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Enhanced Petrogenic Organic Carbon Oxidation in Shales on Ridges Compared to Valleys

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The oxidation of petrogenic organic carbon (OC_{petro}) during shale weathering releases atmospheric CO_2, modulating Earth's climate over geologic timescales. Recent global estimates indicate that oxidative weathering of OC_{petro} in near-surface rocks releases ~68 Mt C yr^{-1} to the atmosphere (Zondervan et al., 2023), underscoring the long-term climatic significance of this process. However, these estimates do not resolve how OC_{petro} oxidation varies spatially between distinct geomorphic settings such as ridges and valleys. Ridges commonly develop thicker weathering zones than valleys due to the combination of potentially deeper groundwater tables, slower erosion and enhanced extensional fracturing on convex surfaces. We hypothesize that the thicker weathering zone on ridges increases the residence time of OC_{petro} in the weathering zone, promoting greater oxidative loss of OC_{petro} relative to adjacent valleys.

We analyzed paired ~10 m drill cores from the Eocene Cozy Dell Shale in the western Santa Ynez Mountains, California. The ridge core shale exhibits tan-brown coloration, low core recovery rates, pervasive fracturing, and deep Fe-oxide staining, indicating intense and deep oxidative weathering, whereas the valley core shows gray color, higher core recovery rates, and minimal fractures at depth, consistent with shallower oxidative weathering. In situ ^{10}Be derived soil production rates together with weathering zone thicknesses derived from carbonate weathering fronts (estimated from Ca and Sr depth profiles), indicate longer OC_{petro} residence times within the ridge weathering zone (> 90 kyr) relative to the valley (~ 7-15 kyr). The ridge also exhibits substantially lower total organic carbon (TOC) concentrations (0.2 ± 0.1 wt %) compared to the valley (1.3 ± 0.7 wt %). Integrating TOC, grain size corrections (Al/Si) and radiocarbon (^{14}C) measurements, we estimate that ~90% of OC_{petro} has been oxidized by the time carbon reaches the ridge surface, whereas only ~50% of OC_{petro} oxidizes by the time carbon reaches the valley surface. These results highlight that ridge-valley contrasts in residence time exert a first-order control on OC_{petro} oxidation. Accounting for such landscape heterogeneity is therefore essential for improving constraints on shale-derived CO_2 fluxes in the long-term carbon cycle.