

STUDIES OF POTENTIAL METAZOAN BIOMARKERS AND ENVIRONMENTAL CHANGE DURING THE METAZOAN RADIATION

The capacity to make completely new kinds of structural materials (eg lignin, cellulose) or to modify existing molecules to improve their function, has resulted in the occurrence of phylogenetically distinctive biomarkers (Brocks & Summons, 2003). Biomarkers that we associate with modern-day oxygen-producing cyanobacteria and steroids that require molecular oxygen and oxygen-specific enzymes for their biosynthesis can be found in rocks as old as 2700 million years. This is consistent with the notion that oxygen from oxygenic photosynthesis played a role in the deposition of banded iron formations and that the ready availability of reduced minerals and volcanic gases acted as a buffer to keep atmospheric oxygen concentrations low. The ‘sudden’ development of oxidized soil profiles about 2300 myr ago, together with S-isotopic indicators, suggests that the oxygen rise occurred in a stepwise manner. No definitive biomarker studies are yet available for this ‘Great Oxidation Event’ but this is obviously a research priority. The Neoproterozoic oxygenation step, or steps, should have been accompanied by burial of a significant quantity of organic matter. Such enhanced OM burial rates would be in accord with the occurrence of the first, large-scale, petroleum-prone basins in several locations (Oman, Australia and Siberia) from about 550-540 million years ago. The oils from these deposits, and abundant sedimentary bitumens from the same era, are geochemically distinct and unlike those from any other period in Earth history. Moreover, they contain

very unusual steroid molecules that might be attributable to primitive animals, that is, sponges (eg McCaffrey et al. 1994).

Steroid biomarkers for early animals; biomarkers for reconstructing paleoenvironment

The application of molecular biomarkers to the study of early metazoan evolution has received relatively little attention, but has much to commend it since primitive, soft-bodied animals are likely to have had poor physical preservation and little potential for leaving a trace fossil record. Sponges, which are almost certainly a paraphyletic grade at the base of the animal tree (Peterson et al., 2004, 2008, Sperling et al., 2007), are also hosts to a large diversity of symbiotic microorganisms, encompassing microalgae, bacteria, archaea and fungi, and a variety of unusual and conventional steroid structures have been detected in their extracts (Aiello et al. 1999). So caution must be exercised in targeting fossil molecular markers for sponges. It appears, however, that numerous steroids are synthesized *de novo* by sponges

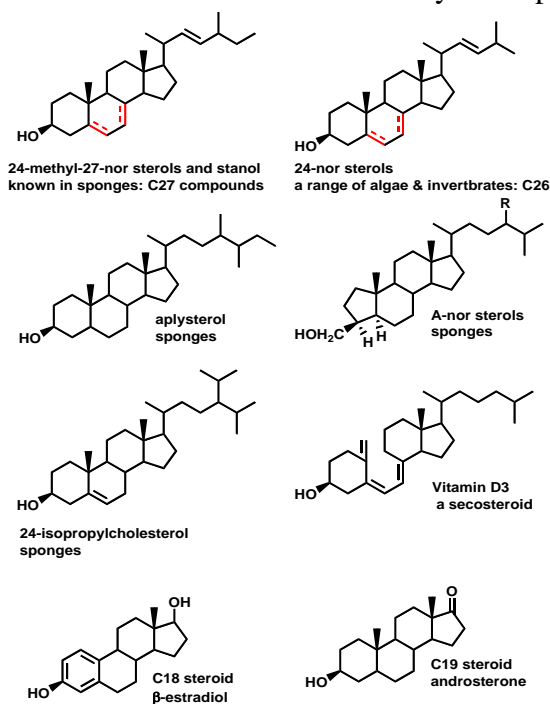


Figure 1. Structures of structurally distinctive sterols that are known to occur in metazoa. Most of the illustrated transformations of the basic steroid skeleton are not known to be exercised by protists. These compounds are, or could be, the biogenic precursors to geologically stable and, as yet, incompletely characterized steranes that we have observed in recent (unpublished) work in the Oman.

(Silva et al., 1991) and that 24-isopropylcholestanes are reliable molecular fossil markers for sponges (McCaffrey et al. 1994) since the precursor 24-isopropylcholesterols and related structures (Bergquist et al. 1986, 1991a,b) appear to be ubiquitous lipid components of the demosponges. Choanoflagellates, the nearest living protistan relative of sponges, have not yet been shown to make this sterol although further studies are required to establish this with more confidence (Kodner et al., 2008).

Over the past five years we have gathered molecular evidence, in the form of uncommon sterane distributions in marine source rocks from the South Oman Salt Basin (SOSB), for a radiation in Porifera occurring prior to 630 Ma (Grosjean et al. 2005; Love et al. 2006). With samples being gathered by our geological colleagues, we are now examining a much broader sample suite that spans ca. 500-800 Ma to evaluate demosponge biomarkers at all stratigraphic levels and across different sediment lithologies. Our aim is to investigate

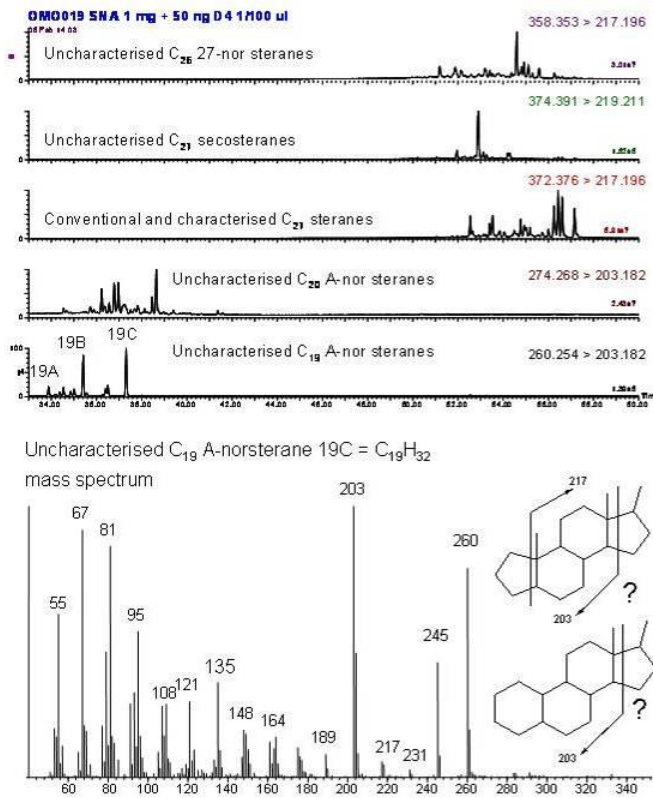


Figure 2. Top panel shows selected GC-MS-MS (MRM) chromatograms for some of the abundant steranes in an early Cambrian oil (Q oil) from Oman. Only the C₂₇ steranes (middle trace) have been previously characterized by geochemists. The bottom panel shows a mass spectrum of one of these compounds and two putative structures. Since the mixtures are too complex to obtain nmr spectra for further structural assignment, we will use judicious chemical synthesis of likely alternative isomers to formally assign structures and, thereby, better understand their organismic origins.

rock units from a representative set of Neoproterozoic-Cambrian sedimentary basins and, at the same time, analyze our findings in the context of geological, isotopic and other biomarker data that speak to local and global environmental change.

Description of Research: Sedimentary rocks of Neoproterozoic-Cambrian age are being analyzed for organic carbon contents, biomarkers and stable isotopes of organic carbon, nitrogen and, where possible, sulfur. We use protocols developed and proven through two decades of research. Specific details of these methods are accessible

at (<http://eaps.mit.edu/geobiology/biomarkers/methods.html>). Improvements to the procedures for analysis of low TOC sediments were recently reported by Sherman et al. (2008).

Together, these data will provide a window into the environmental, biological and secular controls on organic matter composition and accumulation in relation to their sedimentary facies. They will give particularly insightful clues about prevailing paleoenvironmental conditions (eg Peters et al. 2005). Accordingly, we are examining abundances of high molecular weight alkanes (from algal biopolymers), extended acyclic isoprenoids (archaea), carotenoids and porphyrins (diverse phototrophs), C₂₆₋₃₀ regular steranes (algae), 2-methylhopanes (cyanobacteria) and 3-methylhopanes (methylotrophs) as well as molecular and isotopic indicators of paleoredox, salinity and water column stratification. 24-Isopropylcholestanes (demosponges) are measured together with other possible metazoan steroids such as 27-norsteranes, ring-A contracted steranes and putative 19-norpregnanes (Figs 1 and 2). Where the abundances of individual compounds allows, compound-specific isotope analysis of n-alkanes, isoprenoids, steroids, hopanoids and porphyrins are also being conducted.

Significance: With the exception of the attribution of 24-isopropylcholestanes in 'Infracambrian' sediments and oils to stromatoporoids or other sponge ancestors (McCaffrey et al., 1994), there is no generally accepted biomarker record for animals. This new research will systematically evaluate this issue with potential to develop markers that could be applied to the Phanerozoic and the study of mass extinction events and the subsequent recovery of biodiversity. This research addresses goals 5, 6 and 7 of the Astrobiology Roadmap (<http://astrobiology.arc.nasa.gov/roadmap/>).

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