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Center for Environmental Kinetics Analysis

CEKA

The Center for Environmental Kinetics Analysis: an NSF- and DOE-funded Environmental Molecular Science Institute (EMSI) at Penn State

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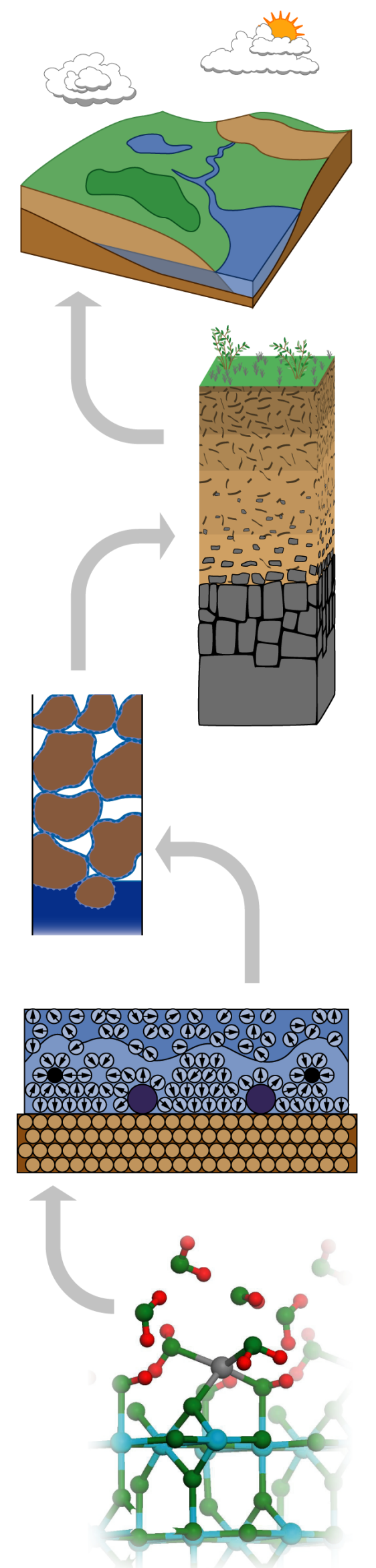


CEKA Structure and Research

Physicochemical and microbiological processes taking place at environmental interfaces influence natural processes as well as the transport and fate of environmental contaminants, the remediation of toxic chemicals, and the sequestration of anthropogenic CO_2. A team of scientists and engineers has been assembled to develop and apply new experimental and computational techniques to expand our knowledge of environmental kinetics. We are also training a cohort of talented and diverse students to work on these complex problems at multiple length scales and to compile and synthesize the kinetic data. Development of the human resources capable of translating molecular-scale information into parameters that are applicable in real world, field-scale problems of environmental kinetics is a major and relatively unique objective of the Institute's efforts. The EMSI team is a partnership among 10 faculty at The Pennsylvania State University (funded by the National Science Foundation Divisions of Chemistry and Earth Sciences), one faculty member at Juniata College, one faculty member at the University of Florida, and four researchers drawn from Los Alamos National Laboratory, Pacific Northwest National Laboratory, and Lawrence Berkeley National Laboratory (funded by the Department of Energy Division of Environmental Remediation Sciences). Interactions among the applied and academic scientists drives research approaches aimed toward solving important problems of national interest.

The Institute is organized into three interest groups (IGs) focusing on the processes of dissolution (DIG), precipitation (PIG), and microbial reactions at surfaces (BIG). Some of the research activity from each IG is highlighted to the right. The IGs interact with each other as each interest group studies reactions across the molecular, microscopic, mesoscopic and, in most cases, field scales. For example, abiotic dissolution and precipitation reactions of Fe oxides as studied in the Dissolution IG provides the baseline for kinetic behavior as the BIG researches the interaction of microorganisms with these same minerals. The attachment of bacteria and redox chemistry that occurs between microorganisms and minerals are critical factors in maintaining groundwater quality and remediation of many toxic waste sites and is one of the main thrusts of research within our EMSI. The IGs also participate in using visualization tools to promote greater understanding of complex environmental data. As a whole, CEKA is also working to compile environmental kinetics data into a cyberinfrastructure and database. The database can be accessed at: http://keystone.ist.psu.edu/

Most Recent CEKA Publications

Navarre-Sitchler, A. and Brantley, S. (under review) Basalt Weathering Across Scales, For: Earth and Planetary Science Letters

Washton, N.M., Brantley, S.L.and Mueller, K.T. "Probing the molecular-level control of aluminosilicate dissolution: A sensitive solid-state NMR proxy for reactive surface area". Submitted to Geochim. Cosmochim. Acta.

Campen, R.C., and Kubicki, J.D. (2007) Calculating gas phase energies of an α(1–4) linked disaccharide: electronic structure theory and classical atomistic simulation. Journal of Molecular Structure: THEOCHEM, Vol. 806, Issues 1-3, 31 March, p. 9-22

Conrad C. F., Icopini G. A., Yasahura, H., Bandstra J. Z., Brantley S. L. and Heaney P. J. (2007) Modeling the Kinetics of Silica Nanocolloid Formation and Precipitation in Geologically Relevant Aqueous Solutions. Geochimica et Cosmochimica Acta Vol. 71, Issue 3, 1 February 2007, p. 531-542

Lichtner, P.C. and Kang, Q. (2006), Comment on: "Upscaling geochemical reaction rates using pore-scale network modeling" by Li, Peters and Celia, Adv. Water Res., in press.

Kang, Q., Lichtner, P.C., and Zhang, D., "Lattice Boltzmann pore-scale model for multi-component reactive transport in porous media", Journal of Geophysical Research, in press.

Bandura A.V., Sofo J., and Kubicki J.D. (2006) Derivation of force field parameters for SnO2-H2O surface systems from DFT-PW calculations. Journal of Physical Chemistry B, 110(16); 8386-8397.

Fry R., Kwon K., Kubicki J.D., and Mueller K.T. (2006) Investigation of surface complexation of nucleotides with metal oxide surfaces. J. Am. Chem. Soc. In prep.

Goldman S.D. and Kubicki J.D. (2006) Quantum mechanical modeling of equilibrium isotope fractionation of iron between organic and inorganic complexes. Geochim. Cosmochim. Acta, submitted.

Ketchum, B. 2006. Center for Environmental Kinetic Analysis: Biogeochemists spanning scales of space and time. The Geochemical News, No., 126, p. 29-33.

Kwon K.D., Vadillo-Rodriquez V., Logan B.E., Kubicki J.D. (2006) Interactions of biopolymers with silica surfaces: Force measurements and electronic structure calculations. Geochimica et Cosmochimica Acta, Vol. 70, Issue 15, 1 August 2006, p. 3803-3819.

Lichtner, P.C. and Carey, W.J. "Incorporating solid solutions in geochemical reactive transport equations using a kinetic discrete composition approach," Geochimica Cosmochimica Acta, 70, 1356-1378.

Paul, K.E., Kubicki, J.D. & D. L. Sparks (2006) Sulfate adsorption at the Fe-(hydr)oxide-H2O interface: Results from hybrid MO/DFT cluster and periodic ab initio DFT slab calculations. International Journal of Soil Science, Submitted.

Ruebush, S., Brantley, S.L., and Tien, M. Reduction of soluble and insoluble iron forms by membrane fractions of Shewanella oneidensis grown under aerobic and anaerobic conditions. Applied and Environmental Microbiology, Apr. 2006, p. 2925–2935 Vol. 72, No. 4.

Nangia Shikha, Nancy M. Washton, Karl T. Mueller, James Kubicki, and Barbara J. Garrison, "Study of a Family of 40 Hydroxylated β-Cristobalite Surfaces Using Empirical Potential Energy Functions". Accepted, J. Phys. Chem. C

Tribe L., Kwon K., Trout C.T., and Kubicki J.D. (2006) Molecular orbital theory study on surface complex structures of glyphosate on goethite: Calculation of vibrational frequencies. Env. Sci. Technol., 40(12); 3836-3841.

Trout C.T. and Kubicki J.D. (2006) Al3+ and benzene interactions with Suwannee fulvic acid. Geochim. Cosmochim. Acta, Submitted.

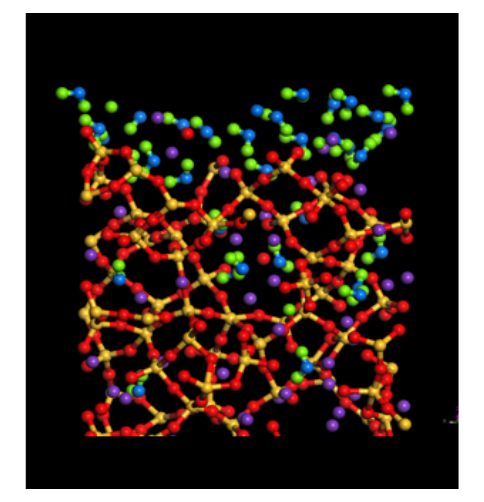
Zhang, Z., Fenter, P., Kelly, S.D., Catalano, J.G., Bandura, A.V., Kubicki, J.D., Sofo, J.O., Wesolowski, D.J., Machesky, M.L., Sturchio, N.C., and Bedzyk, M.J. 2006. Structure of hydrated Zn2+ at the rutile TiO2 (110)-aqueous solution interface: Comparison of X-ray standing wave, X-ray absorption spectroscopy, and density functional theory results. Geochimica et Cosmochimica Acta, Vol. 70, Issue 16, 15 August 2006, 4039-4056.

Dissolution Interest Group

Reactive Surface Area in the Environment

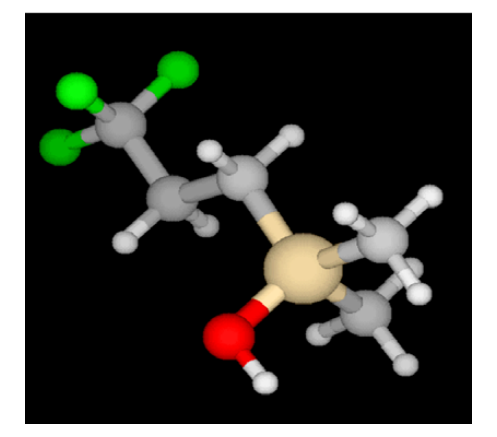
Our research question: In order to normalize reaction rates in environmental dissolution studies, how do we effectively evaluate the reactivity of a surface? Should we use a "surface area" measurement to normalize dissolution rates that lacks chemical specificity or information?

In this research, we have developed a proxy for "reactive surface area", with both a macroscopic and atomistic interpretation, that will help environmental researchers effectively compare dissolution data across spatial and temporal scales for (acid-mediated) dissolution processes.

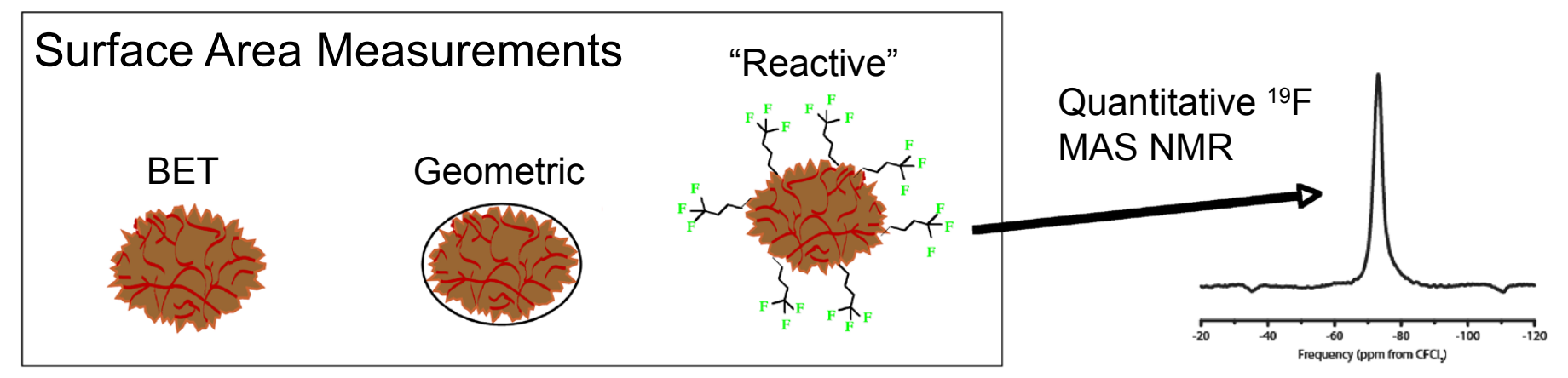


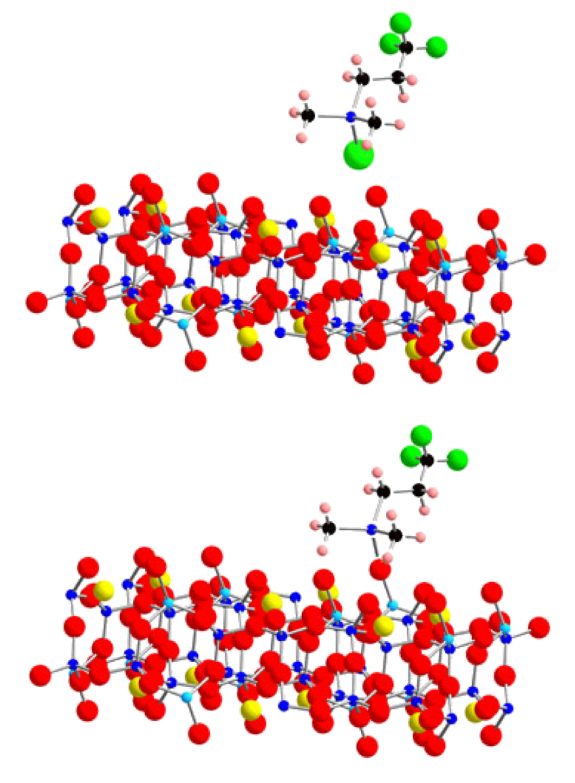
The interface between solution and a complex oxide surface

Research Approach



TFS molecule



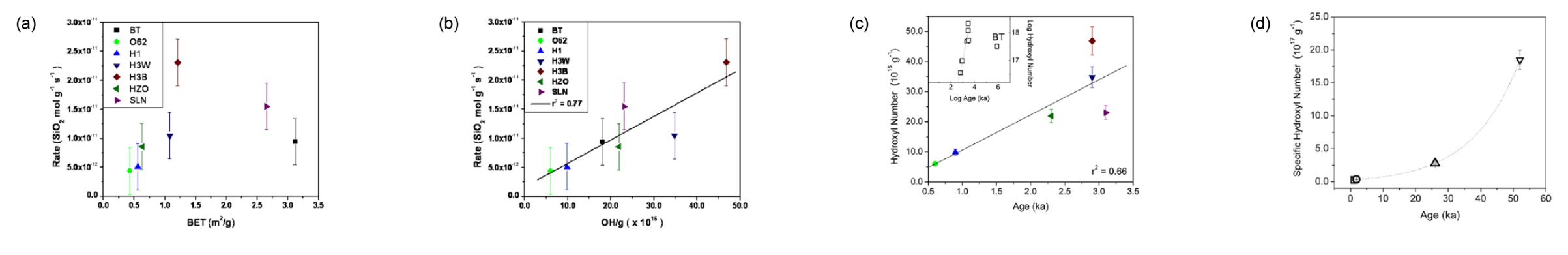


Covalent attachment of TFS to an oxide surface

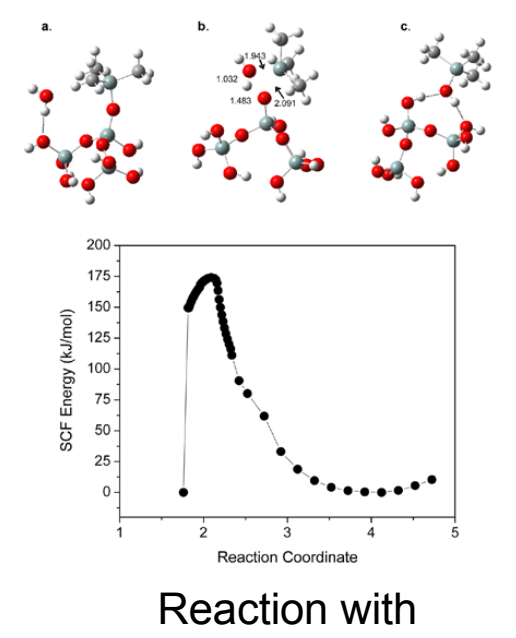
We have previously shown that a sensitive and chemically direct measure of hydroxyl reactivity for low surface area oxides is obtainable through silanization, a surface modification technique that is chemically specific and selective. Using a fluorinated organosilane probe molecule - 3,3,3-(trifluoropropyl)dimethylchlorosilane (TFS) - we quantitatively measure the number of reactive hydroxyl species on two suites of naturally or laboratory weathered volcanic glasses. The first, a suite consisting of six Icelandic glasses and one ignimbritic sample from the Bishop Tuff CA, was chosen to investigate the correlation between the acid-mediated dissolution rates and the reactive surface area (here, defined as, the concentration of specific surface hydroxyl sites). The second suite of four volcanic samples comprises a chronosequence from Kozushima, Japan. The Kozushima samples were acquired to investigate the effects of field weathering on the number of reactive hydroxyl species. Taken together, these samples allow an investigation of surface-specific chemical reactivity, the tie between reactive chemistry and acid-mediated dissolution rates, and the change in surface reactivity as a function of weathering across scales spanning from the laboratory to the field.

Results

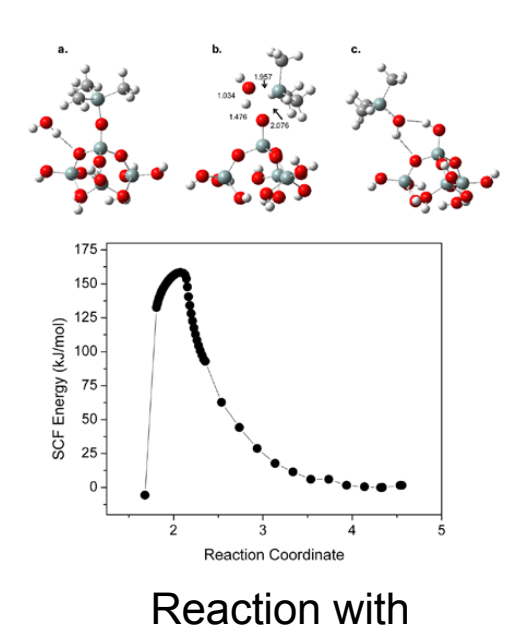
(a) The lack of correlation between dissolution rate and surface area for the first suite of six Icelandic glasses led to our investigation of reactive hydroxyl content, and (b) the correlation between the dissolution rate (normalized to sample mass) and specific hydroxyl number (OH/g) is very strong. (c) For this suite of glasses, weathered under very different conditions, there is also a correlation between specific hydroxyl number and age. (d) To further probe this correlation, we obtained a natural chronosequence of samples and measured a similar increase in reactive sites with age since eruption.



Computational Analyses



Reaction with Q^2 silicon



Reaction with Q^3 silicon

To further understand the interfacial chemistry controlling the dissolution of the volcanic glass samples, we have modeled the reaction pathway for covalent attachment of a TFS molecule to an oxide cluster using density functional theory (DFT) in Gaussian 03. The reaction coordinate in this computational experiment is the distance between the oxygen of the surface cluster and the silicon on the silane molecule. As shown in the energy diagrams at the left, which correspond to gas phase reactions, the activation energy for condensation with a Si Q^2 surface species is approximately 175 kJ mol^{-1}, while reaction with a Si Q^3 species requires an activation energy of approximately 158 kJ mol^{-1}. Further computations will include solvent effects, and these will be compared to values obtained through kinetic experiments performed in our laboratory.

Conclusions

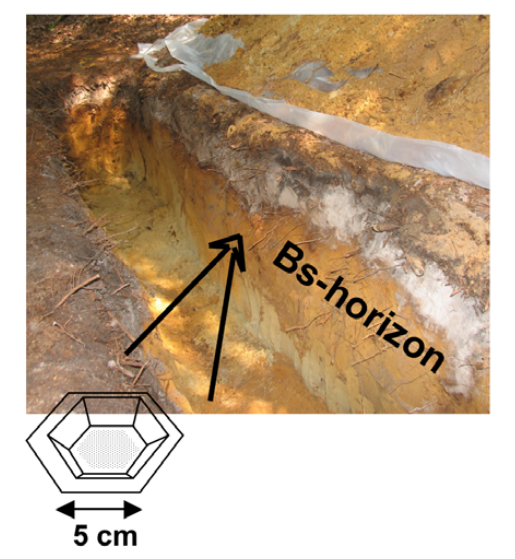
- Reactive hydroxyl group measurement via an NMR active probe molecule (TFS) has been accomplished on very low surface area oxides. Hydroxyl site density is demonstrated to be an appropriate normalization factor for acid-mediated dissolution kinetics.
- The correlation between the measured reactive hydroxyl site density and the dissolution rate under acidic conditions is excellent, crossing scales from the molecular (spectroscopic) scale to the laboratory.
- Density functional calculations provide insight into reaction products, mechanisms, and energetics, crossing scales from the water-solid interface to the atomic scale.

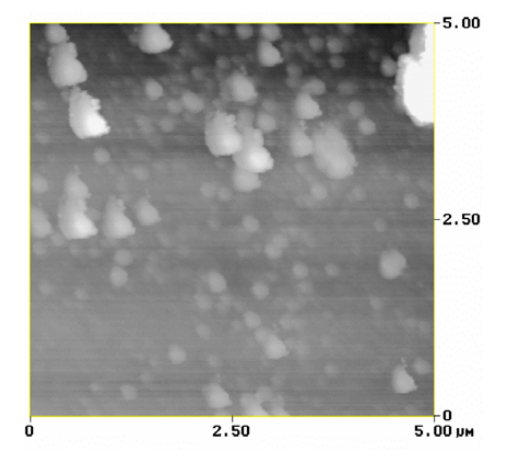
Precipitation Interest Group

Background

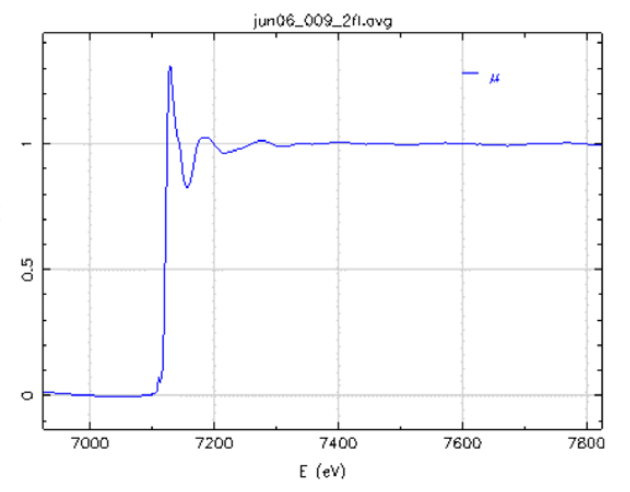
Prof. Carmen Enid Martinez and graduate student Katya Bazilevskaya have collaborated with DOE-affiliate Glenn Waychunas to explore the mechanisms of heterogeneous nucleation and growth in soil environments. Recent studies have demonstrated that heavy metal retention in soils occurs not through adsorption on silicate grains but on thin coatings of Fe-Al oxyhydroxides. Using grazing incidence X-ray absorption spectroscopy (GIXAS) at SSRL, Bazilevskaya and her advisors are exploring the deposition of Fe and Al oxides on quartz substrates placed in natural soil environments. These field-level results are being compared to laboratory analyses of mixed Fe-Al hydroxide deposition on quartz surfaces. This work should offer insights into scaling from lab experiments to the natural processes that govern soil reactions.

Heterogeneous Nucleation - Field Component





AFM image of the surface of quartz wafer retrieved from the field.

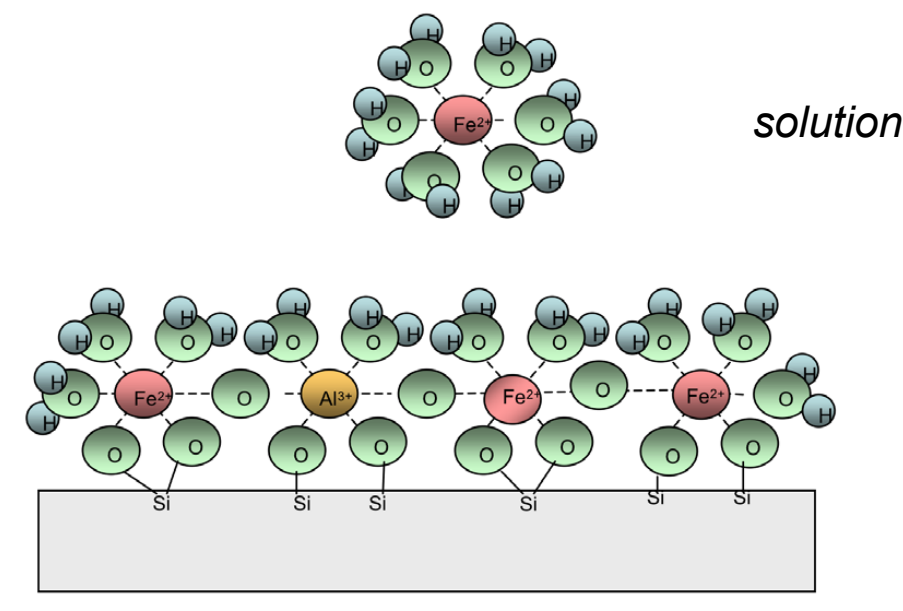


Fe K-edge EXAFS of the field quartz wafer obtained by GIXAS surface technique

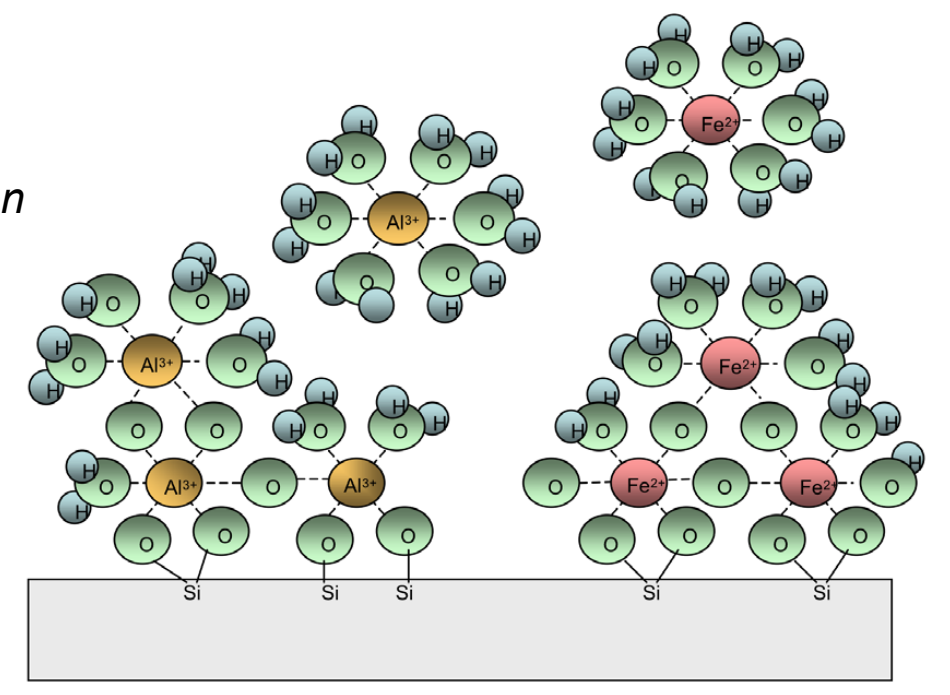
Quartz crystals were placed in a Bs (iron-rich) Spodosol soil horizon and retrieved after one year. Since GIXAS analyses can provide information on the type of surface complex, Bazilevskaya et al. are trying to differentiate among Fe-O-Fe, Fe-O-Al and Fe-O-C local bonding environments. This information is valuable in understanding the chemical state of Fe during coating formation in situ. The GIXAS spectra showed a distinctive Fe-edge, which indicate the presence of iron in a natural coating.

Heterogeneous Nucleation - Lab Component

In tandem with their field work, Bazilevskaya performed a series of experiments to find the optimal experimental conditions for the synthesis of a reasonably flat even coating (less than 10 nm in surface roughness), as is required for the GIXAS technique. She found that slow oxidation of Fe(II) at pH 5 for 2 hours results in relatively even coatings with a surface roughness of 10 nm. In contrast, it is difficult to control the thickness of coatings deposited from Fe(III) solutions due to the rapidity of Fe polymerization.



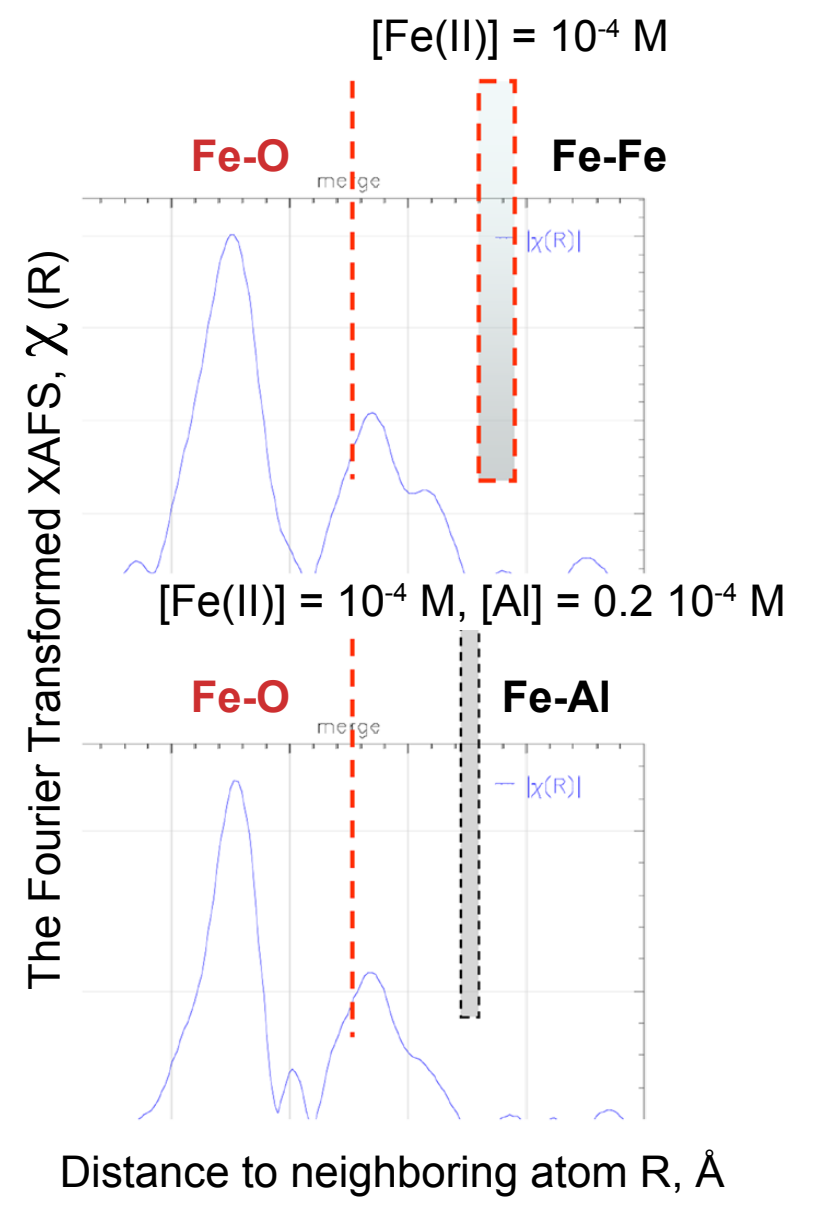
Formation of even co-precipitated Fe-Al coating on the quartz surface



Formation of rough coating due to rapid polymerization at the quartz surface

Interaction of Fe and Al on Surface Coatings

If Al co-precipitates with Fe on quartz surfaces, the structure of the coating is different from that of a pure Fe film. Using GIXAS, Bazilevskaya has calculated radial structure functions for pure Fe and for Fe-Al coatings on quartz. These suggest that the presence of Al in solution changes the average distance from a given Fe atom to its second neighbor.



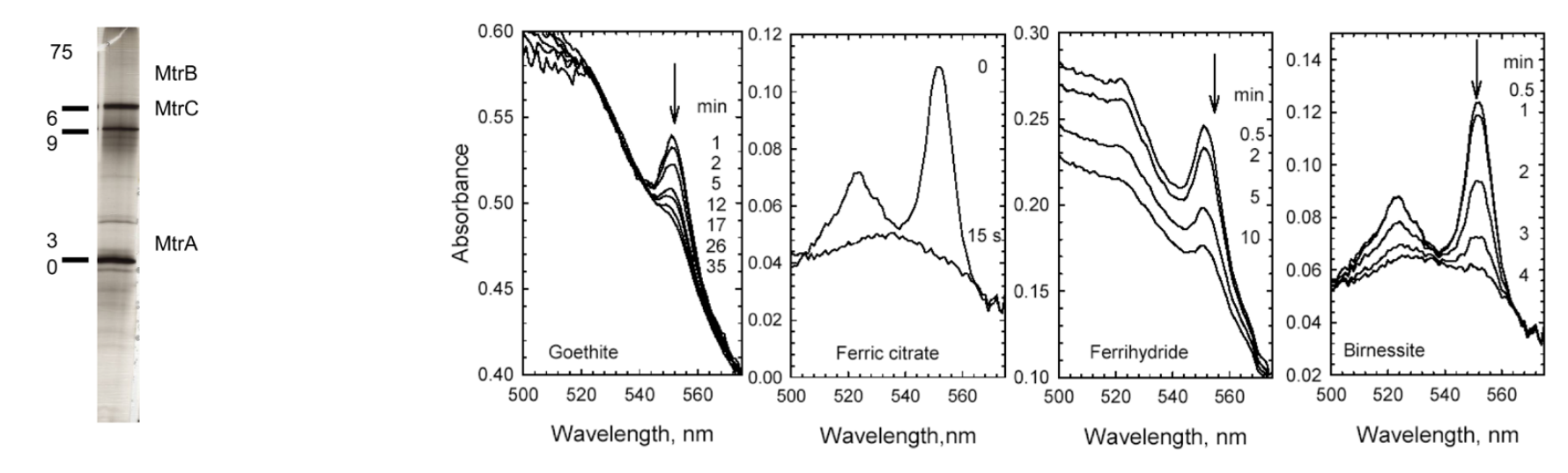
Bioreactions Interest Grouop

Introduction

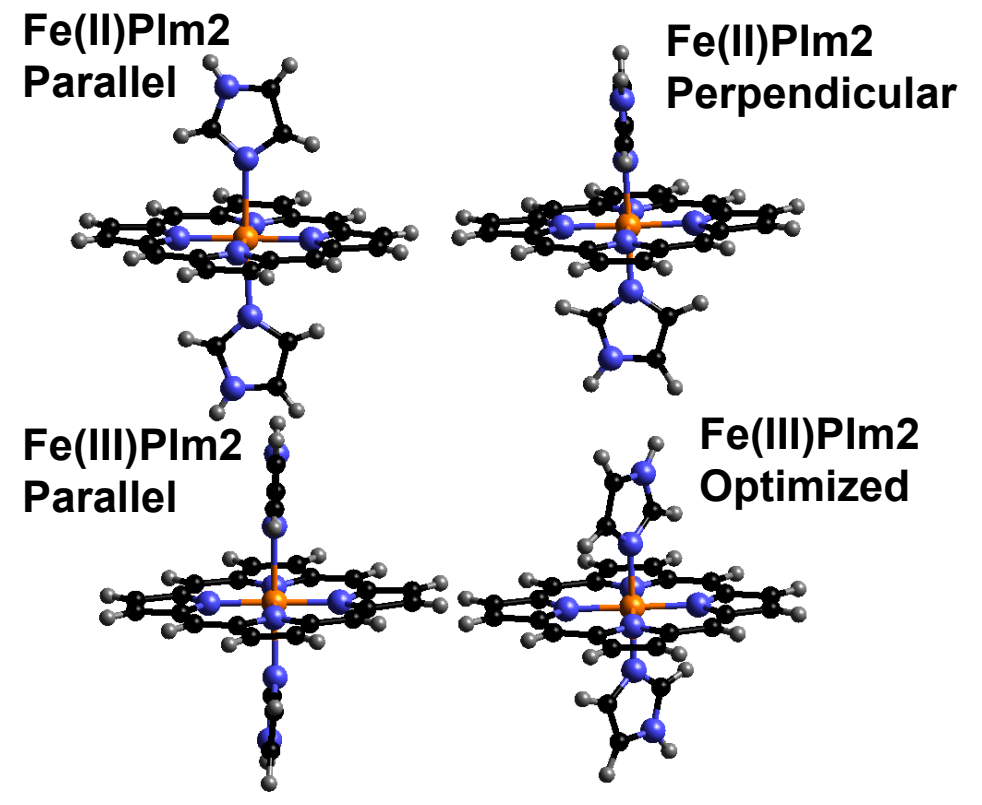
In the absence of oxygen, microorganisms have the ability to couple anaerobic growth, and link respiratory proton translocation with the reduction of alternative electron acceptors. One such organism with great respiratory plasticity is *Shewanella oneidensis* MR-1. This facultative anaerobe has the ability to reduce soluble and insoluble metals (Fe(III) and Mn (IV)) as well as toxic heavy metals such as U(VI) and Cr (VI) terminal electron acceptors. Genetic studies have identified genes (proteins) involved in this process. At CEKA, graduate students Yufeng Qian, Daniel Ross, Camille Stephen and faculty members Susan Brantley, James Kubicki, and Ming Tien are characterizing this electron transport process. We seek to identify the sequence of *in vivo* protein partners; when structures are available, model electron transport through these hemeproteins to metal oxides, obtain kinetic constants from stop flow studies, steady state kinetic studies and whole cell studies. This kinetic scale-up process is the research vehicle to understand this process.

Proposed Mechanism of Electron Transfer to Insoluble Iron Oxide

At the outer membrane of *S. oneidensis*, we have purified MtrA/B/C as a protein complex. The complex was purified by ion exchange chromatography and then gel filtration. SDS-PAGE shows that the complex is over 95% pure. This complex may constitute the terminal electron acceptor since it is able to reduces complex is able to reduce goethite, ferric citrate, ferrihydride and birnessite.



Modeling Electron Transport

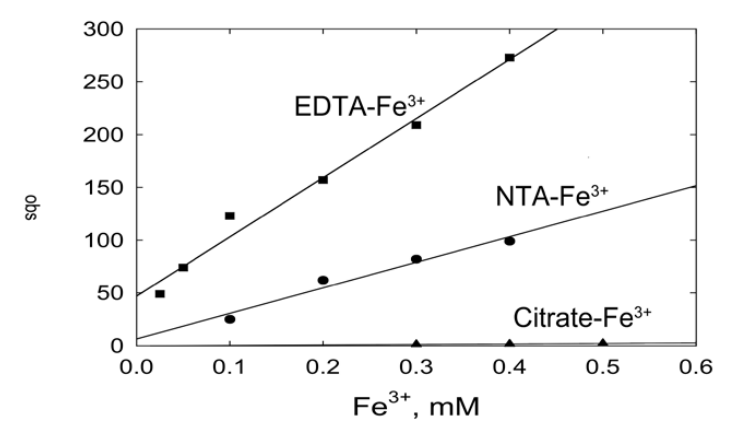


Electron transfer through the heme groups of cytochromes is thought to be a key process in dissimilatory Fe-reducing bacteria. Quantum mechanical calculations (Mitin and Kubicki) are being conducted to examine the structures of these hemes with regard to oxidation state. The figures to the left (P = porphyrin; Im2 = 2 Imadazoles) predict that the lowest energy state for the low-spin Fe(II) heme model is a perpendicular configuration of the imadazole groups rather than the parallel configuration. Also, starting with a parallel configuration of the imadazole groups in the oxidized heme, the imadazoles remain parallel but rotate relative to the porphyrin ring.

Kinetic Studies of S. Oneidensis MR-1 Iron Reductases

We are performing kinetics studies at three scales: transient state studies with the stop flow, steady state studies with isolated membrane fractions and with whole cells in cultures

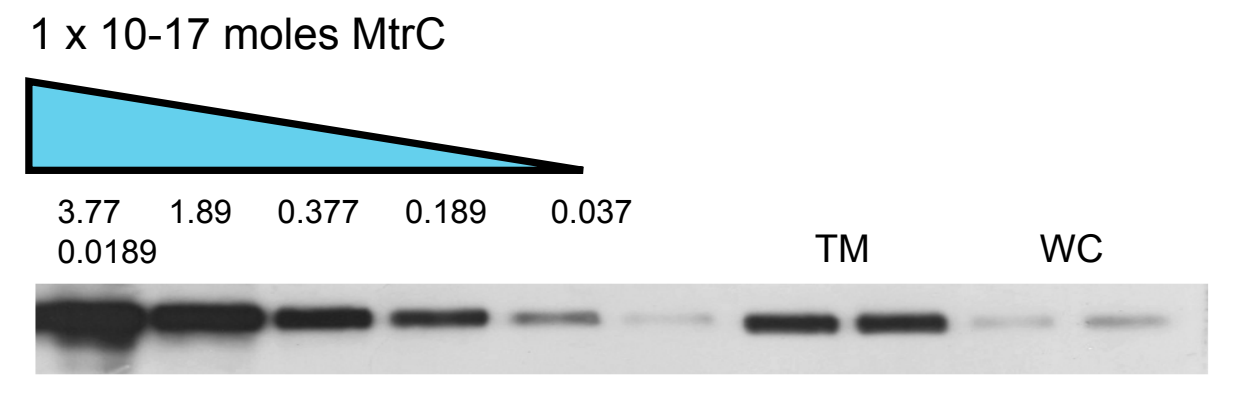
Transient State States - Molecular Scale

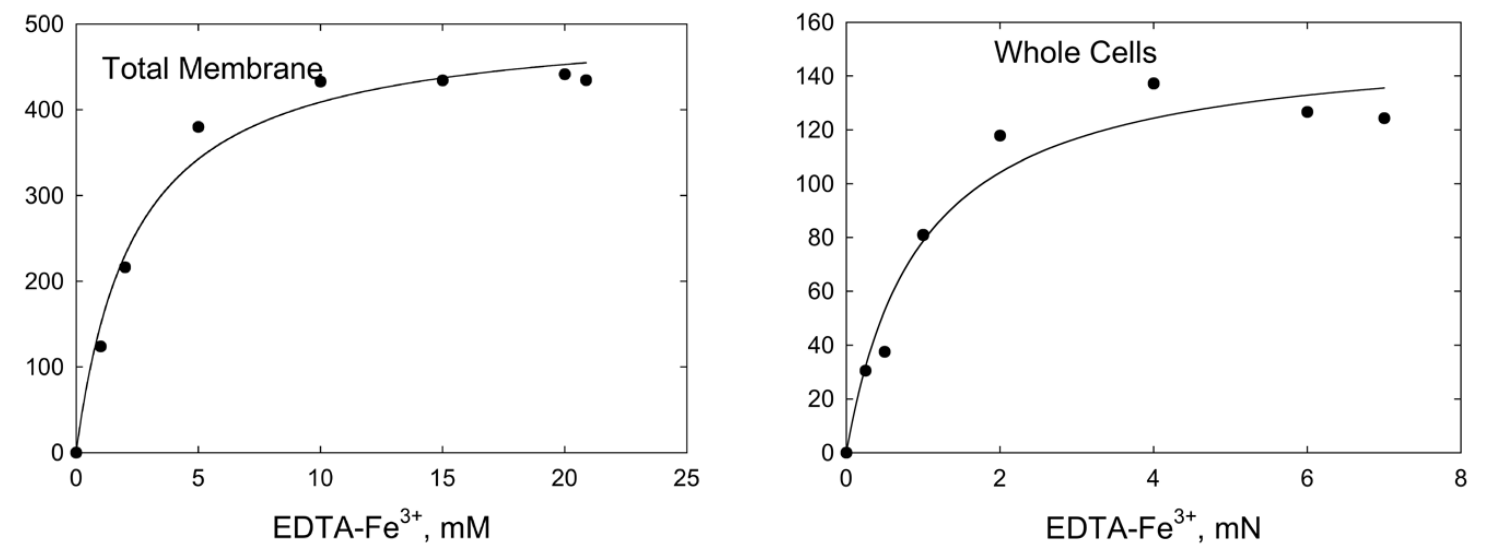


	MtrC ($\mu M^{-1}s^{-1}$)
Citrate	0.46
EDTA	1.58
NTA	0.34

In collaboration with John Zachara at PNNL, we have performed transient kinetic studies with the hemeproteins of the outer membrane. The MtrC used in the stop flow studies were obtained from Liang Shi at PNNL. Rate constants were obtained from the slopes of the plot shown on the left and given in the table.

In Vitro and *In Vivo* Steady State Kinetics





Normalization of steady state rates allows for transient state comparison and hopefully elucidation of mechanism. Rate constants for MtrC were calculated from studies where the mtrC content was determined with antibodies. Second order rate constants are extracted from steady state data for analysis. (k_{cat}/Km = second-order rate constant ($M^{-1}s^{-1}$))