A thermodynamic-kinetic model for organic matter degradation in marine sediments

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The microbial degradation of organic matter in marine sediments links short residence time atmospheric, oceanic, and terrestrial carbon pools with the long-term, geologic carbon cycle. Therefore, developing models that describe and predict the fate and transport of organic matter over a range of timescales is critical for interpreting paleo-carbon records and predicting how anthropogenic activities will perturb the modern global carbon cycle. However, existing organic carbon degradation models are weakly constrained and usually use parameters that are calibrated on the basis of site-specific observations. They do not unambiguously relate these parameters to factors that influence organic matter degradation dynamics such as the type and composition of the depositional environment, the microbial community structure and the bioenergetic constraints that govern the consumption of organic compounds. In an attempt to address these issues, we are proposing an organic matter degradation model that scales the rates of organic matter degradation to the chemical potentials of organic compounds *in situ*. This approach utilizes the extensive thermodynamic database that now exists for a broad range of aqueous, crystalline, liquid and gaseous organic compounds as well as group additivity algorithms that make it possible to reliably estimate the thermodynamic properties of organic compounds for which no data have been reported in the literature. Within this formulation, the type of organic matter deposited can be specified along with the environmental conditions (temperature, pressure, types and concentrations of electron acceptors) that this organic matter is exposed to in order to quantify the fate of organic matter deposition in any marine environment.

Spiral growth on calcite and the effect of the Ca^{2+} to CO_3^{2-} ratio

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Understanding the fundamental aspects of crystal growth helps us interpret the dynamic geochemical processes in nature. The wide-spread occurance of calcite and its rapid reaction rate make it an interesting crystal for theoretical study. The high Ca^{2+} to CO_3^{2-} ratio of natural waters is rarely considered in models intended to describe calcite growth. Our aim was to develop a theoretical method for determining the critical step length of inequivalent steps associated with a dislocation source and to test it on experimentally produced spirals. We investigated the effect of a range of Ca^{2+} to CO_3^{2-} activity ratios on growth of spiral pyramids on calcite. Experiments were performed at constant supersaturation with ion activity ratios ranging from 0.1 to 100. Atomic force microscopy (AFM) revealed a change in pyramid geometry that correlated with $(Ca^{2+})/(CO_3^{2-})$. These changes arise from inequivalency in obtuse and acute step growth velocities. In general, growth velocity decreases when Ca^{2+} dominates. Acute step velocities are more affected by changes in Ca^{2+} to CO_3^{2-} ratio than obtuse steps, probably because of dissimilar dehydration frequency and different configuration for surface-ordered water on the geometrically inequivalent steps. Thus ion activity ratio plays a large role in step growth kinetics on calcite surfaces. Ion selectivity at kink sites is a key for understanding the atomic-scale processes responsible for crystal growth. Kinetic models to describe growth of minerals in natural systems should include parameters for the ion activity ratio as well as the degree of supersaturation.

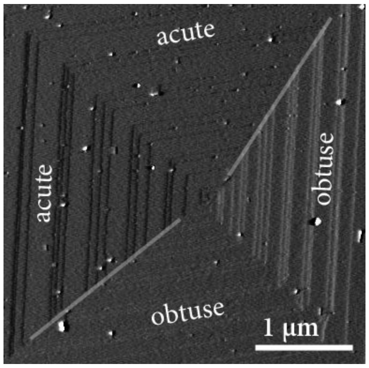

Figure 1: A spiral growth pyramid on a $\{10\bar{1}4\}$ cleavage face.