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Quantifying pyrite oxidation driven pCO_2 changes during the Last Glacial Maximum

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Sea level and pCO_2 records show a strong correlation for much of the Pleistocene. However, for pCO_2 values below 190 ppm, the two variables appear uncorrelated. This disconnect precedes glacial terminations by thousands to tens of thousands of years. One of the more recent explanations suggests that this disconnect is caused by pyrite oxidation on subaerially exposed shelf sediments [1].

Current estimates suggest that over the last 3 Ma, about 120 to 900 Pmol pyrite were oxidized during sea level lowstands [1, 2]. Depending on the reaction pathway, this releases between 2 and 4 mol CO_2 per mol pyrite. Furthermore, the effects on marine dissolved inorganic carbon (DIC) and alkalinity also depend on the reaction pathway. In the presence of carbonates, DIC and alkalinity can both increase by up to 4 mol. But in the absence of carbonates, DIC remains unchanged but alkalinity decreases by 4 mol.

Here, we use a modified Harvardton-bear chemical oceanography model [3] to evaluate how pyrite oxidation affects the marine carbonate system and pCO_2. Using the pyrite oxidation rates of Kölling *et al.* [1] to create carbon and alkalinity fluxes, we show that pyrite oxidation is likely to increase atmospheric pCO_2 by about 8 ppm. If we additionally consider the oxidation of organic matter, this value can increase up to 16 ppm. Our results confirm that pyrite oxidation during sea-level lowstands significantly impacts atmospheric pCO_2 [e.g., 1, 2, 4], and may play a pivotal role in triggering glacial terminations.

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

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

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

[4] Yao *et al.* (2021), *Earth and Planetary Science Letters* 568, 117015.