

**The role of spatial heterogeneities in the apparent age dependence of dissolution and precipitation rate constants in porous media**

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As fluid flows through porous rock, dissolution and precipitation reactions exchange material between the fluid and the reactive surface of the medium. The effective reaction rate at which this exchange occurs is of fundamental importance to many applications, such as carbon sequestration, but remains poorly understood. Laboratory and field measurements of rate constants for common materials yield quantitatively different values. Furthermore, rate constants have been observed to decrease with time according to an inverse power law. We propose that transport and material properties at the pore network scale, such as spatial heterogeneities in the pore size distribution, are critical to the quantitative understanding of reactivity and aging. Using a combination of length and time scale analysis and pore network simulations, we examine situations both near and far from equilibrium. In the latter case, we build on the reactive infiltration literature to show that rapid reactions cause changes in the network properties and flow patterns, thereby affecting the reaction rate itself and introducing feedback. Near equilibrium, fluctuations may lead to a slow evolution of the pore size distribution and spatial heterogeneities. We find that spatial heterogeneities play a critical role in controlling transport of solute through the medium, and can modify the measured reactivity even at apparent concentrations within the so-called dissolution plateau.