

OSMIUM ISOTOPE EVIDENCE FOR TRANSIENT EPISODES OF LATE ARCHEAN ENVIRONMENTAL OXYGENATION AND OXIDATIVE CONTINENTAL WEATHERING. B. Kendall¹, R. A. Creaser², C. T. Reinhard³, T. W. Lyons⁴, and A. D. Anbar^{5,6}, ¹Department of Earth & Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L3G1, Canada (email: bkendall@uwaterloo.ca), ²Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G2E3, Canada, ³School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332, USA, ⁴Department of Earth Sciences, University of California, Riverside, California 92521, USA, ⁵School of Earth & Space Exploration, Arizona State University, Tempe, Arizona 85287, USA, ⁶Department of Chemistry & Biochemistry, Arizona State University, Tempe, Arizona 85287, USA.

Authigenic Mo and Re enrichments and Mo, U, S, N, and Se isotope data from organic-rich mudrocks of the Mt. McRae Shale (drill core ABDP-9, Hamersley Basin, Western Australia) point to the production and accumulation of mild amounts of photosynthetic O₂ in surface environments at 2.5 Ga [1-7]. This evidence for O₂ accumulation may represent one of a series of transient oxygenation and oxidative continental weathering events ("whiffs" of O₂) in the Archean, and thus a non-linear topology of initial environmental oxygenation until the 2.45-2.32 Ga Great Oxidation Event (GOE). Alternatively, small linear stepwise increases in atmospheric O₂ allowed mild environmental oxygenation and oxidative weathering to occur continuously and with increasing intensity towards the GOE.

Distinguishing between the two hypotheses is critical for understanding the dynamics of planetary oxygenation on Earth and ultimately the evolution of complex life. Hence, we obtained new Re-Os isotope data from organic-rich mudrocks in ABDP-9 where high authigenic enrichments of Re and Mo were observed previously and suggested to originate from oxidative weathering of crustal sulfide minerals [1].

Regression of Re-Os isotope data from eight samples (plus four replicate analyses) from 148.09-148.15 m together with previous data from organic-rich mudrocks at 145.22 m, 146.08 m, 147.10 m, and 148.32 m [1] yields a 16-point Re-Os isochron age of 2495 ± 14 Ma (2σ , Mean Square of Weighted Deviates [MSWD] = 2.2; the age uncertainty includes the ¹⁸⁷Re decay constant uncertainty). The new Re-Os age is statistically identical to a 5-point Re-Os age of 2495 ± 20 Ma (2σ , MSWD = 0.95) from organic-rich mudrocks at 128.71-129.85 m in ABDP-9, and to a U-Pb zircon age of 2504 ± 5 Ma from a tuffaceous bed within the Mt. McRae Shale [8]. Hence, post-depositional processes have not significantly affected Re, Os, and likely Mo (because all three metals are siderophilic, chalcophilic, and redox-sensitive). Our findings refute the recent claim that the Mt. McRae geochemical data can be explained by later Proterozoic metasomatic alteration [9].

The initial ¹⁸⁷Os/¹⁸⁸Os isotope ratio from the Re-Os regression of the organic-rich mudrocks at 145.22-148.32 m is 0.34 ± 0.19 (2σ), which is statistically higher than the magmatic/hydrothermal (mantle) baseline of 0.11 at 2.5 Ga. Together with the authigenic Re and Mo enrichments in these samples, the initial ¹⁸⁷Os/¹⁸⁸Os suggests that oxidative mobilization of radiogenic Os, Re, and Mo occurred together from crustal sulfide minerals and that all three metals were transported together to Hamersley Basin seawater.

A decline in Mo and Re enrichments above 143 m in ABDP-9 was previously attributed to falling environmental O₂ levels or an expansion of euxinic conditions due to higher seawater sulfate availability from increased oxidative weathering of crustal sulfides [1, 4, 5]. The Re-Os regression for organic-rich mudrocks at 128.71-129.85 m yields an initial ¹⁸⁷Os/¹⁸⁸Os of 0.06 ± 0.09 (2σ) that is statistically indistinguishable from the mantle value [1], pointing to minimal riverine transport of radiogenic crustal Os. Hence, the high Re and Mo enrichments and more radiogenic seawater ¹⁸⁷Os/¹⁸⁸Os at 145.22-148.32 m captures transient oxygenation.

We infer that environmental oxygen levels fluctuated between the evolution of oxygenic photosynthesis at least 3 Gyr ago and the Great Oxidation Event [10-12]. An important remaining question is whether transient oxygenation events increased in magnitude, frequency, and duration towards the Great Oxidation Event.

References: [1] Anbar A. D. et al. (2007) *Science*, 317, 1903-1906. [2] Kaufman A. J. et al. (2007) *Science*, 317, 1900-1903. [3] Garvin J. et al. (2009) *Science*, 323, 1045-1048. [4] Reinhard C. T. et al. (2009) *Science*, 326, 713-716. [5] Duan Y. et al. (2010) *GCA*, 74, 6655-6668. [6] Kendall B. et al. (2013) *Chem. Geol.*, 362, 105-114. [7] Stüeken E. E. et al. (2015) *Geology*, 43, 259-262. [8] Rasmussen B. et al. (2005) *Geology*, 33, 725-728. [9] Fischer W. W. et al. (2014) *Goldschmidt Conference Abstract*. [10] Lyons T. W. et al. (2014) *Nature*, 506, 307-315. [11] Crowe S. A. et al. (2013) *Nature*, 501, 535-538. [12] Planavsky N. J. et al. (2014) *Nature Geosci.*, 7, 283-286.