Paleoenvironmental Interpretations of Late Devonian biotic turnover in Western Canada Sedimentary Basin: Evidence from stable isotopic analyses of Geoporphyrins

The Late Devonian marks a period of significant global biotic change, beginning with a major extinction pulse at the Frasnian-Famennian stage boundary at 375Ma, constituting one of the "Big Five" radical mass extinctions, and ending with the Hangenberg event at the Devonian-Carboniferous boundary (359Ma). The Hangenberg is a less studied extinction interval associated with the deposition of organic rich black shales in epicontinental and epeiric basins across the globe inferred to result from widespread ocean anoxia.

In the present study, we report the results of an analysis of the biogeochemical impact of such ecosystem restructuring. The stable isotopic composition of total organic carbon and bulk nitrogen were measured for black shales (Exshaw Formation) deposited during the Devonian-Carboniferous boundary interval at seven locations representing a range of water depths and depositional environments in the Western Canada sedimentary basin. High total organic carbon values reflect increase in the fraction of organic carbon burial. Nitrogen isotopic excursions ranged from 1 - 8‰ indicating a more diverse paleogeographic trend and C/N ratios across the basin suggest varied depositional environments and a broad range of burial and uplift history. Extractable organic matter includes biomarkers related to phytoplankton sources, including porphyrins such as vanadyl deoxyphylloerythroetioporphyrin (DPEP) derived from chlorophyll and higher molecular weight porphyrins potentially derived from bacteriochlorophylls produced in euxinic waters.

The difference in isotopic composition between bulk organic matter and porphyrins presents a novel approach to describing the relationship between Devonian photosynthetic communities and water column chemistry. OAEs are interpreted as high-productivity events supported by upwelled nutrients. A deficit in fixed nitrogen is a likely outcome of denitrification at the redox interface, and organic nitrogen would cycle through the water column and reenter the photic zone as re-mineralized ammonium ion. Thus, nitrogen isotopic difference between biomass and chlorophyll and bacteriochlorophyll derivatives can be used to assess the reutilization of upwelled ammonium by phytoplankton versus fixation of atmospheric nitrogen by the photoautotrophic cyanobacterial population. Lower values of $\delta^{15}N$ could possibly suggest upwelling of recycled ammonium rather than diazotrophic assimilation, which we predict will be confirmed by the isotopic composition of bacteriochlorophyll derivatives.