1.1 billion-year-old porphyrins evidence photosynthesis 600 million years earlier than previously established

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Porphyrins are the molecular fossils of chlorophylls. *Our recent discovery of porphyrins from 1.1 billion-year-old marine black shales of the Taoudeni Basin in Mauritania pushes back the geological record for photosynthesis by 600 million years.* These porphyrins are nitrogen-containing molecules preserved from bacterio-chlorophylls, and measurements of their nitrogen isotopic composition provides quantitative information about the type of organisms in past ecosystems that utilized sunlight energy to synthesize organic compounds for nutrition.

Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometry resolved and identified porphyrins from the tens of thousands of other organic compounds in this highly-preserved shale. Indeed, FT-ICR MS was able to identify the elemental composition and structure for many nickel and vanadyl porphyrins.

The porphyrin nitrogen isotope ratio is different in this shale than in younger sediment. *The isotopic offset between sediment nitrogen and the porphyrin nitrogen measured in this experiment indicates cyanobacteria were the dominant photosynthesizing organisms 1.1 billion years ago in the Taoudeni Basin.* The data indicate that purple sulphur bacteria and green sulfur bacteria also thrived, while larger planktonic algae were scarce.

The populations of bacteria through the mid-Proterozoic (1.8 to 0.8 billion years ago) and the perceived later transition to a more eukaryotic world - filled with large, active organisms - is one of the most intriguing yet unresolved phenomena of Precambrian biology.

Facility: 9.4T FT-ICR mass spectrometer, MagLab's ICR Facility

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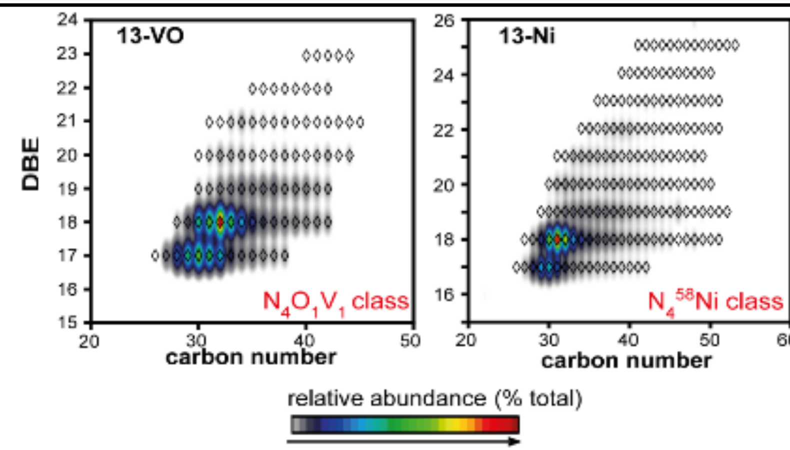

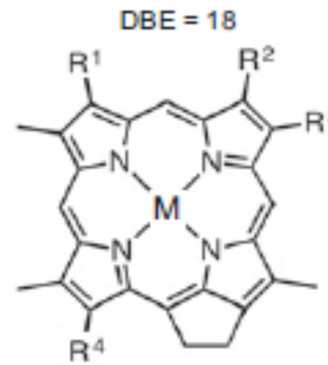

(2) DPEP

2a $R^2 = CH_3$, $R^{1,3,4} = CH_2CH_3$ (C_{32})
2b $R^{1,2} = CH_3$, $R^{3,4} = CH_2CH_3$ (C_{31})
2c $R^{2,3} = CH_3$, $R^{1,4} = CH_2CH_3$ (C_{31})
2d $R^2 = H$, $R^{1,3,4} = CH_2CH_3$ (C_{31})
2e $R^1 = H$, $R_2 = CH_3$, $R^{3,4} = CH_2CH_3$ (C_{30})
2f $R^4 = H$, $R_2 = CH_3$, $R^{1,3} = CH_2CH_3$ (C_{30})

Top: Identification of two classes of Ni- and VO-porphyrins by FT-ICR MS, plotting relative abundance versus double-bond equivalents (DBEs) and carbon number. **Left:** The structure of C_{30} to C_{32} DPEP, one of the many porphyrin structures identified, supports phototrophs as dominant photosynthesizing organisms on Earth 1.1 billion years ago. Identified porphyrins likely derived from oxygenic phototrophs and anoxygenic phototrophic bacteria.