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Potential competition between pyrite and petrogenic carbon oxidation during shale weathering

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The chemical weathering of fine-grained sedimentary rocks (shales) can strongly influence the geologic carbon cycle. Specifically, while silicate weathering generates alkalinity that promotes marine carbonate formation and CO_2 drawdown, the oxidation of sulfides and organic matter in organic-rich shales can lead to CO_2 emissions. Determining the net carbon budget of shale weathering is complicated by the stratigraphic heterogeneity of shales, potential competition on available O_2 between these reductants, as well as tectonic and climatic conditions that modulate the vigor and timescale of biogeochemical reactions.

To investigate how these aforementioned factors influence carbon fluxes during shale weathering, we developed a one-dimensional reactive transport model that includes uplift, fluid flow, redox reactions, and mineral hydrolysis. Using this model, we first considered the weathering of two groups of organic matter (labile and recalcitrant to oxidation) and pyrite in a homogenous bedrock to test for selective preservation of these electron donors during weathering. Intriguingly, our results show that the presence of pyrite can limit the amount of petrogenic carbon oxidation through its effect on subsurface oxygen levels, especially with a fast uplift rate. Going forward, we will add complexity to this model by considering stratigraphic patterns in lithology as well as silicate weathering (for example, albite conversion to halloysite/kaolinite). We will base these more complex simulations on new drill core observations of the Middle Eocene Cozy Dell Formation from the ridges of the Santa Ynez Mountains, California, USA. Data on local uplift rates, bulk-rock geochemistry, and micro-scale weathering processes for these cores will allow us to design realistic reactive transport simulations to constrain how, for example, stratigraphic variability in initial pyrite concentrations affects other weathering processes and the net carbon budget for shale weathering.