Zinc sorption on hydroxyapatite: Systematic uptake and EXAFS studies

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The systematics and mechanisms of Zn sorption on hydroxyapatite (HAP) in pre-equilibrated suspensions open to air were characterized using a combination of batch sorption experiments, X-ray diffraction (XRD), and extended X-ray absorption fine-structure spectroscopy (EXAFS). Experiments were conducted over a range of pH values and Zn concentrations to assess the dominant Zn sorption mechanisms. Sorption isotherms of Zn(II) on HAP at pH 5.0 and 7.3 show an initial steep slope, followed by a plateau up to $[Zn] \leq \sim 750\ \mu M$, whereas at $[Zn] > 750\ \mu M$ a sharp rise in the pH 5.0 isotherm suggests precipitation, and slight continued uptake in the pH 7.3 isotherm is suggestive of an additional uptake mechanism. At pH 9.0, the isotherm shows a steep uptake step at $[Zn] \leq 0.8\ \mu M$, followed by an increasing linear trend up to $[Zn] = 5\ \mu M$, without any indication of a maximum, suggesting that precipitation is an important uptake process at this pH.

Zn *K*-edge EXAFS results show a first oxygen shell at 1.96-1.98 ± 0.02 Å in sorption samples with $[Zn]_{tot} \leq 250\ \mu M$ at pH 5.0, 7.3, and 9.0, consistent with tetrahedral coordination of Zn. EXAFS results reveal additional P and Ca backscatters, supporting formation of an inner-sphere Zn surface complex. In contrast, EXAFS and XRD data indicate that precipitation of $Zn_3(PO_4)_2 \bullet 4H_2O$ (hopeite) dominates the mode of Zn uptake at $[Zn]_{tot} \geq 3$ mM at pH 5.0. Linear combination fits of EXAFS data reveal a mixture of inner-sphere Zn surface complexation and precipitation of $Zn_5(OH)_6(CO_3)_2$ (hydrozincite) in sorption samples for $[Zn]_{tot} = 5$ mM at pH 7.3, and for $[Zn]_{tot} = 1$ mM at pH 9.0. The different mechanisms of Zn uptake by HAP suggest that immobilization of Zn, as well as the potential for remobilization, depends sensitively on solution conditions, including pH, Zn concentration, and the presence of dissolved CO_2.

Determination of cation exchange rates in synthetic birnessite using time-resolved synchrotron X-ray diffraction

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Birnessite is the most abundant and chemically important layer-structure Mn-oxide phase found in soils, desert varnishes, and ocean nodules. For this work, we measured changes in unit cell parameters over time to quantify the degree of cation exchange as a function of concentration. Aqueous K^+, Cs^+, and Ba^{2+} cations at varying concentrations at pH 7 were exchanged for interlayer Na^+ in synthetic birnessite using a simple flow-through cell, and the exchange products were monitored via time-resolved X-ray powder diffraction at the National Synchrotron Light Source. Powder X-ray diffraction patterns were collected every 2-3 minutes.

Rietveld analyses (using the GSAS program) of X-ray diffraction patterns for K- and Ba-exchanged birnessite revealed a decrease in unit cell volume over time; in contrast, Cs substitution increased cell volume. For all three cations, the exchange occurred in two stages. A rapid and dramatic change in unit cell volume was followed by a modest adjustment over longer timescales. Fourier electron difference syntheses revealed that the rapid, initial stage of exchange was marked by major re-configurations of the interlayer species, whereas the second, protracted phase of substitution represented ordering into the newly established interlayer positions. We calculated normalized volume contraction (or expansion) coefficients for the period of rapid initial exchange for each cation solution concentration. Specifically K-exchange at 0.05M, 0.01M, and 0.001M resulted in volume contraction coefficients of $1.51E^{-3}\ min^{-1}$, $4.68E^{-4}\ min^{-1}$, and $1.69E^{-4}\ min^{-1}$ respectively. These values yield the following rate equation that corresponds to the rate of cation exchange:

$$\log [\text{Rate Volume Contraction}] = 0.5524 \log [\text{KCl}] - 2.1469.$$

Further refinements of the Ba^{2+} and Cs^+ exchange results will result in a comparison of the rate of exchange for different cations.