

Quantifying the effect of shelf pyrite oxidation on the marine carbonate system during the Last Glacial Maximum

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The Quaternary period (~2.58 Ma to present) is characterised by glacial-interglacial cycles. During glacial periods, large amounts of ice accumulate in continental ice sheets, effectively removing water from the ocean. This process lowers the global sea level by up to 130 meters below its current value.

Previous studies showed that the repeated flooding and subaerial erosion of shelf sediments oxidised between 120 to 900 Pmol pyrite over the last 3 Ma [2, 3]. Since pyrite oxidation releases 2 mol sulfuric acid for each mol pyrite, this process affects the marine pH, either directly by adding protons, or indirectly by releasing CO₂ from carbonates. This process is thought to generate between 1 to 2 Pmol CO₂/kyr during glacial sea-level low stands, and it has been argued that this CO₂ injection might initiate (or contribute to) glacial terminations [2].

While the flux rates and their phase are reasonably constrained, it is unclear how the marine carbonate system buffers them. We use a modified Harvardton-Bear 3-box model [1] to evaluate how these fluxes affect marine carbonate chemistry. Our results suggest that pyrite oxidation during the Last Glacial Maximum (LGM) would have increased pCO₂ by up to 10 ppm by the end of marine isotope stage 2 (MIS 2). The exact amount and the timing of the pCO₂ release depend critically on the alkalinity production during pyrite oxidation.

Depending on the pyrite oxidation pathway, this reaction can affect just the marine dissolved inorganic carbon (DIC) pool, both DIC and marine alkalinity, or just marine alkalinity. We find that the resulting pCO₂ signal is more pronounced for pyrite oxidation reactions with high DIC:ALK ratios. Our results broadly confirm the idea that pyrite oxidation might contribute to glacial terminations, although our modelled pCO₂ changes are smaller than previously thought.

[1] Boudreau et al. (2010), *Global Biogeochemical Cycles* **24** (4).

[2] Kölling et al. (2019), *Nature Geoscience* **12** (11), 929-934.

[3] Markovic, Paytan & Wortmann (2015), *Biogeosciences* **12** (10), 3043-3060.

