Timing the Paleozoic Oxygenation of the Deep Ocean

Jean Clemente, 2023

The history of marine redox is deeply tied to the direction of evolution. The permanent oxygenation of the deep ocean has received much attention in this regard, but the timing of this transition are poorly constrained. For instance, several lines of evidence point to a marine oxygenation event associated with the first Devonian "forests" (~380 Ma), but few long-term and global records of Paleozoic marine redox are available to test whether this represents a perturbation or state shift in marine O_2 structure.

In this study, I constructed a history of deep ocean redox from the late Cambrian to the Late Devonian using thallium isotope compositions (reported as ε^{205}Tl) of black shales in northwestern Canada (the Road River Group and Canol Formation) and a subset of samples from different global basins. Briefly, I extracted the authigenic (pyrite-bound) fraction of dated rocks, then purified the dissolved thallium through ion exchange chromatography. Thallium concentration and isotope compositions were measured on a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS).

The dataset records a negative excursion from ε^{205}Tl ≈ –2 to –5 beginning in the late Silurian (~425 Ma). Thallium isotope compositions gradually returned to crustal values (ε^{205}Tl ≈ –2) by the Late Devonian (380 Ma). From comparison to Tl cycling in modern basins, I infer that these isotopic changes likely reflect the global ε^{205}Tl of contemporaneous seawater and were driven by a significant enhancement of manganese oxide burial from the oxygenation of the deep ocean. This dataset indicates the earliest timing of post-Cambrian deep ocean oxygenation yet proposed, co-occurrent with the rise of the earliest land plants ~420 Ma. Further work must explore the return to crustal, anoxic ε^{205}Tl values (~ –2) by the Late Devonian.

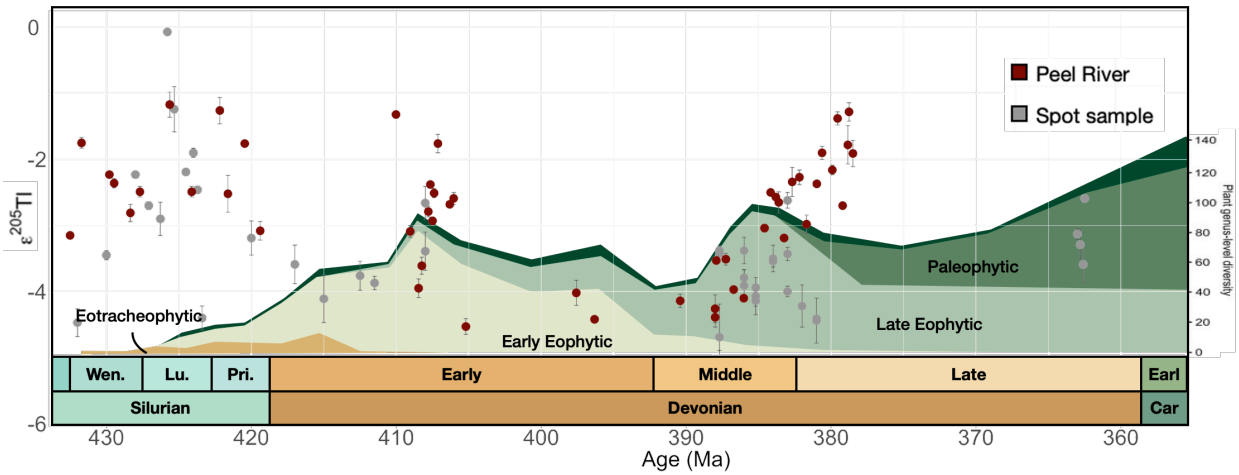

Figure 1. Seawater ε^{205}Tl from the late Silurian to the Late Devonian, overlain by trends in the genera-level diversity of early terrestrial plant groups.

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