

A MID-LIFE CRISIS FOR EARTH'S GREENHOUSE. Stephanie L. Olson,¹ Christopher T. Reinhard², and Timothy W. Lyons¹, ¹University of California—Riverside, Riverside, CA 92521, ²Georgia Institute of Technology, Atlanta, GA 30332

The temporal proximity between oxygenation events and Snowball Earth events in the Proterozoic supports speculation that a reduced gas, most likely biogenic CH₄, regulated Proterozoic climate—compensating for the Faint Young Sun and explaining the apparent dearth of Mesoproterozoic glacial deposits. Although low O₂ and SO₄²⁻ conditions in the Proterozoic likely favored large CH₄ fluxes from the marine biosphere, the geologic record does not provide quantitative constraints on either biogenic CH₄ fluxes or the CH₄ content of the Proterozoic atmosphere. Characterization of the Proterozoic greenhouse is further complicated by: (1) strong nonlinearity in biospheric CH₄ fluxes as a function of marine SO₄²⁻, which arises because both CH₄ production and CH₄ consumption are affected by SO₄²⁻; and (2) strong nonlinearity in the atmospheric lifetime of CH₄ as a function of atmospheric *p*O₂, which reflects the competing effects of O₂ content and UV shielding by ozone in oxidizing atmospheres.

We use an Earth system model to quantify CH₄ fluxes on the Proterozoic Earth and to critically evaluate the role of CH₄ in regulating Proterozoic climate. Our model consists of a 3D marine biogeochemical model, a 2D climate model, and a 1D atmospheric photochemical model. We find that although oxidant-deficient conditions in the Proterozoic would have allowed substantial CH₄ production in, and escape from, the ocean, CH₄ survival in the atmosphere would have been severely limited by rapid photochemical destruction under the atmospheric *p*O₂ conditions suggested by the Proterozoic Cr isotope record (<10⁻³ times present atmospheric level). Thus, in light of recent *p*O₂ constraints, our numerical results suggest the absence of a substantial CH₄ greenhouse and introduce a potential Mesoproterozoic climate paradox. Our results, however, do not preclude a critical role for CH₄ in triggering Neoproterozoic climate collapse. Instead, our model highlights a dynamic relationship between atmospheric O₂, the marine biosphere, and climate, and provides a novel mechanism for triggering Snowball Earth events via perturbation to the CH₄ cycle.

We suggest that a minor oxygenation event in the Neoproterozoic enhanced UV shielding of CH₄ via ozone and allowed the buildup of a CH₄ greenhouse—which resulted in the drawdown of atmospheric CO₂ to precariously low levels through silicate weathering feedbacks. In this scenario, the resulting CH₄ greenhouse is inherently unstable because rapid destabilization of the atmospheric CH₄ reservoir would be triggered by either: (1) a return to low O₂, as suggested by some proxy records, or (2) the accumulation of SO₄²⁻ in the ocean as a consequence of progressive Earth system oxygenation, which would severely throttle CH₄ supply via inhibition of methanogenesis and enhanced anaerobic oxidation of CH₄. Regardless, during the ensuing glaciation, inhibition of chemical weathering, combined with continued anaerobic respiration, would allow dramatic reduction of the marine SO₄²⁻ reservoir—priming the marine

biosphere to generate huge CH₄ fluxes upon deglaciation and leaving the Earth system vulnerable to repeated climate perturbation until a critical oxygenation threshold was achieved in the latest Neoproterozoic or later.