Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.18650

# Ferruginous vs. euxinic conditions through ocean history as regulated by the thermodynamics, kinetics, and competition of microbial pathways

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Microbial metabolisms underpin geochemical cycling in nearly all of the Earth's biosphere. Anaerobic pathways, such as iron and sulfate reduction and methanogenesis, have existed over most of Earth history and have been central in shaping the chemistry of the oceans and atmosphere. The governing principles by which such metabolisms contribute to water-column chemistry, however, are incompletely understood in natural systems where microbes compete for resources. Contrary to common assumptions, thermodynamics often fails to reproduce the observed metabolic succession. In a new approach, we account for the combined and coupled controls by thermodynamic, kinetic, and population dynamics factors, as well as hydrodynamic regimes, on the composition and metabolic rates of anaerobic microbial communities and the resultant water chemistries in coastal water columns. Together, these controls explain the microbiology and chemistry of modern lakes and seas, and constrain the variability expected in Earth's oceans over time. We find, in particular, that microbial sulfate reduction can account for a significant fraction of organic matter remineralization without producing measurable concentrations of aqueous sulfide, at times under conditions in which sulfate reduction is much less thermodynamically favored than iron reduction. Except for the photoferrotrophy-dominated conditions in the Archean, a significant proportion of iron reduction in the water likely occurred abiotically by the produced hydrogen sulfide, with microbial iron reduction being relegated to sediments. Simulations constrain the concentrations of sulfate, iron, and methane in marine coastal waters and explain the predominance of ferruginous conditions, coexisting at times with mid-water euxinia, through most of the Precambrian. They also provide an interpretative framework for the commonly used indicators of water-column chemistry (such as $Fe_{pyr}$:$Fe_{HR}$ ratios) that have been preserved in the rock record.