

Sub-mM levels of sulfate and inefficient AOM in Proterozoic oceans

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Seawater sulfate is widely assumed to have reached mM levels during the Proterozoic eon (0.6-2.5 Ga). In particular, broadening of the S-isotopic range of marine sulfides following the Great Oxidation Event (GOE) around ~2.4-2.65 billion years ago is thought to reflect an increase in seawater sulfate levels, promoted by enhanced oxidative weathering on land. The resulting increase in seawater sulfate levels, however, remains largely unquantified. Using mass balance considerations, we show that seawater sulfate levels must have remained below 1.5 % modern values (<0.5 mM) throughout most of Proterozoic as pelagic sulfate reduction provided a strong sulfate sink from the GOE until the oxygenation of the deep ocean. Diagenetic modeling shows that the S-isotopic composition of Proterozoic marine sulfides can be reproduced under these relatively low sulfate levels if the coastal oceans contained tens of μM of oxygen. At hundreds of μM of sulfate, kinetic suppression of sulfate reduction in anoxic deep ocean would channel carbon mineralization through methanogenesis. Low sulfate concentrations would also suppress the rates of sulfate-driven oxidation of methane (AOM). Aerobic and anaerobic oxidation of methane, collectively, would remove around 20-40% of the methane produced through methanogenesis, while the rest of methane would enter the atmosphere, leading to high atmospheric methane levels (~30ppmv) and greenhouse warming throughout the Proterozoic.