Isotopic Consequences of the Great Oxidation Event

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Carbon isotopic records demonstrate that a massive carbon cycle perturbation occurred in close association with the Great Oxidation Event (GOE) between 2.4 Ga and 2.2 Ga. This C-cycle perturbation includes a protracted period of anomalously positive $\delta^{13}C$ values, known as the Lomagundi event, and one of the largest known negative $\delta^{13}C$ excursions, known as the Shunga event, which occurs at its terminus.

Here we use a numerical carbon cycle model to explore the linkage between carbon cycle perturbation, ocean chemistry, and Earth surface oxidation. Our numerical model contains boxes representing sedimentary and oceanic reservoirs, and tracks the fluxes and isotopic compositions of carbon, calcium, sulfate, and phosphate, as well as ocean chemistry parameters including pCO_2, pH, and calcite saturation.

We perturb our model from a postulated pre-GOE state using a step function in external net O_2 input. This perturbation represents a driver of Earth surface oxygenation external to the exogenic cycle (i.e. hydrogen loss to space or less reducing mantle degassing). In the model the excess O_2 is absorbed by increased sulfide weathering on land, leading to delivery of sulfate to the ocean. The increased delivery of sulfate drives elevated organic carbon burial, as we allow the C:P burial ratio of organic carbon to respond to the O_2-to-SO_4 ratio. This feedback is based on the notion that in low-O_2 / low-SO_4 (pre-GOE) and high-O_2 / high-SO_4 (modern) oceanic states iron oxide precipitation acts as a strong sink for dissolved phosphate, while in the intermediate low-O_2 / high-SO_4 state iron removal is dominated by pyrite precipitation allowing for elevated phosphate regeneration. Thus, a positive feedback arises where O_2 production from organic carbon burial triggers additional sulfide oxidation which leads to further organic carbon burial. This process continues until the sulfide reservoir is depleted after which $\delta^{13}C$ values return to near zero and the model settles into a new steady state with a higher pO_2. Intriguingly, under certain model parametrizations we find that that a large negative excursion is produced at the termination of the positive one. The abrupt termination of the pyrite sink results in the diversion of the massive O_2 flux to organic carbon oxidative weathering, resulting in a huge pulse of light carbon to the ocean. In addition to carbon, our model predicts massive perturbations to the isotopic systems of S and Ca, offering the opportunity to test whether our model offers a realistic abstraction of the events at start of the Proterozoic.