Photochemical modelling of atmospheric oxygen levels reveals three stable states

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Various proxies and numerical models have been used to constrain O_2 levels over geological time, but considerable uncertainty remains. Previous investigations using photochemical models have predicted how O_3 concentrations vary with assumed ground-level O_2 concentrations, and indicate how the ozone layer might have developed over Earth history. However, these earlier models all utilised fixed mixing-ratio boundary conditions. This modelling assumption requires verification that predicted fluxes of biogenic gases are realistic for the Earth system, and critically, can produce equilibrium solutions that are unstable.

Here, we use a 1-D photochemical model with fixed flux boundary conditions, to simulate how O_3 and O_2 concentrations vary as O_2 (and methane) fluxes are systematically varied. We demonstrate that stable equilibrium model solutions only exist for trace, very low, and very high-O_2/O_3 cases, separated by regions of instability. In particular, the model produces no stable solutions with ground O_2 concentrations between $3x10^{-5}$ and 9% PAL. Weakly oxic atmospheres ($7x10^{-7} < pO_2 < 3x10^{-5}$ PAL) exist only for a narrow range of O_2/CH_4 fluxes. A fully UV-shielding O_3 layer only exists in the high-O_2 states, potentially explaining why land-dwelling life evolved only relatively recently. While many Earth system feedbacks are not included, our atmospheric modelling suggests that previously predicted atmospheric O_2 concentrations between approximately 10^{-4} and 10% PAL may not be photochemically stable, requiring a re-thinking of Earth's middle ages.