hopanes, and steranes appear to be below detection from the interiors and exteriors of these seven samples. However, multiple samples from the Carawine Formation contain polycyclic aromatic hydrocarbons (PAHs) and diamondoids. These molecules may represent the oldest reported authigenic hydrocarbons, yet the origin of these molecules is uncertain. Replicate analyses of exact duplicate samples by additional organic geochemical laboratories will test the robustness of these current results. Interestingly, analysis of an RHDH2A drill core sample from the Carawine Formation recovered in the 1980s revealed an abundance of hydrocarbons that were absent in the new AIDP-2 Carawine Formation drill core material, suggesting contaminants were introduced during drilling, sampling, sawing, and/or storage.

[1] Brocks, Logan, Buick, & Summons (1999), *Science* 285, 1033-1036. [2] Summons, Jahnke, Hope, & Logan (1999), *Nature* 400, 554-557. [3] Rasmussen, Fletcher, Brocks, & Kilburn (2008), *Nature* 455, 1101-1104.

REE and Neodymium isotopes in sedimentary organic matter

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Sedimentary Organic Matter (OM) collected from various depositional environments, i.e. rivers (n=25), estuaries (n=18), ocean (n=15), and cold seeps (n=12), was extracted using a mixed hydrogen peroxide/nitric acid solution, after removal of carbonate and oxy-hydroxide phases with dilute hydrochloric acid.

Our results indicate that the abundance of REE in sedimentary OM is six-to-seven orders of magnitude higher than in river water or seawater. The mean REE concentration in the H₂O₂ leachates for samples from rivers, estuaries, coastal seas and open ocean is relatively similar: ΣREE = 107 ± 89 ppm (mean ± s). In comparison, the OM fractions leached from cold seep sediments display higher concentration levels (285 ± 150 ppm). The H₂O₂ leachates for most sediments exhibit remarkably similar shale-normalized REE patterns, all characterized by a mid-REE enrichment compared to the other REE. This suggests that the distribution of REE in leached sedimentary organic phases is controlled primarily by (bio) geochemical processes (i.e. complexation), rather than by the composition of the source from which they derive (e.g. pore water, river or seawater).

The Nd isotopic compositions for OM leached from river sediments are very similar to those for the corresponding detrital fractions. In contrast, OM extracted from marine sediments display εNd values that typically range between the εNd signatures for terrestrial OM (inferred from the analysis of the detrital fractions) and marine OM (inferred from the analysis of local surface seawater). An interesting exception is the case of cold seeps OM leachates, which sometimes exhibit εNd values markedly different from both terrigenous and surface seawater signatures. This suggests that a significant organic fraction in these environments may be derived from chemosynthetic processes recycling pore water REE characterized by a distinct isotopic composition.

Overall, our results suggest that organic matter probably play an important role in the oceanic REE budget, through direct scavenging or remineralization within the water column. In addition, the use of Nd isotopes in sedimentary OM phases could offer interesting future applications in paleoenvironmental studies.