

Surface-Specific Response of Interfacial Water to Arsenate Adsorption on Oxide Minerals

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Chemical reactions at the interface between water and metal oxide mineral surfaces affect contaminant fate and transport, nutrient availability, carbon cycling and sequestration, and nanoparticle mobilization. The interfacial region represents a chemical and structural transition zone. Water molecules adjacent to the surface occur in discrete positions, with this ordering decaying to that of the bulk fluid with increasing distance from the mineral surface. It is in this ~1 nm-thick interfacial region that many critical environmental and geological reactions occur. In situ surface X-ray scattering measurements have been used to investigate how interfacial water near aluminum oxide surfaces responds to changes in fluid composition, specifically pH variations and the addition of dissolved arsenate. In pure water, the arrangement of water molecules varies among different crystallographic surfaces of alumina. Weakly-ordered water occurs above the (001) surface, while water shows a high degree of spatial ordering above other surfaces. This behavior is unaffected in dilute salt solutions at pH 5, 7, and 9, the range of pH conditions relevant to most natural aquatic systems. However, the addition of arsenate to solution results in a full restructuring of water near (001) surfaces following the adsorption of this oxoanion. In contrast, interfacial water adjacent to the (012) surface is generally unperturbed by arsenate adsorption, maintaining a highly ordered state under all conditions. We hypothesize that these disparate impacts of arsenate on interfacial water are controlled by differences in the charge states and affinities for hydrogen bonding among the functional groups that dominate each surface. Such adsorbate-induced interfacial water restructuring may represent an overlooked component of chemical reactions at environmental interfaces. Thermodynamic models of interfacial reactions may require distinct capacitance terms to describe the reactivity of surface with and without adsorbates. In addition, the subset of mineral surfaces that likely display adsorbate-induced water restructuring may show distinct effects of ions on dissolution and growth kinetics compared to surfaces with stable interfacial water structures.