

Molecular dynamics and kinetic modeling of rough calcite surface dissolution

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The dissolution and precipitation of carbonate minerals is a natural chemical process that is interesting to industry and essential to the environment. The transition state theory (TST) is one of the most successful theoretical approaches to describe the kinetics of carbonate dissolution on the molecular level [1,2]. Each elementary dissolution event consists of an ion detachment process coupled with the loss of ion-ion interactions within the solid phase and gain of water-ion interactions for both leaving and newly exposed surface sites. In the TST framework, the rate constant is linearly proportional to the frequency of ions attempting to escape the surface position and exponentially proportional to the energy barrier for ion departure. The latter is inversely proportional to the extent of surface ion hydration and directly proportional to the coordination number of the departing surface ion.

It remains a challenge to parametrize the TST experimentally, and most studies have used ad-hoc values for energy barrier and frequency factor [2]. In particular, the frequency prefactors are challenging to estimate, due to many diverse and complex ion-departure pathways from non-uniform calcite surfaces.

Here, we show how the statistical analysis of an ensemble of molecular dynamics trajectories of spontaneous Ca^{2+} and CO_3^{2-} ions departures from the non-uniform calcite allows us to estimate frequency factor in TST theory, distribution of dissolution rates. We also calculated the energy barrier for the dissolution process as a function of the composition of its coordination shell.

Collectively, we show how molecular modeling can provide a robust parameterization of the TST rate equations – which in turn allow larger-scale kinetic modeling of the dissolution process, the evolution of the surface roughness, ion/isotope exchange, and their extension to stressed surfaces (e.g., pressure solution scenario).

[1] a) Lasaga, A.C. *Kinetic Theory in the Earth Sciences*, Princeton, 1998; b) Morse, R.S et al. *Chem. Rev.*, 2007, 107, 342-281

[2] a) Lasaga, Luttge, *Science* **291**, 2400–2404 (2001), b) Kurganskaya, Luttge *Acs Earth Space Chem* **5**, 1657–1673 (2021).