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Oxygenation of the surface ocean, global methanotrophy, and the Great Oxidation

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The balance of evidence suggests that oxygenic photosynthesis evolved by 2.7 Ga, several hundred million years prior to the Great Oxidation at 2.4 Ga, but the mechanisms preventing a rise of atmospheric oxygen in this interval remain unclear. Here we use a new model of the Late Archean world to link scenarios for the early emergence of aerobic ecosystems to changes in both the organic carbon isotope record, and the redox state of the Earth's atmosphere. We show that if oxygenic photosynthesis spread globally prior to the Great Oxidation, this would have produced widespread oxygen oases in the surface ocean, while levels of oxygen in the atmosphere remained low. The most isotopically-light organic carbon ($\delta^{13}C_{org}$approaching -60‰) in the sedimentary record dates from 2.7 Ga. We show that this could have been produced in environments that spatially concentrate aerobic methanotrophy, either in shelf seas (or lakes) near microbial mats, or in upwelling zones where methane from the deep ocean would have been free to mix with a supply of oxygen from the shelf seas. Aerobic methanotrophy in the open surface ocean explains the prevalence of $\delta^{13}C_{org}$ ≈-45‰ prior to 2.4Ga. Subsequent weakening of the $\delta^{13}C_{org}$ signal can be explained by a shift toward anaerobic methanotrophy as sulphate weathered from the land started to build up in the ocean. Widespread methanotrophy would have restricted the (balanced) fluxes of methane and oxygen escaping from the ocean. This results in a low concentration of methane in the atmosphere once oxygen levels start to rise prior to the Great Oxidation. The influence of hydrogen escape in driving the actual rise in atmospheric oxygen is then reduced, resulting in a less abrupt and probably episodic rise in atmospheric oxygen. This scenario likely requires additional biosphere feedbacks to complete the atmospheric transition.