

Using thermodynamics to address landscape-scale weathering questions

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A major effort of low-temperature geochemistry has focused on understanding the process of weathering and how it sculpts landscapes and forms the weathered regolith that mantles our planet. To understand these processes is intellectually rich because weathering includes all aspects of the surface earth from the upper limits of vegetation to deep groundwater, i.e., the critical zone (CZ). Much of the effort to understand weathering has focused on measuring rates of biogeochemical processes and assigning reaction kinetic constants to primary rock-forming minerals, primary accessory minerals, and secondary minerals. But earth surface settings are often considered to be rate-limited by transport (TL). To predict TL rates relies on knowledge of equilibrium solubilities rather than kinetic constants; thus, investigating TL “kinetics” is an exercise in incorporating thermodynamic constants into models of transport (diffusion, advection). Weathering of minerals that become 100% depleted in regolith well below the land surface are usually modelled as TL. When such minerals display reaction fronts that are wide relative to the depth of weathering advance under a hilltop, 1D modelling is a good approximation (as long as flow occurs far from the stream and the slope is not steep). However, when the reaction front is narrow, advection through the front is limited. In that case, diffusion limits the solute transport across the front, and groundwater flow must change direction. This means that estimates of weathering advance rates are not accurate when they are based on simple models that posit 1D advection at a constant velocity. Predicting outflow chemistry of TL weathering in watersheds is thus an exercise of mapping shallow and deep groundwater flowpaths and solute chemistry in the context of reaction fronts and using equilibrium solubilities to make predictions. With such an approach, we can begin to understand weathering release rates in the context of wide reaction fronts (throughflow occurs) or narrow reaction fronts (lateral flow occurs).