Tracking the Rise of Eukaryotes to Ecological Dominance with Zinc Isotopes

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The shift from cyanobacterial- to eukaryote-dominated primary productivity in the oceans fundamentally altered global biogeochemical cycles. Yet, there are poor constraints on when this transition occurred. Zinc is an important, often co-limiting nutrient for eukaryotes in the oceans today. Given the importance of Zn in the modern oceans, we developed a Zn isotope approach to track the extent of Zn limitation and eukaryotic production through Earth's history. Specifically, we use the isotopic systematics of the pyrite ($\delta^{66}Zn_{pyr)}$, rock extracts (bitumen) and kerogen pyrolysate ($\delta^{66}Zn_{org}$) within euxinic black shales. We show that $\delta^{66}Zn_{pyr}$ of euxinic core-top muds from the Cariaco basin capture the global deep seawater signature, validating its use as a seawater proxy. Additionally, we propose that $\Delta^{66}Zn_{pyr\text{-}org}$ can be used to track surface water zinc bioavailability. Based on an extensive new sedimentary zinc (Zn) isotope record across Earth's history, we provide evidence for the onset of the eukaryotic regulation of the marine Zn cycle at ~800 Myr ago. This shift marks a transition to eukaryotic-dominated primary productivity, which in light of the microfossil and organic biomarker records strongly suggests that eukaryotes evolved early but rose to ecological dominance much later. Furthermore, the Zn dataset provides a new foundation for understanding the impact of extensive carbon fixation by eukaryotes on the global carbon cycle and climate system.