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Environmental Controls on the Occurrence of Bicycloalkanoporphyrins in Ancient and Modern Sediments

JAMES M. FULTON AND SANJUKTA DHAR

Baylor University

Presenting Author: james_fulton@baylor.edu

The occurrence of chlorophyll derivatives in marine sediments record the input of organic matter from photosynthetic organisms. Chlorin derivatives predominate in relatively young sediments, and porphyrins are common in older organic matter-rich sediments from throughout the Phanerozoic. Many natural porphyrin structures have been identified in ancient sediments, with the most common being deoxophyloerythroetioporphyrin (DPEP), a cycloalkanoporphyrin (CAP) which includes a distinctive fifth "E" ring that helps identify it as a chlorophyll derivative. Another group of porphyrins are the bicycloalkanoporphyrins (BiCAPs), which have a sixth ring that derives from the condensation of esterified functional groups at the 13^2 and 17^3 positions of chlorophyll. The production of the sixth ring has been associated in some case with herbivory but also with organic matter decomposition in anoxic sediments. Here we examine the distributions of porphyirns in a black shale deposited during the Devonian-Carboniferous Hangenberg biotic crisis in the Western Canada Sedimentary Basin. At 10 of 11 core locations, DPEP was the most abundant porphyrin, but there was a general trend toward greater BiCAP content with closer proximity to the continental margin, suggesting greater oxygen exposure and potential for aerobic heterotrophy. We also examined the distribution of chlorin precursors to DPEP and BiCAP porphyrins in Pleistocene and Holocene sediments of Great Salt Lake, Utah; Fayetteville Green Lake, New York; and the Black Sea. These sediments encompass deposition in hypersaline, redox-stratified marine and freshwater, and oxygenated freshwater basins. Generally, chlorin structures including the sixth ring structure were most abundant in older, saline/hypersaline sediments, suggesting these environments are most favorable for postdeposition BiCAP formation. Notably, the large freshwater lake phases (Bonneville and Little Valley) from Great Salt Lake sediments included a greater proportion of pheophytin-a, pyropheophytin-a, and pyropheophorbide-a which are more likely to degrade to DPEP-type structures rather than BiCAPs.