

## Links between climate and the oxidative weathering of organic matter and its carbon dioxide emissions

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The oxidation of organic carbon in sedimentary rocks (petrogenic organic carbon,  $OC_{petro}$ ) releases  $CO_2$  from long-term storage in the lithosphere, and consumes atmospheric O<sub>2</sub>. Alongside volcanism, the oxidative weathering of  $OC_{petro}$  is the main source of  $CO_2$  to the atmosphere over millions of years. The balance between  $CO_2$  release during the oxidation of sedimentary rocks and CO<sub>2</sub> drawdown by silicate weathering and organic carbon burial sets the net carbon budget during weathering and erosion. However, OC<sub>petro</sub> oxidation is poorly understood, both in terms of the rate at which it releases  $CO_2$  and the factors that interact to drive the reaction. Trace metals associated with organic matter in rocks, such as rhenium (Re), can be released to the dissolved load of rivers during oxidative weathering. Quantifying dissolved Re fluxes therefore has the potential to provide insight into the oxidative weathering processes involved. Here, we use Re to track the rate of  $OC_{petro}$  oxidation in the rapidly eroding mountain river catchments of the western Southern Alps, New Zealand; alongside river catchments that have lower erosion rates but drain rocks with higher organic carbon contents in the Mackenzie River Basin, Canada. In New Zealand, physical erosion is found to be a first order control on the oxidative weathering fluxes, but catchments dominated by valley glaciers and exposed to frost-shattering processes experience a further two to three times elevation in  $CO_2$  emissions relative to catchments with less glacial cover. Data suggest that the modern-day Mackenzie River catchment presently acts as a  $CO_2$  sink of  $\sim 1.2$  tC km<sup>-2</sup> yr<sup>-1</sup> as a result of the carbon transfers by weathering and erosion, driven by a large organic carbon burial flux. However, under glaciated conditions, this large basin may have operated as a  $CO_2$  source, through enhanced  $OC_{petro}$  oxidation and reduced organic carbon burial fluxes. We propose that mountain glaciation can result in an atmospheric  $CO_2$  source during weathering and erosion, as fresh minerals are exposed for weathering in an environment with high oxygen availability. This provides a previously unrecognised counter-mechanism against global cooling over geological timescales, which may have operated over the late Cenozoic and over multiple glacial-interglacial cycles.