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EXAFS Study of Zn(II) Adsorption Complexes at the Calcite Surface

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Beamline(s): X11A

Introduction: Uptake of Zn(II) by calcite in sorption experiments may include adsorption processes, incorporation of Zn(II) into the calcite structure, and the formation of Zn-hydroxy-carbonate precipitates [1,2]. In this study, we performed EXAFS analyses of dilute Zn(II)-calcite adsorption samples to characterize the interaction between Zn(II) and the calcite surface at the molecular scale.

Methods and Materials: The calcite sorbent used in this study had an N₂-BET surface area of 10 m² g⁻¹. Before reaction with Zn(II), calcite-water suspensions of 0.1 or 0.5 g calcite L⁻¹ were equilibrated at atmospheric CO₂ pressure for 2 months, yielding an equilibrium pH of 8.3. The suspensions were then spiked with appropriate aliquots of a 0.01M ZnCl₂ stock solution to achieve initial Zn concentrations of 1, 5 or 10 μM. After reaction for 48h, the suspensions were filtered through 0.22 μm filter paper to collect the wet calcite solids for EXAFS characterization. Room temperature scans were taken at the Zn K-edge, using a 13-element solid state fluorescence detector. A number of reference Zn solid standards were also run for comparison with the Zn-calcite adsorption samples. Data analysis was done with WinXAS2.0 [3], in combination with the FEFF7 code [4], following standard procedures.

Results: Figure 1 shows the k³-weighted χ spectra of the Zn(II)-calcite adsorption samples, along with those of the Zn reference compounds. Precipitation of hydrozincite or ZnCO₃ had not occurred to a significant extent in the sorption experiments, as indicated by the dissimilarity in the spectra of these compounds versus those of the Zn adsorption samples. The adsorption spectra are also different from the spectrum of a dilute Zn-calcite solid solution, which indicates that during the reaction time allowed, no significant incorporation of Zn into the calcite structure had occurred. The Fourier transforms of the k³-weighted χ spectra are shown in Figure 2. Fitting results indicated a first-shell Zn-O radial distance of ~1.95 Å for the adsorption samples. This radial distance is typical of Zn complexes in tetrahedral coordination with first-neighbor O. Peaks present in the RSFs located beyond the first O shell were successfully fit with O, C and Ca shells located at radial distances consistent with Zn positioned in unoccupied Ca sites at the calcite surface, most likely at kinks and step sites, which contain CO₃ ligands that are only partially coordinated by lattice atoms. We therefore conclude that Zn(II) forms tetrahedral inner-sphere complexes at the calcite surface that are linked to Ca lattice atoms via surface CO₃ groups.

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References:

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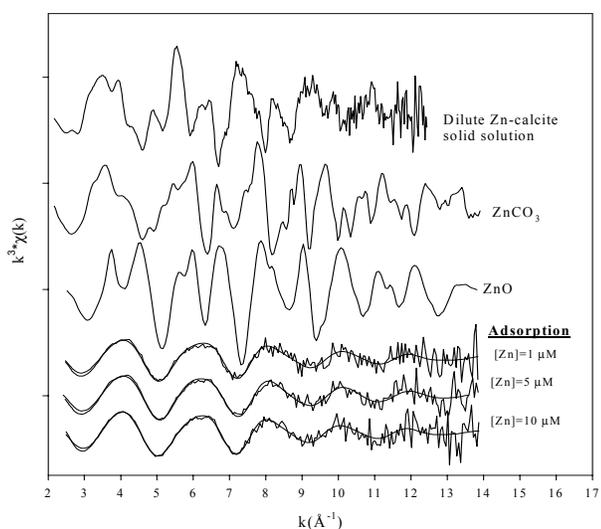


Figure 1. χ spectra of the various samples

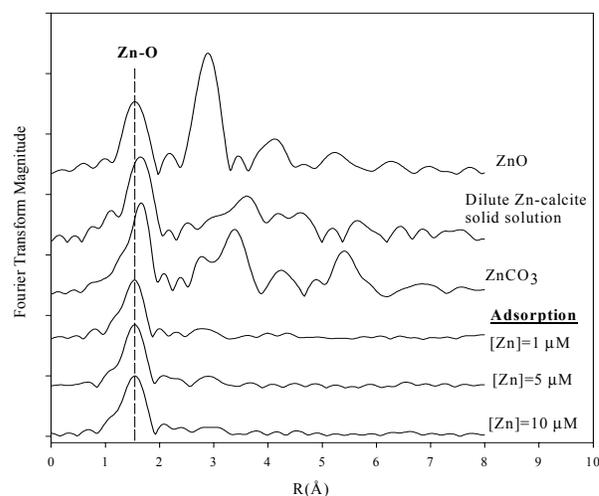


Figure 2. RSFs of the various samples