FINAL REPORT

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PROJECT TITLE: RELEASE OF OXIDE-BOUND TOXIC METALS BY NATURALLY-OCCURRING AND CONTAMINANT-DERIVED ORGANIC COMPOUNDS: THE ROLE OF COMPLEXANT, REDUCTANT, AND ADSORPTIVE CHARACTERISTICS

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INTRODUCTION

Natural organic compounds and contaminant-derived organic compounds can substantially alter the speciation and geochemical behavior of contaminant metals in subsurface environments. Our goal, as part of the Co-Contaminant Subprogram, was to: (i) develop analytical methods for identifying and quantifying organic compounds affecting toxic metal speciation; (ii) evaluate their reductant, complexant, and adsorptive characteristics of organic compounds with regards to important contaminant metals; (iii) determine reaction kinetics, mechanisms, and energetics for metal-organic interactions; and (iv) provide the basis for predicting toxic metal oxidation state, speciation, and mobility.

The publications and manuscripts listed in this report serve as the principal products of this research. Our research group also contributed to the goals of the Co-Contaminant Subprogram by participating in scientific and planning discussions, by assisting in the design of experiments in other laboratories, and by performing laboratory experiments and chemical analyses in support of research performed at Oak Ridge and PNL.

SUMMARIES OF COMPLETED WORK

Godtfredsen, K.L. and A.T. Stone "Solubilization of Manganese Dioxide-Bound Copper by Naturally-Occurring Organic Compounds" Environ. Sci. Technol. 28, 1450-1458 (1994).

Before our work was begun, it was widely understood that adsorption/desorption reactions control toxic metal and radionuclide migration rates in the subsurface. The effects of mineral surface properties and inorganic solution speciation on adsorption/desorption had been extensively explored in carefully-controlled laboratory experiments. Little was known, however, about the participation of natural organic compounds and contaminant-derived organic compounds in adsorption/desorption reactions.

All experiments involving the MnO_2-Cu^{II} system began by pre-equilibrating the adsorbate and the mineral adsorbent for 17 hours. Reaction began by adding representative low molecular weight organic compounds or natural organic matter samples; filtration of suspension aliquots and atomic absorption spectrophotometry

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(AAS) allowed dissolved and particulate manganese and copper to be distinguished. This relatively simple system allowed us to explore all the ways in which subsurface organic compounds solubilize toxic metals and radionuclides: (i) organic compounds may form complexes with the metal ion of interest, shifting speciation from the adsorbed to the dissolved phase; (ii) adsorbed organic compounds may compete with metal ions for available surface sites; (iii) adsorbed organic compounds may facilitate metal ion adsorption through ternary complex formation; (iv) reductive and ligand-assisted dissolution of the mineral adsorbent may lower the number of available surface sites, forcing the metal ion of interest to desorb; and (v) reductive dissolution generates Mn(II), which competes with copper for available surface sites.

Low molecular-weight organic compounds with well-established reductant and complexant properties were used to obtain a detailed understanding of the five solubilization processes just listed. Hydroquinone and pyruvic acid serve as reductants but possess negligible complexant properties; copper release by these low molecular-weight organic compounds arises from Mechanisms iv and v. Oxalic acid and citric acid possess both reductant and complexant properties; copper release in the their presence arises primarily from mechanisms i, iv, and v. An important aspect of the work with low molecular-weight organic compounds is the quantification of each solubilization process. Plots of dissolved manganese as a function of time provide information about changes to the mineral adsorbent, while plots of dissolved copper as a function of dissolved manganese provide information about the degree of copper-organic compound complex formation that is taking place.

The findings obtained with low molecular-weight organic compounds allowed us to proceed with experiments involving Georgetown Site water (GTW) and four other natural organic matter samples. Natural organic matter adsorption was slight, but sufficient to block reactions of the low molecular-weight organic compounds pyruvic acid and oxalic acid. Plots of dissolved manganese as a function of time and dissolved copper as a function of dissolved manganese help quantify differences in the reductant and complexant properties of the five natural organic matter samples. Georgetown Site water possesses complexant properties that are more pronounced than its reductant properties.

Stone, A.T. and K.L Godtfredsen "Solubilization of MnO$_2$-Bound Cobalt, Nickel, and Copper Following Acidification, Metal Ion Addition, and Low Molecular Weight Organic Compound Addition" (Manuscript in preparation for submission to Geochim.

In order to learn more about processes governing metal ion solubilization, our study was expanded to include two additional sorbed metal ions (cobalt and nickel) and a wider range of pH conditions.

Among +II metal ions, complex formation constants with oxygen donor ligands (e.g. oxalic acid and citric acid) decrease in the order: $Cu^{II} > Ni^{II} > Co^{II} > Mn^{II}$. As a consequence, solubilization arising from Mechanism i (complex formation in solution) should be less pronounced for Ni^{II} and Co^{II} in comparison to Cu^{II}.

Experiments performed with nickel are complicated by slow rates of Ni^{II} ligand exchange relative to Cu^{II}. Indeed, our experiments indicate that sorbed nickel is relatively insensitive to the complexant properties of low molecular weight organic compounds during the timescales of our experiments; nickel solubilization occurs primarily through reductive dissolution of the MnO_2 adsorbent mineral, which forces nickel into solution. When MnO_2 reductive dissolution rates are low, the amount of nickel solubilized per mole of MnO_2 dissolved tends to be high.

Experiments performed with cobalt are complicated by oxidation of sorbed Co^{II} to Co^{III} during the 17-hour pre-equilibration period. Cobalt oxidation is accompanied by manganese reduction; stoichiometric amounts of Mn(II) appear during the pre-equilibration procedure. The fraction of cobalt oxidized increases as the pre-equilibration time is increased and as the pH is increased. Both cobalt oxidation states are capable of forming complexes with oxalic acid and citric acid, but Co^{III} ligand exchange kinetics are slow relative to the timescales of our experiments. Reduction of Co^{III} to Co^{II} is believed to play an important role in cobalt solubilization.

Detailed descriptions of MnO_2 reductive dissolution and adsorbed metal ion release as a function of pH are important aspects of this work. A lag period is observed between the time that organic reductants have been added and Mn^{II} appears in solution. The lag period shortens when the pH is decreased and when other sorbable metal ions are present (e.g. cobalt, nickel, and copper). Two factors explain this pH dependence: (i) surface reduction reactions generally occur more quickly at lower pHs and (ii) the affinity of Mn^{II} for the MnO_2 surface decreases as the pH is decreased. Sorbable metal ions shorten the lag period by competing with Mn^{II} for

available surface sites.

Stone, A.T. and K.L Godtfredsen "Solubilization of MnO$_2$-Bound Cobalt, Nickel, and Copper Upon Natural Organic Matter Addition (Manuscript in preparation for submission to Limnol. Oceanogr.)

As discussed in the preceding paper, the response of adsorbed cobalt and nickel to additions of low molecular-weight organic compounds is very different from the response of adsorbed copper. The metal ion properties responsible for this observation also affect response to natural organic matter addition.

Five natural organic matter samples were examined in this study. Georgetown Water (GTW), Dismal Swamp Water (DSW), and Suwannee River Water (SRW) were collected as raw water from south coastal swamplands, and refrigerated prior to use. Suwannee River Humic Acid (SRHA) and Suwannee River Fulvic Acid (SRFA) were prepared by the International Humic Substances Society (IHSS). The IHSS procedure begins with XAD-8 column extraction of a hydrophobic fraction. Once this fraction has been extracted off the column, pH adjustment allows further fractionation into fulvic acids (soluble at all pHs) and humic acids (insoluble at acidic pH but soluble at alkaline pH.) The IHSS samples are deficient in metal ions, inorganic anions, and hydrophilic organic compounds relative to the raw water samples.

Procedure 1 involves bringing MnO$_2$ and metal ion into contact before natural organic matter (NOM) addition. Procedure 2 involves bringing NOM and metal ion into contact before MnO$_2$ addition. With Cu, both procedures yield the same results, since Cu adsorption/desorption and Cu-NOM complex formation reactions are relatively fast and reversible. Procedure 1 yields greater amounts of Co and Ni adsorbed than Procedure 2. With Co, our hypothesis is that Procedure 2 results in the formation of Co^{II}-NOM complexes that prevent Co oxidation by the MnO$_2$ surface. (Co^{II} is sorbed more weakly than Co^{III}.) With Ni, our observations reflect slow rates of ligand exchange and adsorption/desorption. Ni-NOM complexes do not dissociate quickly enough for significant sorption to occur.

The five NOM samples used in this work bring about MnO$_2$ reductive dissolution at different rates. MnO$_2$ reductive dissolution rates can also be increased by increasing the NOM concentration. When differences in reductive dissolution rates are accounted for (using dissolved metal ion versus dissolved Mn^{II} plots), Cu is the

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most sensitive of the three metal ions towards differences in the complexant properties of NOM samples. Ni is insensitive to NOM complexant properties. Ni release appears to be strongly related to the MnO_2 reductive dissolution rate; as the dissolution rate increases, the rate of Ni release decreases. The behavior of Co in the presence of NOM is intermediate between Cu and Ni. It is difficult to draw conclusions about Co desorption by NOM because of the coexistence of Co^{II} and Co^{III} on the MnO_2 surface.

This work, along with the two preceding manuscripts, serves as the first attempt by geochemists to simultaneously account for the effects of complexation and redox reactions on sorption/desorption behavior. This work provides information and concepts that can assist the study of sorption/desorption and redox reactions in more complicated systems such as laboratory flow-through columns (e.g. Jardine and Taylor, 1995; Klausen et al., 1997).

Coughlin, B.R. and A.T. Stone "Non-Reversible Adsorption of Divalent Metal Ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II}) onto Goethite. Effects of Acidification, Fe^{II} Addition, and Picolinic Acid Addition" <u>Environ. Sci. Technol.</u> <u>29</u>, 2445-2455 (1995).

MnO_2(birnessite) carries a net negative charge throughout the pH domain of natural subsurface environments, and sorbs +II metal ions primarily via ion exchange at Mn^{IV} vacancy sites. FeOOH(goethite), in contrast, carries a net positive charge at all but the very alkaline pHs, and sorbs +II metal ions primarily via surface complex formation. The widespread occurrence of FeOOH(goethite) within subsurface environments and its demonstrated importance as an adsorbent for toxic metals and radionuclides make it a good candidate for study.

Divalent metal ion adsorption onto FeOOH(goethite) exhibits typical "adsorption edge" behavior; adsorption rises from zero to 100 % as the equilibration pH is increased within a very narrow range. Kinetic studies of divalent metal ion adsorption reveal an initial, rapid stage followed by a much slower reaction linearly related to the equare root of time. The accepted mechanism is that divalent metal ions first adsorb onto exterior surfaces, diffuse into internal binding sites, and become bound within the oxide interior.

When preequilibration above the adsorption edge is followed by acidification below the adsorption edge, nearly complete metal ion release is expected. Prior

research has shown, however, that metal ions become more difficult to recover as the pH and the time of preequilibration step are increased. Ainsworth et al. (1994) observed that the magnitude of hysteresis for three metal ions adsorbed onto hydrous ferric oxide decreases in the order $Co^{II} > Cd^{II} > Pb^{II}$. Although Co^{II} and Cd^{II} are apparently incorporated into the oxide, Pb^{II} appears to remain on the surface and resists incorporation, most likely because of its larger ionic radius.

We began by repeating the preequilibration and acidification experiments of Ainsworth et al. (1994) using FeOOH(goethite). Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II} all exhibited hysteresis, with the extent of hysteresis increasing as the preequilibration pH was increased. A separate set of experiments examined metal ion release upon addition of 1000 μM picolinic acid. With Co^{II}, Ni^{II}, and Cu^{II}, the amount released after 24 hours of contact with picolinic acid matched the amount released by acidification. logK values for picolinic acid complexes of Mn^{II} and Pb^{II} are lower than for the other three metal ions, and a lower percentage of these metal ions were recovered. When the picolinic acid concentration was increased, the extent of metal ion desorption after 24 hours of contact increased. A limiting value of the extent of metal ion desorption was obtained at very high picolinic acid concentrations, which relates to the hysteresis effect.

In subsurface sediments undergoing changes in redox status, concentrations of Fe^{II} can be significant. Adding 1000 μM Fe^{II} caused a significant <u>increase</u> in the adsorption of Co^{II}, Ni^{II}, and Cu^{II} onto FeOOH(goethite), but had no measureable effect on the adsorption of Pb^{II}. We postulated that added Fe^{II} causes significant reworking of the FeOOH(goethite) surface. Pb^{II} may resist incorporation into the reworked surface, owing to its large radius relative to the other $+II$ metal ions examined.

Picolinic acid possesses two Lewis base functional groups that are ortho- to one another on a benzene ring. Owing to the chelate effect, coordination of both Lewis base groups to a central metal ion is more stable than "bridged" coordination to two metal ions. As a consequence, picolinic acid is not an effective ligand for ternary complex formation.

Coughlin, B.R. and A.T. Stone "Release of Goethite-Bound Divalent Metal Ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II}) Upon Addition of Fumaric Acid, Maleic Acid, Malonic Acid, and Citric Acid (Submitted to <u>Water Research</u>, under revision)

Fumaric acid, maleic acid, malonic acid, malic acid, and citric acid are important biologically-derived (hydroxy)carboxylic acids produced by bacteria and other organisms in the subsurface. Malonic acid and citric acid are employed as wet chemical reagents in energy-related activities. Fumaric acid, maleic acid, and malonic acid possess two Lewis base groups, and are therefore not capable of ternary complex formation. Malic acid possesses three and citric acid possesses four Lewis base groups. This work examines the ability of all five (hydroxy)carboxylic acids to affect the sorption behavior of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II} onto FeOOH(goethite).

For oxygen-donor ligands such as the ones included in this study, logK values for Cu^{II} are considerably larger than logK values for Mn^{II}, Co^{II}, Ni^{II}, and Pb^{II}. Cu^{II} can therefore be used to screen organic ligands for possible effects on metal ion sorption/desorption. Maleic acid and fumaric acid have a negligible effect on Cu^{II} adsorption, while malonic acid causes a significant decrease in Cu^{II} adsorption. These results are consistent with expectations based upon equilibrium model calculations.

The effect of malic acid addition depends upon the metal ion under examination. The three metal ions with the largest logK values for malic acid complexation (Co^{II}, Ni^{II}, and Cu^{II}) are either insensitive to malic acid addition, or exhibit a slight increase in extent of adsorption. The two metal ions with the lowest logK values for malic acid complexation (Mn^{II} and Pb^{II}) exhibit moderate increases in adsorption following malic acid addition.

Results obtained with citric acid are quite different from those obtained with the other four organic ligands. When the amount of citric acid added is low, metal ion sorption increases significantly for all +II metal ions included in the study. The extent of metal ion sorption increases as more citric acid is added, up to the point where the surface becomes saturated with sorbed citric acid molecules. Citric acid is believed to enhance metal ion sorption via ternary complex formation. The number and arrangement of ligand donor groups within the citric acid molecule are apparently sufficient for efficient bridging between two metal ions to occur.

If higher amounts of citric acid are added, appreciable concentrations of citric acid appear in solution. As metal ion-citric acid complexes form in solution, the extent of metal ion sorption finally begins to decrease. The extent to which citric acid affects metal ion adsorption differs slightly among the five +II metal ions examined, reflecting differences in logK for metal ion-citric acid complex formation.

Natural organic compounds and contaminant-derived organic compounds that affect metal ion subsurface chemistry are themselves subject to oxidation, hydrolysis, and other transformation processes. In some instances organic transformation products influence metal ion speciation in ways that are distinct from the parent compounds. In order to fully assess metal ion speciation in the presence of organic co-contaminants, it is important to understand rates and mechanisms of transformation reactions, and to identify transformation products.

Identifying and measuring the concentrations of synthetic chelating agents and their transformation products was an important task for the Co-Contaminant Subprogram. EDTA, NTA, IDA, citrate, and other chelating agents of interest are polycarboxylate anions that are difficult to analyze using conventional analytical methods. Analysis by gas chromatography and high pressure liquid chromatography requires derivatization. (The low concentrations and complex matrix of subsurface samples makes derivatization difficult.) Ion chromatography has been successfully applied in the past, but the method is sensitive to the pH and major ion composition of the sample, and it is difficult to distinguish free from metal ion complexed species.

This objective of this work was to separate and quantify solutions of free chelating agents, Co^{II}-chelating agent complexes, and Co^{III}-chelating agent complexes using capillary electrophoresis (CE) with UV/visible spectrophotometric detection. CE is a highly efficient separation technique that is based upon differences in electrophoretic mobility between analytes. The electrophoretic mobility is a function of ion charge and hydrodynamic radius. Methods development is much simpler with CE than with the analytical methods mentioned in the preceding paragraph; it was possible for all analyses to be performed using the same equipment settings and the sample electrolyte medium (25 mM phosphate buffer (pH 7) containing 0.5 mM tetradecyltrimethylammonium bromide as an electroosmotic flow modifier.)

The CE equipment that we used in our work (Waters Corp. Quantum 4000 Capillary Ion Analyzer) allowed us use the following detection wavelengths: 185 nm, 214 nm, 254 nm, and 315 nm. At 185 nm, any compound containing a carbonyl group absorbs appreciably. Using this detection wavelength, we were able to separate and

quantify a mixture of 15 (amino)carboxylic acid chelating agents. The detection limit was typically 10 - 20 μM. (Unlike the other (amino)carboxylic acids, free EDTA adsorbs to the capillary wall, which causes peak broadening and a slightly poorer detection limit.)

We observed a strong correlation between the thermodynamic stability of Co^{II} and Co^{III} complexes with (amino)carboxylic acid chelating agents and our ability to obtain linear calibration curves with them. Of the two oxidation states, Co^{II} yields complexes with lower values of logK and that undergo more rapid ligand exchange. As a consequence, only very strong chelating agents (e.g. DTPA and EDTA) yield linear calibration curves with Co^{II}. Co^{III}, in contrast, yields complexes with high values of logK that are substitution inert within the timescales of CE analysis; linear calibration curves were obtained with every Co^{III}-(amino)carboxylic acid complex examined.

As part of this work, we collaborated extensively with Harvey Bolton and Don Girvin. The PNL group sent samples from microbial microcosms, and we investigated whether the breakdown products of biodegradation could be identified and measured in the growth medium that was being employed. (Growth medium contains a considerable number of inorganic and organic compounds that absorb light at 185 nm, and hence yield capillary electrophoresis peaks; our principal task was to distinguish chelating agents and their breakdown products from these background peaks.)

McArdell-Burgisser, C., A.T. Stone and J. Tian "Reaction of EDTA and Related (Amino)carboxylic Acid Chelating Agents with CoOOH(Heterogenite) and MnOOH(Manganite)" (Manuscript in Preparation)

The capillary electrophoresis (CE) technique described in the preceding manuscript enables us to determine chelating agent and metal ion speciation in unprecedented detail. This technique can now be used to explore physical, chemical, and biological processes affecting toxic metals, radionuclides, and synthetic chelating agents in subsurface environments.

Co^{III} is known to be associated with iron and manganese oxides in aquatic environments (Murray and Dillard, 1979; Dillard et al., 1981; Crowther et al., 1983). We are interested in whether this adsorbed or precipitated Co^{III} is available for reaction with dissolved chelating agents, and what the nature of the reaction products

might be.

We decided to begin our studies with the phase heterogenite (CoOOH) for the following reasons: 1) CoOOH consisting solely of Co^{III} is readily synthesized; 2) the crystal structure, morphology, and domain size can be determined by electron microscopy, X-Ray diffraction, and EXAFS (with the assistance of Prof. David Veblen of Johns Hopkins University and Prof. Alain Manceau of the Joseph Fourier University in Grenoble, France); 3) $Co^{III}(O,OH)_6$ octahedra within the CoOOH structure are chemically similar to Co^{III} adsorbed or precipitated within iron and manganese oxides; and 4) Co^{II} and Co^{III} complexes generated from reaction with added chelating agents can be resolved and identified without interference from Fe or Mn complexes from a supporting phase.

EDTA can react with CoOOH in two ways. As a ligand, EDTA can bring about the CoOOH dissolution, yielding $Co^{III}EDTA^-$ as the sole reaction product. As a reductant, EDTA can generate Co^{II} and one or more EDTA oxidation products. The EDTA oxidation products, in turn, possess their own ligand and reductant properties, and undergo additional reactions with CoOOH and Co^{II}.

When the CoOOH loading (in moles/L) is much higher than the EDTA concentration, reaction proceeds primarily via ligand-assisted dissolution; the concentration of $Co^{III}EDTA^-$ is much higher than concentrations of other reaction products. Once the EDTA concentration exceeds the CoOOH loading, the redox reaction becomes dominant. The appearance of $Co^{II}EDTA^-$ is the clearest indication of this, although ED3A and other EDTA oxidation products are also present. The distribution of products also depends in a complex way upon pH. The rate of the redox reaction is relatively independent of pH, while the rate of ligand-assisted dissolution increases as the pH is decreased from 7.0 to 4.6.

In the reaction between CoOOH and NTA, the redox reaction is more important than the comparable reaction involving EDTA. Trends in product distribution as a function of chelating agent concentration, CoOOH loading, and pH are very similar to those observed with EDTA. IDA, the oxidation product of NTA, is readily identified by CE. Independent experiments have indicated that IDA can bring about the ligand-assisted dissolution of CoOOH, but exhibits negligible reductant reactivity.

The reduction potential for the MnOOH(manganite)/Mn^{2+} half-reaction is nearly equal to that for the CoOOH(heterogenite)/Co^{2+} half-reaction. Despite this fact, MnOOH reacts solely via the redox reaction; CE and spectrometric evidence indicates that dissolved Mn^{III} complexes do not form during reaction with EDTA, NTA, and IDA.

McArdell-Buergisser, C., A.T. Stone, B. Lanson, A. Manceau, and C.-F.Tien "Formation of Isomeric Co^{III} Complexes with Iminodiacetate During Ligand-Assisted Dissolution of CoOOH(Heterogenite)" (Manuscript in Preparation)

When the non-chiral chelating agent iminodiacetic acid (IDA) is brought into contact with CoOOH(heterogenite), two distinct diastereomers are formed that possess the stoichiometry $Co^{III}(IDA)_2^-$. Changing the CoOOH(heterogenite) synthesis procedure yields particles with dissimilar morphologies (i.e. different relative areas of important cleavage planes) and dissimilar structural properties (i.e. domain size and defect density.) Upon addition of IDA, particles produced by different synthesis procedures yield different ratios of the two diastereomers. The diastereomer ratio is also changed when the IDA concentration, CoOOH loading, and pH are changed.

In support of this work, two CoOOH(heterogenite) preparations have been extensively characterized using redox titration, electron microscopy, X-Ray diffraction, and EXAFS (with the assistance of Prof. David Veblen of Johns Hopkins University and Prof. Alain Manceau of the Joseph Fourier University in Grenoble, France). Since the IDA molecule is non-chiral, production of the two diastereomers must depend upon the relative abundance of two or more chiral sites on the CoOOH(heterogenite) surface.

Computer-generated structures of CoOOH(heterogenite) have been used to explore the stereochemistry of possible IDA reactions with each of two cleavage planes, with edge sites, and with defect sites within the CoOOH(heterogenite) structure. Possible mechanisms affecting the relative yields of u-fac, mer, and s-fac isomers have been proposed.

Stone, A.T., K.L. Godtfredsen, and B. Deng "Sources and Reactivity of Reductants Encountered in Aquatic Environments", In: "Chemistry of Aquatic Systems: Local and Global Perspectives", G. Bidoglio and W. Stumm, Edit., Kluwer Publishers, Dordrecht, The Netherlands (1994).

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There is growing recognition that chemical and biological processes within subsurface environments are closely linked, and that an integrated approach is needed to understand and predict toxic metal and radionuclide behavior. What is commonly referred to as "bioremediation" encompasses reactions and phenomena that have been studied in considerable detail by geochemists. Two reviews have been written that seek to to convey important information and concepts from geochemistry and inorganic reaction chemistry to scientists interested in bioremediation and biogeochemistry.

The first of these two reviews is concerned with metal-organic redox reactions. Subsurface organisms excrete molecules that intentionally or inadvertently reduce metal oxidants in the surrounding medium. Functional groups and molecular structures can be used to distinguish organic compounds that react rapidly with metal oxidants from those that do not. A number of organic intermediates and reaction products have been identified, which have made it possible to outline possible sequences of electron transfer steps.

Some organic redox reactions involve stoichiometric conversion of reactants to products (e.g. oxidation of hydroquinone to benzoquinone) while others generate a complex mixture of products, most typically via radical intermediates (e.g. oxidation of phenols to coupled and polymeric reaction products.) When stiochiometric conversion takes place, thermodynamic calculations that predict reaction progress as a function of pH and concentrations of participating species are readily performed. When a complex mixture of products is generated, it is often still possible to identify the rate-limiting step, and draw quantitative conclusions about reaction energetics (e.g. generation of phenoxy radicals during the oxidation of phenols.)

Metal ion-organic compound electron transfer can occur via an outer sphere mechanism (where the inner coordination sphere of the metal ion remains intact) or via an inner sphere mechanism (where the organic compound is bound directly to the metal ion center.) Inner sphere reactions are acutely sensitive to the coordination properties of both the metal ion and the organic compound. Rates of electron transfer can be limited by rates of ligand exchange at the metal center.

Changes in metal ion oxidation state yield pronounced changes in solubility. For this reason, many environmentally-important redox reactions involve precipitation, dissolution, sorption, or desorption. Bonding arrangements and the stoichiometries of

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surface species are inherently more difficult to determine than for corresponding dissolved species. For this reason, much less is known about surface redox reactions than about redox reactions in homogeneous solution.

Stone, A.T. "Reactions of Extracellular Organic Ligands with Dissolved Metal Ions and Mineral Surfaces", In: "Geomicrobiology: Interactions Between Microbes and Minerals", Mineralogical Society of America, Washington, DC (1997).

The second of two reviews is concerned with metal ion complexation by biologically-derived organic molecules. Organisms intentionally excrete organic ligands to serve a variety of physiological functions. In some instances the organic ligand performs it's intended function entirely outside of the organism (e.g. formation of an insoluble precipitate with a contaminant metal ion.) In other instances, the organic ligand captures metal ions from the extracellular medium and facilitates transport into the organism. (The charge, hydrophobicity, and stereochemistry of the metal ion-organic ligand are important, since receptor site selectivity often is based upon these properties.)

Functional groups and structures participating in metal ion coordination can readily be identified, and provide the basis for estimating the magnitude of equilibrium constants for metal ion complex formation reactions. Some degree of competition between metal ions and protons for available ligand donor sites always takes place. Similarly, organic ligands must compete with hydroxide ions for coordination of available metal ions. The affinity of hydroxide ions for $+III$ and $+IV$ metal ions, for example, is so great that only multidentate organic ligands are capable of solubilizing these metal ions within the environmentally-relevant pH range.

Equilibrium calculations have been performed that show the speciation of Cu^{II}, Fe^{III}, and Al^{III} as a function of pH in the presence of a number of biological chelating agents. It becomes apparent that organic ligands that perform effectively under acidic conditions do not necessarily perform well under alkaline conditions (and vice versa.) Changes other medium characteristics (e.g. major ion composition, presence of natural organic matter) can also influence the ability of organic ligands to distinguish between nutrient metal ions and toxic metal ions. Organic ligands typically coordinate one metal oxidation state more strongly than another, and hence have an important effect on redox potential and the energetics of redox reactions.

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Although a great deal has been learned in recent years regarding organic ligand adsorption onto mineral surfaces, our knowledge of surface speciation and the coordination chemistry of the surface is still rather limited. The most successful approach to date has been to assume that surface complexes are analogous to solution complexes, once corrections have been made for long range electrostatic interactions (e.g. adsorption of an anionic organic ligand onto a positively charged oxide surface.) The distinction between organic ligands that exclusively adsorb and organic ligands that bring about ligand-assisted dissolution is not clear at present.

Three figures are used to illustrate the enormous range in functional groups and structures found on biological organic ligands. Metal ion coordination strategies employed by organisms have evolved throughout earth's history, and probably represent optimal solutions to physiological, biochemical, and geochemical design constraints.

CONCLUSIONS

Several knowledgeable researchers in the areas of inorganic coordination chemistry, mineral/water interface chemistry, and the geochemistry of subsurface environments were already part of the Co-Contaminant Subprogram when our participation began. Our group was able to add expertise in organic analytical chemistry, organic structure-property relationships, and metal-organic reaction chemistry to the Subprogram effort.

One set of accomplishments was made in our laboratory before we began using capillary electrophoresis. Using known low molecular-weight organic reductants and complexants, five distinct metal ion desorption mechanisms were for the first time distinguished and quantified. Rates and extent of desorption could be related to fundamental properties of the surfaces, metal ions, and organic compounds employed in the experiments. Once this work was accomplished, it was possible to distinguish and quantify processes controlling metal desorption behavior following natural organic matter addition.

Co-Contaminant Sub-Program needs motivated us to develop capillary electrophoresis for the identification and quantification of synthetic chelating agents, their breakdown products, and their complexes with +II and +III metal ions. The tremendous potential of this technique has been effectively demonstrated by our first

publication on this area. The ability to monitor chelating agent breakdown reactions, and to speciate metal ions and chelating agents in biological reactors and under near-field subsurface conditions is unprecedented.

Our work with CoOOH(heterogenite) and MnOOH(manganite) represents the first application of capillary electrophoresis to the study of heterogeneous geochemistry. Despite the similar redox potentials of the corresponding +II/+III half-reactions, CoOOH and MnOOH exhibit considerable differences in reaction chemistry. CoOOH reacts via both ligand-assisted dissolution and reductive dissolution, while MnOOH reacts via reductive dissolution only. This work provides clear evidence that EDTA, NTA, and other synthetic chelating agents can be degraded by nonphotochemical, oxidative processes under conditions representative of subsurface environments. The high resolution power of capillary electrophoresis has also enabled us to distinguish diastereomers produced by the reaction of IDA (iminodiacetic acid) with the CoOOH(heterogenite) surface. IDA serves as an effective probe for determining the bonding arrangements and stereochemistry of surfaces sites.

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