

ENVIRONMENTAL CONTROLS ON THE PRESERVATION OF ATMOSPHERIC SULFUR IN NEOARCHEAN MARINE FACIES. A.J. Kaufman¹, I.N. Zhelezinskaia¹, J. Farquhar¹, D.T. Johnston², S. Olson³, T. Lyons³, M.C. Koehler⁴, and R. Buick⁴, ¹Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, 8000 Regents Drive, College Park, MD 20742-4211 <kaufman@umd.edu>, ²Harvard University, 20, Oxford Street, Cambridge, MA 02138, ³Department of Earth Science and NASA Astrobiology Institute, University of California, Riverside, CA 92521, ⁴Department of Earth & Space Sciences and Astrobiology Program, University of Washington, Box 351310, Seattle WA 98195.

Introduction: Like Titan, Saturn's orange shrouded moon, the anoxic atmosphere enveloping the Archean Earth may have contained enough methane to form an organic haze [1, 2, 3], which would have attenuated the solar UV flux and thereby protected surface environments from high energy radiation [4]. Based on recent computer models and laboratory experiments [e.g. 5, 6], a methane haze would form if the CH₄/CO₂ ratio was >0.2 (relative to 0.005 in the modern oxygenated atmosphere). Based on atmospheric models, the methane haze would form at ~60 km height above the surface; however, as solid haze particles condensed and grew they would settle to an altitude of ~20 km and may be heterogeneous with latitude [4]. A thinner organic haze (and lower optical depth) would accumulate in low latitudes due to vertical atmospheric motion at the equator.

An increase in the biological production and utilization of methane in the Neoproterozoic (ca. 2.7 to 2.5 Ga; [7]) suggests the possibility that the greenhouse gas would accumulate to high enough concentrations in the atmosphere to form an organic haze, which may have influenced atmospheric sulfur chemistry. It has been suggested that the photolysis of volcanogenic SO₂ and the production of elemental sulfur (S₈) and sulfate (SO₄²⁻) aerosols with mass-independent sulfur isotope signatures in an anoxic atmosphere [8] – which rained down and were preserved in Earth's surface environments – may have been affected by the presence or absence of an organic haze. For example, an organic haze has been invoked to explain temporal shifts of Δ³⁶S/Δ³³S data arrays in Mesoproterozoic successions [9], and then again for several coupled Neoproterozoic C/S isotope excursions in Western Australian and South African strata characterized by δ¹³C values of organic matter that are < -37‰ and Δ³⁶S/Δ³³S data arrays of < -1.0 [2, 3].

Discussion: Geochemical investigations of two new scientific cores, drilled by the Agouron Foundation, intersecting ~2.7 Ga Neoproterozoic marine sedimentary facies in Western Australia are used here to explore hypotheses related to the cycling of sulfur by photolytic reactions in an anoxic atmosphere. We interpret multiple sulfur isotopic data to reflect atmospheric condi-

tions dominated by an organic haze, which were overprinted in shallow environments through microbial sulfur cycling. Multiple sulfur isotope measurements reveal significant differences between shale- and carbonate-dominated facies of the subtidal Jeerinah Formation and of the intertidal to supratidal carbonates of the overlying Carawine Dolomite. Bulk shale samples are characterized by δ³⁴S, Δ³³S, and Δ³⁶S relationships that are similar to those established for other shale-dominated successions of broadly equivalent age. We interpret this signal as inherited from photolytic fluxes of elemental sulfur from the atmosphere overprinting biological contribution of sulfide from sulfate reduction by sulfur-sulfide exchange. In contrast, a large δ³⁴S range (>35‰) and persistently negative Δ³³S compositions observed in carbonate associated pyrite (CAP), coupled with systematic deviations from expected Δ³³S/δ³⁴S and Δ³⁶S/Δ³³S reference arrays, suggest that the major sulfur source to this environment was sulfate, which carried an atmospheric signature and was isotopically redistributed through microbial sulfate reduction.

Conclusions: These observations support the view that Neoproterozoic oceanic sulfate had a negative Δ³³S signature. Furthermore, geochemical modeling suggests that deviations of data from established reference arrays may result from both changes in atmospheric reactions associated with the shielding effects of an organic haze and in the degree of microbial recycling of organic carbon in the oceans.

References: [1] Pavlov et al. (2001) *Geology*, 29, 1003–1006. [2] Zerkle et al. (2012) *Nature Geoscience*, 5, 359–363. [3] Izon et al. (2015) *Earth Planet. Sci. Lett.*, 431, 264–273. [4] Wolf and Toon (2010) *Science*, 328, 1266–1268. [5] Trainer et al. (2004) *Astrobiology*, 4, 409–419. [6] Domagal-Goldman et al. (2008) *Earth Planet. Sci. Lett.*, 269, 29–40. [7] Eigenbrode and Freeman (2006) *Proc. Nat. Acad. Sci. USA*, 103, 15759–15764. [8] Farquhar et al. (2000) *Science*, 289, 756–758. [9] Farquhar et al. (2007) *Nature*, 449, 706–709.