

## Application of a triple oxygen isotope photochemical model to palaeo-atmospheric O<sub>2</sub>

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Strong evidence for the Great Oxidation Event (GOE) comes from the disappearance of mass-independent fractionation of sulphur isotopes in the geological record at ~2.4 Ga, but the mechanisms behind the GOE and the magnitude of the partial pressure of atmospheric oxygen ( $pO_2$ ) during the subsequent Proterozoic remain under debate. A promising proxy for post-GOE  $pO_2$  is the  $\Delta^{17}O$  value of sedimentary sulphate, which indicates the triple oxygen isotope composition of palaeo-tropospheric O<sub>2</sub>, itself dependent on  $pO_2$ ,  $pCO_2$  and primary productivity. However, despite being a direct record of atmospheric composition, the interpretation of  $\Delta^{17}O_{SO_4}$  values in terms of absolute  $pO_2$  remains challenging. Here, we present a newly-developed triple oxygen isotope photochemical model, which predicts  $\Delta^{17}O$  values in O<sub>2</sub> and sedimentary sulphates under various atmospheric compositions. Our preliminary results demonstrate sensitivity of  $\Delta^{17}O_{O_2}$  to oxygen and carbon dioxide concentrations, as expected, and suggest that O<sub>2</sub> concentrations lower than ~1% of present atmospheric levels (PAL) may not be required to reproduce even the most negative  $\Delta^{17}O$  measurements from the mid-Proterozoic rock record. This expands on our recent 1-D photochemical modelling results [1], which show model atmospheres with either trace ( $< \sim 3 \times 10^{-6}$  PAL) or high ( $> \sim 1\%$  PAL) levels of O<sub>2</sub>, while solutions with intermediate O<sub>2</sub> concentrations appear to be unstable to small perturbations in redox fluxes. Both of our modelling approaches are consistent with a relatively rapid transition from trace  $pO_2$  to much higher levels at the GOE. In our models, this is caused by strong feedbacks in the atmospheric chemistry involving oxygen and ozone, but it is likely that this effect will be exacerbated in future work coupling the model to biogeochemical cycling at the lower boundary.

[1] Gregory, Claire & Rugheimer (2021), *EPSL* 561.