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Drivers for secular marine iodate variations across Earth history

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Iodate (IO_3^-) abundances in ancient seawater have been widely applied as a redox indicator for marine and atmospheric oxygenation. A compilation of carbonate I/Ca data, representing the evolution of the seawater IO_3^- reservoir, reveals two baseline shifts through Earth's history: (1) the initial appearance of non-zero IO_3^- concentrations corresponding to the Great Oxygenation Event (GOE) and then maintained at a low baseline through the Early Paleozoic, and (2) a shift to the near-modern levels during the Late Paleozoic to Mesozoic. However, due to limitations of current knowledge in quantifying the requirements of IO_3^- accumulation in surface seawater, the drivers of these stepwise variations remain unclear.

Here, we quantify the conditions that allow the appearance and sustaining IO_3^- accumulation in the surface ocean by employing two complementary approaches: (1) cultivating *Shewanella oneidensis* MR-1 under controlled low O_2 environments to determine the O_2 threshold for IO_3^- reduction; (2) determining broader conditions maintaining IO_3^- abundances via an Earth System Model with an active iodine cycle and incorporating atmospheric and oceanic biogeochemical and physical processes (cGENIE).

Our experiments show that IO_3^- reduction in the medium did not occur until dissolved O_2 decreased below 0.1µM, presumably representing the molecular threshold triggering activity of IO_3^- reduction enzymes. This threshold provides the minimum O_2 estimation during the first baseline shift in IO_3^- reservoir. Following the GOE, cGENIE simulations suggest that IO_3^- abundances equivalent to the Proterozoic baseline (50 nM IO_3^-, or 0.5µmol/mol I/Ca) could be sustained with 3-4% PAL O_2 and <10% of modern PO_4 concentrations. The second baseline shift in I/Ca occurred during the Paleozoic-Mesozoic, when atmospheric oxygen neared modern abundances. However, cGENIE predicts it should have occurred much earlier, as only 30% PAL O_2 was enough to accumulate modern-like IO_3^- (>250 nM), even with high Phanerozoic [PO_4]. This discrepancy indicates this second baseline shift in I/Ca in the Phanerozoic may have been driven by factors beyond atmospheric oxygenation, including nutrient levels and deep ocean oxygenation. Together, our model and experimental results indicate that IO_3^- baseline changes through Earth history are sensitive to O_2 variations as well as additional, non-redox factors that were not previously considered.