

# **In Situ Silicate Reaction Rates In Sandy Aquifers**

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Despite numerous kinetic studies in soils and watersheds, the studies of reaction kinetics in groundwater systems are scarce. Yet, aquifers are sources of drinking water, major sites for water-rock interactions, and a significant segment of the hydrological cycle and global elemental cycling. In situ rates were derived and compiled from inverse mass balance modeling of solute fluxes along flow paths. The travel time was bounded by corrected  $^{14}\text{C}$  ages or flow modeling, and the surface areas were either estimated from gas adsorption isotherms or geometric calculations. The surface area normalized rates for plagioclase, K-feldspar, and hornblende are two to five orders of magnitude slower than those from laboratory experiments at comparable temperature and pH but at far from equilibrium conditions, and also much slower than those derived from studies of soils and watersheds. Inverse methods pose the challenge of non-unique solutions, which impose a great limitation of field studies. Hence, we are conducting a number of controlled laboratory experiments and geochemical modeling studies to understand specific processes and mechanisms.

We advance two hypotheses for explaining the field-lab discrepancy. First, the secondary minerals rinding on feldspars are not at local equilibrium with groundwater, as traditionally assumed, but their slower precipitation rates can raise the groundwater saturation state with respect to feldspars to very close to equilibrium, and thus retard the feldspar dissolution rates. Feldspar dissolution reaction in aquifers is within a complex web of reactions, in which secondary clay precipitation plays a key role. Second, a thin (~ 10 nm) amorphous layer, possibly leached in origin, is found on feldspars that we examined. The presence of the amorphous layer on naturally weathered feldspars requires re-consideration of the details of surface reaction controlled mechanism.