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A New Look at an Old Idea: The Structure of Oxide Mineral Surfaces and the Role of Metal Centers in Intermediate Co-ordination Environments as Adsorbed Ions

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The complex relationship between the atomic and micro-topographic structure of oxide surfaces and their consequent reactivity in adsorption, dissolution-growth and other processes constitutes the chemical basis for many mineral-fluid interactions that regulate and modulate our chemical environment. Here, nonsteady state wet chemical dissolution data are combined with Hydrothermal Atomic Force Microscopy (HAFM), Scanning Tunneling Microscopy (STM), and optical Second Harmonic Generation (SHG) data to re-examine ideas proposed decades ago by Parks and others that metal ions are potential determining ions when adsorbed on their corresponding metal oxide surfaces. The oxide minerals corundum, hematite, goethite, and cubic indium sesquioxide all exhibit reproducible dissolution transients in response to pH jumps to pH 1 from higher pH. The transients are consistent with the dissolution, at low pH, and regeneration at higher pH, of a reservoir of metal centers at the surface that can be defined as "active" for dissolution at pH 1. Our working hypothesis is that such metal centers may be considered adsorbed to the mineral surface rather than part of the solid structure. These metal centers may occupy surface sites different from those expected of a simple termination of the bulk structure. HAFM experiments, including pH jumps, indicate that on hematite (001) surfaces, at pH 1 and at 125 C, monolayer step motion remains so slow as to be virtually indistinguishable from zero. Thus, the dissolution transients cannot be easily attributed to micro-topographic approach to steady state, or to an initially elevated rate of step motion or straightening. We must therefore look even more closely at the surface for the origin of the material dissolved in the transients. In-situ STM imaging in neutral solutions and 0.1M HNO_3 solutions show that the hematite (001) surface is remarkably inert, even at the atomic scale. Image sequences of up to 1 minute, showing different surface domains, show that few surface atoms appear to move under these conditions. However, preliminary aging experiments for several hours with in-situ STM at pH 1 initially show pervasive non-periodic (adsorbed?) surface sites, but relatively clean, ordered surfaces later in the experiment. These observations are consistent with the dissolution of "adsorbed" material in the dissolution transients. Finally, we utilized in-situ optical second harmonic generation (SHG) to study the (001) sapphire-water interface. In a total internal reflection geometry, SHG is sensitive to interfacial electric fields as well as to the structure of near-surface water. The nature of the non-linear optical effect that produces SHG light also makes SHG inherently interface sensitive. SHG signal in our experiment is pH and ionic strength dependent, and allows us to locate a point of zero salt effect independently of interpretation of titration stoichiometry. Such pH and ionic strength dependencies have previously been interpreted as directly related to surface potential. Preliminary experiments on annealing and subsequent aging of the sapphire (001) surface suggest that, upon annealing, the surface becomes less able to produce SHG and that with aging in water this ability is partially restored. These results have yet to be reconfirmed, but are intriguing given the nonsteady state and STM experiments discussed above. In summary, the hematite (001) surface (and by extension perhaps other oxide surfaces as well) appears to be surprisingly inert at low pH, but also remarkably kinetically labile, in terms of molecular-scale processes, at circum-neutral pH than generally accepted at present. In the early 1960s and 1970s, Parks and others considered the role of, for example, Fe^{3+} as a potential determining ion when adsorbed to hematite surfaces: could the adsorption of aqueous Fe(III) hydrolysis species of pH dependent charge, control the formation of surface charge on hematite? Since that time, an "inert surface, proton adsorption-desorption" model has most often been used to describe oxide surface charge in a simple manner. Our combined data set, including adsorption modelling, is generally consistent with and prompts us to re-examine this earlier approach.