Mid-Proterozoic Atmospheric O_2 Levels Re-Calculated From $\Delta^{17}O$ Values in Sulfates Using a Detailed 1-D Photochemical Model

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Estimates of atmospheric O_2 concentrations during the mid-Proterozoic eon, 0.8-1.8 Ga, range from <0.1% to ~10% of the present atmospheric level (PAL). Recently, triple oxygen isotope mass-independent fractionation (MIF) measurements ($\Delta^{17}O$) from sedimentary sulfates in Canada's 1.4-Ga Sibley basin (Crockford et al., Nature, 2018) have been used to constrain atmospheric O_2 and marine productivity (GPP) during this time. This isotopic signal is produced during ozone formation in the atmosphere and is transferred to sediments during oxidative weathering of pyrite, FeS_2. It is eliminated by isotopic exchange with water during respiration and photosynthesis. Previous calculations using a box model coupled to a biogeochemical model (CANOPS) suggest O_2 levels between 0.1 and 1% PAL (Planavsky et al., Astrobiology, in press). Our more detailed atmospheric model allows O_2 levels up to ~8% PAL, with a most likely level around 3% PAL. The main difference between our calculation and the earlier one is that the ozone layer moves downward into the troposphere at low pO_2, allowing direct photochemical transfer of positive $\Delta^{17}O$ from ozone to gaseous H_2O, which then rains out of the atmosphere. Residual O_2 is thus more negative than found previously. Lower pO_2 values are possible if gas transfer between the atmosphere and surface ocean (and/or terrestrial microbial mats) can exceed the traditional *piston velocity* or if sulfate is recycled within the surface ocean (or lake) after it is formed. Oxidation of biogenic methane can also provide a way for O_2 to leave the atmosphere, allowing O_2 fluxes to exceed the piston velocity.