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Crystallographic Facet Effects on the Mechanism Controlling Antimony Isotope Fractionation During Adsorption on Iron and Manganese Oxides

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Mineral surfaces represent critical reactive interfaces governing the environmental migration and transformation of metals and metalloids. Variations in crystallographic facets can substantially influence surface coordination environments and, consequently, isotope fractionation behavior. However, facet-dependent controls on antimony (Sb) adsorption and stable isotope fractionation remain poorly constrained. Here, we integrate facet engineering, batch adsorption experiments, synchrotron-based X-ray absorption spectroscopy (XAS), stable Sb isotope analysis, and density functional theory (DFT) calculations to systematically investigate Sb(V) adsorption and isotope fractionation on well-defined facets of hematite and α-MnO_2. For hematite, the (012) facet exhibits significantly higher Sb(V) adsorption capacity than the (001) facet. Molecular-scale analyses reveal dominant edge-sharing complexes on (001), whereas both edge-sharing and corner-sharing configurations occur on (012). Correspondingly, stronger Sb–Fe coordination on (012) results in smaller equilibrium isotope fractionation ($\Delta^{123/121}$Sb_ads–aq = −0.98 ± 0.2‰) relative to (001) (−1.41 ± 0.3‰). Fractionation is controlled primarily by equilibrium processes and remains insensitive to pH and initial Sb concentration. For α-MnO_2, only facets parallel to the c-axis are reactive. Although the (310) facet displays higher apparent adsorption rates and capacities than (100), surface area normalization indicates comparable intrinsic reactivity. Identical isotope fractionation on both facets ($\Delta^{123/121}$Sb_ads–aq = −0.44‰) confirms adsorption onto structurally equivalent surface sites. XAS and DFT results demonstrate that Sb(V) forms bidentate double corner-sharing complexes on shared reactive sites, stabilized by Mn 3d–O 2p–Sb 5p orbital hybridization. These findings establish a direct linkage between facet-dependent coordination structures and equilibrium isotope fractionation. While differences in surface complexation dictate adsorption strength and fractionation magnitude, facet variation alone does not induce additional isotope effects when reactive sites are structurally identical. This work provides a mechanistic framework for predicting Sb isotope behavior at mineral–water interfaces and advances the application of stable isotopes in tracing metal(loid) cycling and interfacial processes.