

Dichotomy of the rates and controls on geochemical reactions in heterogenous pore networks into two transport regimes

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At all scales, rock pore networks can be separated into a well-connected backbone network with fast fluid velocities that advect solutes to and from reactive minerals and a poorly connected secondary network with slower velocities and possibly the predominance of diffusive transport to and from reactive minerals. The dichotomy of the pore network into these two flow and transport regimes also splits the pore network into two regimes of different rates of and controls on geochemical reactions. In fast pathways, mineral reaction rates are a function of the intrinsic rate constant and mineral surface because fast advection maintains low concentrations of reaction products. In contrast, in slow pathways, reaction products increase in the fluid to concentrations where reaction rates become a function of transport of solutes away from the reacting mineral. The overall, effective reactivity of the porous rock is then a composite of reactions in these two regimes, with the effective reaction rate scaling with (1) the total surface area of mineral in the backbone network and (2) the solute gradient and interface area between the backbone and secondary network. Consequently, the effective reaction rate is dominated by fast reactions in the backbone network in early times when surface area is high, but as fast reactions deplete reactive mineral in the backbone, transport of solutes from the secondary network dominate the flux of solute out of the domain and the effective reaction rate slows. At this point weathering is transport limited in this system; however, the chemical signature of transport limitation in the effluent is diluted by fluid that continues to flow through the backbone network without accumulating solutes from mineral dissolution. Thus, the saturation indices of reactive minerals in the total effluent reflect the controls on weathering only in the backbone regime and are not reliable indicators of the transport control on weathering. We show this behavior in results from both laboratory mineral dissolution experiments and reactive transport simulations and develop quantitative approaches to predicting mineral reaction rates in heterogeneous pore networks from characteristics of backbone and secondary networks.