



## Carbon dioxide emissions by rock-derived carbon weathering

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Earth's past and future climate is thought to be affected by carbon dioxide (CO<sub>2</sub>) concentrations in the atmosphere. On geological timescales, the concentrations of atmospheric oxygen and carbon dioxide are regulated by the inorganic and organic carbon cycles, which can both act as atmospheric CO<sub>2</sub> sources. Oxidative weathering reactions play a major role in the release of CO<sub>2</sub> to the atmosphere through: i) the oxidation of sulphides, production of sulphuric acid and the subsequent dissolution of carbonate minerals; and ii) the oxidation of rock-derived organic carbon (OC). While the CO<sub>2</sub> drawdown by silicate mineral weathering by carbonic acid is relatively well studied, quantitative estimates of carbonate weathering by sulphuric acid and oxidation of rock-derived OC remain poorly constrained in many settings. Here we aim to better understand the controls (e.g. erosion rates, oxygen supply, rock sulphide and OC contents, etc.) involved in releasing rock-derived carbon (inorganic and organic) to the atmosphere during oxidative weathering of rocks and to provide quantitative estimates of resulting CO<sub>2</sub> fluxes. We present new catchment-scale insight from shale and marl dominated watersheds: i) Laval, Bouinenc, Brusquet, and Moulin river catchments in Draix (France), and ii) Waiapoa and Waiapu river catchments on New Zealand's North Island. The study areas largely contrast in physical erosion rate (t/km<sup>2</sup>/yr, i.e. sediment yield), sulphide content and vegetation cover. The studied rivers mostly drain shales, which are the major source of rock OC, and contain sulphide minerals (e.g. pyrite), and trace metals (e.g. Rhenium - Re). Using time series river water samples from the basins, we investigate dissolved chemistry to track oxidative weathering reactions. We exploit the previously established association of rock OC and Re during chemical weathering and use dissolved Re flux as a proxy for rock OC oxidation rate. The source of Re is assessed by tracing other dissolved products of chemical weathering in river water (e.g. Re/SO<sub>4</sub> and Re/Na ratios). The fluxes of dissolved Re, along with percentage of Re derived from rock OC and ratio between OC and Re stored in un-weathered material, provides us with a robust field-based estimations of CO<sub>2</sub> released during rock weathering. We compare these new measurements to a growing global dataset to examine the rates and controls on CO<sub>2</sub> release by oxidative weathering of sedimentary rocks.