TRACKING THE EMERGENCE AND EXPANSION OF EUKARYOTIC PHYTOPLANKTON AND METAZOA IN PROTEROZOIC OCEANS.

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Introduction: Biomarker records from thermally well-preserved Proterozoic sedimentary rocks can capture the evolving community structure of marine primary producers and provide insight into the timing of metazoan emergence during this critical time in Earth's history. The mid-Proterozoic (1800-1000 Ma) was characterized by a remarkably long period of geochemical and climatic stability resulting from redox-dependent feedbacks within the coupled nutrient-carbon-oxygen cycles imposed on planktonic life in the surface ocean. Evidence from a wide array of geochemical proxies and the fossil record shows a dramatic transition from the persistently reducing mid-Proterozoic Earth system to a world of dramatic change and instability in ocean-atmosphere redox, the carbon cycle, climate and biological innovation sometime later during the Neoproterozoic era (1000-542 Ma). Consistent with this body of work constraining ocean and atmospheric chemistry, lipid biomarker assemblages suggest that primary productivity in the mid-Proterozoic ocean was dominated by communities rich in bacteria as revealed by a dearth of sterane biomarkers [1], [2], [3], [4].

Although microfossil ([5], [6], [7]) and molecular clock evidence ([8]) both suggest that the eukaryotic domain had diverged by at least 1500 Ma, the abundance of any algal/eukaryotic contributions to marine planktonic communities was likely very low. In support of this, evidence for diverse eukaryotic microfossil assemblages and heterotrophic protists is not found until much later in the Neoproterozoic from about 800 million years ago and younger ([9], [10]). In contrast to the mid-Proterozoic, a diverse array of sterane biomarkers from algae and demosponges (metazoa) are abundant and readily detectable in thermally well-preserved 713-540 Ma Neoproterozoic-Cambrian rocks and oils from South Oman Salt Basin ([11], [12]) that post-date the first of two globally extensive Neoproterozoic glaciation events (the Sturtian glaciation at ca. 715 Ma). The sterane compounds detected in these South Oman rocks have been shown as unequivocally genuine primary lipid biomarker signals since they are found to be bound into the kerogen and measured via hydropyrolysis (HyPy). We are seeking to bridge this important temporal gap by examining the early Neoproterozoic lipid biomarker record for an expansion in eukaryotic abundance and diversity, prior to the Sturtian glaciation, using analytical approaches that largely remove concerns of contamination by younger hydrocarbons. This work allows us to construct a detailed and robust record of surface ocean ecology during the early Neoproterozoic.

Sample Information: Sedimentary rocks from the Nankoweap Butte and Sixtymile Canyon sections within the ca. 742 Ma Walcott Member of the Kwagunt Formation, Chuar Group, Grand Canyon, were screened for lipid biomarkers using parallel analysis of solvent extraction from the whole rock powder alongside fragmentation of the extracted kerogen via continuous-flow hydropyrolysis (pyrolysis using high pressure hydrogen, HyPy). The resulting *free* and *bound* biomarker pools were separately characterized and compared in detail using full scan and metastable reaction monitoring (MRM)-GC-MS to assess the relative abundance and taxonomic affinities of bacterial and eukaryotic organisms that thrived in this Neoproterozoic marine paleoenvironment. We report the oldest occurrence of demonstrably kerogen-bound C_{27}-C_{29} steranes with C_{27} compounds dominant, comprising 80-94% of the total sterane (C_{27}-C_{29}) response. These results suggest significant eukaryotic input relative to bacterial biomass, with red algal clades as the dominant eukaryotic phytoplankton (as suggested by the strong C_{27} sterane response).

These data show that a Neoproterozoic marine microbial ecology with abundant eukaryotic primary producers and consumers was established by at least 742 Ma, briefly pre-dating the first Neoproterozoic glaciation event.

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