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Shelf pyrite weathering as negative feedback to glacial pCO_2 during the Eocene-Oligocene Transition

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The Eocene-Oligocene transition (EOT) is characterized by a global cooling trend, falling sea levels, and the onset of Antarctic glaciation. Previous studies have investigated the interactions and feedbacks between ocean circulation, weathering, and atmospheric CO_2 levels during this time, but the role of biogeochemical sulfur cycling on climate change remains largely unexplored. Here we show that the emergence of icehouse conditions is coeval with declining marine sulfate S and O isotope values [1]. We posit that the change in marine sulfate isotope ratios is best explained by oxidative weathering of subaerially exposed shelf sediments during sea-level lowstands [2], which transfers sulfur from the sedimentary pyrite reservoir to the marine dissolved sulfate reservoir. Glacial lowstand-induced pyrite weathering proceeds through reactions similar to acid mine drainage, generating sulfuric acid that further liberates CO_2. Mass balance calculations suggest that the magnitude of sulfuric acid triggered CO_2 release across the EOT is sufficient to affect the marine carbonate system. Depending on the specific reaction sequence, shelf pyrite weathering has the potential to raise pCO_2 (e.g., pyrite oxidation has raised pCO_2 by 10 ppm at the end of the last ice age [3]), acting as a negative feedback mechanism to stabilize ice-sheet growth. Similar feedback responses of sulfur cycling to glaciations have also happened in other geological times [4, 5].

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