Assessing bound molecular & stable isotopic information preserved in Archean sedimentary kerogens

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The technique of continuous-flow hydropyrolysis (hydrogen pyrolysis, termed *HyPy*) has proven capabilities for accessing *in situ* ancient kerogen-bound organic molecules [1-3]. Analysis of organic matter in rocks older than 2.5 Ga has been hampered by high thermal alteration of such rocks, which results in the loss and/or degradation of any original biomarker constituents. The main organic matter phase present in Archean rocks (>99 wt%) is overmature biogenic kerogen. Archean sedimentary organic matter can exhibit a wide range of ^{13}C-depleted bulk carbon isotopic signatures (ranging from -30 to -55‰), not generally found in younger rocks, which may reflect the balance of enigmatic biological source organisms in the Archean ocean.

The *HyPy of kerogen* approach generates a source of unambiguously syngenetic molecular remains (hydrocarbons and polar compounds) which can be quantified and generates sufficient products for detailed compound-specific carbon isotopic analyses. Overall product yields from HyPy of kerogens from 2.7 Ga Jeerinah Formation black shales were significantly lower than kerogens prepared from 2.6 Carawine dolomites and their PAH profiles displayed a significantly lower degree of alkylation indicating poorer preservation [3], likely reflecting a higher degree of thermal alteration for black shales promoted by organic matter-acidic clay mineral interactions during burial maturation. Absolute yields of PAH compounds released by HyPy of kerogens were typically at least an order of magnitude higher than for the extractable PAH released by solvent extraction for the same rocks [3]. The PAH and *n*-alkanes generated by HyPy from kerogen in this study constitute the most ^{13}C-depleted molecular signatures reported for Archean organic matter [3], strongly supporting that these are primary Archean organic molecules. Hopanes and steranes were undetectable in all HyPy products of Archean kerogens analysed using multiple reaction monitoring (MRM)-GC-MS, consistent with the high thermal maturity of Archean kerogens [3].

[1] Love *et al*. (1995) *Org. Geochem.* **23**, 981-986.
[2] Marshall *et al*. (2009) *Precam. Res.* **155**, 1-23.
[3] French *et al*. (2015) *PNAS* **112(19)**, 5915-5920.