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Two-stage oxidation of petrogenic organic carbon in a rapidly exhumed mountainous river catchment

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Petrogenic organic carbon (OC_{petro}) has conventionally been regarded as a non-degradable entity, and therefore is excluded from the carbon cycle. The perception might be even more widely accepted for an active orogen considering that the steep topography and limited soil development associated with the exposure of fresh bedrocks through rapid uplift facilitate the efficient transfer of massive quantities of OC_{petro} to marine burial. In this study, we aimed to test this perception by examining the maturity and geochemical characteristics of OC_{petro} from various compartments of the catchment, where the exhumation and erosion rates have been estimated to be in the range of 1.5-10 mm/yr and 5-30 mm/yr, respectively, in eastern Taiwan and its downstream submarine canyon. The degrees of graphitization of OC_{petro} in weathered materials were lower than those in parent rocks, slate and black schist, with more disordered (low crystallinity) OC_{petro} coupled with higher radiocarbon activities (younger). For comparison, the maturities of river sediments were within the range of the two major carbonaceous parent rocks. For marine sediments, the abundance of highly graphitized OC_{petro} increased with travel distance from the estuary. The Raman results, combined with isotopic and abundance data of organic matters, suggest that OC_{petro} may have experienced two-stage oxidation. The first stage involves the production of disordered OC_{petro} through in-situ alteration, that is potentially aided by the so-called priming effect. Once eroded into the river channel, the mixture of disordered and highly graphitized OC_{petro} appears to be barely affected by fluvial processes, but experiences preferential oxidation during marine transit, a pattern consistent with previous studies on the Amazon and Himalayan systems. Based on OC contents and radiocarbon activities, the OC_{petro}-derived CO_2 emission flux is estimated to range around 30-60 $tC/km^2 \cdot yr$, which surpasses the fluxes for Amazon River (~0.18 $tC/km^2 \cdot yr$) and Mackenzie River (<1 $tC/km^2 \cdot yr$) by at least one order of magnitude. Overall, the rapid transformation and selective oxidation of OC_{petro} along the short hillslope-river-submarine routing enables enormous CO_2 emissions, highlighting the importance of integral investigation into detailed OC_{petro} oxidation from source to sink in small mountainous catchments in tectonically active context.