

Direct observations of ion adsorption and interfacial hydration with resonant anomalous X-ray reflectivity*

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In-situ characterization of ion adsorption structures and the associated changes to interfacial hydration structures is essential for a complete understanding of hydration at mineral-water interfaces. Water is partially ordered at mineral-water interfaces with a detailed hydration structure that depends on the local atomic configuration of the mineral surface [1]. Ion adsorption is expected to disrupt the interfacial hydration structure but the ability to observe these changes requires element- and interfacial-specificity. This difficulty can be overcome using Resonant Anomalous X-ray Reflectivity (RAXR), which combines the interface sensitivity of conventional X-ray reflectivity with the element-specific sensitivity of X-ray absorption spectroscopy. The distributions of Rb⁺ and Sr²⁺ at the muscovite (001)-water interface were determined with RAXR revealing critical differences between two ions: while Rb⁺ adsorbs exclusively as an inner-sphere species, Sr²⁺ coexists in both inner- and outer-sphere configurations. An ion-specific perturbation of the interfacial hydration layer is also directly observed from these data. RAXR measurements of arsenate (AsO₄³⁻) adsorbed on α -Al₂O₃ also revealed a coexistence of inner- and outer-sphere species. The ability to observe directly outer-sphere species provides fundamentally new insights into ion distributions at mineral-water interfaces, and suggests that this aspect of the interfacial structure may be relatively common. More generally, these results show that the complex inter-relationships controlling ion adsorption at mineral-water interfaces (e.g., including electrostatic interactions, mineral-water hydration and ion hydration) can be observed directly.

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References

[1] Fenter P., and Sturchio N.C., Prog. Surf. Sci. **77**, 171 (2004).