Minimal cadmium-isotopic variations during a 'whiff' of O_2 at 2.5 Ga

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Numerous geochemical proxies suggest that 'whiffs' of molecular oxygen (O_2) predated the Great Oxidation Event (GOE; ~2.4 billion years ago, or Ga). Because the 'whiffs' of oxygen are suspected to be of a cyanobacterial origin, we might expect concurrent perturbations to the marine nutrient biogeochemistry associated with the emergence of this metabolism. Evidence for such perturbations is lacking. Here, we explore cadmium (Cd) abundance and isotopic compositions in the sedimentary rocks that host perhaps the most compelling evidence for a pre-GOE "whiff" event: the ~2.5 Ga organic-rich Mt. McRae Shale (Western Australia).

In the modern ocean, dissolved Cd displays a nutrient-like profile. Uptake by phytoplankton fractionates Cd: the light isotopes are assimilated into organic matter and the residual seawater is enriched in heavy isotopes. Because the Cd that is ultimately delivered to sediments is primarily associated with organic matter and sulfides, the Cd isotopic compositions of certain marine sediments can elucidate changes in the composition of ancient seawater and thus nutrient biogeochemistry.

We observe minimally-varying Cd-isotopic compositions in the upper Mt. McRae Shale despite pronounced Cd enrichments associated with the 'whiff' interval. Moreover, the entire interval is characterized by Cd-isotopic compositions that are lighter than modern seawater or recognized marine Cd sources. Burial of light Cd-isotopic compositions could reflect incomplete consumption of a large dissolved Cd reservoir, though supporting geochemical data indicate that this explanation is unlikely. Alternatively, our data can be taken as reflecting seawater compositions in the Hamersley Basin. This result would require that either the sources or sinks of Cd in the pre-GOE Hamersley Basin were markedly different from today.