Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.28680

Microscopic structural transformation of cesium adsorbed on clay minerals: Dependence on cesium concentration

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Clay minerals influence the environmental behavior of many elements through adsorption reactions. For example, the radioactive cesium (Cs) released by the Fukushima Daiichi Nuclear Power Plant accident in Japan was strongly adsorbed on clay minerals, causing its fixation in the surface layer of the soil even 10 years after the accident.

However, the adsorption reaction on clay minerals remains unclear due to their complexity. The clay minerals have multiple adsorption sites with varying affinities and capacities, and the dominant adsorption site changes depending on ion concentration. Most molecular-level studies of Cs adsorption have been conducted at high concentrations (ppm level or higher), but in the environment, Cs is typically adsorbed at much lower concentrations (ppt level). This discrepancy raises concerns about the applicability of laboratory findings to real environmental behavior.

To address this issue, this study systematically examined adsorption structures over a wide concentration range using molecular-level experiments and density functional theory (DFT) calculations. Adsorption experiments were performed with Cs concentrations ranging from 10^{-9} to 10^{-1} M to prepare samples with different dominant adsorption sites. These samples were analyzed using X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), and high-energy resolution fluorescence detection X-ray absorption near-edge structure (HERFD-XANES). Additionally, stable structure and bonding characteristics were simulated using the Vienna Ab initio Simulation Package (VASP) and the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER).

The adsorption isotherm results identified three distinct adsorption sites, while XRD confirmed systematic changes in the interlayer spacing. EXAFS analysis showed that the distance between Cs^+ and neighboring oxygen atoms varied with adsorption site changes. Combining these findings with DFT calculations, the study found that Cs^+ first adsorbs onto frayed edge sites (FES) with a narrow interlayer spacing. As concentration increases, Cs^+ adsorbs onto FES with wider interlayers, eventually causing interlayer collapsing at higher concentrations. In addition, HERFD-XANES results revealed that the interaction between Cs^+ and clay minerals remained primarily ionic, irrespective of the adsorption site. This was consistent with DFT-based bonding evaluations, offering crucial insights into Cs adsorption behavior in natural environments [1].

Reference: [1] A. Yamaguchi et al., Sci. Total Environ. 964, 178585 (2025).