ONSET OF OXIDATIVE URANIUM MOBILIZATION ON THE LATE ARCHEAN EARTH? B. Kendall[1], G. Brennecka[1], S. Weyer[2] and A. D. Anbar[1,3], [1]School of Earth and Space Exploration, Arizona State University, Tempe, AZ, 85287, USA, [2]University of Frankfurt, Institute of Geosciences, Altenhofer Allee 1, D-60431 Frankfurt, Germany, [3]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, 85287, USA.

Introduction: Geochemical data on the redox-sensitive elemental abundances and isotopic compositions of Late Archean (2.7-2.5 Ga) black shales and banded iron formations suggest cyanobacterial oxygenic photosynthesis led to mild oxygenation of the Late Archean surface ocean and accumulation of trace amounts of free oxygen in the atmosphere. Authigenic enrichments of Re and Mo in Late Archean shales are interpreted to reflect oxidative weathering of crustal sulfide minerals and transport of the oxidized species ReO_4^- and MoO_4^{2-} to sites of anoxic deposition on the seafloor. However, uniformly low U abundances in the same shales suggest biospheric O_2 levels were too low for oxidative U mobilization. We test this hypothesis using the emerging U isotope paleoredox proxy.

Mt. McRae U isotope stratigraphy: Here, we report a stratigraphic shift to heavy U isotope compositions ($\delta^{238}U$) in the 2.5 Ga Mt. McRae Shale (Hamersley Basin, Western Australia) that coincide with excursions to elevated Re and Mo abundances [1], heavier Mo isotope compositions [2] and a change in S and N isotope systematics [3-5]. Recent Black Sea organic-rich sediments and ca. 260 Ma black shales have $\delta^{238}U$ (–0.06 to +0.43 ‰) heavier than average upper crust (–0.46 to –0.20 ‰, represented by granites and basalts) and modern seawater (–0.41 ± 0.03 ‰; 2σ) [6]. The heavy $\delta^{238}U$ in black shales reflects preferential incorporation of heavy U isotopes from seawater. Thus, the excursion to heavy $\delta^{238}U$ (> –0.20‰) in the Mt. McRae Shale implies the presence of a small U inventory in the overlying water column and weak authigenic U enrichment in these shales. Light $\delta^{238}U$ in the stratigraphically underlying and overlying shales is similar to crustal (detrital) $\delta^{238}U$, suggesting U concentrations in the overlying water column was vanishingly small.

Implications: Mass-independent fractionation of S isotopes in the Mt. McRae Shale indicates atmospheric pO_2 remained below 0.001% of present atmospheric levels (PAL) [3,5]. The partial pressure of free O_2 at which detrital uraninite can resist oxidative dissolution is poorly constrained, with a loose upper limit of 1% PAL [7,8]. Modelling of the effects of ongoing Late Archean oxygenic photosynthesis under a low-O_2 atmosphere suggests subaerial weathering of crustal sulfides and oxidative mobilization of Re and Mo can occur whereas detrital uraninite remains stable [9]. The low authigenic U enrichments (typical enrichment factors [EF] of 1-2) relative to Re (EF up to 75) and Mo (EF up to 55) are consistent with weaker subaerial U mobilization compared to Re and Mo.

The heavy $\delta^{238}U$ signature is not accompanied by a clear shift to higher U EF. However, the EF are defined relative to average upper crust, which may not be representative of background sedimentation, thus complicating interpretation of a limited range of low EF. We suggest the U isotope signature is more sensitive to authigenic enrichments based on simple mass-balance calculations. For example, assuming a fractionation factor of ~0.5‰ between anoxic sediments (0.15‰, mid-point of Black Sea sediments) and the crust (–0.35‰) [6], a mix of 40% authigenic U and 60% detrital U would result in shale $\delta^{238}U$ of –0.15‰.

A low oceanic U inventory suggests seawater $\delta^{238}U$ would be highly sensitive to U removal into reducing sediments, resulting in lighter dissolved $\delta^{238}U$ along the oceanic transport path. Preservation of a heavy $\delta^{238}U$ signature may then reflect the survival of enough dissolved U during shallow-to-deep water transport to enable fractionation of sediment $\delta^{238}U$ relative to average crust.

Our findings raise the possibility that the oxidative part of the U marine geochemical cycle commenced beneath a low-O_2 atmosphere during the Late Archean. Consistent with previous geochemical data, the stratigraphic shift from light to heavy $\delta^{238}U$ in the Mt. McRae Shale might correspond to an increase in oxidative weathering rates associated with increasing biospheric oxygenation. The subsequent return to light $\delta^{238}U$ may reflect exhaustion of the local water column U inventory by enhanced sediment removal during an episode of middle water column euxinia [5].

References:

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