Mercury isotopes as a novel proxy of photic zone euxinia

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Photic zone euxinia (PZE) is a condition where anoxic, H_2S-rich waters occur in the photic zone. PZE has been invoked as an impediment to the evolution of complex life in the Precambrian, and as a kill mechanism during Phanerozoic mass extinctions. However, finding reliable evidence for PZE in geological records has been difficult. Here we propose a potential new proxy for PZE based on mercury stable isotopes. We measured Hg mass independent isotope fractionation (MIF) in 1.64 Ga Barney Creek Formation (McArthur Basin, northern Australia), which has been previously found to record episodes of PZE based on evidence from organic biomarkers diagnostic of anoxygenic phototrophs (e.g., green and purple sulfur bacteria). These bacteria require light and H_2S to survive and thus the biomarkers diagnostic of these bacteria have been considered as the key evidence of PZE. We found strong negative shifts in Hg MIF (up to ~ -0.2 ‰) that show excellent stratigraphic correlation with the appearance of biomarkers in some drill cores. The negative shift of Hg MIF during episodes of PZE is consistent with previous experimental findings that Hg develops negative MIF (depletion of ^{199}Hg and ^{201}Hg in the residual Hg(II)) during photoreduction of Hg(II) when it is complexed with reduced sulfur ligands, as opposed to positive MIF when it is complexed with non-sulfur ligands. The increase in reduced sulfur concentration in the photic zone during PZE may have resulted in significant change in Hg coordination chemistry and likely changes in Hg MIF. However, other mechanisms, such as enhanced terrestrial Hg input into the ocean due to enhanced continental weathering and erosion that stimulated euxinia, may also contribute to the negative shift of Hg MIF. However, not all drill cores show the correlation between biomarkers and Hg MIF, which requires further studies. Based on the current data, we suggest that Hg MIF is a promising proxy of PZE.