Kinetic concepts for quantitative prediction of fluid-solid interactions

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The paradigm: ΔG_r governs surface reactivity

The 100 year evolution of our understanding of crystal growth and dissolution kinetics has been punctuated by key milestones: the role of kinks on stepped surfaces; the role of screw dislocations, sustaining growth at low overstep; the link between defects, hollow cores, macroscopic etch pits. For crystal dissolution, these relationships were formalized in the stepwave model [1], which linked etch pit nucleation, step generation, and global retreat of the crystal surface. Underpinning these conceptual advances is an assertion of the fundamental link between mass action and kinetics, of chemical potential as the primary driver of rates of physical process. This condition is the common basis for “classical” rate equations, embracing many laboratory observations.

The problem: relict surface reactivity = variation

This assertion creates two problems, spatial and temporal: 1) reaction mechanism involves collisions at crystal surface sites and is thus atomic in dimension; in contrast, ΔG_r is macroscopic; 2) if the surface reacts towards “equilibrium” from an open, unsaturated regime, it inherits topography inconsistent with the “driving force”, however defined [2]. This reactivity mismatch yields evolving, non-steady-state surfaces, that breed heterogeneous rate ranges, characterized by *rate spectra* (below): the rate span reflecting site diversity established under previous ΔG_r regimes. In crystals with slow kinetics, large ΔG_{crit} and activation energies, the time required to attain a “steady state” may exceed the crystal’s lifetime.

The promise: model rate spectra

We exploit this complexity, using spatial and temporal analysis of rate spectra to yield kinetic information from material properties *and* reactive history. These deconvolution results provide key feedbacks to complementary simulations. Integrated modelling (MD-parameterized KMC + reactive transport) can explore the limits of spectral distributions (in both frequency and content), and thus develop realistic predictive tools [3,4].

[1]Luttge et al. (2013) Elements **9/3**:183-188; [2]Arvidson & Luttge (2010) Chem Geol **269**:79-99; [3]Fischer & Luttge (2017) EPSL **457**:100-105; [4]Kurganskaya & Luttge (2013) JPC **C117**:24894-24906.