Cation Sorption at the Barite (001) and (210)-Water Interfaces

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Here, we use barite as a model substrate to understand divalent cation interactions with ionic crystals. The coverage and location of either lead (Pb) or strontium (Sr) sorbed to the (001) and (210) surfaces were studied as a function of $[Pb]_{aq}$ or $[Sr]_{aq}$ using in situ specular x-ray reflectivity (XR) and resonant anomalous x-ray reflectivity (RAXR). In the presence of Pb, the XR signals become progressively more distorted as $[Pb]_{aq}$ increases, implying the presence of Pb alters the structure of the two surfaces. In contrast, the presence of Sr has smaller effects on the XR. The interfacial structural changes imply Pb and Sr sorption and that the extent of Pb sorption may be greater than that of Sr sorption.

The specific Sr or Pb sorption behavior at the (001) and (210) surfaces was measured using RAXR. At both surfaces, Sr and Pb incorporate into the topmost barite layer and adsorb inner-sphere with a small outer-sphere fraction. At both surfaces, roughly half the sorbed Sr is incorporated and the other half is adsorbed, regardless of concentration. Pb is similarly partitioned half incorporated and half adsorbed at both surfaces at low concentrations ($[Pb]_{aq} \leq 75$ μM), but not at higher concentrations. At $[Pb]_{aq} \geq 200$-225 μM, less than a third of the Pb sorbed to the (001) is incorporated, but up to three-quarters of Pb sorbed to the (210) is incorporated. The total coverages of Sr and Pb at each surface varies depending on concentration. At $[Sr \text{ or } Pb]_{aq} = 25$-75 μM, the amount of sorbed Sr or Pb is ~0.6-1.2 Sr or Pb per nm^2 at the (001) and ~0.4-0.5 Sr or Pb per nm^2 at the (210). At $[Sr \text{ or } Pb]_{aq} = 200$-225 μM, the Sr coverage is similar to that measured at lower concentrations, but the Pb coverage is greater: ~2.8 Pb/nm^2 at the (001) and ~1.0 Pb/nm^2 at the (210). At the highest concentration of Pb measured, $[Pb]_{aq} = 800$-900 μM, ~3.9 Pb/nm^2 sorbs to the (001), while only ~1.9 Pb/nm^2 sorbs to the (210). These results suggest that the (001) has a higher sorption capacity than the (210), despite sorption occurring simultaneously through incorporation and adsorption at both surfaces.