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## Investigating the influence of preferential flow on geochemical weathering in the critical zone using high resolution reactive transport models

The critical zone (CZ) represents a major life-sustaining realm of the terrestrial surface. It spans from canopy to bedrock and is regulated by chemical, physical, and biological processes that influence flows of water, solute, gases, and sediment. The CZ encompasses the shallow subsurface, a region of reaction, unsaturated flow, and transport that is comprised of soils and/or regoliths derived from the chemical and mechanical breakdown of bedrock to saprolite. Chemical weathering of primary minerals in the subsurface is an important but poorly understood processes involved in the formation, transformation, and functioning of the CZ. This research is motivated by evidence that preferential flow paths may drastically alter chemical weathering patterns observed in the subsurface CZ. In the shallow subsurface, preferential flow or non-uniform flow can occur through rock fractures, which are caused by mechanical stresses induced by tectonic activity and topography. We present results of a twodimensional, hydro-geochemical model of a CZ hillslope that is used to study the influence of such "relict" fracture networks in low permeability saprolite on flow and subsequent weathering in the CZ. The model is implemented using the reactive transport code PFLOTRAN. Preferential flow fields are generated using multiple realizations of random fracture networks in a hillslope transect. Flow and transport through the fracture network systems are then compared to homogeneous and correlated random fields (sequential Gaussian simulation). Model parameters are constrained by observations from the Boulder Creek Critical Zone Observatory (BCCZO), which include extensive hydrologic, geochemical, and geophysical datasets. We found that preferential flow through fractures drastically alters how water from hydrologic inputs (e.g. precipitation, snow melt) propagates through the subsurface, resulting in a bimodal water-flux response downstream that becomes more defined as fracture density increases. Although local chemical equilibrium arises in all cases, geochemical weathering simulations show that preferential flow through fractures greatly alters weathering patterns relative to the homogeneous or correlated random systems, since reactants are quickly delivered to areas of the subsurface domain that would otherwise remain inert. We also use the model to provide additional insight on the discrepancy between laboratory and field weathering rates seen in the literature and investigate the relative roles of advection and diffusion in fractured saprolite system.