Determining the Complete Thermodynamics of Calcite Kink Sites for Crystal Growth and Dissolution

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The competition between growth and dissolution is of key interest in determining the evolution of a crystal system. In the case of many materials where slow growth is observed, the kink sites play an important role in determining where any loss or gain of mass to the crystal will occur. Despite this, it is rare that the thermodynamic stability of individual kink sites is known for a solid growing from solution, except that the average value for a stoichiometric amount is constrained by the solubility of the material. Here we consider the case of the growth of calcium carbonate ($CaCO_3$), which is a highly abundant biomineral fulfilling many roles in nature, including the sequestration of carbon from the environment. In particular, the focus will be on the most stable polymorph at ambient conditions, calcite, which often exhibits predominantly the $(10\bar{1}4)$ surface. The interface of this surface with water has been extensively studied using atomic force microscopy [1,2] and X-ray reflectivity [3,4], both of which indicate the presence of ordered water layers.

In this study the focus will be on extending a recently proposed method for determining standard free energies of ion binding at solid-liquid interfaces [5] to predict the 16 distinct kink site free energies at the acute and obtuse steps of calcite. Here the standard free energies for dissolution will be presented based on using both alchemical methods, in which an ion is transferred from the kink site to a 1 M aqueous solution, and via methods in which the ion is removed by following an explicit pathway as a function of distance from the kink site. Both sets of free energies obtained from the two different approaches are found to be consistent with the expected bulk dissolution free energy of calcite, while being radically different from each other. The origin of this difference can be traced to the existence of a substantial interfacial potential at the calcite-water interface due to the ordering of water dipoles. The significance of these results for the growth and dissolution of calcite from aqueous solution will be discussed.

References

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