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Estimating the redox state of the Mesoproterozoic ocean: constraints from microbial culture and Earth System Model

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The Mesoproterozoic atmosphere is constrained as having <1% present atmospheric levels (PAL) of oxygen (O_2), yet multiple lines of geochemical evidence indicate the potential for higher levels spatially or temporally in portions of the ocean. For example, the iodine content of carbonates provides evidence for the accumulation of low but present levels of the oxidized iodine species, iodate (IO_3^-) in the Mesoproterozoic surface ocean. However, the redox threshold at which IO_3^- reduction becomes favorable has not been quantified, which limits quantitative constraints from the carbonate-iodine record. Here, we quantify the conditions that allow sustained low level IO_3^- accumulation in the surface ocean. Specifically, we compared two approaches: (1) an Earth System Model with an active iodine cycle and incorporating atmosphere and ocean biogeochemical and physical processes (cGENIE); (2) we cultivated *Shewanella oneidensis MR-1*. under controlled low [O_2] environments to determine relationships with IO_3^- reduction for the Earth System Model.

We simulated iodine distribution under possible Proterozoic atmospheric [O_2] and ocean nutrient conditions. At low [PO_4] relative to modern, [O_2] <10% PAL is sufficient to accumulate near-modern [IO_3^-]. When [O_2] rises >10% PAL, surface ocean [IO_3^-] starts to be sensitive to both [O_2] and primary productivity. Our laboratory experiments provide complimentary constraints. Shewanella reduce IO_3^- at low but present [O_2] and such IO_3^- reduction rates increase in sequential experiments which maintain [O_2] at lower values. Together, our model and experimental results indicate that changes in the steady state of carbonate-iodine contents in the Mesoproterozoic and elsewhere in Earth history can provide quantitative constraints on [O_2] variations. Meanwhile, surface ocean [IO_3^-] may be sensitive to additional, non-redox factors that were not previously considered.