Multiple sulfur isotopes from the 2.45-2.2 Ga old Turee Creek Group and the rise of atmospheric oxygen

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The Turee Creek Group (TCG) in Western Australia shows evidence for continuous deposition across the Great Oxidation Event (GOE), and thus provides a unique opportunity to examine the nature, rate, and duration of the rise of atmospheric oxygen on Earth during the Paleoproterozoic. Here, we report bulk and *in situ* ion probe multiple (^{32}S, ^{33}S, ^{34}S, ^{36}S) sulfur isotope measurements of sedimentary pyrite from three drill cores obtained in BIFs of the underlying Boolgeeda Iron Fm., glacial diamictites of the Meteorite Bore Member, quartzites of the Koolbye Fm. and overlying carbonates of the Kazput Fm.

Bulk isotope analyses and mean values of ion probe analyses appear remarquably coherent throughtout the three drill cores. Evidence for mass-independent sulfur isotope fractionation (MIF-S, $\Delta^{33}S$) between -1.4 to +3.4‰ in authigenic pyrite indicates that the TCG and associated glacial events were deposited during the initial stages of the GOE when pO_2 remained below ~10^{-5} Present Atmospheric Level. Several sedimentary intervals display no MIF-S and a 93‰ range in mass dependent sulfur isotope fractionation between -36.6 to 57.4‰. This suggests that microbial sulfate reduction under changing sulfate concentrations occurred intermitently, thus indicating that atmospheric O_2 rised occasionnally to sufficient levels to permit oxidative weathering of sulfides on the continents. Multiple generations of pyrite are preserved, typically represented by primary cores with high $\delta^{34}S$ values (>+10‰) and no or minor MIF-S signal, overgrown by euhedral rims with $\delta^{34}S$ near mantle values (0±5‰) and displaying significant MIF-S. The preservation of sharp sulfur isotope gradients and absence of MIF-S signal in pyrite cores suggest that the rise of oxygen occurred intermitently and was followed by abrupt drops. Alternatively, these core-rim zonation patterns may reflect a secondary process associated with pyrite remobilisation during low grade metamorphism.