

# Molecular Recognition at Organic Acid-Calcite Interface

HENRY TENG<sup>1</sup>, YANG CHEN<sup>2</sup>, AND ELLI PAULI<sup>1</sup>

<sup>1</sup>Department of Chemistry, The George Washington University, Washington, DC, USA (hteng@gwu.edu)

<sup>2</sup>Department of Geosciences, Nanjing University, PRC

Interactions of aqueous organic acid with calcite crystal face find their occurrences in many natural processes such as biomineralization and metal ion sequestration. They may also be one of the critical gateways in understanding the origin of homochirality in terrestrial biomass because of the possibility of chiral adsorption of amino acids on mineral surfaces. It is generally accepted that, due to the similarity between carbonate anion ( $\text{CO}_3^{2-}$ ) and carboxyl group ( $-\text{COO}^{1-}$ ), the interaction is fulfilled by carboxylic acid adsorbing onto the crystal faces through electrostatic attractions of  $-\text{COO}^{1-}$  and terminal  $-\text{Ca}^+$  surface site. This indicates that, given the ordered atomic arrangement in crystal lattice, the interaction has to be crystallographic direction specific. Previous studies of calcite-aspartate (Asp) interactions documented such direction-specific nature, and also raised questions regarding the involvement of specific functional groups and the geometry of the surface binding. Issues needing to be addressed include (1) the roles of amino acids' side chain functional group and the  $\alpha$ -amine group; (2) the effect of side chain length; and (3) the coordination of multifunctional groups in surface binding.

In this study, we investigated the binding direction and geometry of organic acid, including biological amino acid, on calcite surface by examining the possible molecular recognition between aqueous ion and crystal face. Experiments were conducted using a 'molecular probing' approach where the structure and composition of the organic acid used were varied systematically relative to Asp. The results show that when the chirality of the organic acids was maintained, such as in the case of alanine, glutamic acid, and serine, the reactions took place only on one side of the  $c$ -glide plane on the  $\{10\bar{1}4\}$  faces and the side preference depended upon the chirality of the organic acids. When the chirality was removed, such as in the case of succinic acid, the  $c$ -glide plane lost its control on the reaction. Instead, two new directions,  $[42\bar{1}]$  and  $[010]$ , along with the inherent  $[\bar{4}41]$  and  $[48\bar{1}]$ , developed and the new directions were different from the ones stabilized by Asp,  $[45\bar{1}]$  and  $[41\bar{1}]$ . Additionally, the Asp-preferred directions did not appear when the side chain length or functional group was changed, such as in the case of alanine, glutamic acid, and serine. These results will be discussed in terms of electrostatic matching, geometric correspondence, and stereochemical conformity between the organic acids and various steps on the  $\{10\bar{1}4\}$  faces. On the basis of these observations, we propose a general binding geometry for multi-functional organic acids to interact with calcite surfaces.