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Characterization of c.3.5 billion-year-old organic matter

One of the major challenges in Earth Sciences is to construct a robust picture of the diversity and timelines of the early forms of life from the fossil record. Several decades have passed since the first description of recognisable early Archaean microfossils which were purported to be ancient bacteria (e.g., Dunlop et al., 1978; Buick et al., 1981; Awramik et al., 1983; Schopf, 1993; Rasmussen, 2000). However, morphology-focused imaging techniques of fossil-like objects and stable isotope (C, N, and S) compositions of putative organisms have relentlessly failed to prove their biological origin (e.g., Brasier et al., 2002; Schopf et al., 2002; Ueno et al., 2004).

Finding evidence for traces of early life on Earth is difficult due to the problems faced in assessing both the syngenicity and the biogenicity of preserved organic matter in Archaean sedimentary rocks. Since the syngenicity of the soluble organic matter fraction is difficult to demonstrate, studies focus on the insoluble organic fraction (kerogen) in order to ascertain biomarkers. It is generally accepted that the insoluble organic matter (kerogen) is syngenetic with the host rock and several features of the kerogen confirm its formation simultaneously with the solidification of the siliceous matrix of the cherts. Raman spectroscopy has recently become a very popular analytical technique used by Earth and Planetary scientists, for example Precambrian palaeobiology. Raman spectroscopy has been used to demonstrate a carbonaceous composition for putative microfossils in Early Archaean age rocks (Westall and Rouzaud, 2004). In some cases, Raman spectroscopy has been used to infer a biological (Schopf et al., 2002) origin of putative microfossils. On the other hand, Raman spectra have been cited as evidence of a non-biological origin for microfossils (Brasier et al., 2002). However, studies have shown that non-biological and biological organic matter display similar Raman spectra (Wopenka and Pasteris, 1993). The carbon first-order spectra for these isolated kerogens are typical spectra obtained from disordered sp^2 carbons, and have a similar line-shape to the spectra acquired by Brasier et al. (2002, 2005). The results and subsequent interpretation clearly show that the organic matter in the Warrawoona cherts are not graphitic as previously reported. Geochemical maturation or metamorphism of almost all naturally occurring organic matter, whether biological, abiological or meteoritic in origin, might be expected to give rise to essentially similar assemblages of thermally stable products — interlinked PAHs that have experienced geological conditions that result in carbonization and graphitization. Therefore, Raman spectroscopy of over-mature kerogen cannot provide definitive evidence of biogenicity by itself.

Obtaining information about the chemical and physical macromolecular structure of insoluble carbonaceous materials is best accomplished with a combination of catalytic hydropyrolysis and solid-state spectroscopic techniques. Currently, we are undertaking catalytic hydropyrolysis (HyPy) to obtain molecular information. Catalytic hydropyrolysis is used instead of standard pyrolysis due to the higher yields of products routinely obtained when using an effective hydrogen donor, which is particularly appropriate for hydrogen-lean carbonaceous materials such as Archaean kerogens. Organic contamination of geological samples appears to be a common phenomenon. Insoluble organic matter is composed of a covalently bound cross-linked polymer-like macromolecular network in which potential contaminating solvent soluble/extractable bitumen from a younger geological source may become trapped. Therefore, we investigated solvent extracted isolated kerogen in order to eliminate false biomarker signals arising from potentially contaminating younger organic matter trapped in the kerogen macromolecular structure.

An initial HyPy treatment up to 330 °C was performed to remove any residual bitumen prior to the high temperature run (to 520 °C). Over 99% wt. of aromatic hydrocarbons were released in the latter high temperature step. Significantly this adds confidence that, in general, the aromatic compounds reported represent genuine kerogen-bound molecular constituents. The Strelley Pool Chert isolated kerogen hydropyrolysates contain a diverse range of 1 to 7-ring PAH compounds, with phenanthrene (3-ring) or pyrene (4-ring) PAH as the major components. Although the chromatograms are complex, the PAHs do not show a high degree of branched alkylation of aromatic side-chains and C_1- and C_2-substituted PAHs are the dominant alkylated forms. The PAH profiles are fairly similar to those observed by Brocks et al. (2003) from HyPy of 2.5 Ga kerogens from Hamersley Group (Western Australia). For comparison, an unmetamorphosed Mesoproterozoic isolated kerogen from the Urapunga 4 drill core that intersects the 1.4 Ga Velkerri Formation, Roper Group, NT, Australia, was analysed. The total PAH profiles for Strelley Pool Chert and Urapunga 4 kerogens have similar features, with the less mature Urapunga 4 aromatic compounds not surprisingly exhibiting a greater degree of alkylation. Moreover, these are distinct from those obtained from HyPy treatment of the insoluble carbonaceous material found in Murchison meteorite.

Similarities in molecular profiles exist between HyPy products of Strelley Pool Chert kerogens and an unmetamorphosed Mesoproterozoic kerogen from Roper Group (ca. 1.4 Ga), which is biogenic in origin, suggesting that the Strelley Pool Chert kerogens may also be derived from diagenesis and thermal processing of biologically derived organic matter. A combination of Raman spectroscopy, for identifying the least metamorphosed kerogens, used together with HyPy, for liberating trapped and bound molecular components of these kerogens, offers a powerful strategy for assessing the origins of Earth's oldest preserved organic matter.

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The Vendian (Ediacaran) in the geological record

Fifteen years in Western Australia brought me into contact with Reg Sprigg, the finder in 1947 of the Ediacara "jellyfish" and Martin Glaessner, who was at first sceptical, but who later described them brilliantly My interest was aroused in 2001 by seeing spectacular Ediacara fossils at the Natural History, London, and Western Australian, Museums and I searched for a "global review" of the occurrences of these soft-bodied fossils, but could only find brief summaries. So I decided to research the subject (McCall, 2006), little realising its immense breadth!

Most antipodeans probably think that it started with Ediacara in the Flinders Ranges of S. Australia but this is not so. It emerges that *Aspidella* (now an Ediacara synonym) was described by Billings from Newfoundland in 1872. Furthermore Range and Schneiderhohn collected *Rangea* and *Pteridinium* from Namibia between 1908 and 1914, though they were not formally named until the 1930s Nevertheless it was Sprigg's find which set the world of geology alight, closely followed by that of a school boy, Roger Mason, of frondose.*Charnia* in the Charnwood Forest of England.

Eight major provinces are described (McCall, 2006). The Avalon occurrences in Newfoundland were described first in 1969 and another extensive province in NW Canada embracing the NW territories, Yukon and British Columbia from 1977 onwards. At the same time extensive developments were described in great detail from Russia including Ukraine (Podolia), the White Sea Coast, Urals and Olenek, Angara and Magadan regions of Siberia. Less extensive or less well-researched occurrences include Carmarthenshire, Wexford, North Norway, Spain, Sardinia, Iran, Oman, India, China, Algeria, Morocco, Brazil, Argentina, Uruguay, USA (Carolina, California, Nevada), Mexico (Sonora).

The Ediacara soft-bodied fauna invaded the extensive shelf seas formed after the break-up of Rodinia. It was a cosmopolitan fauna extending across the globe, but each province has its own peculiar faunal character.