Heavy Metal and Radionuclide Sorption on Mineral Surfaces: The Role of Anionic Ligands

D.O.E. Project # 54860

Participants:
(alphabetical order)

John Bargar *
Rizlan Bencheikh
Matthias Kohler **
James Leckie
Jinhe Li
Yanping Liao
George Redden
Maya Trotz
Mario Villalobos
David Villarreal

Stanford University
Dept. of Civil and Environmental Engineering
Stanford, CA

*** Stanford Synchrotron Radiation Laboratory**

****U.S. Geological Survey**
Menlo Park, CA

Objectives

Characterize the Effect of Anionic Ligands on Heavy Metal Partitioning at Oxide Mineral Surfaces:

Anionic ligands can increase or decrease the sorption of heavy metals on mineral surfaces. As a result, synthetic and naturally occurring ligands and chelators will affect the rates of heavy metal migration in soils and groundwater, and the chemical, redox, and microbially mediated transformations. Chelating compounds are often components of complex waste mixtures that have been released to the environment. Microorganisms and plants also produce a wide range of metal chelating compounds. The chemical stabilities of these compounds span a wide range and are themselves dependent on their speciation with metals and surfaces.

The complexity of metal - ligand - surface interactions make it apparent that equilibrium sorption models should be based on, at least generally, the actual physical and chemical mechanisms, rather than purely empirical partitioning coefficients. The more the models reflect actual physical/chemical processes, the better will be their ability to extrapolate to conditions outside the experimental parameter space rather than only interpolate within it. Therefore, this project attempts to obtain a set of macroscopic and molecular level details that should help constrain the model simulations.

Experimental Systems in This Project:

Metals (cations): UO_2^{2+}, Sr^+, Pb^{++}
Ligands: Citrate^{3-}, NTA^{3-}, EDTA^{4-}, CO_3^{2-}
Surfaces: Gibbsite, Kaolinite, Goethite

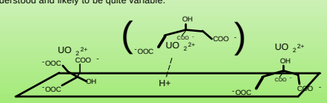
Establish Consistency between A Range of Experimental Observations and Modeling:

Application of chemical processes to environmental issues requires a predictive capability. Several models and variations have been proposed to describe the surface chemistry that controls the partitioning of chemical species between solid and solution phases. Although these models are often successful at simulating experimental data, they are often unconstrained. Different models, or different parameter sets for an individual model, will often yield equally acceptable data simulations. This means that predictions outside the experimental conditions (extrapolation) are risky and additivity of modeling results for individual systems has rarely been demonstrated.

An objective of this project is to determine whether results from multiple experimental techniques applied to the same system conform to a self-consistent interpretation that can be used to constrain or validate model simulations.

Hypotheses

Decreased metal sorption in the presence of anionic ligands and chelators can generally be explained by the formation of soluble metal-ligand species. Increased sorption in the presence of anionic ligands is also observed, as was the case for the goethite-citrate-uranyl system, although the mechanisms are less well understood and likely to be quite variable.



Note that extended bridging structures can have charge centers located at significant distances from the surface. Models that employ electrostatic free energy expressions will have to account for these displacements (e.g., Filius et al, 1998). A consequence of a structure of the first type where particle charge may be net positive, but with a significant population of negatively charged carboxylic groups, could be that increases in ionic strength would lower the free energy of reaction with a cationic species (UO_2^{2+}). Whether this interaction is best described by an electrostatic (outer-sphere) interaction or as a covalent bond has been one focus of this project.

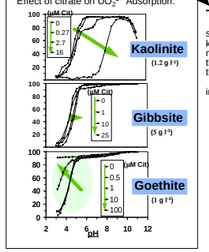
Relevance

Metal-complexing ligands affect the solid-solution partitioning of metals. This will play a role in metal transport and bioavailability in aquatic systems and can be employed to either enhance or decrease the mobility of contaminant metals in soils and groundwater.

The nature of metal-ligand surface complexes will be related to the degree to which changes in other system components (solutes, pH) affect changes in metal mobility and bioavailability.

Knowledge of the actual types of surface complexes helps to constrain the surface complexation models used to simulate experimental data. This should improve the capabilities of these models by reflecting more closely actual surface chemistry. This should lead to models that are more robust in environmental applications and that are better suited for interpreting experimental observations.

Effect of citrate on UO_2^{2+} Adsorption:

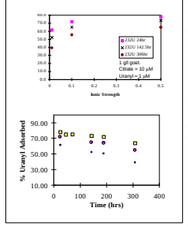


Initial Observations

The initial study (Redden et al., 1996, 1998) demonstrated that the effect of citric acid on uranyl sorption depends on properties of the mineral surface. Citric acid decreases sorption of uranyl on kaolinite. In the gibbsite system, little effect was seen although higher concentrations of citric acid may have been necessary to induce a response. Citric acid significantly enhanced uranyl sorption in the presence of goethite. The obvious effect is seen in the low pH range but this does not imply that the state of sorbed uranyl in the upper pH range remains unchanged.

The relative concentrations at which the effect of citrate on uranyl was observed implies that the important parameter may be the citrate:surface ratio rather than the citrate:uranyl ratio.

Uranyl Adsorption on Goethite - pH 3.5: Kinetics and Ionic Strength Dependence



Ionic Strength Effect

The effect of ionic strength on sorption is often interpreted in terms of the electrostatic models for surface complexation. Decreasing sorption of ionic species with increasing ionic strength implies that the surface complex is a weaker outer-sphere complex which is easily displaced by other electrolyte ions or is less favorable due to a reduction of the near surface electrostatic potential field. If increases in ionic strength have little effect on sorption, the implication is that the complex is a strong covalent or ionic bond.

In this system, an "inverse" ionic strength effect was observed. Increases in ionic strength were found to increase the sorption of uranyl in the presence of citrate. This trend has rarely been reported. A hypothesis that is consistent with this observation is that in the low pH range where citrate increases uranyl sorption, the goethite surface is made up of negatively charged, surface-bound citrate, but still has a net positive charge from proton adsorption. The increase in ionic strength may make the cation-anion interaction between uranyl and surface-citrate more favorable by reducing positive potential near the surface. The actual location of the negative charge from citrate will be an interesting issue since it may not reside immediately adjacent to the surface, and is likely to extend further into solution.

Proton Stoichiometry for Citrate Sorption

In the low pH range, citrate speciation is primarily a mix between the unprotonated and singly protonated forms. Adsorption on the goethite surface, even at pH 3.5, results in production of H^+ in solution. This is consistent with the formation of negatively charged surface-citrate sites. At higher pH values, H^+ consumption is observed. The actual stoichiometry of the sorption reaction cannot be directly deduced from the results shown in the right-hand column of the table since, if an electrostatic surface complexation model is accepted, the release of protons will be buffered by the change in net surface charge, i.e., the reduction in surface potential will result in a parallel consumption of protons at surface hydroxyl sites. The stoichiometry, however, should be reflected in a valid model simulation of the sorption data.

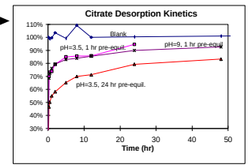
Summary of proton stoichiometries for the Citrate / Goethite system

pH	Sorption Density initial / final (μmole / g)	Sorption Density initial / final ($\#$ / nm^2)	ΔH^+ / Δ UO_{ads}
4.0	0 → 4.8 4.8 → 9.7 9.7 → 14.6 14.6 → 80.5	0 → .071 .071 → .14 .14 → .21 .21 → 1.2	0 → .04 .04 → .08 .08 → .14 .14 → .72	8 .54 .2 .3
6.0	0 → 5.0 5.0 → 10.1 10.1 → 15.5 15.5 → 101	0 → .073 .073 → .15 .15 → .23 .23 → 1.5	0 → .044 .044 → .09 .09 → .14 .14 → .92	-1.8 -1.9 -1.9 -1.4
8.0	0 → 5.0 5.0 → 10.1 10.1 → 15.5 15.5 → 101	0 → .073 .073 → .15 .15 → .23 .23 → 1.5	0 → .044 .044 → .09 .09 → .14 .14 → .92	-1.7 -1.5 ? -1.3

Desorption Kinetics of Citrate

The issue of thermodynamic equilibrium, reversibility of sorption reactions, and mass balance is important in studies of this type. The desorption of citrate was studied by equilibrating citrate and goethite at low pH (where sorption is 100%) for different lengths of time, then adjusting the systems to pH = 12 to remove citrate. The result is consistent with what is often observed in this type of experiment where longer pre-equilibration periods result in longer desorption, even for non-porous materials. Desorption under these conditions continued for more than 72 hours. Verification of mass balance was done by adding concentrated base (approximately 2 M NaOH). The recovery of citrate was approximately 95%.

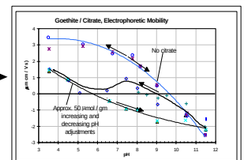
Desorption is expected to be slow for multi-functional ligands since, if more than one functional group is bonded to the surface, removal from the surface requires that all bonds be broken simultaneously. The change in desorption rates could indicate that the bonding arrangement changes ("matures") with time. This, in turn, would have a bearing on subsequent interaction with uranyl and how the sequence of component addition affects the short term species distributions.

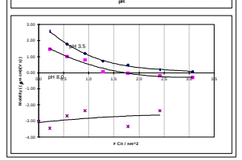


Electrophoretic Mobility

The electrophoretic mobility of the goethite with and without citrate was studied to see if the particle surface charge was qualitatively consistent with the sorption results and proton stoichiometry. The results shown below are for short equilibration times, but the effect of citrate is clearly seen. (Interpretation of the mobility is not attempted since derivation of the zeta potential from theoretical arguments is based on Stokes Law and the assumption that particles are spherical.)

Citrate reduces the surface charge over the pH range where citrate adsorption is significant. This is consistent with the formation of a negatively charged, covalently bonded citrate molecule. One feature that is surprising is that with increasing citrate concentration, citrate continues to reduce the surface charge up to an apparent surface coverage of 4 molecules per nm^2. This surface coverage exceeds the likely surface site density for goethite (2-10 sites/nm^2) and possibly the geometric space available. One possibility is that less than 100% of the citrate is sorbed. Alternatively, the way in which citrate is bound may change with surface coverage, e.g., bound by only one functional group.



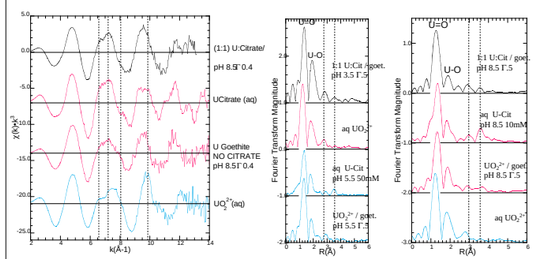


EXAFS

An analysis of the goethite | citrate | uranyl system was conducted using Extended X-ray Absorption Fine Structure spectroscopy. This technique probes the atomic composition of the volume immediately surrounding a target atom, uranium in this case. We want to know whether UO_2^{2+} is associated with citric acid on the goethite surface, and how the association compares to uranyl-citrate solution complexes.

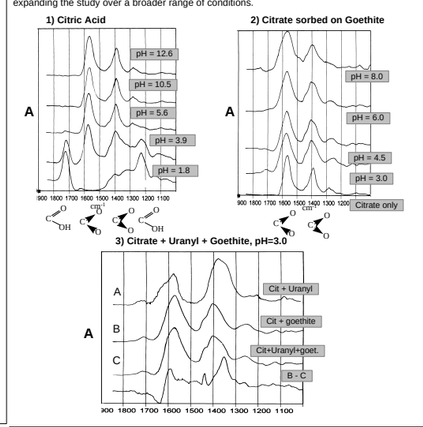
The objective is to develop consistency with the stoichiometric and structural interpretations for possible surface complexes that result from surface complexation model simulations of the experimental data, and with the other experimental observations presented in this poster. This is valuable since it can provide additional constraints on the range of surface reactions used to model the data.

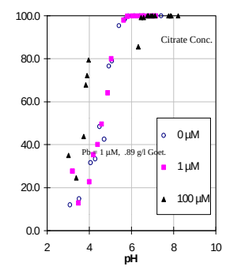
Although preliminary, an interpretation of the spectra is that at low pH uranyl forms an outer-sphere complex with a negatively charged surface-citrate site. This is based on the similarity of the spectra for free UO_2^{2+} ion, and the ternary system. At higher pH, although uranyl is still 100% sorbed, the state may be a mixture of goethite-UO_2^{2+}, and goethite-citrate-UO_2^{2+} complexes with UO_2^{2+} is covalently bound to citrate.



ATR - FTIR

A preliminary study of citric acid sorption with and without uranyl, using ATR - FTIR, shows that citrate is not an outer-sphere complex at pH 3.5 except to the degree that hydrogen bonding may be involved. In addition, the presence of uranyl appears to affect a portion of the carboxylic groups. Although EXAFS suggests that an outer-sphere complex between surface-citrate and uranyl is possible, the bonding may still be a stronger hydrogen or covalent bond. As with the EXAFS study, spectra from additional model compounds are being acquired in addition to expanding the study over a broader range of conditions.





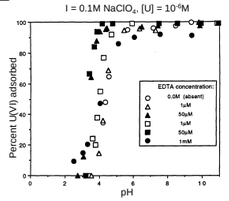
Lead - Citrate - Goethite

The binary lead sorption edge lies between pH 3-6 as expected (Balistrieri et al., 1982; Hayes, 1987; Muller et al., 1992). Like the uranyl-citrate system, equimolar citrate concentrations do not affect the sorption behavior of lead to goethite. A 100 fold excess of citrate to lead increases the sorption of lead to goethite in the lower pH region, although the effect of citrate is less than that for uranyl. Citrate forms weaker solution complexes with lead than with uranyl. This may be related to the difference in adsorption between lead and uranyl. This also implies that at least for uranyl, citrate speciation at the surface involves a covalent complex bridging structure since purely electrostatic interactions would be expected to be more similar for lead and uranyl. Nowack and Sigg (1996) found that at equimolar Pb and EDTA concentrations, Pb sorbed to goethite as an anionic complex, mirroring the EDTA behavior. In the higher pH region where citrate sorption decreases, lead is still sorbed 100% and is not affected by citrate.

Uranyl - EDTA - Goethite

EDTA has also been shown to promote the sorption of uranyl on goethite. The effect was not as pronounced as in the case of citrate and modeling efforts were not successful at simulating the observed behavior. The enhanced adsorption occurs in the manner of a metal-like ternary surface complex. Since the EDTA is predominantly (>80%) partitioned to the goethite surface at pH < 6, it is possible that EDTA attaches to the goethite in one configuration that creates a higher energy site for the uranyl, leading to modest increases in adsorption in the low pH region.

Adsorption of U(VI) onto 1 g/l goethite
Effect of EDTA
I = 0.1M $NaClO_4$, [U] = 10^{-6}M



Microbial Degradation of Citrate:

A PROBLEM, A TOPIC, AND A FEATURE.

The potential for biological degradation of citric acid presents a problem when conducting sorption experiments, especially where long equilibration times are involved. Since ^{14}C labeled citrate was used in the experiments, and citrate was measured as the ^{14}C content of a sample, loss of volatile 14C degradation products would be misinterpreted as citrate sorption. Conversion to undetected, non-volatile species will affect the thermodyanmic interpretation of solid - solution partitioning of citrate. Therefore, evidence for degradation during the experiments was monitored and steps were taken to maintain sterile conditions.

The fact that citrate can be readily degraded is also a potentially useful attribute with respect to its use for remediation of metal contaminated soils and groundwater. The degradation is likely to be affected by whether citrate is adsorbed or bound to metals. Similarly, the bioavailability of metal-bound citrate is likely to influence the speciation and partitioning of the metal.

SORPTION EXPERIMENTS:

Citrate samples were equilibrated at 25°C for 24 hours and loss of citrate was recorded. The effects of uranyl and goethite were tested.

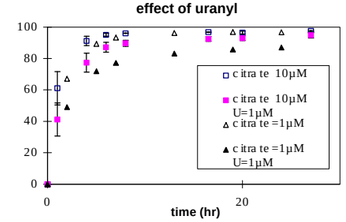
- **In the absence of goethite:**

Without autoclaving, up to 70% of the citrate can be degraded after 24 hours in the absence of uranyl. In the presence of uranyl, less degradation was seen in this time period than for citrate alone.

- **In the presence of goethite:**

Tests showed less than 6% loss of citrate after 24 hours in the presence of goethite.

Degradation of citrate by P. fluorescens - effect of uranyl



Results:

Citrate degradation is highly unpredictable in non-sterile systems. In some cases significant degradation occurred within a day. Replicating experiments remains the best way to check for potential degradation effects in abiotic experiments. Even when precautions are taken to maintain sterile conditions, the possibility of microbial degradation can not be ignored.

The presence of goethite seems to lower the rate of degradation of citrate, possibly due to sorption of citrate to the surface.

Role of microorganisms in the fate of uranyl:

Citrate-uranyl complex degradation:

Pseudomonas fluorescens, a bacteria capable of degrading citrate and some metal-citrate complexes (Joshi-Tope et al., 1995) has recently been shown to be able to degrade the uranyl-citrate complex (see fig). It is not known at this time if the complex itself is metabolized or if dissociation of the complex and release of free citrate is required.

Potential effects on uranyl mobility:

This finding may have profound effects on the mobility of uranyl in a system containing citrate. The abiotic system may not be sufficient to predict the mobility of uranyl in certain DOE sites.

References:
Joshi -Tope, G. and A. J. Francis. 1995. Mechanisms of Biodegradation of metal-citrate complexes by *Pseudomonas fluorescens*. Journal of Bacteriology, **177**, 8, pp 1989-1993

Summary

Citric acid and EDTA have exhibited the ability to promote sorption of heavy metals (uranyl and lead in this study) on goethite. In the case of citric acid, metal sorption appears to be the result of strong covalent bonding of citrate with the iron oxy-hydroxide surface which produces negatively charged binding sites for cations. Whether the interaction between the sorbed-ligand and metal is inner or outer-sphere has not yet been demonstrated and a mixture of species is certainly possible. The nature of the mineral surface is significant since the surface-ligand bond must compete with the formation of metal-ligand solution species. Sorption of citrate on minerals such as kaolinite and gibbsite is not as strong as for goethite.

Since a high surface coverage by the ligand is necessary for significant metal adsorption to occur, and because an "inverse" ionic strength effect was observed, it appears that the near-surface electrostatic potential field is a significant factor in the free energy of the complexation reaction. This and the preliminary EXAFS data support the possibility that interaction between the surface-bound citrate and uranyl is electrostatic. However, FTIR data show a distortion of the carboxylic group environment in the presence of uranyl which suggests that a ligand-like bond also contributes to the surface speciation. Over the pH range where uranyl is predominantly in the sorbed state, the actual type of surface structure can vary although the possibility of an outer-sphere association between a positively charged goethite surface and a citrate-uranyl anion can be discounted.

Conclusions from the experimental results have implications for sorption modeling where fitting the sorption "edge" would not require variations in the complexation stoichiometry or structure in the region where uranyl is 100% sorbed. A robust complexation model should have the mathematical functionality to capture these reactions if extrapolation outside the experimental conditions is important. The structure of the ternary surface complexes may also correlate with the bioavailability of the sorbed metal or ligand.

The actual structure also requires modification of the general electrostatic surface complexation models since the distinction between inner and outer-sphere complexes often follows a parallel assignment of ionic charge to particular planar regions next to the surface. Large molecules such as citrate will have charge centers displaced from the surface. The combination of macroscopic and spectroscopic data should provide an opportunity to constrain the reaction sets that are used to model the sorption behavior.

The issue of thermodynamic equilibrium is a critical concern in these types of studies. Most laboratory based studies are relatively short compared to many environmentally relevant time scales. Two issues that require further study are:

1) The role of metal oxide dissolution: Fe^{3+} and Al^{3+} form some of the strongest complexes with many chelating ligands. Depending on the solubility of the oxide phase, competition by these elements could be expected to displace uranyl, lead, or strontium. The end result could be either sequestration of the organic ligand such that it plays little role in partitioning of the other heavy metals, or competition for surface bound ligand sites.

2) The sequence of exposure of the mineral surface to ligand and metal could be significant. Desorption experiments generally show that longer equilibration times result in longer desorption kinetics and potentially a higher degree of irreversibly sorbed component. This indicates, not surprisingly, that thermodynamic equilibrium, even metastable states, are not necessarily achieved in short time scales. Biological issues will be serious issues for longer term studies.

Publications / Presentations

Bargar, J. R., R. L. Reitmeyer, C. C. Fuller, G. D. Redden, J. A. Davis, et al. (1998). Remediation and reactive transport of uranium(VI) in groundwaters. Stanford, Stanford Synchrotron Radiation Laboratory: 5.

Redden, G. D., J. Li and J. O. Leckie (1995). Influence of citric acid on the adsorption of uranyl ion on goethite. American Geophysical Union, Fall 1995, San Francisco, CA, Am. Geophys. Union.

Redden, G. D., J. Li and J. O. Leckie (1996). Ternary Uranyl-citrate-surface complex formation on goethite gibbsite, and phyllosilicate minerals. American Chemical Society, Spring 1996, New Orleans, LA, Am.Chem. Soc.

Redden, G. D., J. Li and J. O. Leckie (1997). Adsorption of uranium(VI) and citric acid on goethite, gibbsite, and kaolinite: Comparing results for binary and ternary systems. Adsorption of Metals by Geomedia. E. A. Jenne. New York, Academic Press: 291-315.

Redden, G. D., P. Persson, R. Bencheikh-Latmani and M. Trotz (1997). Adsorption of uranyl on gibbsite, kaolinite and goethite in the presence of citric acid. Proton stoichiometry and ITC spectroscopic details for the goethite system. American Chemical Society, Spring 1997, San Fransisco, CA, Am.Chem. Soc.

Heavy Metal and Radionuclide Sorption on Mineral Surfaces: The Role of Anionic Ligands - Carbonate

Mario Villalobos, James Leckie, John Ostergren, George Redden
Department of Civil and Environmental Engineering, Stanford University, Stanford, CA

D.O.E. Project # _____

CARBONATE ADSORPTION ONTO GOETHITE

RELEVANCE

Carbonate Is Pervasive In Natural Aquatic Environments:

- Concentrations are comparable to other major ions: Ca^{2+}, Na^{+}, SO_4^{2-}, Cl^{-}
- Concentrations are a function of mineralogy, pH and P_{CO2}
  - Contributions in river water: Atmospheric CO_2 60%, carbonate minerals 31%, organic matter 7%
- Underground P_{CO2} ranges from 0.35 matm to 50 matm (may reach 200 matm)
- Average carbonate concentrations: 1 mM in rivers, 6.3 mM in groundwater

Carbonate Species Adsorb to Mineral Surfaces

- Carbonate adsorption onto colloidal solids is expected to affect partitioning of other solutes onto surfaces.
- Knowledge of the adsorptive behavior of carbonate is fundamental to understanding and predicting mobility and fate of ionic pollutants.

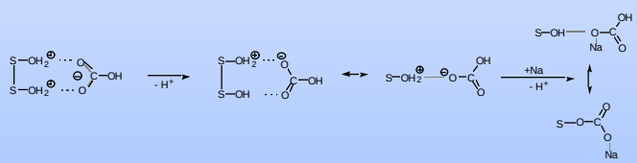
RESULTS:

Carbonate Adsorption on Goethite

- Carbonate adsorption on goethite has been determined experimentally in a closed recirculating gas/liquid system. The equilibrium pH and P_{CO2} of an aqueous suspension is determined after adding known quantities of carbonate.

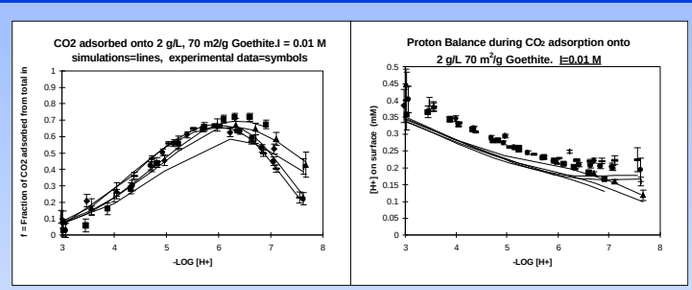
$$[CO_3]_{ads} = [CO_3]_{tot\ added} - [CO_{2(g)}] - [CO_3]_{solution}$$

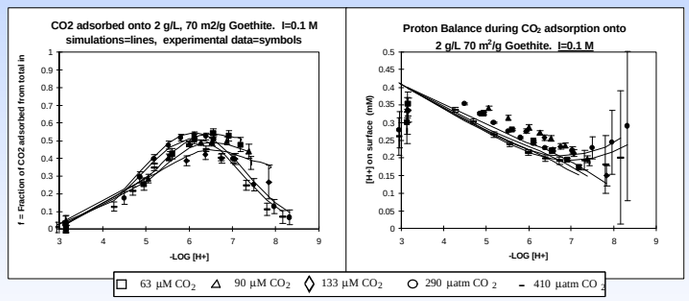
- Adsorption in closed and open systems were studied as a function of pH, total solution carbonate (10 µM to 5 mM), and ionic strength (0.01 and 0.1 M).
- Closed systems with up to 0.133 mM total carbonate showed maximum adsorbed concentrations for pH values between 6 and 7. The estimated site coverage is 14% for a site density of 2.3 sites/nm^2.
- In Open systems, carbonate adsorption (and total carbonate in solution) continuously increased up to the studied pH of 8.5. At this pH and near atmospheric P_{CO2} of 3.4 matm, surface site coverage was close to 40% (assuming 2.3 sites/nm^2). A similar coverage was obtained for the system at 5.5 matm CO_2 at a pH of 7.5.
- Increasing ionic strength significantly decreased adsorption of carbonate onto goethite for pH values < 7.
- The Triple Layer Model (TLM) for surface complexation was used to simulate the carbonate adsorption data. Surface acidity constants for goethite were determined independently from systems without carbonate.
- The best simulation of the carbonate adsorption data was obtained by including reactions for the formation of three different carbonate surface complexes. The surface complex stoichiometries were arrived at from an analysis of all possible charge distribution configurations at the solid-liquid interface.

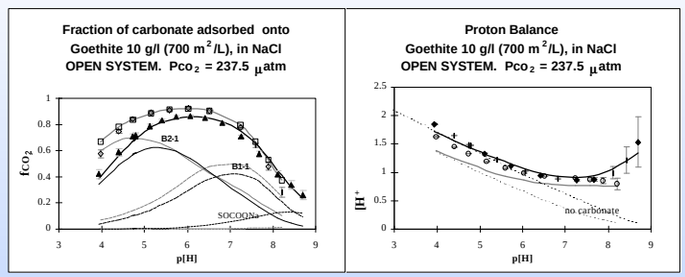


	B2-1	B1-1	M1-1	M0-1+Na
Log K =	30.7	21.5		13.1

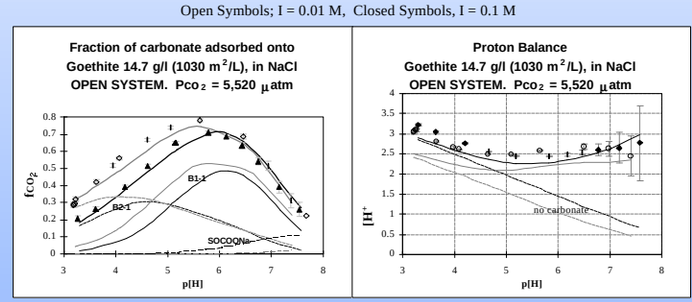
- The TLM cannot be used to distinguish between bonding arrangements having the same stoichiometry and charge distribution (e.g., complexes under M0-1+Na). ATR-FTIR work is currently being conducted to determine whether the possible surface complexes suggested by the TLM modeling exercise are present.

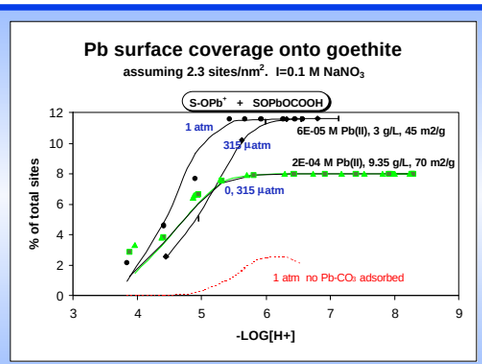






Open Symbols; I = 0.01 M, Closed Symbols, I = 0.1 M





Effect of Carbonate on Pb(II) Adsorption

- Anionic adsorption onto goethite is normally found to decrease in the presence of carbonate (for example for chromate (Cr(VI)) and acetate) (previous work).
- Cationic adsorption effects are more complex due to the formation of soluble and insoluble carbonate species, and the possibility of adsorbing metal-carbonato species. For example, uranyl (UO_2^{2+}) and neptunyl (NpO_2^{+}) adsorption onto aluminosilicate and oxide surfaces decreases in the presence of carbonate. This can be explained by the formation of carbonato complexes in solution that do not sorb strongly. (previous work).
- Preliminary experiments with Pb(II) show the opposite effect of carbonate on metal adsorption. Atmospheric CO_2 shows no difference in the adsorption behavior of Pb onto goethite compared to the absence of CO_2. Increasing the P_{CO2} to 1 atm causes an enhancement in the adsorption of Pb.
- The TLM simulates this effect by including a reaction for the formation of a ternary Pb-bound carbonato complex:

SO-Pb-OCOOH

Selected References

- *Villalobos, M. and J.O. Leckie. (1998). Carbonate adsorption onto goethite: I. Macroscopic adsorption behavior under a wide range of closed and open CO_2 conditions. In progress. To submit to Geochimica et Cosmochimica Acta.*
- *Villalobos, M. and J.O. Leckie . (1998). Carbonate adsorption onto goethite: II. Simulation of carbonate and proton adsorption using the triple layer surface complexation model. Extrapolations to natural environments. (in prep.)*
- *Mason, C.F.V.; W.R.J.R. Turney; B.M. Thompson; N. Lu; P.A. Longmire and C.J. Chisholm-Brause. (1997) Carbonate leaching of uranium from contaminated soils. ES&T. 31, 2707-2711.*
- *Reardon, E.J.; R.D. Kellerman, R.W. Gillham and H.M. Johnston. (1986). Carbonate sorption capacity of iron hydroxide and soil material. In: 2nd. International conference on radioactive waste management, proceedings. Canadian nuclear society, Toronto, Ontario, Canada, 151-157.*