The free energy landscape of growing calcite: Adsorption of ions at kink sites

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Earth's most abundant biomineral, calcite, stands as a model crystal for developing an understanding of how minerals grow. The conventional terrace–step–kink model [1] describes crystal growth as a two step process where the nucleation of a kink site at a step edge is followed by the propagation of the kink sites along the step via a monomer-by-monomer addition. Atomic force microscopy can image the growing surface in aqueous solution and the overall rates of step propagation can be determined experimentally. However, the rates of individual processes, such as single ion additions at the growing crystal, remain unknown. Molecular simulations can help make the connection between the macroscopically observed rates and the underlying atomistic mechanisms. The time required for a step to advance only one nm is on the order of s while the typical limit of classical molecular simulations is that of μs. Enhanced sampling methods are therefore needed to allow fast thermodynamic and kinetic calculations. A previous study from our team obtained the free energy profiles for kink nucleation at the calcite two distinct step geometries. [2] Building on this, results will be presented using the free energy perturbation approach [3] and the parallel-biased metadynamics technique [4], to compute accurate adsorption free energies of ions incorporating at calcite kink sites. These results will serve as an input for a recently proposed general model for predicting growth of macroscopic crystals based on tilings. [5]

[1] Burton, Cabrera, & Frank (1951), *Philos. Trans. R. Soc. London. Ser. A* **243**, 299–358. [2] De La Pierre *et al.* (2017), *Angew. Chemie - Int. Ed.* **56**, 8464–8467. [3] Zwanzig (1954), *J. Chem. Phys.* **22**, 1420–1426. [4] Pfaendtner & Bonomi (2015), *J. Chem. Theory Comput.* **11**, 5062–5067. [5] Anderson *et al.* (2017), *Nature* **544**, 456–459.