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Surface site-specific interactions of aspartate with calcite during dissolution: Implications for biomineralization

H. Henry Teng and Patricia M. Dove

School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, U.S.A.

Abstract

Calcite occurs widely as a mineral component in the exoskeletons and tissues of marine and freshwater invertebrates. Matrix macromolecules involved in regulating the biological growth of calcite in these organisms are known to share a carboxylic-rich character that arises from an abundance of the acidic amino acids aspartate (Asp) and glutamate (Glu). This study determines the interactions of Asp with calcite $\{10\bar{1}4\}$ faces during dissolution using in situ fluid-cell atomic force microscopy (AFM) and macroscopic ex situ optical methods. In control experiments, etch-pit morphologies produced by dissolution in simple undersaturated solutions reflect the inherent symmetry of the $\{10\bar{1}4\}$ faces with a rhombus form. With the introduction of Asp, surface site reactivities are modified to yield isosceles triangular etch pits and hillocks. With continued exposure to Asp-bearing solutions, these triangular pits coalesce and the surface evolves into a network of interconnected tetrahedral etch hillocks. The component tetrahedral ''sides'' have Miller-Bravais indices of (0001), $(\bar{1}101)$, and $(0\bar{1}11)$. These faces intersect the $(10\bar{1}4)$ face in the [010], $[45\bar{1}]$, and $[\bar{4}11]$ directions to compose the three edges of the triangular etch pits. Structural and stereochemical contraints suggest that the $(\bar{1}101)$ and $(0\bar{1}11)$ faces in the hillock are a combination of corresponding faces from the $\{\bar{1}102\}$ and $\{\bar{1}100\}$ crystallographic forms.

Results of this dissolution study are consistent with previous growth experiments showing that Asp causes preferential development of the {0001} and possibly the $\{\bar{1}100\}$ forms of calcite. These observations support mechanisms proposing that the new forms are stabilized by the molecular recognition of Asp functional groups for specific surface sites. Because Asp stabilizes identical faces during growth and dissolution, we suggest that dissolution studies offer an alternative means of determining the crystal forms that develop during biomineralizing processes and a more direct means of identifying those surface sites involved. We demonstrate that the stability of crystallographic directions expressed by step edges is controlled by the relative reactivities of surface sites. Our findings yield new insights into surface structure controls on mineral reactivity.