Lead Adsorption at the Barite (001) – Water Interface

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Lead (Pb^{2+}) adsorption on barite surfaces is a likely initial step for incorporation of lead into barite. Using high resolution X-ray reflectivity (XR) and resonant anomalous X-ray reflectivity (RAXR), we quantified structural changes at the barite (001) – water interface associated with the extent of Pb^{2+} coverage during adsorption. The XR results indicated that adsorption of Pb^{2+} disrupted the barite surface structure through relaxation of the bariums and sulfates (≤ 0.3 Å) in the top two monolayers. These distortions were significantly larger than those observed in the absence of lead. There was also an increase in the electron density at the topmost barium plane, indicating possible exchange of more electron-dense lead for barium. The RAXR results showed that Pb^{2+} adsorbed at $[Pb^{2+}] \geq 8$ μM above which the coverage increased rapidly with increasing $[Pb^{2+}]$. At its maximum coverage, two-thirds of the Pb adsorbed as an inner sphere complex at ~ 2.0 Å, while the other one third of the lead was incorporated into the surface structure at ~0.4 Å below the barite surface. This implies that Pb^{2+} adsorbed primarily as an inner-sphere surface complex and/or was incorporated in the top monolayer of the barite surface. The maximum amount of lead present was greater than 1 Pb^{2+} ions per unit cell area. During desorption experiments, only half of adsorbed Pb^{2+} ions were removed from the surface after exposure to a Pb^{2+} -free barite-saturated solution, indicating irreversible Pb^{2+} adsorption.