Uptake of Cu^{2+} by the calcium carbonate minerals vaterite and calcite as studied by CW and pulse electron paramagnetic resonance (EPR)

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The distribution of trace metals like Mn, Fe, Cu or Cd in the aquatic environment is regulated by redox equilibria, the complexation of the metals with organic and inorganic ligands in solution and at surfaces, and precipitation/dissolution reactions [1]. Due to the high reactivity of the widespread carbonate minerals the speciation of trace metal ions in natural waters is often controlled by carbonate and bicarbonate ions [2]. Furthermore the precipitation of carbonate minerals like calcite ($CaCO_3$) in lakes and oceans provides important pathways of trace metal scavenging by adsorption of the metal ions and coprecipitation during crystal growth. Investigation of the molecular interactions between trace metals and carbonate minerals is relevant for the understanding of the biogeochemical cycles of the metals and their role in the processes of crystal growth and growth inhibition.

Recently, the application of surface-sensitive spectroscopic and microscopic techniques has given more insight into the molecular structure and properties of calcite surfaces and provided a new basis for the interpretation of trace metal sorption on calcite on an atomic level [3,4]. Detailed information about the coordination geometries at individual surface adsorption sites, however, is best obtained with magnetic resonance techniques.

The investigation of the Cu^{2+} uptake by the calcium carbonate minerals vaterite and calcite with continuous wave and pulse EPR gives insight on an molecular level into complexation reactions at the mineral surfaces. The structural assignment is based on a previous study of the complexation of Cu^{2+} with carbonate ligands in aqueous solution [5] and the surface complexation model of Van Cappellen *et al* [6]. Different chemical processes occurring upon addition of Cu^{2+} ions to a $CaCO_3$ suspension have been identified and are shown schematically in Fig. 1.

Rapid dehydration after adsorption of the trace metal ions from solution (A) to the mineral surface (B). The strong surface binding is due to monodentate coordination to three or four carbonate surface ions, comparable to a chelate complexation in solution.

Accumulation of square-planar or square-pyramidal copper complexes (C) at exposed surface sites

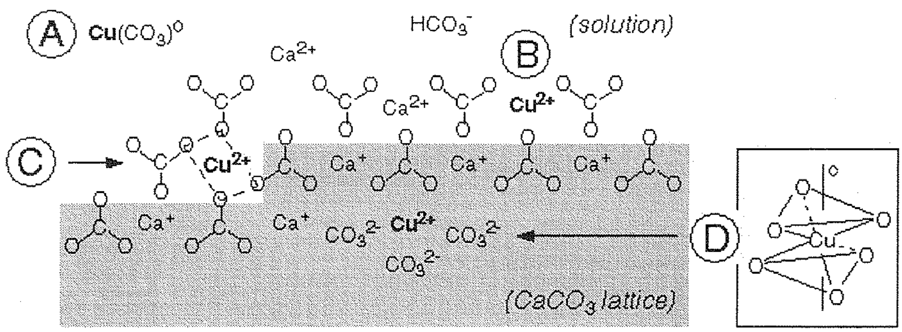

FIG. 1.

like kinks and steps of the solid $CaCO_3$ due to the inhibition of crystal dissolution and growth.

Integration into the calcite lattice where the Cu^{2+} ions exhibit a temperature-dependent Jahn-Teller effect as the nearly cubic symmetry of the ligand field (small trigonal distortion along the c axis, see inset) allows for hopping of the tetragonal distortion axis between three possible orientations (D). The resulting local lattice distortions and vibrations are expected to destabilize the $Cu_xCa_{(1-x)}CO_3(s)$ solid solution.

Our results support the concept of a dynamic calcium carbonate surface, covered by a thin, structured surface layer. The detailed structural information obtained for Cu^{2+} provides a better understanding of the interaction of other foreign metal ions with calcium carbonate minerals.

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