



Chemical Heterogeneity at the Mineral–Water Interface: Implications for Biomineralization and Bioweathering

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The mechanistic understanding of biomineralization and bioweathering processes requires an appreciation of the diversity of coordinative environments present at the mineral–water interface. With the exception of diffusion processes, which are of importance especially in intracellular mineralization, and possible vital effects, thermodynamic and kinetic controls on biomineralization and bioweathering are dependent on the microscopic structure of mineral surfaces. For example, Orme et al. (2001, *Nature* 411, 775–779) showed that the geometric and chemical fit of amino acids binding to calcite surface steps affect the step-edge free energies, which in turn results in a macroscopic change in the crystal shape. It has also been shown that both divalent metals (e.g. Paquette and Reeder, 1995, *Geochim. Cosmochim. Acta* 59, 735–749) and oxyanions (Reeder et al., 2004, *Geochim. Cosmochim. Acta* 68, 4799–4808) show site-specific incorporation at the calcite surface, based on geometrical constraints.

Here we present a surface chemistry model, which offers a detailed description of the bonding environment at the calcite–water interface. This surface chemistry model is a refinement of the original model of Van Cappellen et al. (1993 *Geochim. Cosmochim. Acta* 57, 3505–3518), using the MUSIC approach (e.g. Hiemstra et al., 1989, *J. Coll. Interf. Sci.* 133, 91–104). The surface structure of calcite is based on crystallographic data for calcite, and information on bond-lengths and hydration of the surface lattice (Kerisit et al., 2003, *J. Phys. Chem. B* 107, 7676–7682). The formal charges for carbonate and calcium hydroxyl groups vary depending on their position at the surface, because of differences in the coordination of surface carbon or calcium ions to the bulk

lattice. Hence, sites at the corners of a crystal have a different coordination than those located along an edge or on a plane surface. These differences in coordination affect the chemical reactivity of the sites, yielding a chemical heterogeneous surface. The implications of this surface chemical heterogeneity for interactions between calcite and organic molecules will be discussed.