

THE NITROGEN-ISOTOPIC COMPOSITION OF 1.1 BILLION-YEAR-OLD PORPHYRINS REVEALS OCEANS DOMINATED BY PHOTOTROPHIC BACTERIA

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The oceans of the mid-Proterozoic, 1.8 to 0.8 Ga ago, were devoid of animal-like life. According to recent models, this lack of large multicellular heterotrophs may have been caused by a severe global limitation of the nutrients such as phosphate (Brocks, 2018). Severe nutrient limitation causes low cell densities of primary producers but also gives planktonic cyanobacteria a distinct advantage over microalgae based on their much smaller cell size that promotes nutrient uptake by diffusion. Low cell densities and sizes, in turn, limit the flow of energy and carbon to higher trophic levels, possibly restricting the evolution of energy demanding large organisms (Brocks et al., 2017; Knoll, 2017). This hypothesis is supported by the observation that sterane / hopane ratios are consistently beneath detection limits in the mid-Proterozoic interval ($S/H < 0.001$) and only started to surge to modern levels after ~650 Ma ago (Brocks et al., 2017; Hoshino et al., 2017), around the time when eumetazoan animals emerged (Figure 1). However, it is difficult to exclude the possibility that the extremely low sterane abundances are an artefact of unfamiliar Proterozoic degradation processes. The only other known proxy that may record relative abundances of different primary producers is the nitrogen isotopic composition of fossils chlorophylls (porphyrins) (Higgins et al., 2011).

We present the discovery of intact porphyrins (fossils chlorophylls) from 1,100 Ma old marine black shales from Mauritania (Gueneli et al., 2018). The porphyrins, identified at the molecular level with a 9.4 Tesla Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), are 600 million years older than previous findings. Notably, compound-specific porphyrin nitrogen isotopic compositions ($\delta^{15}N_{por} = 5.6$ to 10.2‰) measured at JAMSTEC are heavier than in younger sedimentary sequences, and the isotopic offset ϵ_{por} between sedimentary bulk nitrogen and porphyrins (-5.1 to -0.5‰) is the lowest detected in any ancient sedimentary sequence. The low ϵ_{por} values point to predominantly cyanobacterial primary production with a contribution from anoxygenic phototrophic bacteria based on the presence of 2,3,6- and 2,3,4-trimethyl aryl isoprenoids. However, ϵ_{por} is inconsistent with a significant algal contribution, validating sterane / hopane ratios beneath detection limits of $S/H = 0.001$ to 0.0002 .

Based on porphyrin and sterane data, planktonic eukaryotic algae, the dominant marine primary producers of the Phanerozoic, did not play a detectable role in mid-Proterozoic oceans (Gueneli et al., 2018). The data supports the view that energy and nutrient limitation at the base of the food web, possibly in combination with low oxygen levels and unstable redox conditions, limited the evolutionary drive towards complex multicellularity and large size.

