Soil Gas Controls on Coupled Pyrite-Carbonate Weathering Dynamics and Carbon Fluxes

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The coupled weathering reactions of carbonate dissolution and pyrite oxidation in shales may act as a primary control on atmospheric pCO_2 and pO_2 on geologic timescales. Despite their potential importance in global biogeochemical cycles, relatively little is known about the dynamic relationships between these reactions in modern catchment systems and their controls on net carbon fluxes. We examine the role of pCO_2 and pO_2 in the weathering zone in setting the balance of pyrite oxidation and carbonate dissolution that occurs in shales. Specifically, we simulate these coupled reactions through CrunchFlow reactive transport modelling of Mancos shale weathering and compare our results to concentration-discharge relationships observed in the East River watershed, CO. Reactive transport simulations across a suite of initial pCO_2 and pO_2 demonstrate that the proportion of protons generated via pyrite oxidation that either (1) act to dissolve additional carbonate or (2) are buffered by alkalinity already in solution changes as a function of the extent of carbonic-acid weathering in the shallow subsurface. Finally, we compare our modelling results with tributary baseflow geochemistry across the East River watershed to calculate implied equilibrium pCO_2 and pO_2. Calculated pCO_2 and pO_2 are anti-correlated across the majority of tributaries and co-vary with net primary productivity, which together suggest the respiration of organic matter in soils exerts a first-order control on the balance of oxidative and acid-base weathering in the East River.