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Lipid taphonomy in the Proterozoic and the effect of microbial mats on biomarker preservation

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ABSTRACT

The pre-Ediacaran biomarker record has several characteristic features that distinguish it from its Phanerozoic counterpart, including high concentrations of unresolved complex mixture (UCM), low concentrations or absence of eukaryotic steranes, and a conspicuous carbon isotopic enrichment of *n*-alkyl lipids relative to bulk sedimentary carbon. We propose that these derive from a common, non-actualistic taphonomy based on the pervasive presence of microbial mats prior to the “Cambrian substrate revolution.” Such mats would have formed a significant mechanical and biochemical barrier to in-falling plankton, leaving a biomarker record dominated by benthic microbial lipids, most of which would have originated from the lower, heterotrophically reworked layers of the mat. Most Proterozoic biomarker assemblages studied in this work derive from shallow-water sediments, where cyanobacteria-dominated upper mats represent a focused source of corrosive molecular oxygen. This “mat-seal effect” was broken with the onset of bioturbation in the Ediacaran and early Cambrian, at which point the primary source of fossil biomarkers switched from the benthos to the plankton.

INTRODUCTION

Fossil hydrocarbons (biomarkers) provide insight into ancient biology that complements the traditional body fossil record (Brocks et al., 2005). Most biomarkers are derived from biolipids that, as a result of diagenetic processes, have become geolipids while retaining significant biological information (Brocks and Pearson, 2005). Like the body fossil record, however, ancient lipid biomarkers are also subject to the many biases of taphonomy or postmortem information loss. Taphonomic processes are typically studied via actualistic experiments under controlled conditions. Even so, it is important to appreciate that taphonomic pathways and preservation potential have changed, sometimes dramatically, over time (Butterfield, 2003).

The Neoproterozoic-Phanerozoic transition was accompanied by revolutionary shifts in ecological structure, most of which can be ascribed to the rise and radiation of animals (Butterfield, 2007). One of the most important innovations was the disturbance of soft sediments and microbial mat cover by infaunal burrowing, with profound effects on contemporaneous ecology (Seilacher, 1999), sedimentology (Droser et al., 2002), and sulfur geochemistry (Canfield and Farquhar, 2009). We argue here that it also fundamentally altered the way in which organic matter was incorporated into the sedimentary record, and how it was eventually preserved. Prior to the Ediacaran rise of bioturbation, biolipid preservation would have followed

distinctively non-uniformitarian pathways due to the prevalence of microbial mats.

THE PROTEROZOIC BIOMARKER RECORD

The published record of pre-Ediacaran (>635 Ma) biomarkers is plagued by instances of secondary contamination (Brocks et al., 2008). As such, we have reanalyzed all units for which we could acquire suitable samples and assembled an unprecedented dataset of biomarkers using the same protocol throughout. Bitumens that pass all current tests for syngenicity range in age from the 742 Ma Chuar Group (Arizona, United States) to the 1640 Ma Barney Creek Formation (Australia) (see Table DR1 in the GSA Data Repository¹). Significantly, a majority of these samples are from shallow marine settings, and all share a combination of characters that is essentially unique to the Proterozoic.

(1) Gas chromatograms of Proterozoic bitumens almost always exhibit a conspicuously higher average base level of so-called unresolved complex mixture (UCM) than their Phanerozoic counterparts (Fig. 1). UCMs consist of thousands of mostly unidentified, branched and cyclic hydrocarbons. A prominent UCM is sometimes encountered in chromatograms of Phanerozoic oils, but in these instances can be recognized as the product of late-stage biodegradation (Peters et al., 2004) after the oil has been expelled from its source rocks and has come into contact with water and microorganisms. By contrast, most Proterozoic bitumens have high UCMs even

when preserved in their original source rock and showing no evidence of secondary alteration. Thus, UCMs are a primary characteristic of Proterozoic bitumens and likely reflect fundamental differences in the biological sources and taphonomy of Precambrian organic matter.

(2) When screened for secondary contamination (Brocks, 2011; Brocks et al., 2008), pre-Ediacaran biomarker assemblages are characterized by conspicuously low concentrations or absence of eukaryotic steranes, even in thermally exceptionally well preserved bitumens. This paucity of early eukaryotic steranes is generally interpreted as a primary ecological signal reflecting the limited ecological significance of eukaryotes (e.g., Anbar and Knoll, 2002), though it might also derive from localized exclusion or larger-scale taphonomic bias.

(3) Proterozoic bitumens typically contain conspicuously higher concentrations of monomethyl alkanes (MMA) and dimethyl alkanes (DMA) (single-chained hydrocarbons with one and two methyl groups, respectively) than their Phanerozoic counterparts (Fig. 1). The isomer and homologue distribution of MMA and DMA in these bitumens is fundamentally different from all known biogenic sources, and the wide variety of fossil structures is probably generated by cracking and rearrangement of functionalized precursors (Alexander et al., 2011; Kissin, 1987). Even so, suitable precursors appear to be abundant in modern microbial mats (Kenig, 2000).

(4) Relative to their Phanerozoic counterparts, pre-Ediacaran biomarker assemblages are characterized by conspicuously depleted (facies 1) or enriched (facies 2) concentrations of phototrophic or archaeal isoprenoids such as pristane (Pr) and phytane (Ph) and their respective breakdown products (Fig. 1).

(5) Proterozoic hydrocarbons are also distinguished from their younger counterparts by the conspicuous ¹³C enrichment of *n*-alkyl carbon skeletons compared to Pr and Ph and bulk sedimentary organic matter (Logan et al., 1995). Because the lipids of living organisms are isotopically depleted relative to their total biomass, such enrichment of *n*-alkyl lipids most likely occurred after the lipids were biosynthesized but prior to final burial. Insofar as Pr is derived primarily

¹GSA Data Repository item 2013025, methods and sample sections, Table DR1 (summary of pre-Ediacaran bitumen occurrences and their relevant characteristics), and Figure DR1 (full-scan mass chromatograms of the saturated hydrocarbon fractions of 11 pre-Ediacaran bitumens), is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

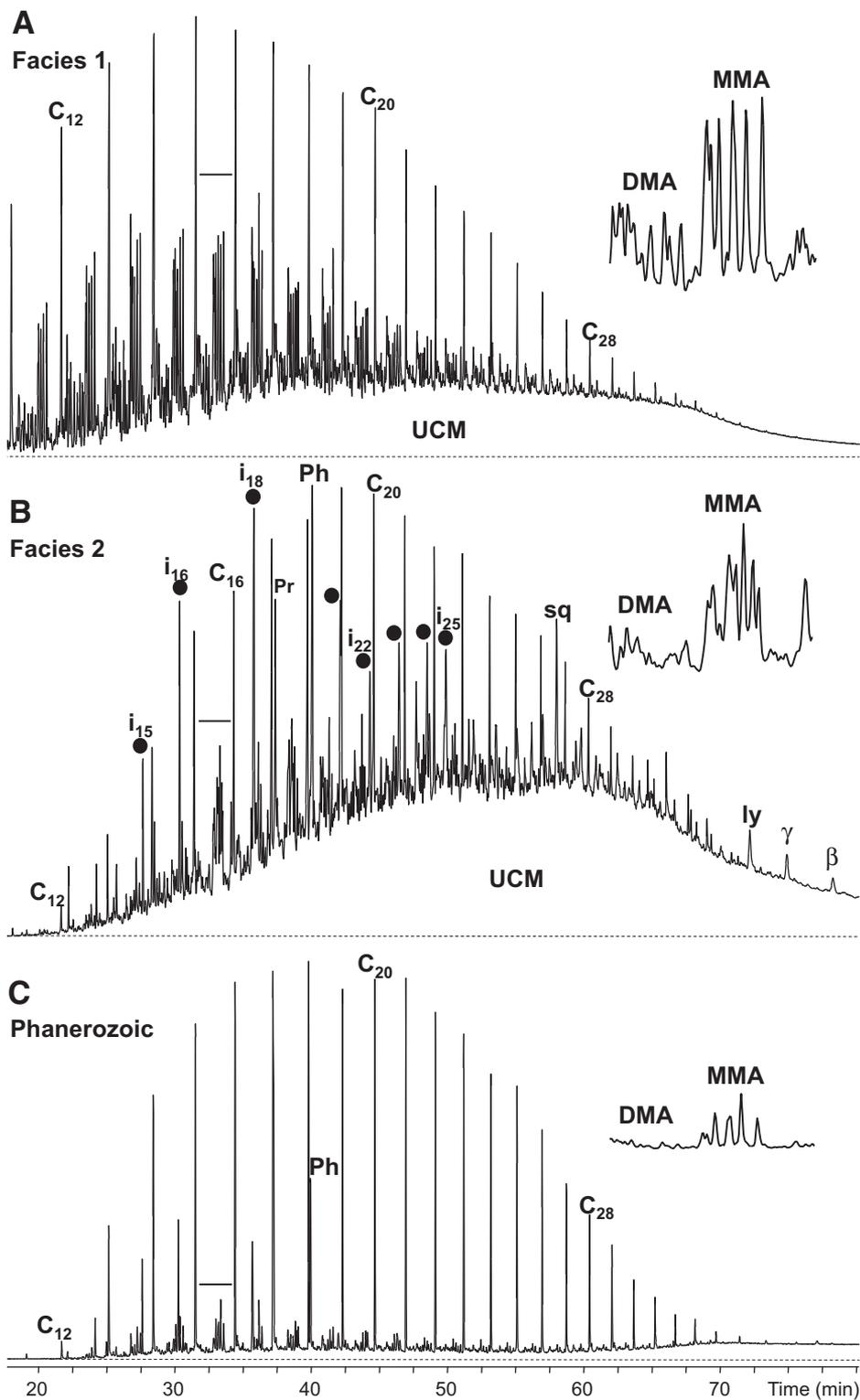


Figure 1. Gas chromatography–mass spectrometry (GC-MS) total ion chromatograms (TIC) of Proterozoic and Phanerozoic saturated hydrocarbon fractions from (A) ca. 1.1 Ga Neryuen Formation (Siberia) as representative of typical Proterozoic bitumen facies 1, (B) 1.64 Ga Barney Creek Formation (Australia; drill core GR-7, 45.35 m) as an endmember of Proterozoic bitumen facies 2, and (C) AGSO-II (Australian Geological Survey Organization) industrial standard, representing a mixture of a variety of typical Phanerozoic oils. Oils may have a slightly different composition than bitumens due to migration effects; however, these effects do not cause the major differences in the chromatograms. Insets show a horizontal magnification of the region between n -C₁₅ and n -C₁₆ (indicated by horizontal line), highlighting the distribution of monomethyl alkanes (MMA) and dimethyl alkanes (DMA). Relative signal intensities in the insets in A–C are to scale. ly—lycopane; γ — γ -carotane; β — β -carotane; C_{*x*}— n -alkanes with carbon number *x*; black dots—acyclic isoprenoids (*i*_{*x*}) with carbon number *x*; Pr—pristane; Ph—phytane; sq—squalane; UCM—unresolved complex mixture.

from photoautotrophic chlorophyll, it provides a clear measure for the degree of heterotrophic reworking in other molecules (Hayes, 1993). According to Logan et al. (1995), the isotopic enrichment of n -alkanes relative to Pr in the Proterozoic resulted from the extended heterotrophic reworking of plankton-derived organic matter in the water column due to the absence of zooplankton and their rapidly sedimenting fecal pellets.

PRE-EDIACARAN VERSUS POST-EDIACARAN LIPID TAPHONOMY

The “Mat-Seal Effect”

Microbial mats have a significant impact on sediment processes and, in the absence of grazing/burrowing animals (e.g., in various extreme environments and prior to the Ediacaran appearance of tissue-differentiating eumetazoans), can form thick cohesive structures with continuous, relatively impermeable internal laminations (Des Marais, 1995). Moreover, the friction of water just above the surface of the mat creates a stagnant boundary layer (De Beer and Kühl, 2001), imposing a further barrier to transport from the water column into underlying sediment.

In addition to their mechanical sealing effects, microbial mats are centers of intense biochemical activity (Des Marais, 1995), representing significant taphonomic hurdles to lipid preservation. In photic-zone settings, the combined activities of (mid-to upper mat) photoautotrophic and (mid- to lower mat) heterotrophic microbes result in steep and highly fluctuating redox gradients, and an accompanying gauntlet of lipid-degrading pathways. The molecular oxygen released by cyanobacteria strongly promotes degradation of organic compounds such as sterols (Harvey and Macko, 1997) and can reach supersaturation levels during daylight hours (Gingras et al., 2011).

The aerobic heterotrophs that reside within and immediately below the cyanobacterial layer of modern microbial mats are highly efficient lipid biodegraders. For example, Jahnke et al. (2004) recorded a 97% loss of cyanobacterial n -heptadecane within the upper 2 cm of an alkaline hot-spring mat, while concentrations of more recalcitrant 7-methylheptadecane and hopanoids declined by 83% and 57%, respectively. Even more rapid decomposition was observed by Wieland et al. (2008) in a hypersaline mat, where total organic carbon declined by 80% within the top 10 mm, and cyanobacterial 8-methylhexadecane and n -heptadecane to below detection limits within 3 mm. By contrast, non-lipid extracellular polymeric substances (EPS) appear to be less prone to degradation with >30% preserved at 9 mm depth in the latter study. Thus, benthic microbial communities in photosynthetic mats will rapidly degrade lipids produced in the water column and in the upper mat, but nevertheless accumulate degradation-resistant biopolymers. If mat ecology was

similar in the Proterozoic, then lipid biomarkers derived from plankton will be underrepresented in the long-term geological archive.

Non-photosynthetic microbial mats in deep-water environments are also likely to have had a strong effect on lipid preservation (e.g., Krüger et al., 2008). Although heterotrophic and chemoautotrophic mats do not produce high concentrations of corrosive oxidants, they nevertheless form significant mechanical and chemical barriers to in-falling plankton. In the absence of bioturbation, such mats may exclude a large fraction of plankton-derived lipids from access to clay minerals, which provide an important pathway for the adsorption and preservation of organic molecules (Hedges and Keil, 1995). Thus, even in deeper-water pre-Ediacaran settings, the sources and taphonomic processing of sedimentary organic carbon were likely distinct from those in the Phanerozoic.

At the same time as they interfere with the delivery of plankton to the sedimentary archive, microbial mats enhance the preservation of benthic organic carbon by providing a seal between overlying oxidant-rich environments and underlying reducing sediments. Thus, mat environments prior to the Ediacaran will have imparted a significant bias in favor of lipids derived from heterotrophs and anaerobes living within and below microbial mats, and against those derived from plankton and upper mat. We term this phenomenon the “mat-seal effect.”

THE BIOMARKER RECORD IN LIGHT OF THE MAT-SEAL EFFECT

Because of the distinct, non-actualistic bias of the mat-seal effect on input and preservation of organic matter, Proterozoic biomarkers cannot be interpreted in the same way as their younger counterparts. Whereas the Phanerozoic marine signal derives largely from plankton (Peters et al., 2004), Proterozoic biomarkers and their isotopes appear to be dominated by sources and processes intrinsic to benthic mats. In this light, the high UCM signature of Proterozoic biomarker assemblages can be viewed as the catagenetic product of heavily biodegraded biomass from the plankton and upper microbial mat, including significant proportions of EPS. Likewise, the high concentrations of MMA and DMA relative to *n*-alkanes most likely derive from the elevated activity of certain heterotrophic bacteria within microbial mats (Kenig, 2000; Shiea et al., 1990), combined with the preferential degradation of labile straight-chain lipids in the upper mat.

The pronounced microbial reworking of lipids in cyanobacteria-dominated mats will also have contributed to the conspicuously low concentrations of eukaryotic steranes and phototrophic isoprenoids in pre-Ediacaran biomarker assemblages (Fig. 1A). Even so, a notable minority of these bitumens contain abundant isopren-

oids and even carotenoid derivatives (Fig. 1B; Table DR1). In our view, the elevated levels of these compounds were probably not generated by cyanobacteria and algae but by anoxygenic phototrophs thriving in a sulfidic horizon deeper in the mat. Under these conditions, isoprenoidal lipids and carotenoids may accumulate through protection by sulfurization (e.g., Sinninghe Damsté and de Leeuw, 1990). This is seen, for instance, in the massive accumulation of carotenoids of anoxygenic phototrophs in the 1.64 Ga Barney Creek Formation (Brocks et al. 2005).

In addition to elucidating biomarker distributions, the mat-seal effect also offers an alternative explanation for Precambrian isotopic ordering (Logan et al., 1995) by removing the site of heterotrophic reworking from the water column to microbial mats. Quantitative treatment of Logan et al.’s heterotrophic model suggests that it can only work where primary organic matter is consistently exposed to high levels of initial degradation followed by significant attenuation, conditions unlikely to have been met persistently in Proterozoic plankton (Close et al., 2011). Such circumstances were much more likely to be encountered as sinking plankton experienced intense aerobic degradation associated with the top of pervasively developed microbial mats, before encountering increasingly anaerobic and preservation-prone conditions within and below the mat. By incorporating signatures from anoxygenic phototrophs assimilating heterotrophically derived (isotopically depleted) CO₂, microbial mats may also explain the marked isotopic variability noted among Proterozoic isoprenoids (Close et al., 2011).

If the mat-seal effect offers a correct interpretation of the Proterozoic biomarker record, then Phanerozoic assemblages from microbial mat facies are expected to show similar signatures. Reports of biomarkers from thermally mature Phanerozoic mat facies are rare and, almost necessarily, represent exceptional metazoan-excluding environments. Intriguingly, however, a biomarker assemblage recovered from a Silurian microbialite in southwestern Poland is characterized by high UCMs and MMAs (Bauersachs et al., 2009), although the presence of abundant steranes reflects a post-Ediacaran invasion of mats by eukaryotes.

The Ediacaran Transition

The Ediacaran Period (635–542 Ma) witnessed the most profound transition in ecosystem function of the past 2.4 b.y. (Butterfield, 2007), a turnover that is also reflected in the biomarker record. Our survey of biomarker assemblages through this interval (see the Data Repository) points to an Ediacaran continuation of elevated UCMs and MMAs, but with the loss of isoprenoid-deprived facies 1 bitumens and disappearance of the most extreme UCM and MMA signals. The carbon-isotopic reversal

between isoprenoids and *n*-alkanes appears to be similarly transitional, persisting in Australia (Logan et al., 1997) but expressing a Phanerozoic-like signature in Siberia (Kelly et al., 2011). The most striking change in Ediacaran biomarkers, however, is a pronounced increase in the abundance of eukaryotic steranes, including high relative abundances of C₂₉ stigmastanes and C₃₀ isopropylcholestanes.

The appearance of isopropylcholestanes of possible demosponge origin just prior to the Ediacaran suggests the evolutionary arrival of simple suspension-feeding animals (Love et al., 2009), offering a biological mechanism for transmitting planktonic biomarkers through the mat and into the underlying sediment. Of fundamentally greater importance, however, was the appearance of organisms capable of actively disrupting the mat seal. Although substantial burrowing/bioturbation is not recognized before the late Ediacaran, macroscopic trace fossils record the activity of large motile organisms by at least 585 Ma (Pecoits et al., 2012), while numerous lines of indirect evidence point to the presence of motile eumetazoans from at least the beginning of the period (Peterson and Butterfield, 2005). As such, we suggest that Ediacaran microbial mats are likely to have been subject to significant, if largely cryptic (cf. Pike et al., 2001; Zhang et al., 2007), bioturbation prior to the more pronounced “substrate revolution” of the early Cambrian, with important implications for contemporaneous sediment permeability, redox chemistry, and biomarker preservation. By disrupting the sealing effect of microbial mats, accruing infaunal activity through the Ediacaran will have been accompanied by increased preservation of plankton-derived lipids, decreasing levels of UCM and MMA, and a shift toward Phanerozoic-style carbon-isotope signatures in *n*-alkanes. Associated changes in styles of benthic photosynthesis are seen in the Ediacaran expansion of thrombolitic microbialites (e.g., Grotzinger et al., 2000) and eukaryotic algae (e.g., Yuan et al., 2011), along with a general marginalization of laminated stromatolites. In addition to enhancing the plankton signal, vertically oriented algal “turfs” will also have contributed more directly to Ediacaran increases in sterane concentrations, with levels remaining conspicuously low where horizontally oriented mat facies persisted into the late Ediacaran (McKirdy et al., 2006).

CONCLUSION

The biomarker record offers a powerful means of tracking evolutionary history in deep time, but like all paleontological data, is biased by context-dependent taphonomic processes. In the presence of a perennial pre-Ediacaran mat seal, for example, it is worth asking whether eukaryotes may have played a more significant role in pre-Ediacaran plankton than suggested

by their limited biomarker expression, and to what degree the Ediacaran–Cambrian rise in sterane concentrations might reflect the progressive opening of a taphonomic window. Certainly the mat-disrupting behavior of early animals induced major changes in taphonomic pathways, with significant impacts on carbon burial efficiency, nutrient availability, and paleontological expression. Such shifts inevitably distort the primary evolutionary signal, but by the same token reflect underlying innovation—in this case the Ediacaran arrival of motile metazoans.

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