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Peggy A. O'Day
Department of Geology
Arizona State University, Tempe

Abstract. The chemistry, mobility, and bioavailability of contaminant species in the natural environment are controlled by reactions that occur in and among solid, aqueous, and gas phases. These reactions are varied and complex, involving changes in chemical form and mass transfer among inorganic, organic, and biochemical species. The field of molecular environmental geochemistry seeks to apply spectroscopic and microscopic probes to the mechanistic understanding of environmentally relevant chemical processes, particularly those involving contaminants and Earth materials. In general, empirical geochemical models have been shown to lack uniqueness and adequate predictive capability, even in relatively simple systems. Molecular geochemical tools, when coupled with macroscopic measurements, can provide the level of chemical detail required for the credible extrapolation of contaminant reactivity and bioavailability over ranges of temperature, pressure, and composition. This review focuses on recent advances in the understanding of molecular chemistry and reaction mechanisms at mineral surfaces and mineral-fluid interfaces spurred by the application of new spectroscopies and microscopies. These methods, such as synchrotron X-ray absorption and scattering techniques, vibrational and resonance spectroscopies, and scanning probe mi-

croscopies, provide direct chemical information that can elucidate molecular mechanisms, including element speciation, ligand coordination and oxidation state, structural arrangement and crystallinity on different scales, and physical morphology and topography of surfaces. Nonvacuum techniques that allow examination of reactions in situ (i.e., with water or fluids present) and in real time provide direct links between molecular structure and reactivity and measurements of kinetic rates or thermodynamic properties. Applications of these diverse probes to laboratory model systems have provided fundamental insight into inorganic and organic reactions at mineral surfaces and mineral-water interfaces. A review of recent studies employing molecular characterizations of soils, sediments, and biological samples from contaminated sites exemplifies the utility and benefits, as well as the challenge, of applying molecular probes to complicated natural materials. New techniques, technological advances, and the crossover of methods from other disciplines such as biochemistry and materials science promise better examination of environmental chemical processes in real time and at higher resolution, and will further the integration of molecular information into field-scale chemical and hydrologic models.

1. INTRODUCTION

Molecular geochemistry is a rapidly developing field that seeks to study chemical reactions at the molecular level through the application of a variety of spectroscopic and microscopic methods. In studies of the chemistry of environmental phenomena or contamination, the molecular reactions in question often involve the transfer of chemical species among aqueous, solid, and gas phases, with and without the intervention of living organisms. It is now generally recognized that the identity and stoichiometry of chemical species taking part in reactions should be constrained independently by spectroscopic or microscopic information and cannot be deduced unambiguously from macroscopic behavior. With regard to environmental contaminants, a high level of confidence in the prediction of chemical reactivity and transport is required, first because of the toxicity and longevity of many contaminants, and second because of the high cost and technical difficulties associated with

remediation. Therefore predictions of chemical reactivity, phase partitioning, and bioavailability in the environment must have high credibility. Extrapolation of chemical environmental processes over ranges of temperature, pressure, and composition requires fundamental mechanistic understanding that is reaction-based, not simply empirical derivatives valid only for the range of experimental data. This requires knowledge of the chemical form, or speciation, of contaminants, information about how contaminants react or transform as physical or chemical conditions change, and observation of how they become immobilized by soils, minerals, plants, or animals.

Although Earth's surface environment encompasses a vast array of chemical processes and transformations, recent applications of molecular methods in geochemistry have been driven to a large extent by concern about the behavior and fate of environmental contaminants, including metals, radionuclides, synthetic organic compounds, and pathogens. Within the broad scope of geo-

chemistry, spectroscopic and microscopic probes have been used to study a wide variety of geologic materials and phenomena. However, the microscopic-scale reactions that control contaminant mobility, and that are particularly difficult to study, occur primarily at the surfaces of Earth solids (inorganic and biological) and their interfaces with aqueous solutions or with air. Because the field of molecular geochemistry has advanced rapidly as a result of contaminant-related research, this paper focuses how molecular techniques are used to study reactions and fundamental partitioning processes in the context of contaminant species and solid-fluid interfaces. Specifically, this review discusses (1) what we have learned from model systems about fundamental chemical processes at mineral-fluid interfaces by using molecular probes, (2) how molecular techniques are applied in field studies to assess contamination and advise remediation, and (3) how new techniques and applications will advance the field of environmental geochemistry, in particular, for the study of relationships between inorganic and biogeochemical reactions and for the integration of molecular reactions into field-scale hydrologic and geochemical models. Because the link between molecular level processes and larger-scale parameterization is essential for implementation into field models, I begin with a brief review of the connection between microscopic and macroscopic chemical formulations in the context of thermodynamics and kinetics, and the current conceptual basis for describing reactions at mineral surfaces.

2. WHY DO WE NEED MOLECULAR INFORMATION?

The application of macroscopic chemical thermodynamics to geologic phenomena has had a profound effect on the study of the Earth's chemical system. The basic principles of thermodynamics developed in the middle to late nineteenth century and early twentieth century have proven remarkably applicable to the quantitative description of natural chemical systems, especially those at higher temperature. Thermodynamics still remains the most widely used tool to describe geochemical processes as a function of temperature, pressure, and composition for a number of reasons. Most importantly, the basic tenets of thermodynamics describe chemical driving forces, or the general notion that there is an overall chemical "push" for substances to react in a certain fashion. Thermodynamics provides a basic road map for predicting what may or may not happen in a given system. More practically, the large and growing number of chemical species contained in thermodynamic databases, and the computerized retrieval, extrapolation, and free energy minimization algorithms that make this information accessible and useful, allow application of thermodynamics to a wide variety of geochemical systems.

Despite this usefulness, thermodynamics has limitations, and these are most often apparent in environmental systems at lower temperatures, in biological systems, and in the description of reactions at phase boundaries. Thermodynamics applies to chemical processes among large numbers (i.e., Avogadro's number) of molecules and deals with overall reactions among a set of chemical species. Strictly speaking, equilibrium thermodynamics tells us nothing about how a chemical system got to its current state. If a system is assumed to be at equilibrium, however, enough thermodynamic data have been collected and synthesized to predict (at least for a fair number of species) what the distribution of aqueous and gas species and solid phases ought to be. Everything at the surface of the Earth is not expected to be at complete thermodynamic equilibrium (otherwise, all living organisms would evaporate into CO₂ and H₂O), but parts of the system and many species are observed to be at local equilibrium or, at least, at dynamic steady state. If we consider, for example, the release of a toxic contaminant into a river, this can be viewed as a perturbation of the local equilibrium, and we can ask questions such as: What reactions will occur? How long will they take? Over what spatial scale will they occur? This leads to a need to identify actual chemical species and reaction processes and to consider both the thermodynamics and the kinetics of reactions.

To illustrate the relationship between thermodynamic and kinetic species and reactions, consider a simple example: the precipitation of solid lead carbonate, the mineral cerussite (PbCO₃(s)), as a sink for lead, a toxic metal, according to the reaction



(see also *Krauskopf and Bird* [1995, chapter 1] for a good introduction to chemical equilibrium). At thermodynamic equilibrium the distribution of lead and carbonate ions between the aqueous solution and the solid mineral is governed by a constant that is a function of temperature and pressure. We can express this relationship using the familiar equilibrium constant (K_{eq}) and the standard free energy of the reaction (ΔG_r^0):

$$K_{\text{eq}} = \frac{a_{\text{PbCO}_3(\text{s})}}{a_{\text{Pb}^{2+}} a_{\text{CO}_3^{2-}}} \quad (2)$$

$$\Delta G_r^0 = -RT \ln K_{\text{eq}} \quad (3)$$

where R is the gas constant, T is temperature, and K_{eq} is the standard state equilibrium constant. Rather than considering only the concentrations of the reactants and products, thermodynamics uses activities a of species, a measure of its chemical "force" or potential that depends on both its absolute concentration and its degree of nonideal behavior. By convention, the activities of chemically pure solids are set equal to 1 ($a_{\text{PbCO}_3(\text{s})} = 1$ in equation (2)). At equilibrium and constant temperature and pressure, (2) provides a reliable description of how

species will partition between aqueous and solid phases. If we consider the actual process represented by (1), however, we find that the reaction is really at dynamic equilibrium, i.e., the reaction is proceeding forward to precipitate cerussite at some rate k_f :



and backward to dissolve cerussite at another rate k_b :



The rate of appearance (or disappearance) of cerussite in the system as a function of time can be written as a difference between the forward and backward rates:

$$\frac{d[\text{PbCO}_3(\text{s})]}{dt} = k_f - k_b \quad (6)$$

These forward and backward rates depend explicitly on the concentrations of the reactants (where brackets denote concentrations):

$$\text{forward rate} = k_f[\text{Pb}^{2+}][\text{CO}_3^{2-}] \quad (7)$$

$$\text{backward rate} = k_b[\text{PbCO}_3(\text{s})] \quad (8)$$

If the reaction is at equilibrium, the forward and backward rates must be equal:

$$\frac{[\text{PbCO}_3(\text{s})]}{[\text{Pb}^{2+}][\text{CO}_3^{2-}]} = \frac{k_f}{k_b} = K_{\text{eq}}^* \quad (9)$$

A constant K_{eq}^* expressing this equilibrium can be calculated from the rates of the forward and backward reactions. This constant is not necessarily equal to the thermodynamic equilibrium constant K_{eq} because it is calculated only from the concentrations of species, not from their activities. If we account for nonideality using activity coefficients, then the concentrations of species multiplied by their activity coefficients would provide activities, and K_{eq}^* in (9) would equal the activity product (often designated Q) for the reaction.

The description of cerussite precipitation given above is an example of an overall reaction: how we might describe the system if it were given enough time to come to equilibrium. However, if we employ probes to examine chemical species at the molecular level, or consider what is happening over a short period of time, we find that the situation is much more complicated. For example, there are aqueous chemical species taking part in pH-dependent reactions that determine the form of carbon in solution and thus affect the precipitation of cerussite:



If cerussite precipitation is followed at the microscopic scale, we find that the actual molecular species involved

in elementary reactions (one-step reactions with a single transition state [Connors, 1990]) might be different from those in (1). In addition to a number of solution species and a solid, species adsorbed to and desorbed from the surface could also be included and described using elementary reactions. As with any chemical reaction, whether it is inorganic or biochemical, we must choose which kinetic species to include in the elementary reactions that make up the overall process, and hopefully we have molecular or chemical information to guide this choice. Kinetic species in elementary reactions are expressed by their concentrations, not their activities. Nevertheless, we can always add up sets of elementary reactions to obtain an overall chemical reaction, and then calculate an equilibrium constant (if activities of species are used instead of concentrations). Thus the set of kinetic species for any overall chemical reaction is generally larger (and usually more complicated) than the set of equilibrium species. The only constraints on overall reactions are that they go in the same direction as ΔG_r^0 and that the overall reaction rate goes to zero at equilibrium [Connors, 1990].

This connection between the rate of an overall reaction and the driving force supplied by thermodynamics can be expressed by including a free energy term in a rate equation [e.g., Aagaard and Helgeson, 1982; Lasaga, 1995]. The free energy of a reaction not at equilibrium (ΔG_r) is given by

$$\Delta G_r = RT \ln (Q/K_{\text{eq}}) \quad (13)$$

where R , T , and K_{eq} have the same meaning as in (3) and Q is the measured ion activity product for the reaction. By comparing the activity product of species observed in the system (Q) with the expected concentration product at equilibrium (K_{eq}), the ratio Q/K_{eq} provides a measure of how far from equilibrium the reaction is and in which direction it is going (note that $Q = K_{\text{eq}}$, and thus $\Delta G_r = 0$, at equilibrium). Thus the rate of precipitation of cerussite given by (1) could be expressed, for example, by an equation of the form [Lasaga, 1995]

$$\text{rate} = k_0 S_{\text{min}} e^{-E_a/RT} f(\Delta G_r) \quad (14)$$

where k_0 is a measured rate constant, S_{min} is a reactive surface area of the mineral, E_a is the apparent activation energy of the overall reaction, and $f(\Delta G_r)$ is a functional term that includes the “driving force” (or chemical affinity) from thermodynamics (equation (13)), which in this example is the degree of oversaturation or undersaturation of cerussite. As was stressed by Lasaga [1995], equation (14) is a general form in which to write rate equations (and it should be noted that many rate expressions do not contain an explicit term for ΔG_r , but instead use concentrations of species only). In general, rate equations derived from experiments have more terms than are shown in (14) to account explicitly for variables such as concentrations of species in solution, pH, ionic

strength, possible catalytic or inhibitory effects, and different forms of expression for $f(\Delta G_r)$. Rate expressions should be able to account for the difference in reaction rate far from and close to equilibrium and cannot assume that the reaction mechanism is the same for both dissolution and precipitation [Nagy *et al.*, 1991; Nagy and Lasaga, 1992].

The role of molecular probes is to provide us with information, either chemical or physical, about the species taking part in reactions so that we can represent them appropriately in either elementary or overall reactions, and then apply (or derive from experiments) rate or equilibrium constants. In the context of environmental systems the first, and sometimes the most difficult, task is determining the species and stoichiometry of reactions that govern the fate of the elements of interest and then deciding whether they can be treated as equilibrium reactions for the timescale of interest. Reactions that occur at surfaces, and the molecular species involved, are inherently difficult to characterize because their concentrations are usually lower than those of bulk species and because they are often transitory. Making the connection between molecular species, the actual atoms and molecules that are detected with spectroscopic and microscopic probes, and thermodynamic and kinetic species, those species chosen to represent macroscopic chemical behavior, is the crux of applying molecular geochemistry to field-scale environmental problems.

3. MOLECULAR PROCESSES AT MINERAL SURFACES

Our current molecular models of surfaces evolved first from macroscopic observations of surface adsorption, hydroxylation, hydration, oxidation/reduction (redox), and electrical charge and have been followed more recently by spectroscopic and microscopic investigations. It is interesting to note that molecular surface complexation models (SCM), which are often used to describe species partitioning between aqueous and solid phases, were proposed largely in the absence of any direct spectroscopic information [Stumm *et al.*, 1970, 1976; Schindler *et al.*, 1976; Schindler, 1981; Schindler and Stumm, 1987]. Because SCM use molecular-based concepts, they have been readily applied to spectroscopic observations, although our growing knowledge of molecular surface reactions demands modifications to these original models (see below). Numerous reviews of mineral/water interface geochemistry and SCM have appeared in articles and texts, including review of surface free energy and concepts of electrified interfaces [James and Parks, 1982; Parks, 1990], a comprehensive review of adsorption processes and SCM [Davis and Kent, 1990], an advanced text on the surface chemistry of soils and surface processes [Sposito, 1984], SCM description and compilation of data for sorption on hydrous ferric oxides [Dzombak and

Morel, 1990], and review of SCM and the use of spectroscopic constraints [Hayes and Katz, 1996].

Conceptual models of reactions at mineral surfaces are depicted in Figure 1. Surface complexation models treat the surface as a chemical species that takes part in reactions. For oxide and silicate surfaces this species is usually designated ($\equiv\text{SOH}$), where S is a metal atom in the bulk mineral (e.g., Si, Al, Fe) and OH represents a hydroxylated surface oxygen atom. If a perfect crystalline mineral is terminated, it must leave "dangling" bonds where metal atoms are exposed. From studies of cleaving minerals in vacuum, it is known that these unsatisfied bonds are highly reactive and almost immediately pick up any available water or gas molecules. In aqueous solutions, mineral surfaces are both hydrated and hydroxylated, and surface sites ($\equiv\text{SOH}$) react by bonding or releasing H^+ , ions, or compounds from solution (the appendix summarizes types of reactions in SCM and the molecular model implied by them). The observation that mineral surfaces can release or accumulate protons as a function of pH led to the idea that minerals have a characteristic pH where net surface charge is zero: the pH point of zero charge (pH_{pzc}) [Parks, 1965; Sposito, 1984]. The pH_{pzc} , which is a surface expression of the bulk crystalline mineral structure in contact with water, is considered to be a fundamental property of mineral surfaces, and pH_{pzc} values have been tabulated from experimental measurements and calculated theoretically (summarized by Davis and Kent [1990] and Sverjensky [1994]).

In SCM, the development of negative or positive charge at mineral surfaces from the adsorption of protons and ions is balanced by attraction of counter ions slightly further out in the interfacial region (Figure 1), which creates an electrical double layer between mineral surfaces and bulk solution. Variations in the stoichiometry of reactions at surfaces (see appendix) arise from the number of SOH groups assumed to take part in a complexation reaction (usually one or two is assumed), from the species bonded to the surface from solution (ions, neutral species), from species released to solution (ions, protons), and from whether bonding is inner sphere (loss of water ligands to form direct bonds between sorbate and sorbent atoms) or outer sphere (retention of water ligands around the sorbate and electrostatic attraction or hydrogen bonding between sorbate and sorbent). Because this approach is completely general, it can be applied to any exchangeable species, not only a mineral surface site. For example, a surface complexation model was recently applied to protonation and metal binding by functional groups on bacterial cell walls [Fein *et al.*, 1997]. It is important to note that all SCM assume equilibrium, i.e., that there is a distribution of species on the left- and right-hand sides of the appendix equations for which there exists a constant K for each reaction at equilibrium (at a given pressure and temperature).

In addition to exchanging species on a mineral sur-

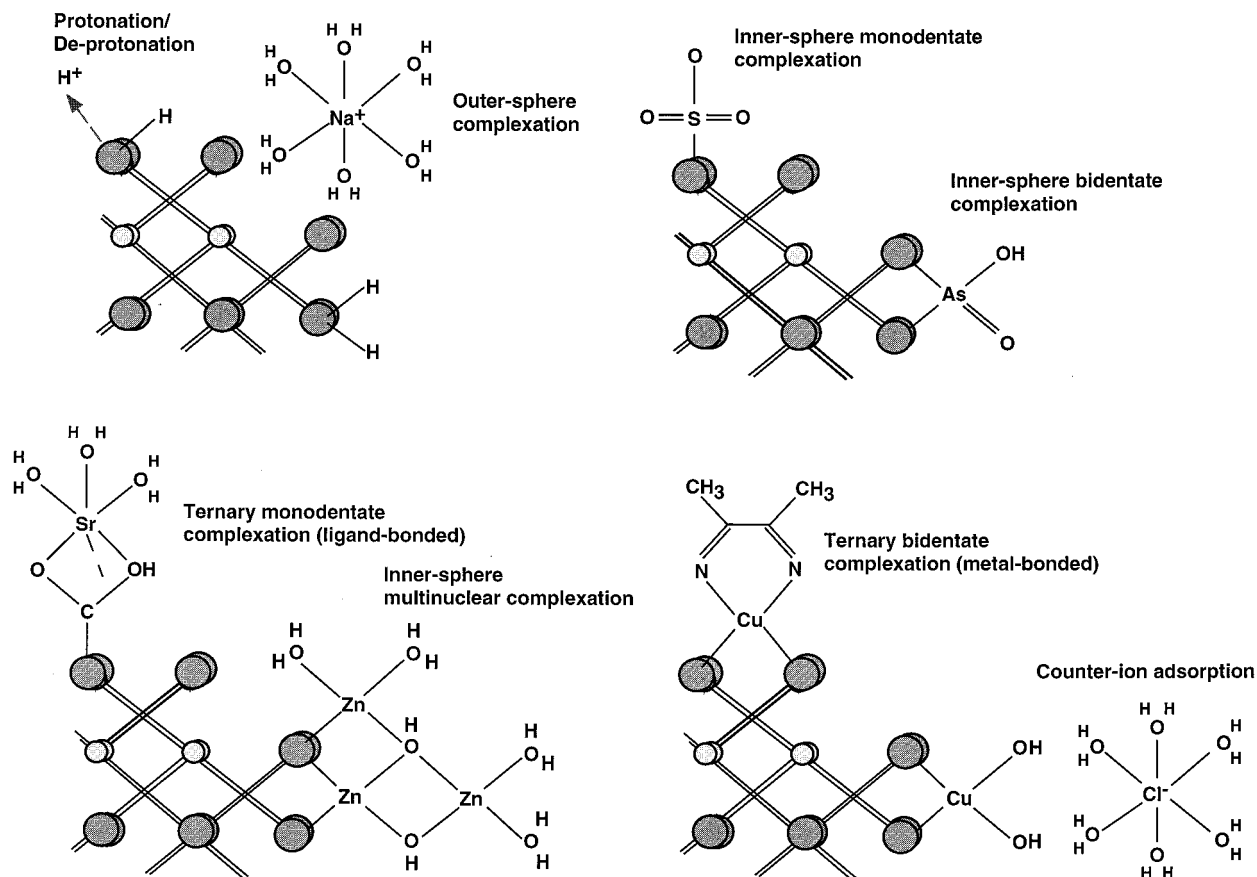


Figure 1. Schematic representation of surface reactions. The surface is a generic oxide mineral (large atoms are oxygen; small atoms are a metal cation such as iron or aluminum) in contact with an aqueous solution containing dissolved ions. Although not depicted for clarity, the oxide surface is completely hydroxylated, and water molecules occupy the surface interfacial region. See the appendix for the surface complexation reactions associated with the molecular models shown here.

face, a number of other chemical processes can take place, including electron transfer (oxidation state changes), coordination changes (number and/or type of ligands around the adsorbed species), relaxation or reconstruction of the surface structure, dissolution of the substrate, and precipitation of new phases. As is discussed below, it is clear that mineral surfaces are dynamic and heterogeneous: more than one of these processes might occur simultaneously, one process may follow another, and reactions do not occur uniformly on surfaces. Different surface phenomena can be represented by reactions that contain a surface species ($\equiv\text{SOH}$), although it is not clear that the SCM approach is necessarily the best chemical representation for all reaction types or for translation to real field systems. In addition to a lack of equilibrium constants for different types of reactions, current SCM contain a large number of adjustable parameters that are difficult to constrain in the field [Davis and Kent, 1990]. The role of molecular probes is to provide evidence for the chemical reactions governing the behavior of species in order to either constrain SCM, or to indicate the appropriate type of reaction (e.g., redox, precipitation). Even with molecular information,

however, it can still be difficult to completely constrain the stoichiometry of all surface reactions, especially with respect to surface geometries, charge of individual complexes, spatial extent of reactions, release of protons to solution, and timescales of reactions. It is the same problem faced when writing elementary reactions in kinetic theory: stoichiometry is very important, but it is difficult (and time consuming) to unambiguously determine it.

4. MOLECULAR METHODS AND TOOLS

The need for direct identification of molecular chemical species to constrain surface and bulk chemical reactions has lead to the increasing application of spectroscopies and microscopies to environmental systems. As pointed out succinctly by Sposito [1986, p. 226], "molecular concepts can be studied only by molecular methods." This mantra of the 1980s has fueled the molecular examination of a number of model systems and, more recently, the study of natural systems. Spectroscopic probes typically provide chemical speciation or bonding

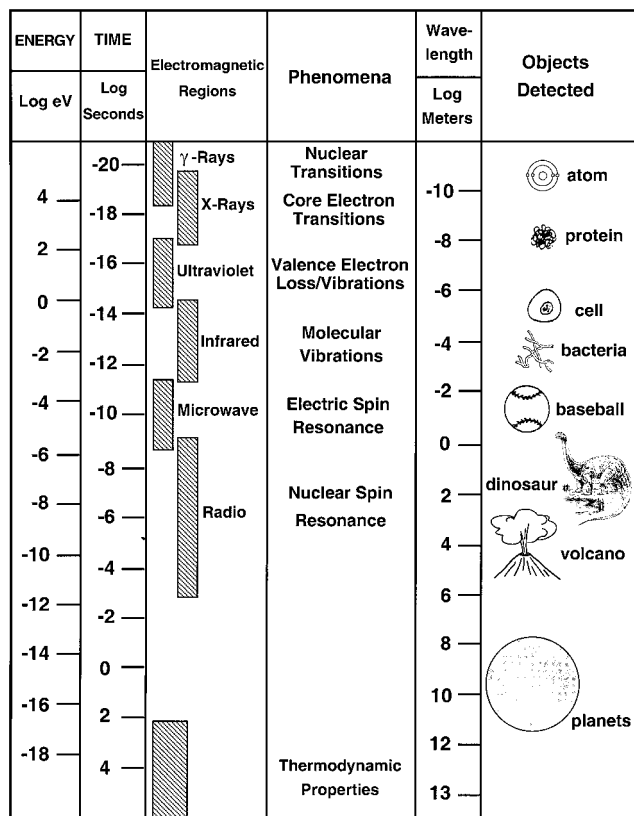


Figure 2. The electromagnetic spectrum. Radiation of different energy or frequency is used to incite specific types of electronic excitations, leading to different types of spectroscopies, or to the study of different time-dependent phenomena. Alternatively, radiation employed to detect an object must have a wavelength equal to or less than the object's dimensions. Modified from *Sposito* [1984], *Calas and Hawthorne* [1988], and *Winick* [1987].

information, while microscopic probes supply images or spatially resolved information. Of course, the use of a single probe never supplies a complete picture of molecular-scale reactions because the information obtained is sensitive to the nature and timescale of the excitation process: each molecular tool is specific, and the information it provides depends on what is being measured. Consequently, different methods are best used in a complementary fashion.

In general, spectroscopy involves the interaction of energy with matter. We can consider energy changes in the equivalent forms of momentum k , frequency ν , or wavelength λ ($= 1/\nu$) as this interaction takes place [e.g., *Calas and Hawthorne*, 1988; *Graybeal*, 1988] (Figure 2). Because atomic processes are quantized, energy of a particular frequency (or equivalently, wavelength) must be applied in order for something to happen. This usually results in an energy change from a ground state to an excited state (a transition). At the atomic and molecular levels, these transitions can be quite complicated, but this can be used advantageously by supplying radiation of the right frequency or energy to incite a particular

kind of transition. Whenever excited states are created, there are many different electronic processes that occur, but just as the mode of excitation is selected, the method of detection can also be selected for a particular kind of information (the other nonselected electronic processes often contribute to "background"). A number of phenomena are possible as energy interacts with matter, and this gives rise to different types of spectroscopies and microscopies [*Calas and Hawthorne*, 1988]: (1) nothing (energy is transmitted with no change in k or ν); (2) frequency does not change, but the interaction affects k , causing elastic scattering and diffraction processes which can provide spatial information; (3) absorption of radiation of a particular frequency ν results in some internal process (e.g., nuclear, electronic, vibrational) that gives rise to a number of absorption spectroscopies; and (4) absorption of radiation of a frequency ν results in an internal process that causes emission of radiation at a different frequency, generating a variety of emission spectroscopies such as inelastic scattering, luminescence, or energy loss.

Given the diversity of excitation phenomena, an amazing array of spectroscopic and microscopic methods have been developed to study a broad range of chemical and physical attributes. Table 1 lists some of the more popular molecular techniques that have been applied to environmental geochemistry and briefly summarizes the kinds of molecular information they provide (acronyms and abbreviations are deciphered in the glossary following the appendix). Readers should consult the review papers and volumes noted in Table 1 for details of each method.

Because each spectroscopic and microscopic technique is a specialty in itself, it is easy to become overwhelmed by the details of theory and methodology (and probably discouraged from using it!). However, the idea behind these probes (energy in, interaction with matter, and energy out) is common to all, and they can be generalized by considering the kind of energy within the electromagnetic spectrum each technique uses (Figure 2). Electromagnetic radiation has both particle and wave properties, and thus light of a particular wavelength also corresponds to a spatial scale of detection. Thus longer-wavelength radiation is used to detect bigger objects, or conversely, to study phenomena that occur over longer timescales [*Sposito*, 1984; *Winick*, 1987]. The form of the excitation radiation (e.g., X rays, electrons, visible light) can be the same as, or different from, that measured after excitation. High-energy radiation (X rays, generated by laboratory or synchrotron sources) causes atomic level excitations (absorption and emission of radiation) that are used to probe bonding states (core or valence level) around an atom (e.g., *XPS*, *Auger*, *XANES*). (Abbreviations in italics are defined in the glossary following the appendix.) If lower energy radiation is used, such as infrared, the vibrational modes of bonds between atoms absorb energy and give rise to absorption spectra (*IR* and *FTIR*). Lasers, which emit

radiation at a single frequency, are commonly used as a radiation source in the ultraviolet, visible, and infrared regions. At still lower energy, microwave or radiowave radiation is applied in the presence of a magnetic field to excite nuclear and electron magnetic resonances (e.g., *NMR* and *ESR*) that are sensitive to the surrounding molecules, from which information about local bonding is obtained. Scattering of radiation is used to obtain spatial information (e.g., X-ray diffraction and scattering), and some methods combine an excitation event at X-ray energies with scattering of radiation (e.g., *SR*, *EXAFS*, or *AFS* and *XSW*).

For all of these techniques, the level and type of quantification that allows extraction of chemical information varies. One of the main distinctions is whether the method provides information about elemental or isotopic abundance, about chemical form, bonding, or speciation, or about both. Quantification of either absolute abundance or chemical speciation requires comparison with standards or known species that are either experimentally determined or theoretically calculated. Spectral quantification ranges from comparative “fingerprinting” (i.e., matching distinctive spectral features of knowns and unknowns) to *ab initio* theoretical calculations of spectra based on quantum chemistry, depending on the technique and its level of theoretical maturity. When shopping for molecular probes for real applications, it is important to consider what chemical information is needed for a particular problem, (e.g., oxidation state of an element, types of ligands, presence or absence of a crystalline structure) and whether or not a technique is amenable to your system (e.g., soil particles, aqueous solution, cell membrane).

While spectroscopies usually tell us something about chemistry, microscopies provide spatial information and arise (generally) from the interaction of energy with matter that either focuses or rasters radiation in some way to produce an image (Table 1). Scanning electron microscopy (SEM), as a familiar example, uses electrons as the radiation source and secondary or backscattered electrons from the target material to construct topography. Microscopies can either be strictly surface sensitive or penetrate into or through the material. A number of electron microscopies (SEM, *TEM*, *HR-TEM*, *STEM*) have become mainstays of Earth, material, and biological sciences because they operate over a large spatial range (micrometers to angstroms) and can image a wide variety of materials [Goldstein *et al.*, 1981]. A drawback to electron microscopies is that they are usually vacuum based (although “environmental” sample chambers allow for the introduction of a gas or water vapor around a sample). The newer family of scanning probe microscopes (SPM), which are not strictly vacuum based, use either electron tunneling (*STM*) or atomic level force interactions (*AFM*) to produce surface images at the angstrom to micrometer scale. Although the nature of the excitation is fundamentally different between *STM* and *AFM*, both share the technology of an atomic-sized

tip positioned by a microcantilever and rastered over a surface. Scanning tunneling microscopy relies on measuring the current produced by the tunneling of electrons between the tip, to which a small voltage is applied, and the surface atoms in order to generate “images” of atoms. Atomic force microscopy is slightly different in that it measures the extremely small deflections of a molecular tip by its interaction with atoms on the surface. Both are capable of producing images of angstrom-scale features, although *STM* at present is much better at atomic imaging than *AFM*, which is better suited for nanometer- to micrometer-scale imaging. These advancements in imaging at the atomic level have dramatically changed the way we view surfaces and their reactions, and new breakthroughs in biological, Earth, and industrial materials using these methods are anticipated.

Some of the most useful molecular techniques applied to environmental geochemistry are those that allow examination of processes in the presence of a water or fluid medium that is relevant to natural conditions. This is not to say that vacuum-based techniques are not useful for interpreting natural materials. In fact, they are particularly good for examining chemistry and structure of the surfaces and interiors of solid particles, and they have been used widely in many aspects of geochemistry [e.g., Buseck, 1992; Navrotsky, 1994]. Water, however, is the primary medium of transport of environmental contaminants; likewise, biochemical reactions take place in aqueous media and often across biological membranes that are water- or fluid-based. Several techniques developed in recent years have proven to be particularly useful for examining reactions that control species partitioning between aqueous and solid phases or for imaging surfaces in nonvacuum environments. The summaries discussed below rely heavily on recent studies that have employed synchrotron radiation-based methods (*XANES*, *EXAFS*, *SR-XMP*, *XSW* and *SR-XAF* analysis), *IR*, *ESR*, and *NMR* spectroscopies, and *SPM* (*AFM* and *STM*), together with more traditional methods such as *SEM*, *HR-TEM*, *EM*, *SIMS*, and *XRD*.

5. RECENT STUDIES IN MOLECULAR ENVIRONMENTAL GEOCHEMISTRY

5.1. Model Systems

A number of model systems have been studied with a variety of molecular probes. Taken together, these studies are supplying a more accurate and detailed picture of reactions at aqueous-solid interfaces from which generalizations can be drawn. Most studies to date have investigated model systems of relatively simple inorganic and/or organic aqueous ions or compounds reacted with pure mineral phases or well-characterized soils and sediments. Fewer studies have investigated reactions involving bacteria or biological molecules, although this is a rapidly expanding field of interest. Increasingly, multiple spectroscopic and microscopic probes are being applied

TABLE 1. Summary of Selected Analytical Methods for Molecular Environmental Geochemistry

<i>Analytical Method</i>	<i>Type of Energy</i>	
	<i>Source</i>	<i>Signal</i>
Absorption, emission, and relaxation spectroscopies		
IR and FTIR	infrared radiation	transmitted infrared radiation
Synchrotron XAS (XANES and EXAFS)	synchrotron X rays	transmitted or fluorescent X rays; electron yield
Synchrotron microanalysis (XRF, XANES)	synchrotron X rays	fluorescent X rays
EELS (also called PEELS)	electrons	electrons
XPS and Auger spectroscopy	X rays	electrons
Resonance spectroscopies		
NMR	radio waves (+ magnetic field)	radio waves
ESR (also called EPR)	microwaves (+ magnetic field)	microwaves
Scattering and ablation		
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X rays (synchrotron or laboratory)	scattered X rays
SIMS	charged ion beam	atomic mass
LA-ICP-MS	laser	atomic mass
Microscopies		
STM	tunneling electrons	electronic perturbations
AFM (also called SFM)	electronic force	force perturbation
HR-TEM and STEM	electrons	transmitted or secondary electrons
SEM/EM with EDS or WDS chemical analysis	electrons	secondary, or backscattered electrons; fluorescent X rays

Abbreviations are defined in the glossary.

to systems to circumvent biases inherent in using any one technique. Summarized below are some general observations and examples from the literature about environmentally relevant surface reactions from the molecular viewpoint.

5.2. What Have We Learned About Surface Reactions From the Study of Model Systems?

5.2.1. Adsorption at mineral surfaces may or may not be strongly controlled by electrostatic attraction/repulsion. This observation was made some time ago from the macroscopic study of charge development and metal ion adsorption on mineral surfaces [James and Parks, 1982] and has spurred the microscopic examination of inner and outer sphere surface complexation. For alkali and alkaline earth cations, and for oxidized anions such as chromate, electrostatic forces are important in controlling sorption because these large ions appear to retain their solvation shells upon sorption and their

attraction to surfaces is governed to a large extent by near-surface electrostatic charge. Evidence from IR, NMR, and XAS studies indicates outer sphere adsorption or mixtures of inner and outer sphere adsorption for these ions depending on the solid [Peterson *et al.*, 1996; Kim *et al.*, 1996a, b; Kim and Kirkpatrick, 1997; Parkman *et al.*, 1998]. For most other cations and anions, including the actinide elements, molecular probes have shown that adsorption occurs primarily via inner sphere complexation (monodentate-tridentate) that is not strongly related to the development of charge on the surface (see reviews by Manceau *et al.* [1992], Fendorf *et al.* [1994], Brown *et al.* [1995], and Schulze and Bertsch [1995]). An example of the lack of correlation between macroscopic sorption behavior and microscopic reactions is illustrated in Figure 3 by the contrasting sorption behavior of $\text{Co}^{2+}(\text{aq})$ on quartz and rutile surfaces [O'Day *et al.*, 1996]. The sorption of the metal cation is not simply related to increasing negative charge on the mineral surface with increasing pH above the pH point of zero

<i>Chemical Information</i>	<i>Notes</i>	<i>References</i>
molecular and lattice vibrations; local (first neighbor) bonding	nonvacuum; bulk liquids, crystalline and amorphous solids	<i>McMillan and Hofmeister</i> [1988]
quantitative local structural information; oxidation state and atomic bonding geometry	nonvacuum; element specific; liquid, crystalline, amorphous and materials	<i>Brown et al.</i> [1988, 1995]
elemental analysis (XRF); oxidation state and atomic bonding geometry (XANES)	vacuum or nonvacuum; spatial resolution, element specific; crystalline and amorphous materials	<i>Smith and Rivers</i> [1995], <i>Smith</i> [1995]
oxidation state and atomic bonding geometry (similar to XANES)	vacuum; high concentrations, crystalline and amorphous materials	<i>Buseck and Self</i> [1992], <i>Champness</i> [1995]
oxidation state; chemical bonding information	vacuum; surface sensitive; spatial resolution	<i>Hochella</i> [1988], <i>Perry et al.</i> [1990]
sensitive to electron density (nuclear shielding); local (first neighbor) bonding	nonvacuum; bulk liquids and solids; requires NMR-active isotope	<i>Wilson</i> [1987], <i>Kirkpatrick</i> [1988]
sensitive to electron density (electron coupling); local (first neighbor) bonding	nonvacuum; bulk liquids and solids; sensitive to low concentrations; requires paramagnetic ions	<i>Motschi</i> [1987], <i>Calas</i> [1988]
quantitative structural information	nonvacuum; crystalline and amorphous materials; microdiffraction with synchrotron sources	<i>Bras et al.</i> [1993]
elemental and isotopic analysis	vacuum; surface sensitive to low concentrations; spatial resolution	<i>Metson</i> [1990]
elemental and isotopic analysis	nonvacuum; sensitive to low concentrations; spatial resolution	<i>Perkins and Pearce</i> [1995]
molecular and atomic-scale surface imaging; surface electronic structure	vacuum and nonvacuum; conducting/semiconducting materials only	<i>Chen</i> [1993], <i>Hochella</i> [1995]
molecular-scale surface imaging	nonvacuum; imaging in air or liquid	<i>Sarid and Elings</i> [1991], <i>Hansma and Hoh</i> [1994]
bulk morphology and crystallinity; particle- to atomic-scale spatial resolution	vacuum or light element atmosphere	<i>Buseck</i> [1992]
morphology over wide magnification; quantitative or qualitative chemical analysis (EDS/WDS)	vacuum or light element atmosphere	<i>Goldstein et al.</i> [1981], <i>Reed</i> [1995]

charge for quartz and rutile. At similar cobalt surface sorption densities, molecular evidence from EXAFS analysis suggests that sorption is controlled in the case of rutile by the availability of geometrically favorable surface sites, and no evidence for precipitation of cobalt is observed. In the case of quartz, the lack of favorable bonding sites leads to the precipitation of a cobalt hydroxide phase at low surface coverages and higher *pH*, and uptake from solution is not correlated directly with surface charge (Figure 3). Model studies have shown that the fit of the adsorbed atom, in terms of ion size, charge, and polyhedral coordination, with the structure of the substrate is an important factor in sorption in addition to macroscopic variables such as *pH*, solution concentration, and surface concentration [Waychunas *et al.*, 1993; Charlet and Manceau, 1992; O'Day *et al.*, 1994a; Bargar *et al.*, 1997a, b; Farquar *et al.*, 1997; Fendorf *et al.*, 1997]. Other studies note the similarities between metal-ligand exchange rates in solution and on surfaces, and

suggest that local bond strength and aqueous coordination chemistry are useful guides for predicting the behavior of metal ions on surfaces [Casey and Ludwig, 1995; Ludwig *et al.*, 1995, 1996; Phillips *et al.*, 1997]. Conflicting spectroscopic and solution chemistry evidence exists, however, regarding the mode of sorption of polyprotic anions such as SO_4^{2-} , PO_4^{3-} , and SeO_4^{2-} . Depending on the spectroscopic method used, the substrate, and the anion concentrations in solution, both inner and outer sphere sorption modes have been proposed, and it is possible that both modes occur [Hayes *et al.*, 1987; Manceau and Charlet, 1994; Persson and Lovgren, 1996; Eggleston *et al.*, 1998].

Evidence from numerous macroscopic studies of adsorption of organic and organometallic compounds onto mineral surfaces has established that complexation is governed by the reactivity of specific functional groups of the organic compound (see summaries by Spósito [1984], Schwarzenbach *et al.* [1993], and Stone *et al.*

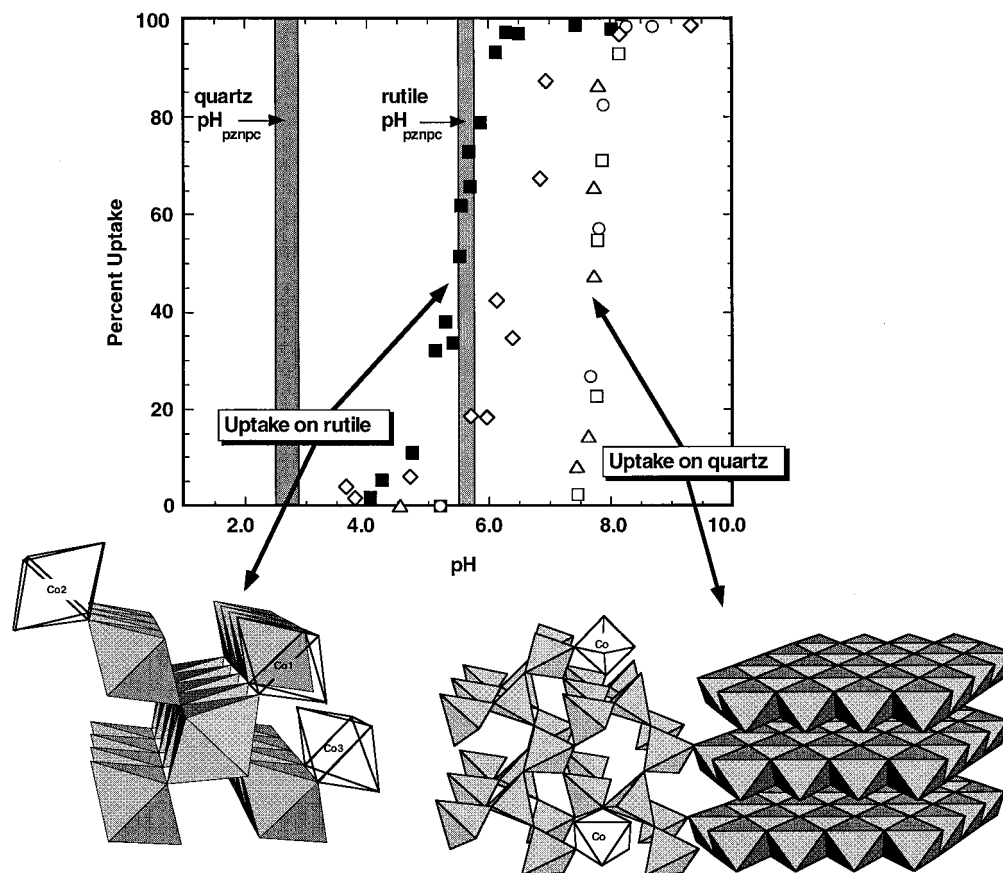


Figure 3. Macroscopic adsorption of $\text{Co}^{2+}(\text{aq})$ on rutile (TiO_2) (solid symbols) and quartz ($\alpha\text{-SiO}_2$) (open symbols) shown as percent uptake from solution as a function of $p\text{H}$ compared with microscopic models of sorption deduced from EXAFS spectroscopy. Above the $p\text{H}$ point of zero net proton charge ($p\text{H}_{pznpc}$) of a mineral, the mineral surface has a net negative charge because protons are removed as $p\text{H}$ increases; below the $p\text{H}_{pznpc}$, the mineral surface is net positively charged because protons are adsorbed. For $\text{Co}^{2+}(\text{aq})$ uptake onto rutile and quartz, sorption of positively charged cobalt does not follow as a consequence of negative charge development on the mineral surface. This behavior is accounted for by sorption onto specific surface structural sites that are more favorable geometrically for sorption on rutile, resulting in cobalt uptake at lower $p\text{H}$, and less favorable for sorption on quartz, leading to suppression of uptake and formation of a cobalt-hydroxide-like precipitate at higher $p\text{H}$. Sources and symbols are as follows: $[\text{Co(II)}]_{\text{tot}} = 1.1 \times 10^{-5} \text{ M}$ and background electrolyte (B.E.) = 10^{-3} M KNO_3 , solid squares (data from James [1971]). $[\text{Co(II)}]_{\text{tot}} = 1.2 \times 10^{-5} \text{ M}$ and B.E. = 10^{-3} M KNO_3 , open diamonds (data from James [1971]). $[\text{Co(II)}]_{\text{tot}} = 3 \times 10^{-4} \text{ M}$; B.E. = 0.01 M (open circles), 0.1 M (open squares), and 1.0 M (open triangles) NaNO_3 (data from O'Day [1992]). (Reprinted and modified from O'Day *et al.* [1996] with permission from Elsevier Science.)

[1993]). A number of bonding mechanisms can be invoked, depending on the chemical nature of the organic functional group and the mineral surface site (Table 2), but the molecular details of these interactions have not been extensively studied by spectroscopic methods. Most characterization has been done with IR and FTIR, which have limited sensitivity, and suggests that many organic ligands can be characterized by inner sphere complexation via a ligand exchange reaction with surface OH groups (see, for example, Zeltner *et al.* [1986], Tejedor-Tejedor *et al.* [1990, 1992], Yost *et al.* [1990], and Biber and Stumm [1994]). A recent detailed study of salicylate anions sorbed to colloidal alumina using absorption and fluorescence excitation and emission spectroscopy has

suggested the presence of up to three distinct inner sphere complexes and one outer sphere complex as $p\text{H}$, ionic strength, and anion concentration are changed [Ainsworth *et al.*, 1998]. Despite this apparent complexity, this study notes the similarity in spectra among aqueous and sorbed Al salicylate complexes, suggesting that the spectroscopic study of aqueous organic complexes may provide useful analogies for surface complexes. For organometallic complexes, evidence primarily from NMR and ESR has indicated the formation of ternary surface complexes (i.e., cation-ligand-surface site) in which surface bonding can occur via the ligand or the metal (Figure 1 and Table 1) (see reviews by Motschi [1987] and Schindler [1990]). These studies suggest that

transition metal ions tend to form direct bonds to oxide surfaces, usually with the organic ligand on the solution side. Likewise, XAS studies of Co, Ni, Cu, Zn, and Pb complexation by humic substances shows that these metals form inner sphere complexes in a specific coordination site of the humic material [Xia *et al.*, 1997a, b]. In contrast, a ^{15}N NMR and XRD study of pyridine adsorption on cation-exchangeable clay (hectorite) concluded that pyridine is hydrogen-bonded to water molecules in clay interlayers and forms water-bridged complexes with interlayer cations such as K^+ , Na^+ , Ca^{2+} [Ukrainczyk and Smith, 1996]. No evidence was found for direct bonds between pyridine and interlayer cations, which is consistent with the aforementioned observation that these larger cations do not easily exchange water ligands and tend to remain fully hydrated.

From these model studies, some generalities are becoming apparent: (1) basic polyhedral units or cation-ligand geometries in solution remain intact upon adsorption; (2) surface ligands form polyhedral linkages with sorbate molecules and compete with solution ligands for bonding, (3) the strength of ion solvation is an important factor in inner versus outer sphere sorption modes, and (4) knowledge from inorganic and organic chemistry regarding coordination polyhedra, metal-ligand bond strengths, and rates of ligand exchange provide useful guides for predicting sorption behavior. Molecular dynamic and *ab initio* calculations are also contributing significant insight into the energetics and geometries of sorbed species (see, for example, Lasaga [1992] and Tossell [1995]). To date, however, the level of detail provided by microstructural observations and calculations has not in general been explicitly transferred to macroscopic sorption models. Several studies in model systems have shown how molecular information can be used to independently constrain reactions in SCM [Waite *et al.*, 1994; Katz and Hayes, 1995a, b], but this approach has yet to be widely applied and tested in field settings. Current SCM are relatively insensitive to microscopic variations and have a number of limitations. Most notably, complexation is treated using one or two surface binding sites which are often arbitrarily chosen; there are a number of poorly constrained adjustable parameters including estimation of reactive surface sites; the ability to account for competition among multiple sorbate ions is poor; and nonideal behavior (i.e., activity coefficients) is modeled by calculation of surface charge at a given *pH* based on adsorption of protons and ions which, as discussed above, may not accurately describe inner sphere sorption.

5.2.2. Sorption of ions from solution is a continuum among mononuclear adsorption, multinuclear cluster formation, and surface precipitation that may or may not be epitaxial. This is another general observation that was originally deduced from macroscopic studies of metal hydroxide sorption and precipitation and surface charge development [James and Healy, 1972a, b, c; James *et al.*, 1975; Farley *et al.*, 1985] and has

TABLE 2. Mechanisms of Adsorption for Organic Compounds in Soils

<i>Mechanism</i>	<i>Principal Organic Functional Group</i>
Cation exchange	amines, ring NH, heterocyclic N
Protonation	amines, ring NH, heterocyclic N, carbonyl, carboxylate
Anion exchange	carboxylate
Water bridging	amino, carboxylate, carbonyl, alcoholic OH
Cation bridging	carboxylate, amines, carbonyl, alcoholic OH
Ligand exchange	carboxylate
Hydrogen bonding	amines, carbonyl, carboxyl, phenylhydroxyl
Van der Waals bonding	uncharged, nonpolar organic functional groups

From Sposito [1984].

since been supported by spectroscopic evidence [Chisholm-Brause *et al.*, 1990a, b; Charlet and Manceau, 1992; O'Day *et al.*, 1994a, b; Katz and Hayes, 1995b; Bargar *et al.*, 1997a]. At low surface sorption densities, ions sorb as mononuclear inner or outer sphere complexes, and surface bonding is generally monodentate or bidentate. Several studies have shown that multinuclear oxygen-bridged cation clusters form at low total sorption densities, generally well below monolayer coverages (<5%) or coverages corresponding to the total number of ionizable protons. The onset of polymerization of metal cations occurs at different sorption densities on different solids, and nucleation and growth of surface clusters is probably influenced by the local polyhedral geometry of the sorbate at a particular surface site [Chisholm-Brause *et al.*, 1990a, b; Charlet and Manceau, 1992; Manceau *et al.*, 1992; Manceau and Charlet, 1992; O'Day *et al.*, 1994a, b; 1996; Bargar *et al.*, 1997a, b].

Early macroscopic studies of metal sorption and surface electrophoretic mobility suggested that hydroxide phases can form in the presence of mineral surfaces from solutions undersaturated with respect to the bulk thermodynamic solubility of the precipitating phase, forming a "surface precipitate" [James and Healy, 1972c; Farley *et al.*, 1985; Dzombak and Morel, 1990]. Spectroscopic studies have since shown that initially small surface clusters can grow to three-dimensional precipitates in which the atomic structure is similar, but not always identical, to the corresponding homogeneously precipitated phases. In addition, spectroscopic and microscopic evidence suggests that newly precipitated or coprecipitated phases can either grow epitaxially (i.e., as an oriented overgrowth) on existing substrates [Charlet and Manceau, 1992; O'Day *et al.*, 1994b, 1996; Chiarello and Sturchio, 1994], form as separate particles [Fendorf *et al.*, 1996; Towle *et al.*, 1997], or form solid solutions in which poisoning of crystallite growth can occur [Waychunas *et al.*, 1993, 1995, 1996; Myneni *et al.*, 1997b]. The implication of these model studies for natural systems is that

equilibrium thermodynamic solubility products of pure phases are not appropriate for describing metal uptake in cases where amorphous, metastable, or solid solution phases are forming. In addition, thermodynamic data for metastable solids are often conflicting or poorly known, and rates of conversion to thermodynamically stable phases in the presence or absence of mineral surfaces or biological mediation have not been investigated for many systems.

5.2.3. Surfaces can dissolve and contribute ions to surface complexes and precipitates, surface reactivity varies as a function of solution chemistry, and surface reactions are spatially heterogeneous. Abundant evidence has accumulated to show that at the microscopic level, mineral surfaces are very heterogeneous. Scanning probe microscopic imaging in particular has highlighted the dynamic nature of surfaces and documented the migration, appearance, and disappearance of surface features such as steps, vacancies, adsorbed atoms, and defects (reviewed by *Hochella* [1995]). For the uptake of species from solution, it has been shown that minerals can either incorporate ions from solutions into their structures, or dissolve and contribute ions to surface precipitates, depending on the solubility of the mineral in solution. For example, carbonates are very soluble and remarkably surface reactive whether close to or far from solution-solid equilibrium. Scanning probe and electron microscopies have shown surface modifications and roughening on the timescale of minutes [*Gratz et al.*, 1993; *Dove and Hochella*, 1993; *Stipp et al.*, 1994], and estimates of real-time dissolution rates for calcite and sulfate minerals (celestite and barite) using AFM have been attempted [*Dove and Platt*, 1996; *Jordan and Ram-mensee*, 1998]. Spectroscopic and X-ray scattering studies of adsorbate ions (both cations and anions) on calcite indicate substitution into the carbonate structure in surface layers for large ions (such as Pb^{2+}) [*Sturchio et al.*, 1997] and to much greater depths below the surface for smaller ions (such as Cd^{2+}) and anions, perhaps due to diffusion or to dissolution and reprecipitation along microfractures [*Pingitore et al.*, 1992; *Stipp et al.*, 1992; *Reeder et al.*, 1994; *Xu et al.*, 1996].

Oxides and sheet silicates are generally less soluble than carbonates and sulfates and apparently experience less surface modification. Solution studies and XAS have suggested that these mineral substrates can dissolve and contribute ions to a new precipitate, either a homogeneous phase or a solid solution with ions from the aqueous phase [*d'Espinose de la Caillerie et al.*, 1995; *Scheidegger et al.*, 1996, 1997]. For example, dissolution of sheet silicates, which releases silicon and aluminum to solution, may lead to the precipitation of gibbsite ($\text{Al}(\text{OH})_3$) or, in the presence of aqueous metal ions, may precipitate a layered metal-aluminum-hydroxide solid solution [*Scheidegger et al.*, 1997; *Thompson et al.*, 1997]. The formation of a solid solution is one explanation for the apparent low solubility of "surface precipitates" relative to pure phases noted above, although

evidence suggests that kinetic and epitaxial effects may also contribute to differences in solubility.

5.2.4. Minerals can donate electrons to and accept electrons from surface species on a local molecular scale, creating electron flow paths and surfaces that are heterogeneous with respect to oxidation state. Electron transfer and changes in oxidation state of elements at mineral surfaces and among sorbed species have been well documented macroscopically (see reviews by *Stone and Morgan* [1987], *Hering and Stumm* [1990], and *White* [1990]). Electron transfer is an important process in solute sorption, in mineral dissolution and precipitation, and at mineral-biological interfaces. Spectroscopic and microscopic tools are especially useful for examining molecular mechanisms of redox reactions. Disequilibrium with respect to oxidation state is the rule rather than the exception for many species in natural systems, so determination of reaction rates is critical. Many common minerals containing transition metals are conductors or semiconductors, making them functionally infinite sources and sinks of electrons as long as the bulk structure is manifest at the surface (which is not always the case). It has been observed that minerals such as sulfides and iron(II)-bearing minerals, which form under reduced conditions, commonly react and oxidize at Earth's surface conditions and become coated by precipitates of oxide or hydroxide minerals, resulting in changes in surface reaction mechanisms and rates [*My-croft et al.*, 1990; *Moses and Herman*, 1991; *Nesbitt and Muir*, 1994; *Peterson et al.*, 1997a]. Molecular spectroscopies and microscopies have been used to characterize the redox heterogeneity of surfaces, the reaction mechanisms of electron transfer, and their rate constants (see reviews by *Bancroft and Hyland* [1990] and *Hochella* [1995]). In some recent examples, *Eggleson et al.* [1996] used a combination of XPS, STM, and Monte Carlo calculations to derive molecular mechanisms and rate constants for electron transfer between pyrite and oxidized Fe(III) surface species (Figure 4). The mechanism of reductive dissolution of birnessite by arsenious acid was examined microscopically using XPS, which identified a Mn(III) surface-intermediate species [*Nesbitt et al.*, 1998]. Heterogeneous oxidation of Mn(II) at hematite and albite surfaces was studied by XPS and micro-XRD [*Junta and Hochella*, 1994]. Subsequently, *Junta-Rosso et al.* [1997] used these microscopic observations in a geometrical description of the reactive surface to develop a kinetic model and then to fit previously published laboratory rate data [*Davies and Morgan*, 1989]. Disagreement over whether or not the spectroscopic observations in the system studied by *Junta and Hochella* [1994] and their subsequent kinetic model were actually applicable to the macroscopic system studied by *Davies and Morgan* [1989] points out the difficulty in developing generally transferable rate laws for specific microscopic reactions (see comment by *Morgan and Davies* [1998], and reply by *Rosso et al.* [1998]).

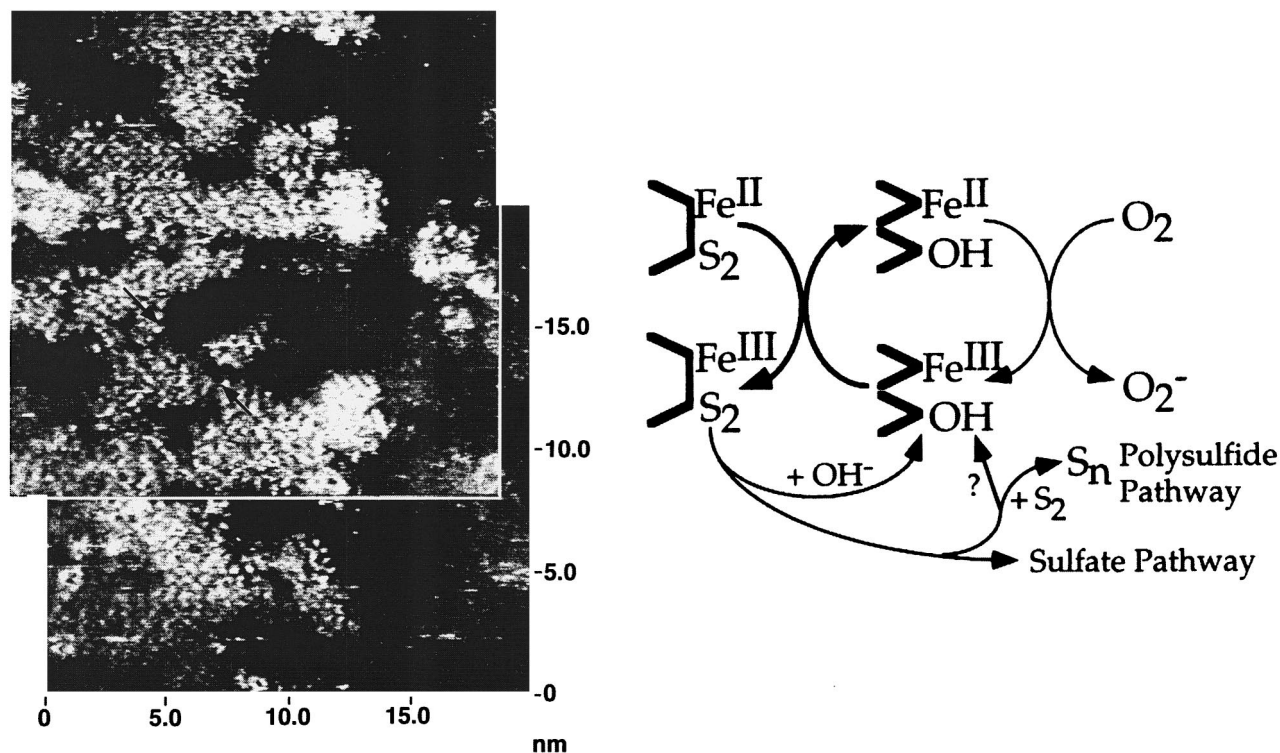


Figure 4. Scanning tunneling microscope image of the surface of pyrite (FeS₂) after fracturing and exposure to air for 26 hours. Arrows show the end points of crystallographically oriented borders between oxidized (dark) and unoxidized (light) areas. The mechanism for surface oxidation deduced from STM, XPS, and Monte Carlo calculations postulates electron transfer between fresh pyrite areas and iron-oxide-like (Fe-OH) sites, and oxidation of S₂. (From *Eggleston et al.* [1996], used with permission from the Mineralogical Society of America.)

5.3. Natural Systems

Molecular probes have been applied to the study of fewer natural systems than model systems because of their inherent complexity, although applications are increasing as the need for more detailed geochemical descriptions of real sites increases. In natural systems, molecular tools can help determine the redox states of elements, the bonding modes of sorbed species, the structure and composition of secondary precipitates, the spatial variability of surface and bulk constituents, and the interactions between microorganisms and mineral surfaces. Metal-contaminated systems (including actinides), with and without organic components, have received the most examination with molecular techniques because of their amenability to spectroscopic probes and the persistence of metals in the environment. Obviously, the application of multiple techniques will supply more detail at the molecular level, but cost and time factors must be weighed against the nature and extent of the environmental problem and the anticipated level of remediation. For many years, standard techniques such as XRD, SEM/TEM, EM, surface area measurements, total element concentration determinations (by *ICP-AES*, *ICP-MS*, or *AAS*), and wet chemical extractions have been used to characterize contaminated soils and sediments. These techniques are still essential for establish-

ing baseline element concentrations and the mineralogy of major phases. Characterization by molecular techniques is most efficient (and interpretable) when used judiciously in addition to standard techniques. Also, combining a bulk technique (such as XAS) and a spatially resolved surface technique (such as SEM or AFM) is important for maximizing information content while assessing heterogeneity.

Because of its element specificity and its ability to provide information about speciation under wet and dry conditions, XAS (both XANES and EXAFS) has proven to be particularly useful for providing chemical information about trace metals and radionuclides at relatively low concentrations (~10 ppm to several weight percent) in natural soils and sediments. Some redox sensitive elements, such as S, Cr, Mn, Se, and As, have rich spectral features in the near-edge adsorption region (XANES spectra) that are excellent chemical fingerprints (Figure 5). In natural systems, knowledge of the oxidation state of these elements is critically important because the oxidation state controls the element's solubility, complexation in solution, bioavailability, and bio-toxicity. Analyses of XANES spectra have been used to identify mixed oxidation states in contaminated soils and sediments without the need for pretreatment or separations. For example, relative proportions of Cr(III) and

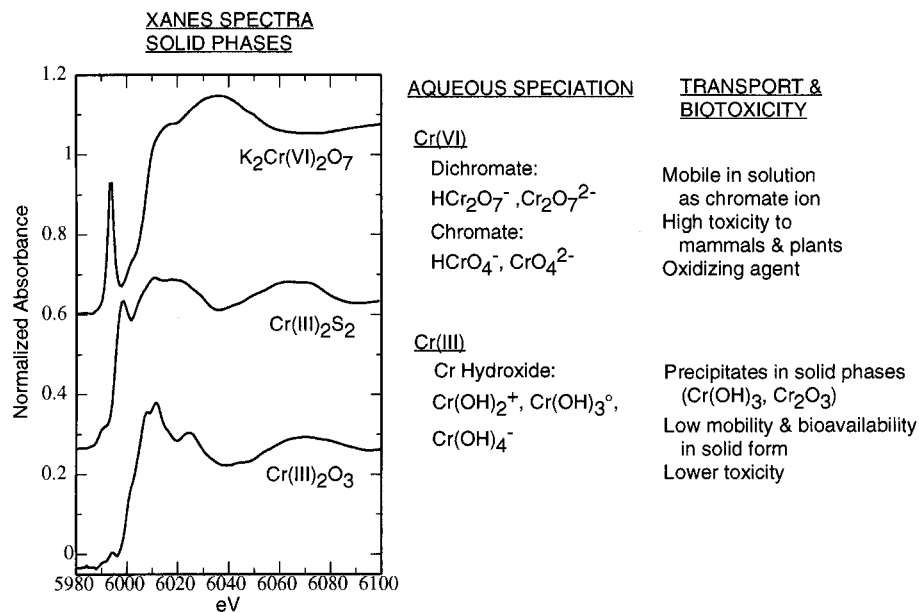


Figure 5. XANES spectrum of chromium, an excellent molecular “fingerprint” for distinguishing Cr(VI) from Cr(III) in solid and aqueous phases. Note the prominent pre-edge feature at ~5990 eV that is diagnostic of Cr(VI). Both the mobility in solution and the biotoxicity of chromium depend to a large extent on its oxidation state.

Cr(VI) were readily estimated in contaminated soils by the height of a prominent pre-edge spectral feature that was calibrated against known amounts of Cr(III)/Cr(VI) in reference compounds [Peterson *et al.*, 1997b]. Likewise, XANES analyses were used to demonstrate the reduction of selenium to monoclinic elemental selenium in contaminated soils from Kesterson Reservoir (California), indicating that selenium was converted in soils from its oxidized, more mobile aqueous form to a reduced, less mobile solid phase [Pickering *et al.*, 1995]. The speciation of organically bound sulfur in marine sediments was studied by XANES and used to identify sulfonates as an important sulfur species in organic-rich sediments [Vairavamurthy *et al.*, 1994]. Studies of soils using spatially resolved micro-XANES analysis, where the X-ray beam is focused to a point of the order of 50–200 μm , can identify mixed oxidation states of elements on microscopic scale [Bertsch *et al.*, 1994; Tokunaga *et al.*, 1994]. Collection of XANES spectra is advantageous because it is relatively fast and less sensitive to noise than EXAFS analysis, so it has a higher practical sensitivity. Analysis of XANES spectra, however, is semiquantitative in terms of determining atomic coordination sites, and thus EXAFS analysis is required to extract interatomic distances. Better theoretical modeling of near-edge absorption structure is an active research area [e.g., Rehr *et al.*, 1998], and in the near future, these models should enhance our ability to quantify XANES spectra.

Several studies of contamination by mining, smelting, and industrial processes such as coal and oil refining have employed EXAFS, along with other techniques, to

characterize the speciation and bonding of metals in contaminated soils and sediments. For example, lead in soils contaminated by different industrial activities was found to be complexed by functional groups of humic substances (salicylate and catechol-type groups) in some cases but occurred as lead sulfate and silica-associated lead in other cases [Manceau *et al.*, 1996]. An array of hazardous trace elements in coal and coal fly ash has been characterized by XAS (reviewed by Huggins and Huffman [1996]). The structure of copper and selenium precipitates in sludges from waste waters produced by seleniferous crude oil refining was determined using a combination of techniques [Manceau and Gallup, 1997], and the speciation of manganese in eutrophic lake water and surface sediment was determined by XAS [Friedl *et al.*, 1997]. In a study of zinc, cadmium, and lead contamination in stream sediments in the U.S. Tri-State Mining District, modes of metal partitioning between aqueous and solid phases were deduced by combining EXAFS analysis with SIMS, SEM, EM, and XRD characterization, and with thermodynamic analysis of stream water chemistry [O'Day *et al.*, 1998; Carroll *et al.*, 1998]. It was found that metals were added to the system through the dissolution of sulfide minerals (primarily sphalerite), and removed from solution by a combination of adsorption and precipitation processes which differed for different metals (Figure 6). Metal behavior was controlled by the amount of iron in the system at a given site, present mostly as amorphous iron oxyhydroxides or goethite, and by stream pH, which increased as groundwater-fed streams lost $\text{CO}_2(\text{g})$ to the atmosphere. Although the primary reaction mechanisms were identified, de-

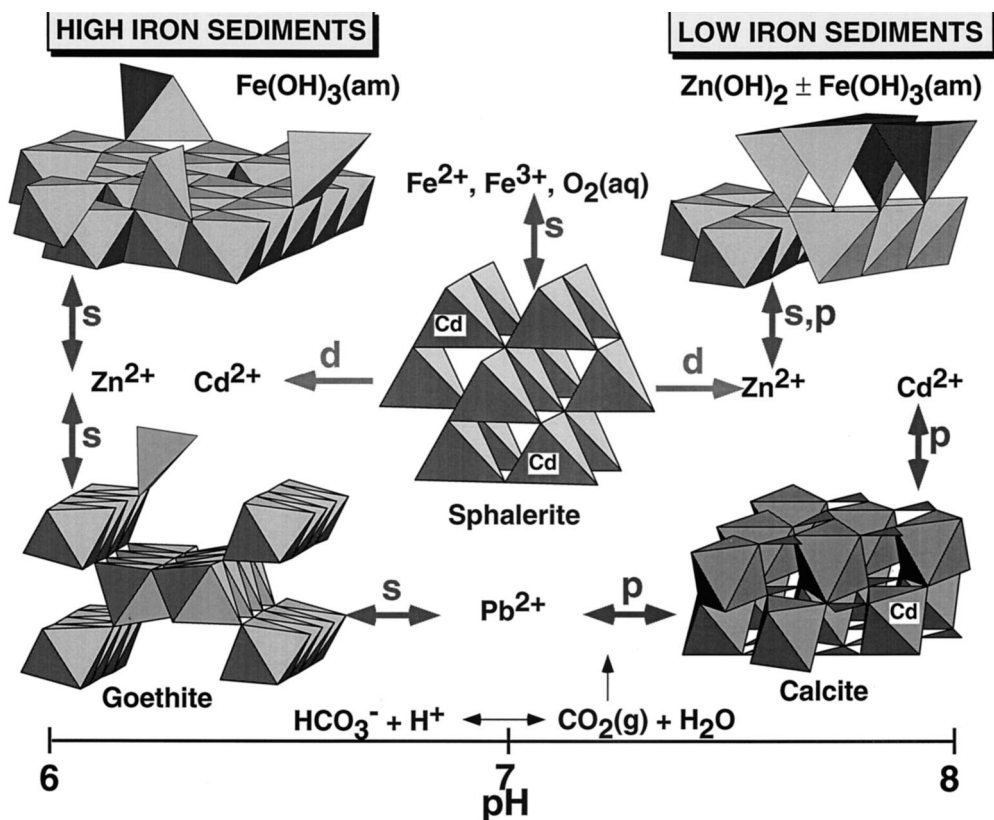


Figure 6. Summary of principal water-sediment reactions that control partitioning of zinc, cadmium, and lead, deduced from EXAFS analysis of contaminated stream sediments from the U.S. Tri-State Mining District [O'Day *et al.*, 1998]. Zinc and cadmium are dissolved (d) from detrital sphalerite, the host ore, into stream waters where dissolution is enhanced by sorption (s) of aqueous iron onto sphalerite surfaces. Removal of aqueous Zn^{2+} , Cd^{2+} , and Pb^{2+} to secondary phases is controlled either by sorption onto goethite or amorphous iron-oxhydroxides in sediments with high bulk iron concentrations, or by competition between sorption on iron minerals and precipitation (p) with calcite in low-iron sediments. In high-iron sediments at $\text{pH} \approx 6-7$, more zinc than cadmium sorbs to iron minerals, and cadmium tends to remain mobile in solution. In low-iron sediments, zinc forms mixed zinc-iron oxyhydroxides, whereas cadmium and lead tend to substitute into calcite with increasing pH. Stream pH increases downstream from groundwater-fed sources as $\text{CO}_2(\text{g})$ degasses from surface water. (From Carroll *et al.* [1998], reprinted with permission from American Chemical Society.)

tailed geochemical modeling was precluded by the lack of rate constants for sphalerite dissolution appropriate to the solution conditions and by the absence of models that could adequately describe continuum adsorption-precipitation processes and competition among contaminants. Nevertheless, the combination of equilibrium thermodynamic calculations and spectroscopic and microscopic probes was successful in identifying the reactions that governed metal uptake and release in this complex system.

The U.S. Department of Energy has estimated the cost of assessment and remediation of facilities, soils, and waters contaminated by radioactive waste from weapons research and processing at over 200 billion dollars [Renner, 1997]. Intensive study of the environmental speciation and chemical behavior of actinides and other radioactive elements such as ^{90}Sr , ^{99}Tc , ^{129}I , and ^{137}Cs is under way. For example, uranium contam-

ination in soils from a former processing facility (Fernald, Ohio) was studied by a combination of X-ray absorption, optical luminescence, and Raman vibrational spectroscopies [Morris *et al.*, 1996]. This multi-pronged approach effectively identified the oxidation state of uranium ($\sim 75-95\%$ U(VI)) and the primary uranium host phases (hydroxides and phosphates), allowing recommendation of remediation strategies at this site, which has been undergoing clean-up since 1989. Other studies are aimed at understanding the speciation of actinides in aqueous solution and complexed with organic ligands [Allen *et al.*, 1996; Clark *et al.*, 1996; Conradson *et al.*, 1998]. Uranium can also be mobilized from sediments and soils by irrigation and can accumulate in significant concentrations by evaporation, as has occurred in evaporation ponds of irrigation water in the San Joaquin Valley, California [Duff *et al.*, 1997]. The solubility and mobility of uranium depends on its oxida-

tion state: U(VI) solids are soluble in surface waters as $\text{UO}_2(\text{CO}_3)_3^{4-}$ aqueous species, whereas reduction to U(IV) and immobilization occurs in sediments and by complexation with organic matter. Synchrotron *XRF* and *XANES* was used by *Duff et al.* [1997] to identify the oxidation state of uranium in pond waters, sediments, and plants. A fraction of the uranium dissolved in pond water was found to bioaccumulate by algae, which created reducing conditions in sediments where uranium was present as mixed U(VI) and U(IV) oxides and complexed with organic matter.

5.4. Biological and Biochemical Systems

A rapidly developing area of research in both the laboratory and the field is the application of molecular methods to biogeochemistry. Although it has been acknowledged for many years that biology plays a role in geochemical systems (see, for example, texts such as *Ehrlich* [1996]), only recently have Earth scientists begun to intently study the role of microorganisms and macroorganisms at the reaction level, from which follows the need for molecular characterization. The development of molecular characterization techniques in biology (in particular, DNA and ribosomal RNA analyses) has had a profound influence. These methods supply detailed phylogenetic information and, by inference, metabolic functions in natural microbial populations (e.g., distinguishing sulfate reducers from methanogens), and have identified entirely new groups of Bacteria and Archaea (reviewed by *Nealson and Stahl* [1997]). This genetic characterization, however, does not supply direct information about the organism's interaction with its environment, i.e., the specific reactions among the cell interior, the cell exterior, the surrounding fluid, and the adjacent minerals, and how they affect the partitioning and mobility of chemical species. As future research unfolds the complexity of the microbiological world, molecular characterization of microenvironments and interfacial reactions will become increasingly important for deciphering the interplay between biology and chemistry in real environments.

Interactions between microorganisms and mineral surfaces are beginning to be investigated by microscopies such as AFM, SEM, and TEM. Several studies have observed surface pitting associated with sites of bacterial adhesion on iron oxyhydroxide and silicate minerals [*Bennett et al.*, 1996; *Grantham and Dove*, 1996; *Maurice et al.*, 1996; *Grantham et al.*, 1997], and others have documented mineral degradation by lichen during rock weathering [*Wierzbos and Ascaco*, 1996; *Barker and Banfield*, 1996]. These studies are aimed at determining if and how microorganisms might enhance mineral dissolution, compared with abiotic dissolution rates and mechanisms, in natural systems. In addition to dissolution, it has long been recognized that organisms can play both active and passive roles in the precipitation of minerals ("biologically controlled" and "biologically induced" mineralization, respectively) [*Lowenstam*, 1981].

Surprisingly few studies, however, have employed direct molecular probes to aid in deducing precipitation mechanisms. In general, most characterization at the microscopic level has been done with TEM, SEM, and *EDS*, which are useful techniques for identifying the mineral products (reviewed by *Fortin et al.* [1997]) but cannot follow precipitation mechanisms in situ. This is an area of study that will certainly receive much attention in the future.

Changes in oxidation state are an important part of bacterial metabolic pathways because organisms use electron transfer for energy [*Lovley and Chapelle*, 1995; *Nealson*, 1997]. The oxidation state of sulfur in thiosulfate was studied by *XANES* spectroscopy, and its role in microbial metabolism was discussed by *Vairavamurthy et al.* [1993]. The speciation of selenium, another element whose oxidation state significantly influences its bioavailability and toxicity, was studied by *XAS* following microbial metabolism of aqueous selenite by soil bacteria and was found to be reduced to elemental selenium [*Buchanan et al.*, 1995]. Phytoremediation, using plants to sequester toxic substances from water, is an area of research that is accelerating in light of its potential as a nondestructive, relatively inexpensive method of removing metals from soils and water. Molecular characterization by *XAS* is beginning to be applied to determine metal speciation; for example, manganese oxidation states have been studied in a metal-accumulating aquatic plant (*Potamogeton pectinatus*) [*Lytle et al.*, 1996] and in rhizosphere of wheat [*Schulze et al.*, 1995]. In these kinds of studies, the objective is to identify changes in the speciation of metals as plants and organisms sequester them, and then link these changes to cellular or enzymatic processes. As with inorganic, kinetically controlled reactions, the number of elementary reaction steps in the biochemical process can be numerous, but presumably there are overall thermodynamic driving forces that organisms exploit for energy and nutrients or to immobilize toxic species. This notion is supported by preliminary observations that metal uptake can be driven by abiotic thermodynamics, rather than only by enzymatic processes [*Nelson et al.*, 1996]. Likewise, recent spectroscopic work has emphasized the need to distinguish between abiotic and biotic reactions in soils, both of which can have similar rates [*Myneni et al.*, 1997a]. For future research in the geobiochemical field, it will be important to (1) distinguish between reactions that are intracellular and linked directly to the metabolism of microorganisms, and extracellular reactions in which organisms supply a favorable surface for reactions to take place or secrete compounds that modify the local solution chemistry, and (2) establish relationships between macroscopic solution chemistry and an organism's solution microenvironment in order to apply thermodynamic constraints and/or kinetic rate laws appropriate to the system.

6. THE FUTURE OF MOLECULAR ENVIRONMENTAL GEOCHEMISTRY

6.1. New Techniques and Approaches

Our understanding of molecular environmental reactions will continue to expand both from the application of existing molecular methods and from new technological advances. Because of their versatility, synchrotron-based techniques are expected to play a prominent role. The recent completion of a new, high-photon-flux synchrotron source, the Advanced Photon Source at Argonne National Laboratory, will provide new capabilities, in particular: lower detection limits and higher sensitivity for conventional XAS and for quicker energy scanning (QXAS) [Wong *et al.*, 1995; Hecht *et al.*, 1996]; higher sensitivity and better spatial resolution for focused-beam applications (micro-XRF, micro-XANES, and microdiffraction) [Smith, 1995; Smith and Rivers, 1995]; access to higher X-ray energies for the study of *K* and *L* absorption edges of more elements; two- and three-dimensional high-resolution imaging and chemical analyses (CT) [Spanne *et al.*, 1994; Bonse and Busch, 1996]; and improved surface sensitivity for grazing-incidence XAS, X-ray reflectivity, and X-ray standing wave measurements [Heald *et al.*, 1987; Bedzyk *et al.*, 1990; White, 1991; Bargar *et al.*, 1996; Sturchio *et al.*, 1997]. These improvements should enhance our ability to study samples of lower concentration (especially relevant to actinide work); to carry out sorption, precipitation, and redox experiments in real time in order to directly couple microscopic reaction mechanisms and rates; to better assess spatial, chemical, and physical heterogeneity in two and three dimensions; and to probe the molecular structure of the solid solution interface with better sensitivity and resolution.

Advances on other technological fronts are expected as well. Continued rapid developments in the scanning probe microscopies promise to expand capabilities for extracting chemical information, in particular, electron tunneling spectroscopy, which provides electronic structure information from individual atoms using STM [Avouris, 1990; Chen, 1993; Becker and Hochella, 1996]. Recent improvements in AFM include a tip tapping-mode and a magnetically driven oscillating probe for less destructive tip-sample interactions with soft materials and improved resolution for imaging in liquids [Lindsay *et al.*, 1993; Han *et al.*, 1996; Warren *et al.*, 1997]. A new cousin in this field, NSOM (also known as SNOM), uses a subwavelength-sized light source and a cantilever system to raster the source a fraction of a wavelength above a surface [Betzig *et al.*, 1991; Valaskovic *et al.*, 1995]. Because light is the excitation source rather than the force of a tip, high-resolution optical spectroscopy is possible (over a spatial scale of about 50 to several hundred nanometers), such as detecting fluorescence from a single molecule in biological materials [Tarrach *et al.*, 1995].

Along this line, we can expect a crossover of tech-

niques currently used in the biological and biomedical fields as the study of environmental biochemical reactions expands. One of the more useful is confocal laser scanning microscopy, which provides high-resolution, three-dimensional imaging of soft materials, currently used in biology to image cells, membranes, neurons, and other biological materials (for example, see edited volumes by Stevens *et al.* [1994] and Pawley [1995]). Of particular interest is the use of fluorescent dyes and ligand probes (fluorophores) that are selectively substituted onto functional groups of organic or biochemical molecules and imaged using laser scanning. Application of fluorophore tags would be extremely useful in tracking the migration and sorption of organic compounds to mineral surfaces, or in monitoring biochemical reactions on mineral surfaces. For all of these techniques it will be especially important to couple molecular observations with parameterization on the macroscopic scale. While they add to our fundamental knowledge of environmental molecular processes, microscopic observations are really most useful when they can be translated to directly useable field parameters: rate or equilibrium constants.

6.2. Integration of Physical, Chemical, and Biochemical Processes in Natural Systems

As the foregoing review of recent work points out, molecular studies are adding a wealth of direct information about chemical environmental processes. For the most part, these studies have addressed basic questions regarding characterization, namely, what is the speciation, bonding, and phase partitioning of hazardous contaminants, and what is the nature of their association with soils, sediments, organic compounds, and biological materials? Although this is a big step forward, to be effective in a field context, molecular studies need to be efficiently integrated with macroscopic geochemical models and with models of physical processes. Only then can overall, quantitative assessments of contaminant mobility, biohazard, and remediation be made. This is not to say, however, that development of a single, overriding computer model is required, only that chemical and physical processes be integrated according to the nature of the problem and the timescale of interest. The level of sophistication of physical and reactive transport models has advanced rapidly in recent years, as has their validation in the field (a series of review articles on reactive transport models is found in the volume edited by Lichtner *et al.* [1996]). With increased computer power, discrete spatial analyses and time integration of physical parameters such as convection, dispersion, and solute transport can be achieved in three dimensions. Inclusion of chemical and biochemical fluid-rock-microbial reactions in physical models requires knowledge of reaction stoichiometries, databases of rate and equilibrium constants, and estimates of mineral surface areas, porosity structure, and microbial mass along with parameterization of physical properties of the system [Rubin,

GEOCHEMICAL ANALYSIS OF NATURAL SYSTEMS

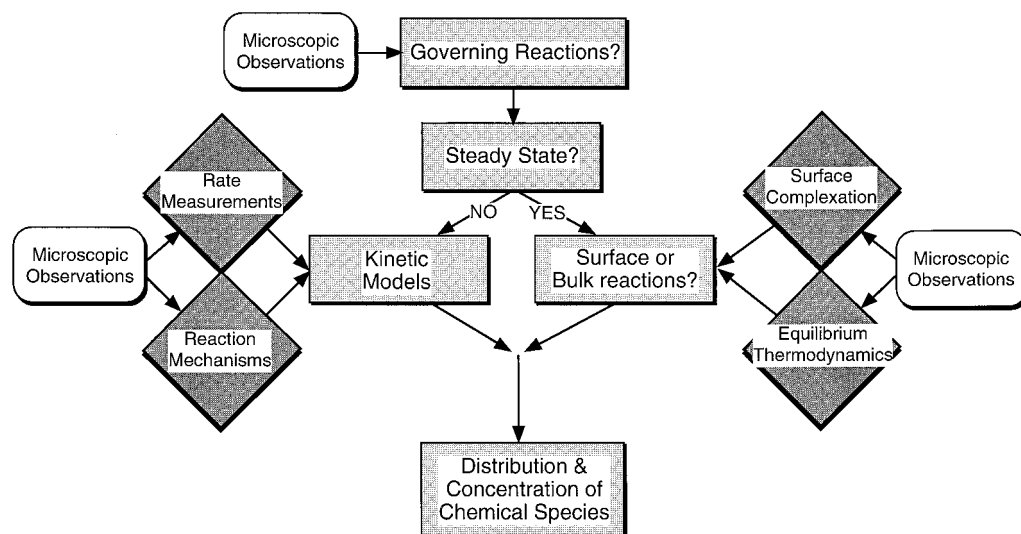


Figure 7. A conceptual hierarchy for modeling contaminated geochemical systems. This scheme can be thought of as a subset of a physical transport or reactive flow model. Microscopic observations can help constrain reactions that directly govern transformations of species of interest, and can be used to help determine whether or not reactions are treated as steady state with respect to the rate of flow or the timescale of the system. Once this is determined, either kinetic or steady state models can be applied for quantitative analysis, which produces a mass-balanced distribution of species in aqueous, solid, and gas phases for the time or space increment of the physical model. Microscopic characterization is needed for choosing the chemical species to include in the geochemical model, and for deducing molecular species and mechanisms to include in kinetic and surface reaction models.

1983; Kirkner and Reeves, 1988; Walter *et al.*, 1994; Lichtner, 1996].

In modeling natural systems from the standpoint of contaminant assessment or remediation, the first consideration is identifying key reactions that govern the behavior of contaminant species, and determining whether or not they are steady state or transient with respect to the rate of groundwater or surface water flow (Figure 7). As the studies discussed here demonstrate, molecular tools are valuable for constraining these governing reactions, which then dictate the choice of model description: kinetic (if rate constants are known for specific reactions), equilibrium, or a combination of both. Equilibrium formulations can include bulk and mineral surface reactions, or a reaction progress approach, *i.e.*, using the chemical affinity of reactions not at equilibrium and irreversible mass transfer as a proxy for absolute-time rate constants [Helgeson, 1979]. It should be pointed out that not all chemical and biochemical reactions in the system need to be, or even could be, quantified at such a high level of detail. In most systems the majority of reactions can be described adequately using equilibrium thermodynamics, particularly for fast reactions such as speciation in solution, for which extensive databases are available. The critical factor is sufficient scrutiny of processes that control the speciation, transformation, and transport of contaminant species of interest, and adequate parameterization over the time-

scale of these processes. In dynamic systems such as marine sediments with steep depth-dependent redox gradients, it may be appropriate to choose a model that tightly couples kinetic reactions and transport (see, for example, Van Cappellen and Wang [1996] and Wang and Van Cappellen [1996]). For systems in which the flow rate is low, the time interval is long, or temperature is high, local chemical equilibrium assumptions may be quite valid [Lichtner, 1996]. Regardless of the model formulation, there is a need for the development of transferable, system-independent kinetic databases, in much the same way that thermodynamic databases have been developed over the years. They should include common inorganic and biologically mediated reactions, be based on well-constrained reaction mechanisms, and adhere to a general form of the rate equation (14). Standardization of kinetic models is complicated by the difficulty in verifying molecular reaction mechanisms under different conditions, but here again spectroscopy and microscopy play an important role in identifying molecular species. Likewise, better integration of surface reactions at mineral and biological interfaces into geochemical and physical models will improve the ability to account for this class of reactions in natural systems.

The application of spectroscopic and microscopic probes to environmental geochemistry has expanded our knowledge of molecular processes in an unprecedented way. There is no doubt that this field of Earth sciences

will continue to grow and play a vital role in integrated, interdisciplinary environmental research, driven by new techniques and by innovative applications of existing methods. Although this review has focused primarily on examples from contaminant geochemistry, the methods touched on here are powerful tools applicable to many areas of geochemistry and biogeochemistry. In order to most effectively employ molecular probes in the study of environmental processes and contamination, the following points should be considered as future areas of research:

1. Judicious and efficient use should be made of molecular spectroscopy and microscopy. Clearly, we cannot study every contaminated site exhaustively with a battery of high-level probes. It is important, however, that contaminated systems be characterized sufficiently in both aqueous and solid phases, and that surface reactions and biological influences be considered. This points to a need to develop a hierarchy and strategies for incorporating molecular methods into studies of contaminated sites.

2. Better model descriptions are needed that reflect the continuum of processes among mineral dissolution, solute surface complexation and nucleation, precipitation of new metastable phases, and transformation to stable thermodynamic phases. For a simple sorbate-sorbent system, these are linked in a general way to the undersaturation or oversaturation of thermodynamically stable phases, but often involve a series of metastable steps along the way (Figure 8). The importance and persistence of metastable surface complexes and phases in the environment is dependent on temperature, time, biological mediation, and chemical affinity, and at present, no model treats these in a comprehensive fashion. Simplification of existing surface complexation models and better integration with thermodynamic data for minerals and solutions is needed to bridge the gap between the laboratory and the field.

3. Kinetic databases need to be developed for reactions that are system-independent and account for biotic and abiotic processes. As was noted above, spectroscopic and microscopic examinations of model systems concurrently with rate measurements are needed for establishing molecular mechanisms and appropriate rate constants. This effort would also be aided by the development of good estimation algorithms or extrapolation methods based on microscopic observations.

4. Finally, research is needed into efficient coupling of chemical and physical parameters, and critical model validation. While the mathematical basis is in place to generate very detailed reactive transport models, the chemical and physical parameters that fuel these models must demonstrate a reliable predictive capability and a realistic estimate of error, not simply the ability to "fit" existing data. Without such stringent validation criteria, chemical and physical models of contaminated systems will have little credibility with the ultimate end users of

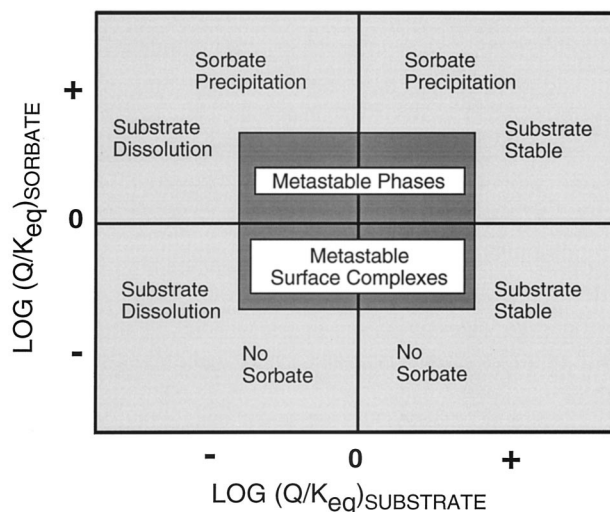


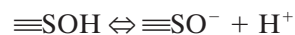
Figure 8. In a simple system with a single solid substrate and aqueous sorbate, the degree of thermodynamic undersaturation or oversaturation, $\log Q/K_{eq}$ (equation 13), provides an overall measure of the driving force for dissolution and precipitation of bulk phases. When surface sorption is included, the formation of mononuclear and multinuclear surface complexes, and incipient surface precipitates, can be viewed as metastable intermediates among the thermodynamically stable end-members. The composition of the metastable surface species may include ions dissolved from the substrate as well as ions sorbed from solution.

the studies: government research and regulatory agencies, the legal system, and the public.

APPENDIX: EXAMPLES OF SURFACE COMPLEXATION REACTIONS

Surface complexation models treat an oxide or silicate surface site as a molecular species ($\equiv\text{SOH}$) that can form bonds with ions and species from solution. In $\equiv\text{SOH}$, $\equiv\text{S}$ is a metal atom in the bulk solid and OH is a surface-exposed oxygen atom with a proton. A variety of reactions are possible depending on the ions or organic species in solution, the number of surface sites that are involved in the reaction, the number of protons released from the surface, and whether or not water takes part in the reaction (hydrolysis).

Protonation/deprotonation

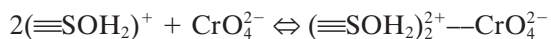
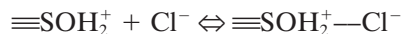
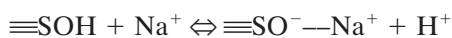


Ion exchange

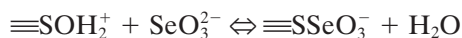
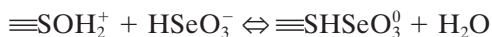
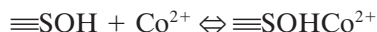


The dash here is meant to imply a solvation shell around the adsorbed ion (see Figure 1).

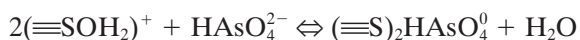
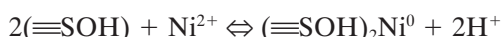
Mononuclear outer sphere



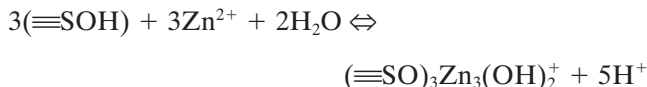
Mononuclear, monodentate, inner sphere



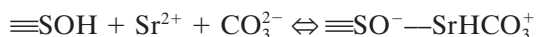
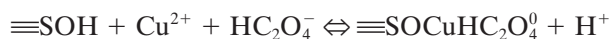
Mononuclear, bidentate, inner sphere



Multinuclear, bidentate, inner sphere



Ternary (metal ion and ligand), monodentate



Precipitation



Note that this reaction is the same as for homogeneous precipitation from solution; the surface does not appear explicitly.

GLOSSARY

- AAS:** Atomic absorption spectroscopy.
AFM: Atomic force microscopy (also known as SFM).
CT: Computerized tomography.
EDS: Energy dispersive spectrometry.
EELS: Electron energy loss spectroscopy.
EM: Electron microscopy.
EPR: Electron paramagnetic resonance (also known as ESR).
ESR: Electron spin resonance (also known as EPR).
EXAFS: Extended X-ray absorption fine structure.
FTIR: Fourier transform infrared.
HR-TEM: High-resolution transmission electron microscopy.
ICP-AES: Inductively-coupled plasma atomic emission spectrometry.
ICP-MS: Inductively-coupled plasma mass spectrometry.

IR: Infrared.

LA-ICP-MS: Laser ablation inductively coupled plasma mass spectrometry.

NMR: Nuclear magnetic resonance.

NSOM: Near-field scanning optical microscopy (also known as SNOM).

PEELS: Parallel electron energy loss spectroscopy.

QXAS: Quick X-ray absorption spectroscopy.

SAXS: Small-angle X-ray scattering.

SEM: Scanning electron microscopy.

SFM: Scanning force microscopy.

SIMS: Secondary ion mass spectrometry.

SNOM: Scanning near-field optical microscopy (also known as NSOM).

SPM: Scanning probe microscopy.

SR: Synchrotron radiation.

SR-XMP: Synchrotron radiation X-ray microprobe.

SR-XRF: Synchrotron radiation X-ray fluorescence.

STEM: Scanning transmission electron microscopy.

STM: Scanning tunneling microscopy.

TEM: Transmission electron microscopy.

WAXS: Wide-angle X-ray scattering.

WDS: Wavelength dispersive spectrometry.

XAFS: X-ray absorption fine structure.

XANES: X-ray absorption near-edge structure.

XAS: X-ray absorption spectroscopy.

XPS: X-ray photoelectron spectroscopy.

XRD: X-ray diffraction.

XRF: X-ray fluorescence.

XSW: X-ray standing waves.

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P. O'Day, Department of Geology, Box 871404, Building PSF 686, Arizona State University, Tempe, AZ 85287-1404. (oday@asu.edu)