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How deep roots slow water, supply reactivity and enhance silicate weathering

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Upland landscapes route infiltrating precipitation to headwater streams, evolve bedrock weathering profiles within hillslopes and sustain some of the highest chemical weathering rates on Earth. While indirect evidence suggests high silicate weathering rates in the vadose zone of upland landscapes, difficulties in accessing fluids in the depth interval below soils and above the water table have prevented direct sampling of water-rock interactions in this compartment of the Critical Zone. Recent efforts to directly monitor both hydrological and geochemical dynamics in the vadose zone of hillslopes have highlighted a feedback between rock moisture and deep plant roots that regulates vadose-zone fluid transit times and the seasonal dynamics of the two key weathering reactants, CO_2 and O_2. Here, we exploit the capabilities of an innovative vadose-zone monitoring system in an upland forested hillslope in the Eel River Critical Zone Observatory (California, USA) to sample *in-situ* water and pore gas composition over a 16 meter weathered bedrock profile over four years of monitoring. A multi-component reactive transport model (RTM) is developed to interpret these data and identify the factors that control the chemical composition of fluid draining from the vadose zone to the water table. The numerical model is calibrated using a series of batch-reactor experiments between fluid and drilling cuttings from the hillslope. We show that solute concentrations are the result of a coupled set of primary mineral dissolution and secondary mineral precipitation reactions that evolve with depth and consistently follow mineralogical analyses of cuttings ranging from soil to fresh bedrock compositions. The RTM shows that timescales of water storage and drainage in the vadose zone are sufficient to allow for a substantial extent of weathering to take place. However, *in-situ* solute concentrations cannot be reproduced by the RTM unless elevated CO_2 derived from plant root respiration is also included in the model. Our model shows that plant roots significantly enhance mineral dissolution 6-10 meters below soil in this upland forested environment. This work highlights a link between the rhizosphere and rock weathering in the vadose zone that impacts nutrient mobilization in forested ecosystems and elemental fluxes in the Critical Zone.