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Molecular Models for Mineral Surfaces: Oxygen Exchange between Water and Aluminum Polyoxocations

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The complexity and heterogeneity of oxide mineral surfaces make it difficult to determine the stoichiometry and rates of elementary reactions responsible for mass transport between mineral surfaces and aqueous fluids. Furthermore, rates of net reactions, such as dissolution and adsorption, are difficult to compare directly to theoretical results for elementary reactions. Some dissolved aqueous complexes contain structural fragments similar to those likely occur at mineral surfaces and can provide insight into structural chemical controls on reaction rates. We have measured rates of steady oxygen exchange reactions between aqueous fluid and the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}(aq)$, ($Al_{13}$) and $GaO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}(aq)$ ($GaAl_{12}$) complexes by ^{17}O NMR spectroscopy. These complexes expose to the solution bound water and bridging hydroxyl groups similar to those likely to occur on Al-(hydr)oxide mineral surfaces.

Except for the identity of the central, tetrahedrally coordinated cation, the Al_{13} and $GaAl_{12}$ complexes have nearly identical structures. Both complexes contain a set of equivalent terminal waters, μ_4-oxo groups interior to the surface, and two distinct types of bridging hydroxyls. We measured the rates of exchange of the bound waters and both types of hydroxyl, but observed no exchange of the μ_4-oxo with solvent. For both complexes, our results indicate a large difference in the lability of the two distinct hydroxyls, which have identical coordinations and nearly indistinguishable Al-O bond distances. We also find that the rate coefficients differ significantly between these two complexes, even though none of the exchanging oxygens are directly bonded to the tetrahedral cation that distinguishes the complexes. Although Al_{13} and $GaAl_{12}$ present nearly identical surfaces to the solution, the oxygen exchange rate coefficients for $GaAl_{12}$ are slower by over an order-of-magnitude for the hydroxyls and a factor of four for the bound waters, which are 0.53 nm from the central cation. These oxygen exchange reactions are elementary, or nearly so, and provide clear tests for computational models. These results suggest that changes in structure interior to the surface can have a large effect on reaction rates at surfaces. Moreover, we observe that the oxygen exchange rates are largely independent of pH and that exchange of bridging hydroxyls occurs many times before complete decomposition of the complex. By analogy, these results suggest that surfaces can re-organize at a rate much faster than dissolution reactions, which must involve breaking of metal-oxygen bonds interior to the surface.