

Kinetics and Mechanisms of Reactions at the Mineral-Water Interface: An Overview

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The study of environmental aquatic chemistry has matured over the past 30 years and with it the understanding of natural aquatic systems has grown. One outgrowth of this more mature understanding is a realization that reactions occurring at mineral-water interfaces are central to many, perhaps most, processes of geochemical importance. The rates of many ecosystem scale or even global scale processes are controlled by mineral-water interfacial reactions. The centrality of reactions at mineral-water interfaces is not a new idea as evidenced by previous research compilations which have emphasized the mineral-water interface to varying degrees (1-9). Rapid advances were made in the 1980's with the advent of a variety of modern spectroscopic techniques that, for the first time, allowed the direct study of mineral surfaces (10). In the last decade, researchers have coupled the detailed knowledge of surface structure available from these spectroscopic techniques with experimental and modeling studies of macroscopic surface behavior. This synergism has resulted in a dramatic increase in the ability to decipher and predict both the mechanisms and kinetics of surface mediated reactions. It is these mechanisms and rates that form the central theme of this volume.

Underlying Themes

The underlying intent in the preparation of this volume was to provide a compilation of papers that focus on the involvement of mineral surfaces in geochemical processes as a topic in and of itself. There is a particular need for a compilation of this sort because the topic encompasses a wide spectrum of researchers including environmental engineers, environmental microbiologists, geochemists, hydrogeologists, limnologists, oceanographers, soil scientists and spectroscopists. The resulting literature is quite fragmented and the rapid pace of progress further exacerbates the problem. The last major compilation dealing primarily with interfacial processes in the environment was based on a symposium held 6 years ago (2). Reflective of the progress made in the intervening time, this volume contains

work that cuts across a much broader spectrum of phenomena. Also indicative of the continuing evolution and maturation of this field is the incorporation of principles from completely unrelated fields of knowledge. Two clear examples of this include the use of the metallurgical corrosion literature to approach the problems inherent with zero valent iron remediation (11) and the use of the glassy-rubbery phase transition of the synthetic polymer literature to explain non-idealities in the sorption of organic contaminants to natural organic matter (NOM)(12,13).

The diversity of reactions that are considered to be surface mediated has also increased over the past decade. It is not only strict sorption/desorption and precipitation/dissolution processes that are important but also the surface mediation of reactions such as electron transfer (eg. 14-17), hydrolysis (18) and various photochemical transformations. In addition certain solid phases, in particular metallic iron, iron oxides and smectitic clays, are capable of transferring electrons in and out of their bulk structure (eg. 19-23). When viewed in this context, minerals should not be considered as passive solids, or even as simple sources of a reactive surface but must be considered as bulk reactants.

An additional emphasis that we hope becomes discernable to the reader is in the presentation of work that uses evolving spectroscopic techniques to complement either experimental data obtained from the macroscopic behavior of surfaces or modeling efforts aimed at a mechanistic understanding of surface mediated reactions. Much of the mechanistic detail that is needed to attain a predictive capability towards mineral surface behavior is derived via combined studies of this type.

Volume Overview

The first section deals specifically with the spectroscopic/ microscopic tools that can be used in concert with macroscopic techniques. The second section emphasizes computer models that are used to elucidate surface mediated reaction mechanisms. The remainder of the volume is organized around reaction type. Sections are included on sorption/desorption of inorganic species; sorption/desorption of organic species; precipitation/dissolution processes; heterogeneous electron transfer reactions; photochemically driven reactions; and microbially mediated reactions. What follows are a few highlights taken from the work presented in this volume.

Spectroscopic/Microscopic Tools. It has been long recognized qualitatively that natural surfaces are heterogeneous, however researchers can now explore surface structure, and the structures associated with phenomena such as sorption or precipitation and dissolution on a microscopic scale in real time. Equally important as real-time capability is the development of both spectrographic and microscopic techniques that allow the imaging of samples under *in situ* conditions (i.e. with water present). Environmental Scanning Electron Microscopy (ESEM), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), Electron Paramagnetic Resonance (EPR), Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR), Mossbauer spectroscopy, X-ray Adsorption Fine Structure (XAFS) and X-ray Adsorption Near Edge Structure (XANES) are all extant ambient techniques that

are applicable to geochemical problems (for a description of these techniques see (10)). A spatially resolved XAFS technique (X-ray spectromicroscopy) has recently been developed that has wide application to geochemical problems (24). Numerous examples of studies using real-time, *in situ* techniques are presented in this volume (25-29).

Modeling of surface reactions has kept pace with the new spectroscopic views of mineral surface structures. Chang et al. (30) and Van Riemsdik and Hiemstra (31) present excellent examples of the incorporation of new surface structure paradigms into computer modeling studies.

These new paradigms can immediately be applied to the many geochemical processes that are in essence surface-mediated. This will result in an improved understanding of geochemical processes on all time scales. Over geologic time, the surface-controlled dissolution of silicates and the precipitation of metal oxides are important sinks and sources, respectively in the global proton balance of surface and groundwaters (32). On more human time scales, carbonate precipitation/dissolution and various adsorption reactions are important buffers. Soil scientists recognize the importance of surface binding to the availability of soil nutrients. Hochella et al. (28) address this issue by applying real-time AFM data to the problem of potassium release from phlogopite. Surface-mediated reactions have been invoked to remove or supply ionic constituents from or to water, poise redox levels, and catalyze photochemical transformations. The importance of heterogeneous electron transfer reactions to the poise of sediment/water systems is probably matched only by the importance of silicate and carbonate dissolution to the buffering of the same systems.

Sorption of Inorganic Species. The intricacies of the sorption of inorganic cations to mineral surfaces is directly addressed by Sparks et al. (33) who point out that "sorption" is a general term that describes the retention of an aqueous species on a mineral by any of a number of processes, only one of which is actual adsorption (i.e. the association of an aqueous species strictly to the surface). Adsorption itself is highly variable with adsorption of radiocaesium being highly selective towards ion exchange type reactions at the edge sites of illite (34) whereas the sorption of Ni^{2+} on clay minerals and aluminum oxides is shown to be a combination of adsorption and the surface precipitation of a mixed nickel-aluminum hydroxide (33). Surface precipitation occurs at Ni^{2+} concentrations well below the solubility limit of $(\text{NiOH})_2$ and is associated with release of aluminum and silicon from the mineral itself. The formation of mixed cation oxide phases appears to be a substitution of trace metals of similar size as Al^{3+} and Si^{4+} for silicon or aluminum in the surface layers. Similar $\text{Fe}^{2+}/\text{Fe}^{3+}$ mixed cation surface precipitates on the surface of magnetite are suggested by Haderlein and Pecher (35). Implicit in these findings is that the formation of mixed cation oxides at mineral surfaces may be quite prevalent in the environment. Furthermore, these precipitates seem very geochemically active as an efficient scavenging mechanism for the removal of trace metal ions and in the enhancement of clay and oxide mineral dissolution. These precipitates also appear quite effective in promoting heterogeneous electron transfer.

Suarez et al. (36) use a combination of FTIR spectroscopy, electrophoretic mobility and pH titration data to deduce the specific nature of anionic surface species sorbed to aluminum and silicon oxide minerals. Phosphate, carbonate, borate, selenate, selenite and molybdate data are reviewed and new data on arsenate and arsenite sorption are presented. In all cases the surface species formed are inner-sphere complexes, both monodentate and bidentate. Two step kinetics is typical with monodentate species forming during the initial, rapid sorption step. Subsequent slow sorption is presumed due to the formation of a bidentate surface complex, or in some cases to diffusion controlled sorption to internal sites on poorly crystalline solids.

Sorption of Organic Compounds. The classic view of the sorption of neutral organic contaminants to sediment holds that hydrophobic forces cause the contaminant to preferentially associate, or partition, to NOM (e.g. 37,38). This linear partitioning model is attractively simple, and to a first approximation, accounts for the behavior of organic contaminant sorption. However the often observed presence of non-linear isotherms, sorption-desorption hysteresis, competitive effects, and slow kinetics indicates that this model does not accurately reflect the complete sorptive process. Weber et al. (13) and Pignatello (12) both address this problem and summarize a new model in which NOM can be viewed as having two physical states: glassy and rubbery. The rubbery state behaves as a classic "partitioning" type sorbent whereas the glassy state acts as a specific site-to-site type sorbent. The proportion of glassy to rubbery states in NOM is a function of the provenance and extent of weathering. This model is promising in that it may provide fundamental insights into the sorption of organic contaminants. This should allow a mechanistic understanding of such poorly understood phenomenon as the meaning of the exponential term in Freundlich isotherms, slow sorption kinetics, and hysteresis. This model may also provide a framework in which compositional differences in NOM and its effect on sorption can be classified.

Mineral precipitation and dissolution: The study of mineral precipitation and dissolution rates is advancing rapidly with the advent of modern spectroscopic techniques, in particular AFM (see (26)) and a review has recently been published that is devoted explicitly to the rates of mineral dissolution (39). Casey et al. (40) point out that in spite of the acknowledged complexity of reactive sites at mineral surfaces, much can be learned by comparing mineral dissolution and growth to the much simpler metal-ligand exchange reactions that occur in solution. This analogy is most useful when using multidentate ligands which more closely resemble the coordination conditions that exist at mineral surfaces. Luther et al. (41) report on a rapid disproportionation reaction of colloidal sized MnO_2 particles when they are complexed to oxalate. The reaction yields Mn^{2+} and CO_2 . In this reaction, solid MnO_2 is not only dissolved but also reduced and is therefore a potential oxidant in natural systems. This reaction is particularly interesting because the colloidal particles involved are only 50 nm in size and as such would be considered soluble in that they readily pass the 0.2 or 0.45 μm pore size filter that is typically used to differentiate soluble from insoluble constituents.

Heterogeneous electron transfer. It has long been obvious that redox conditions in heterogeneous systems are not adequately defined in terms of aqueous parameters (42,43). The underlying reason is that biologic control of redox reactions dominates in the natural environment causing widespread disequilibrium among redox active species. The geochemical importance of heterogeneous redox reactions is underscored by the fact that rapid bacterial reduction of several ferric oxides, manganese oxide, and iron bearing montmorillonite has been demonstrated (44-49).

In recent years, much progress has been made in the understanding of electron transfer across mineral surfaces. Taken as a whole, this work has greatly improved the understanding of redox geochemistry of environmental systems and of the specific processes in operation during the engineered remediation of groundwater. Reactions have been reported in which the bulk mineral is oxidized (e.g. 50,51), is reduced (e.g. 15,16,17,21), and acts to mediate the transfer of electrons between two aqueous species (52). In the first two cases, where the mineral serves as a bulk source/sink of electrons, the structure of the actual surface and how it differs from the structure of the bulk mineral is key to the understanding of the actual electron transfer. Scherer et al. (11), working within the context of metallic iron oxidation, presents three models for the redox behavior of surface oxide layers. Evidence suggests that surface oxides can act as passivating layers, as semiconductors, or as sites for the formation of redox active surface complexes. These behaviors are not mutually exclusive and may often operate concurrently.

Surface passivating layers are further discussed by White and Peterson (53) in the oxidation of magnetite by Cr^{6+} and by Fendorf (29) in the reduction of pyrolusite by Co^{2+} -EDTA complexes. In both cases, surface passivation removes the bulk mineral from further reaction with the solution and significantly reduces the redox capacity of the mineral.

In addition to exchanging structural electrons, ferric oxyhydroxide minerals also act to mediate electron exchange from surface bound Fe^{2+} to several reducible pollutants of environmental concern (52). In this case, the redox capacity of the mineral is not limited by the formation of a passivating layer because the bulk reductant is aqueous ferrous iron and reactive surface sites are continually regenerated. Haderlein and Pecher (35) review the environmental factors affecting the reactivity of surface bound Fe(II) in heterogeneous systems.

In contrast to the behavior of oxide minerals, iron bearing montmorillonite is capable of being reversibly reduced (21,54,27). A variety of inorganic reductants have been shown to be capable of reducing montmorillonites including hydrazine (55), sodium sulfide (56), benzidine (57,58), dithionite (59), and tetraphenylboron (27). Exposure to oxygen re-oxidizes the clay. The mechanism of electron transfer with the iron, which is located in the inner octahedral layer of these clays, is not fully understood but apparently occurs across the outer layer of tetrahedrally coordinated silicate (27,57,58,60). Using XANES and EXAFS techniques, Hunter et al. (27) examine structural changes induced in the clay matrix by the reduction of tetrahedral iron.

Photochemical reactions. Photocatalyzed degradation of pollutants at semiconducting surfaces has been reported for a long time. The majority of this work has been done in simple laboratory systems. Waite et al. (61) present data on the photocatalyzed oxidation (on TiO_2) of a complex algal toxin in the presence of a large excess of other, poorly defined, algal exudates. Composite systems of this sort are more representative of natural systems in which poorly defined humic or fulvic acids and various microbial exudates are common. Waite et al. (61) suggest a conceptual model for this system in which the background organics (algal exudates) sorb to TiO_2 and form long-lived radicals which in turn oxidize the pollutant (algal toxin). Interestingly, the long-lived radicals appear to desorb and primarily react with the algal toxin in solution rather than on the surface.

Microbially Mediated Reactions. In many respects the true geochemists of the world are the prokaryotic bacteria. These microbes are universally abundant and catalyze so many geochemically important reactions that the distinction between "biotic" and "abiotic" reaction is often unclear. Biotic reaction mechanisms have been observed on scales ranging from electron transport across the fluid interface of mineral grains (44,48,62) to the microbial involvement in weathering and elemental cycling on a global scale (63,64). Tebo and He (65) provide an excellent overview of the diversity of microbes that are involved in the oxidation of Fe(II) and Mn(II) . New insights into the mechanism of the microbial catalysis of Mn(II) oxidation are also presented. It seems possible that the enzymes responsible are relatively general and may be capable of oxidizing a variety of trace metal ions (66). While it is not always clear what metabolic benefit is derived from the oxidation of metal ions, it is clear that microbial cycling of Fe(II) and Mn(II) is central to many environmental processes.

Progress in this field is being driven by dramatic advances in molecular biology. It is now possible to study microbes at the molecular level. The ability to form genetic mutants and thereby manipulate internal metabolic processes means that a detailed understanding of the metabolic pathways is possible. This, in conjunction with the newest techniques in electron microscopy that allow imaging under ambient conditions (e.g. 66), are allowing further insight into the mechanisms of microbial processing at mineral interfaces.

Conclusion

This volume summarizes an increasingly clear understanding of reaction mechanisms at mineral surfaces on the part of researchers in the field. Along with this understanding comes the attendant realization of the complexity of these reactions. Long standing impediments to the detailed understanding of these complex surface processes are falling as experimental techniques in spectroscopy/microscopy and molecular biology continue to evolve. We hope that as the reader progresses through this volume, new conceptualizations of mineral surfaces and their reactivity will arise and ultimately lead to new avenues of research into the effects of mineral surfaces on the aqueous environment at large.

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