

Phanerozoic trends in seawater nitrogen isotope composition from geoporphyryns

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The nitrogen (N) stable isotope record of seawater is reflected in the organic components of marine sediments. However, the majority of deep-time N isotope data comes from total organic carbon (TOC) or kerogen, which tends to homogenize primary, secondary, and diagenetic isotopic signals. In contrast, porphyrins, the degradation products of chlorophyll, are diagenetically stable, readily extractable, and originate from surface ocean-dwelling photosynthetic organisms. Recent analytical developments have allowed for the rapid acquisition of porphyrin $\delta^{15}\text{N}$ values [1]. In addition to recording primary N sources, the isotopic difference between porphyrin and corresponding biomass has been shown from laboratory culture to vary taxonomically. The utility of this approach has been demonstrated for the extraordinarily negative porphyrin $\delta^{15}\text{N}$ values during Cretaceous Oceanic Anoxic Event 2 [2-3], which also show that export production throughout the event was ~80% eukaryotic [3]. These negative values differ from distinctively positive modern ocean $\delta^{15}\text{N}$, exposing our limited understanding of the complex N cycle deep in the past. This motivated us to study a range of organic sediments spanning the last ~600 million years. We will present porphyrin $\delta^{15}\text{N}$ records to investigate the evolution of the marine N cycle during the Phanerozoic and during critical events in Earth's redox history (e.g., OAEs). Preliminary results show that the preservation of porphyrins is heterogeneous and is dependant on source rock lithology, with shales being the richest reservoirs. In such samples as measured to date, $\delta^{15}\text{N}$ values are generally negative ($< -3\text{‰}$). We propose that such values reflect a fundamentally different mode of ancient N cycling linked to major changes in global marine redox budgets.

[1] Higgins et al. (2009) *Anal. Chem.*, **81**, 184-192. [2] Kashiyama et al. (2008) *Org. Geochem.* **39**, 532-549. [2] Higgins et al. (2012) *PNAS* **109**, 2269-2274.