## Toward a Conceptual Model of the Calcite Surface

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Calcite has received increased interest recently because of its geologic, biologic and industrial importance. Improved ability to model its behaviour will improve prediction of contaminant uptake or release in environmental systems and permeability changes in oil and gas reservoirs. It will help optimise production of materials engineered for specific properties such as high transparency for optical devices, high reflectivity for paper fillers or site-specific interaction for sequestering of isomers. Perhaps one of the most exciting applications is improved design for complex materials that mimic shells, where layers of organic molecules control  $CaCO_3$  crystal type and form. Better fundamental understanding of the function of enhancers and inhibitors to adsorption, mineral growth and dissolution will lead to progress in each of these fields.

The increase in interest has provoked increased activity in formulating mathematical models to describe geochemical processes affecting the calcite surface. For a model to be effective, it must be based on a conceptual model that is realistic. In many cases, conventional wisdom about surface hydration and hydrolysis on metal oxides has simply been adopted and applied to the carbonate system, but there is good experimental evidence to suggest that this does not give the most reliable description.

Work of many researchers has failed to provide a reproducible value for calcite's  $pH_{pzc}$  (point of zero charge); it varies with sample history and solution composition. Electrophoretic mobility of calcite particles is a function of solution concentration of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> (or HCO<sub>3</sub><sup>-</sup> or  $H_2CO_3^{o}$ ), and is independent of pH, leading to the interpretation that  $H^+$  and  $OH^-$  are not potential determining ions and pH<sub>pzc</sub> is a meaningless term for describing calcite's behaviour. However, substantial evidence from several surface-sensitive techniques proves the persistence of hydrolysis species at the calcite surface, even in the violent conditions of ultra-high vacuum. The apparent conflict is resolved by a slight modification of the Electrical Double Layer (EDL) Model. At the surface, H<sup>+</sup> and OH<sup>-</sup> are chemi-bonded. At the Stern layer, adsorption attaches the potential-determining ions, Ca<sup>2+</sup> and  $CO_3^{2-}$  (or other carbonate species), but the hydrolysis layer holds them in outer-sphere coordination. With dehydration, loss of the hydrolysis species results in direct contact between adsorbed ions and the bulk termination, so innersphere sorption is exactly equivalent to extension of the three-dimensional bulk network, which we call precipitation. Attachment of ions with size and charge compatible with Ca and CO<sub>3</sub> likewise results in co-precipitation and solid-solution formation.

In building representative mathematical models, we are faced with occasional incompatibilities between the thermodynamic and molecular-level approaches. Macroscopic treatment of interface processes inherently averages over many individual processes that may be going on simultaneously. Local, very site-specific investigations help to sort out some of the complexity, but it is difficult to describe inhomogeneous systems and conditions near equilibrium where slight local variability leads to apparently incongruous behaviour. A new conceptual model, to be presented, simplifies descriptions.