

## **Impact of surface functional group coordination state on the response of interfacial water structure to arsenate adsorption**

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Chemical reactions at metal oxide mineral-water interfaces affect contaminant fate and transport, nutrient availability, carbon cycling and sequestration, and nanoparticle mobilization. These reactions occur at surface sites having multiple possible coordination states that interact with both adsorbates and interfacial water. Surface X-ray scattering measurements have been used to investigate how surface site coordination state dictates ion adsorption mechanisms and interfacial water structure, and the feedback between these, on aluminum oxide surfaces. Surfaces of corundum dominated by singly coordinated functional groups induce strong ordering of interfacial water. In contrast, the (001) surface of corundum, which is dominated by doubly coordinated functional groups, induces weak water ordering that is largely unaffected by pH. This suggests that the charge state of functional groups plays an important role in inducing interfacial water ordering. The adsorption of arsenate to the (012) surface of corundum weakly perturbs the interfacial water structure above this surface. In contrast, arsenate adsorption on the (001) induces a substantial restructuring of interfacial water. These distinct responses of interfacial water to arsenate adsorption to the (001) and (012) surfaces is observed at both pH 5 and 9. Interfacial water structure on the (001) surface shows a dependence on arsenate surface coverage. These observations demonstrate the fundamental role of surface sites in controlling interfacial structure and suggest that water restructuring may contribute to the energetics of interfacial reactions.