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Assessing the utility of Hg isotopes as evidence for atmospheric organic haze during the late Archean

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The late Archean atmosphere underwent dynamic compositional changes leading up to the Great Oxidation Event (GOE), which in turn modulated the incident UV flux to the Earth's surface. The extent and timing of UV changes is unknown, but it has been suggested that the formation of organic haze layers could have blocked incoming UV radiation. Stable mercury (Hg) isotopes have the potential to record UV flux changes, because mass independent fractionation of Hg isotopes (Hg MIF) occurs in a limited number of processes – mainly by photochemical transformations that require UV radiation.

Previous investigations of carbon and sulfur isotopic systematics in late Archean (~2.7-2.5 Ga) sedimentary rocks (WRL-1 and RHDH2a drill cores, Pilbara Craton, Western Australia) reveal periodic C-S isotopic anomalies that could indicate a bi-stable, oscillating hazy atmosphere [1]. Hg MIF measured in the GKF01 drill core (Griqualand Basin, South Africa) shows little or no fractionation (-0.2 to -0.01‰, +/- 0.07‰) coincident with S isotopic anomalies [2]. The lack of Hg MIF despite Hg enrichment was hypothesized to be a consequence of UV-blocking organic haze.

We conducted a preliminary investigation of Hg isotope fractionation in the AIDP-3 drill core (Roy Hills black shale member, Pilbara Craton, Western Australia; depth range = 68.22-164.12 m), which is spatially and temporally equivalent to the WRL-1 and RHDH2a cores, and also temporally overlaps the GKF01 core. Hg concentrations throughout the section showed similar enrichment to those seen in the GKF01 drill core, with concentrations ranging from 0.13 to 0.99 ppm. We observed no significant Hg MIF (δ^{199}Hg and δ^{200}Hg) to within +/- ~ 0.05‰. This is consistent with prior Hg elemental and isotope analyses in the WRL-1 core. Future examination of MIF-S and other geochemical tracers is needed to determine if the AIDP-3 core provides independent evidence of organic atmosphere haze, as suggested previously.

[1] Izon, G. et al. (2015) *Earth and Planetary Science Letters*, *431*, 264-273. [2] Zerkle, A. L. et al. (2020) *Nature communications*, *11*(1), 1-9.