Complete simulation of deglacial changes in atmospheric ¹⁴C/C: Implications for ocean circulation changes and CO₂ release

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We present a new deglacial budget (production and decay) of ¹⁴C, the first to correctly predict the preindustrial global activity of ¹⁴C. While ¹⁴C production change accounts for most of the overall decline in atmospheric ¹⁴C/C (i.e., $\Delta^{14}C_{atm}$) since the Last Glacial Maximum, it fails to explain the rapid observed $\Delta^{14}C_{atm}$ swings during deglaciation. We use a carbon cycle model to separate the contribution of ocean CO₂ release and circulation changes to the $\Delta^{14}C_{atm}$ history, which together yield an exceptional match to available terrestrial $\Delta^{14}C_{atm}$ data, both in terms of overall deglacial $\Delta^{14}C_{atm}$ decline and millennial scale variations. The previously hypothesized but not yet identified stagnant "mystery reservoir" in the ice age ocean is not required in our simulations.

Ocean chemistry before and after the rise of atmospheric O₂

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The tight coupling among the biogeochemical cycle of O₂ and those of the major redox-sensitive elements, such as C, Fe and S [1-3], implies that the rise in atmospheric O₂ was likely preceded. accompanied and followed by radical rearrangements in the cycles of these elements. Indeed, the rise of O₂ appears to be recorded in a variety of marine geochemical and isotopic records, especially those of Fe and S. Among others, these include traditional and massindependent S isotope ratios [4,5], Fe isotope ratios [6], detrital O₂-sensitive mineral grains [7], and banded iron formations [7]. Qualitative understanding of these records hinders insight into events that fundamentally reshaped Earth's surface environment. I have developed a chemically detailed, spatially resolved model of the coupled marine biogeochemical cycles of S and Fe [8], which I use here to provide quantitative constraints on ocean chemistry before and after the rise of O_2 .

Prior to the rise of O₂, the main S reservoirs in the ocean are sulphate and thiosulphate, with concentrations up to ~60 and ~10 µM, respectively, consistent with recent constraints from mass-independent S isotopes in VMS deposits [9]. Elemental S particles (S_8) , which settle rapidly, reach only sub-nanomolar concentrations, but contribute much of the S flux to the sediments. A balance between riverine and hydrothermal supply of Fe²⁺ and its oxidation in the photic zone governs water-column Fe2+ concentrations, which do not exceed 5 µM, unlike suggestions that mineral solubility allowed Fe²⁺ concentrations as high as ~100 μ M [7]. After the rise of O₂, sulphate becomes essentially the only marine S reservoir, and its concentration exceeds 1 mM. Sulphide concentrations in hydrothermal fluids exceed those of Fe, resulting in a decline of the hydrothermal Fe influx. Deposition of Fe (as Fe³⁺-hydroxides) becomes limited to near-shore environments.

Among other topics, I will discuss the implications of these results to the records S isotope ratios, to metabolic S and Fe utilization, and to the observed Precambrian sedimentary record.

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