

Structure and surface complexation of the calcite-water-interface

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Calcite, the most stable polymorph of CaCO_3 at ambient conditions, is ubiquitous in natural systems and controls to a large degree the geochemistry of environmental settings like terrestrial soils and sediments, lacustrine- or seawater. Due to the reactivity of its surface, calcite has impact on the mobility of nutrients and contaminants in subsurface environments. Electrostatic phenomena at the calcite-water-interface are of interest in many fields ranging from environmental studies, through oil recovery from chalk reservoirs, to industrial applications e.g. in the cement or paper production.

In this study we present an updated view of the structure of the calcite(104)-water interface on the basis of a new extended crystal truncation rod data set, which allows to resolve previous ambiguities with respect to the coordination sphere around the surface Ca-ions and the relaxation of surface atoms within the top four mono-layers. The structural aspects are related to a newly developed electrostatic triple layer surface complexation model (SCM), describing the calcite-water-interface chemistry. For the first time, direct information on the inner surface potential of calcite, as measured with a calcite single crystal electrode, is included in the data constraining the calcite SCM, besides zeta potential data. All model parameters like ion binding constants and especially the Helmholtz capacitances are in a physically and chemically reasonable range. The surface protonation constants for surface calcium and carbonate groups, $\log K_{>\text{CaOH}-0.5/\text{CaOH}2+0.5}$ and $\log K_{>\text{CO}3-0.5/\text{CO}3\text{H}+0.5}$, respectively, are in good agreement with MUSIC¹ calculations.

1. T. Hiemstra, P. Venema and W. H. VanRiemsdijk, *Journal of Colloid and Interface Science*, 1996, **184**, 680-692.