

# Coupled C-S-Fe cycles on early Earth and far beyond

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The balance between burial and oxidation of organic matter (OM) and pyrite is the first-order control on oxygen levels in the atmosphere and oceans. Traditionally, researchers have used proxy records of changing carbon and sulfur isotope compositions of seawater DIC and sulfate, respectively, to model long-term trends in atmospheric oxygen. The idea is that OM burial, quantifiable via C isotope fractionation during C fixation, tracks net photosynthesis and corresponding oxygen release to the biosphere. Iron availability is central in these calculations because reduced sulfur is buried as pyrite, typically with diagnostic S isotope consequences, and oxygen is released. Conversely, pyrite oxidation during weathering is a critical oxygen sink. Widespread anoxia over geologic time increased dissolved Fe availability and thus pyrite formation, while also enhancing OM and pyrite burial, releasing oxygen, and highlighting the importance of multiple associated feedbacks. Thus, recent arguments for anoxic, ferruginous deep oceans that persisted well into the Paleozoic are of elevated importance.

Recent studies focused on these C-S-Fe relationships are exploring the patterns and consequences of microbial evolution, fingerprinted principally through genomic and geochemical data and mapped on top of the biospheric expressions of coupled cycles and specifically their relationships to the parallel evolution of oxygen. As these cycles drove oxygen variability, they also set the stage for concomitant microbial innovation and metabolic proliferation through a dynamic redox landscape in the oceans marked by expanding and contracting microbial niches, while also driving the emergence and ecological impacts of a wide swath of metabolisms through increasing availability of oxygen and additional oxidants (e.g., nitrate and sulfate).

This presentation will recap the history of interwoven microbial metabolisms for C, S, Fe, and N and the corresponding redox backdrop. Among the primary topics covered will be the cycling of methane as related to microbial evolution of methanogenesis and methanotrophy and climate through greenhouse warming and haze formation. Also key are the production and preservation of methane as tied to marine oxygen and sulfate concentrations, including the role of AOM; other controls on atmospheric methane accumulation, including time-varying photochemistry; and, by extrapolation, methane's potential as a biosignature gas around exoplanets.