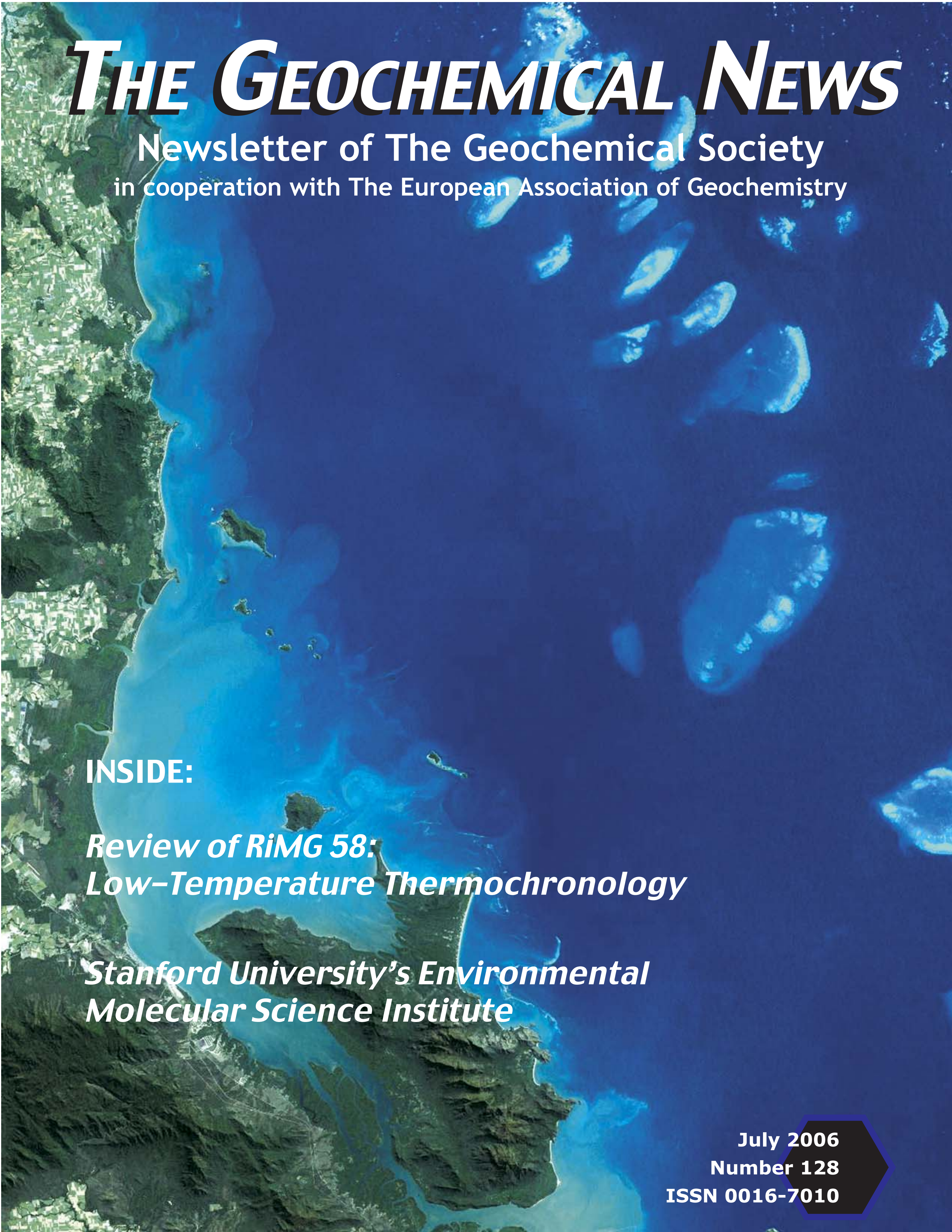

THE GEOCHEMICAL NEWS

Newsletter of The Geochemical Society
in cooperation with The European Association of Geochemistry

INSIDE:

Review of RiMG 58:
Low–Temperature Thermochronology

Stanford University's Environmental
Molecular Science Institute

July 2006
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THE GEOCHEMICAL SOCIETY

The **Geochemical Society** is a nonprofit scientific society founded to encourage the application of chemistry to the solution of geological and cosmological problems. Membership is international and diverse in background, encompassing such fields as organic geochemistry, high- and low-temperature geochemistry, petrology, meteoritics, fluid-rock interaction, and isotope geochemistry. The Society produces a ***Special Publications Series***, ***The Geochemical News*** (this quarterly newsletter), the ***Reviews in Mineralogy and Geochemistry Series*** (jointly with the Mineralogical Society of America), the journal ***Geochimica et Cosmochimica Acta*** (jointly with the Meteoritical Society), and co-publishes the electronic journal ***G³*** (jointly with the American Geophysical Union: AGU); grants the ***V.M. Goldschmidt***, ***F.W. Clarke*** and ***Clair C. Patterson Awards***, and, jointly with the European Association of Geochemistry (EAG), the Geochemistry Fellows title; sponsors the V.M. Goldschmidt Conference, held in North America in odd years and elsewhere in even years, jointly with the EAG; and co-sponsors the Geological Society of America annual meeting and the AGU spring meeting. The Society honors our first President, F. Earl Ingerson, and our first Goldschmidt Medalist, Paul W. Gast, with the ***Ingerson*** and ***Gast Lectures***, held annually at the GSA Meeting and the V.M. Goldschmidt Conference, respectively. The Geochemical Society is affiliated with the American Association for the Advancement of Science and the International Union of Geological Sciences.

Members of the Organic Geochemistry Division are individuals with interests in studies on the origin, nature, geochemical significance, and behavior during diagenesis and catagenesis of naturally occurring organic substances in the Earth, and of extraterrestrial organic matter. GS members may choose to be affiliated with the OGD without any additional dues. The OGD presents the **Alfred E. Treibs Award** for major achievements in organic geochemistry, and **Best Paper** awards (student and professional) in organic geochemistry.

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THE GEOCHEMICAL NEWS
July 2006

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Cover: Landsat image (photo credit Dr. Darrel Williams, Landsat Project Scientist, NASA/GSFC) showing part of Australia's Great Barrier Reef, including Hinchinbrook Island in the lower center.

From the GS President,

As I sit here writing this message as the President, I am wondering if any of you have ever puzzled over the question of why scientists in some disciplines such as marine geochemistry or seismology seem better organized than those in disciplines such as terrestrial geochemistry. My own puzzlement over this question was stimulated one day by a question from an administrator at the U.S. National Science Foundation (NSF), who asked me something like, "Why don't terrestrial geochemists support one another?" Upon discussion, I discovered that it was this person's perception that our communities do not generally review each others proposals highly nor generally support community activities in geochemistry. In subsequent discussion, it became apparent that the administrator held the opinion that not only is the geochemical community not organized, but it also lacks the ability of asking or answering "big" questions. It became clear to me in this discussion that the perceived inability to ask "big" questions on the part of the terrestrial geochemical community was a liability in terms of promoting better funding scenarios fot this field.

Of course, these are only one person's perceptions. I would like to discuss implications of these points here (albeit with a regrettably U.S.-centric focus). However, I believe that the problems I discuss below are not limited to the U.S. and I wonder how the Geochemical Society might help create opportunities for change. In addition, where some geochemical sub-disciplines have been successful in promoting organization, I would hope that these groups could help other groups make similar strides forward.

Although I cannot address whether geochemists truly are harder reviewers than those in other disciplines, I would like to relate a pertinent observation. While serving on two committees for the U.S. National Science Foundation, I reviewed submitted proposals as well as all reviews and all funding decisions with respect to those proposals for one period of time. I observed a very high quality of scientific proposal among the geochemical programs I was asked to peruse, but a very, very low funding rate. For example, the average scores for funded proposals and for the top ten declined proposals in one geochemical program in Spring 2004 were 4.31 and 4.07, respectively, out of a highest possible rating of 5. The high ratings for proposals that were funded are evidence of the high quality of funded research and education. The high ratings for proposals that were declined indicates that funding is limited to the point that some very good (score of 4) to excellent (score of 5) research and educational activities were not funded that year. I conclude that, if geochemists do rate each other's proposals harshly, then truly wonderful proposals are being rejected at the NSF in geochemistry.


Susan Brantley

Amazingly, as part of my NSF committee service, I also remember one proposal that received 9 reviews, none of which were lower than an Excellent! Of course, it was funded. This exceptional proposal requested funding for a community resource that serves a large number of scientists and that greatly benefits the entire community. It represented a sub-community of geochemists that had banded together to seek support for an expensive set of geochemical resources. Other proposals for infrastructure and tools included a $13-million proposal to fund an exceptional community effort among U.S. seismologists to deploy a network of seismic stations around the world, to enable community seismic data storage and handling, to provide mobile seismic equipment, and to generate seismological outreach and education programs. This proposal was also funded. While some scientists believe that such well-funded group efforts siphon money from single investigator projects, I have observed that such group efforts promote community among scientists and promote the sharing of resources. Community and shared resources then further scientific advance.

I think that the time has come to organize geochemists into similar networks that can address big questions that we can only answer as organized groups.

Why has this not generally happened in terrestrial geochemistry? It certainly has happened in marine geochemistry: look at the superb wealth of information we have about elemental concentrations as a function of depth in the world's oceans. Marine geochemists have successfully organized internationally to obtain the funding needed for ships and marine experiments to map out the chemistry of the world's oceans. Future such efforts are now being articulated to augment this data in ways that may help us puzzle out important questions related to productivity and carbon cycling in today's oceans.

I think the reason terrestrial geochemists have not similarly organized is that we have not needed to do so – but we now are facing such a need.

Why have we not needed to organize? We are interested in the chemistry of about 100 components (e.g. elements) that form almost 3000 phases (e.g. minerals) in terrestrial systems. Furthermore, we are interested in the speciation and isotopic composition of these elements. Speciation and phase identity varies significantly from system to system and controls bioavailability and both elemental and isotopic distribution. The data we need as geochemists are vary widely over space and time. Despite (or perhaps because of) this complexity, the extreme heterogeneity of the surface earth has meant that no matter how limited a geochemist's budget, it has often been possible to measure something locally on the cheap and still make interesting geochemical observations that are publishable.

Why do we need to organize now? As our understanding of the heterogeneity and complex inter-relationship of chemical, physical, and biological factors controlling the surface earth deepens, we now recognize we must work in teams of interdisciplinary scientists to unravel important questions. In addition, tools of analysis for geochemistry and molecular biology are extremely expensive. Thus the nature of the science has driven the creation of teams needing expensive budgets to answer fundamental questions.

The funding situation worldwide has both promoted this activity and hindered it. In many countries, agencies have developed programs capable of funding large teams of interdisciplinary scientists, but in general these programs are of the "here today, gone tomorrow" variety. Thus no core programs in the U.S. have the necessary funding to support the interdisciplinary core of scientists that have educated themselves to tackle the important questions of the surface earth.

I write this letter to seek information about whether you agree with these thoughts and whether these observations have parallels in other countries. I am also wondering if it is appropriate for the Geochemical Society (GS) to help to articulate how better organized teams lead by geochemists might be able to address important fundamental questions about the surface earth. If such activity is appropriate for the GS, how best might we proceed with both national and international activities? Please consider emailing me your thoughts or discussing this topic with me in Melbourne in August.

Susan L. Brantley, GS President

GS News and Notes

Goldschmidt 2006 – Melbourne Australia
27 August - 1 September 2006

http://www.goldschmidt2006.org/.

The Melbourne Goldschmidt Conference is fast approaching! The early registration deadline is **June 30, 2006**. Remember that GS and EAG members qualify for a substantial registration discount. If you are not already a member of GS or EAG, then please join before you register to take advantage of this member benefit. With support from the National Science Foundation, the Geochemical Society will be awarding $40,000 (US) in student travel grants to the Melbourne Goldschmidt Conference. Recipients shall appear in the August issue of Elements.

Goldschmidt 2007 – Cologne, Germany (19-24 August 2007): Preparations for next year's Goldschmidt Conference are already underway. Dr. Herbert Palme (herbert.palme@uni-koeln.de) is the conference organizer.

Goldschmidt 2010?

The GS Board of Directors will be examining North American bids for the 2010 Goldschmidt Conference during the 2006 annual board meeting on August 26, in Melbourne, Australia. If you, your university, or your city are interested in submitting a bid, please contact the GS Business Office at gsoffice@geochemsoc.org.

2006 Geochemical Society Award Recipients Announced!

V.M. Goldschmidt Medal: Susan Solomon (US National Oceanic & Atmospheric Administration - Boulder)
F.W. Clarke Medal: Alexis Templeton (University of California – San Diego)
C.C. Patterson Medal: Fred Mackenzie (University of Hawaii – Manoa)

GS/EAG Fellows

William H. Casey (University of California – Davis), Bor-ming Jahn (Institute of Earth Sciences – Taipei), Brian N. Popp (University of Hawaii – Manoa), Jacques Schott (Laboratoire des Mecanismes et Transferts en Geologie – Toulouse)

GS Logo Contest

Thank you to everyone who participated in the GS Logo Contest. We received nearly 140 entries. As of this writing, the selection committee has been narrowing down the field.

GS at GSA Meeting & Exposition

The GS Program Committee will be organizing a number of sessions at the 2006 GSA Meeting and Exposition held in Philadelphia, PA from 22-25 October 2006. GS Members qualify for discounted registration. GS will also have a booth in the exhibition.

Elsevier Publication Discount

Through an agreement with Elsevier, Geochemical Society members can take advantage of a 25% discount to their full line of books, including the paperbacks editions of the Treatise on Geochemistry.
Order forms can be found either in Geochemical News, or on-line at: http://gs.wustl.edu/join/elsevierbooks.pdf

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Seth Davis

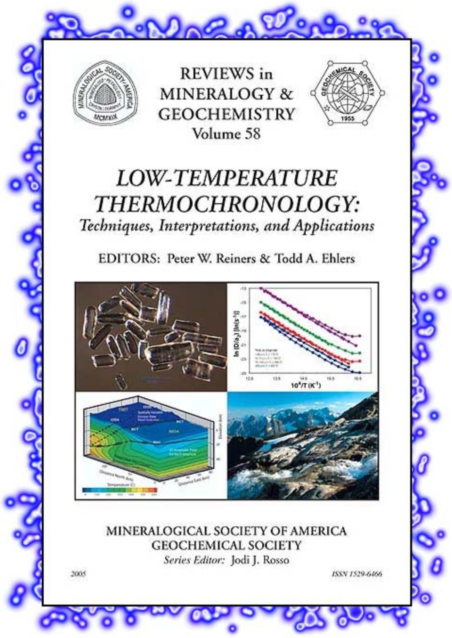
Book Review

Low-Temperature Thermochronology: Techniques, Interpretations, and Applications

edited by Peter Reiners and Todd Ehlers

Review by Geoffrey Batt
Senior Lecturer, ExxonMobil Teaching Fellow
Royal Holloway University of London
Egham, TW20 OEX, UK

Coming in what is, arguably, the 100th anniversary of the birth of quantitative geochronology – in Rutherford's 1905 Silliman lecture at Yale, which was then published in a seminal paper the following year – "Low-Temperature Thermochronology: Techniques, Interpretations, and Applications", volume 58 in the long-running *Reviews in Mineralogy and Geochemistry* series, offers a timely review of the dynamic offspring of this field – the discipline of thermochronology.



REVIEWS in MINERALOGY & GEOCHEMISTRY
Volume 58

LOW-TEMPERATURE THERMOCHRONOLOGY:
Techniques, Interpretations, and Applications

EDITORS: Peter W. Reiners & Todd A. Ehlers

MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY
Series Editor: Jodi J. Rosso

2005 ISSN 1529-6466

Thermochronology extends and enhances chronological constraint by pairing it explicitly with the extraction of information about the thermal history of geological materials and systems. This approach is based on the interplay between the accumulation of the daughter product of some nuclear decay reaction within a rock (geochronology) and the removal of that daughter product by thermally activated diffusion processes.

Low temperature mobility of the daughter products of radioactive decay initially so concerned pioneering geochronologists that many isotopic decay systems were abandoned as un-reliable dating methods – a label that has until recently stuck with them in the minds of some workers. Following the maxim that noise is just signal that we have yet to understand, however, (or in the more prosaic imagery of the introductory chapter to the volume – taking lemons and making lemonade), more recent work constraining the diffusional nature, and consequent thermal control, of open system behaviour in geochronological systems has turned this weakness on its head and led to the foundation of the now vibrant field of thermochronology. Indeed, the significance of this understanding to the development of the field is amply demonstrated by the Editor's dedication of the volume to pioneering experimental petrologist William Luth.

The understanding and application of thermochronological processes has touched on and advanced an array of fields where temporal constraint of thermal change is a significant feature, with notable applications to tectonics, landscape development, sedimentary basin studies, ore genesis, and novel applications continuing to develop – as strongly evinced in this comprehensive volume.

This review comprises 22 chapters, each focussed on a specific aspect or sub-discipline of thermochronology and its corollaries, and written by an individual or small group of co-authors acknowledged as among the leading figures in the relevant area. With 22 such contributions and close to 50 listed authors, there can be few practising thermochronologists not touched in some way by either contributing to or reviewing (formally or on the informal grapevine) one or more of the papers presented. The structure and coverage of individual chapters ranges widely, including elements of historical perspective, analytical techniques, kinetics and applications to differing extents. The level of the contributions similarly varies – with some pitched at an introductory level accessible to novice graduate students or the interested generalist, while others (notably, and perhaps not unexpectedly, contributions on novel methodologies in ^{4}He/^{3}He thermochrometry and quantitative modelling of isotopic data) clearly aim at a more experienced practitioner.

This diversity is at once a strength and weakness to some degree – the lack of consistent voice and level make it difficult to digest the volume as a whole, and perhaps for any one group to fully appreciate the offering. As a reviewer, however, I must admit that I have to reach fairly deeply to come up with that somewhat petty criticism – and the volume as envisaged by the editors – a genuine community-wide project encompassing the diversity of a broad and active field – could work no other way, in that each aspect is presented by leading specialists with the knowledge and experience to do it justice. That the editors managed to extract cogent manuscripts from so many of the leading practitioners in this field to a strict production timetable is impressive enough in itself.

For workers new to thermochronology or perhaps unaware of its own evolutionary timeline, the opening chapter, co-authored by the volume editors together with Peter Zeitler, represents a concise, well written introduction to the subject. As befits the nature of the review volume, this encompasses both a pithy and relevant historical overview and a dynamic vision for the future challenges and potential of the field.

Although not explicitly divided as such, the following chapters are loosely collected around a number of general themes, beginning with a series of introductions to the analytical dating techniques that best lend themselves to thermochronological investigation. Chapters 2-4 outline various aspects of fission track analysis and chronometry – significant both as a tool in its own right, and for its historical role as providing much of the early empirical insight into thermochronological behaviour. Chapter 5 introduces the principal complement to this approach, reviewing the fundamentals of chronometric techniques based around noble gas daughter isotopes (K-Ar, $^{40}Ar/^{39}Ar$, and (U-Th)/He analysis), while chapters 6 and 7 present two of the more significant recent developments in this area. While most interest (and published data) in (U-Th)/He chronometry has focused on the low-temperature constraint afforded by apatite, efforts have recently expanded constraint of helium diffusion systematics into a wider array of minerals, and chapter 6 describes the recently popularised use of zircon in this approach.

Perhaps of more note, chapter 7 presents a novel and exciting methodology termed "^4He-^3He thermochronology" by its developers (the authors, unsurprisingly, of this chapter), in which samples are subjected to high-energy proton irradiation to produce a uniform distribution of ^3He across a crystal. Subsequent joint analysis of the ^3He and ^4He isotopes then provides both direct constraint of the diffusion kinetics of the sample and a proxy for the relative distribution of radiogenic ^4He, both of which contribute to more complete understanding of sample history, providing higher orders of insight than bulk integration dating techniques.

Chapters 8 and 9 move on from analytical methodology to introduce practical use of thermochronological constraint in different styles of geological problem, reviewing the application of thermochronology (zircon fission track and $^{40}Ar/^{39}Ar$, respectively) to detrital materials. Although sacrificing the spatial and structural control afforded by bedrock sampling, sedimentary samples compensate for this loss through their provision of a picture of the integrated character of a source region at the catchment scale – and more importantly, its temporal evolution, through monitoring changing thermochronological patterns through a stratigraphic sequence.

Chapters 10 through 15 present reviews of a range of approaches to the modelling and interpretation of thermochronological data, and it is here, perhaps, that the volume best takes itself beyond specialist application and becomes of primary interest to a more general readership – laying bare the "black box" of methods used by many workers to make geological sense from these isotopic systems, and making clear the true nature and significance of thermochronological data. In some respects (and certainly without diminishing its value in any way), this could be viewed less a review volume than a toolkit – offering up well-signposted methods ready for application to the resolution of geological problems.

Indeed, chapters 16 through 21 proceed to do just that, laying out a series of both general and specific case studies illustrating the use of thermochronological data in different settings and to address an array of geological problems, including, variously, extensional tectonics, sedimentary basin evolution, problems of denudation and exhumation, hydrothermal ore deposits, and even, in the extra-terrestrial realm, meteorites. Given the breadth of the volume, it seems almost churlish to note gaps in its coverage[1], but in this context the absence of a paper reviewing the application of thermochronological techniques to convergent orogenic regions does seem notable, given both the historical part played by studies in orogenic settings in the European Alps, the Himalaya and elsewhere in the evolution of thermochronological understanding, and equally the significance of thermochronology to orogenic problems.

The volume finishes with a concluding 'chapter' (though here this is something of a misnomer, as the section is in effect a series of disconnected snippets and might better be thought of as a diverse appendix) introducing and providing directions for the use and, significantly, the free downloading, of an array of computational modelling tools designed by the various contributors for use in the simulation and interpretation of thermochronological data. Laying out and encouraging the use of these computational tools is a final demonstration of the openness and collegiality of those involved in the production of this volume, and of the discipline as a whole, and this section perhaps more than any other seems purpose-built to achieve the Editor's stated aims that "…this volume will likewise encourage continued innovation and discoveries in [the field of thermochronology] that synergizes the work and imagination of geochemists, geodynamicists, tectonicists, geomorphologists, and others."

Overall, this volume presents neither a collection of esoteric concepts and aspirations, nor the final word in a mature field of study – rather, it lays out the state of a confident and vibrant research community, and invites engagement. Whether practicing or aspiring researchers in the field itself or merely touched by the implications of thermochronological constraint in a myriad of geological fields, this volume is sure to be of interest and benefit to a broad swathe of students and professionals interested in quantitative understanding of Earth Science.

Footnote

[1] And here I must confess a degree of bias, as this is an area of my own research interest.

The Stanford Environmental Molecular Science Institute

A Focus on Chemical and Microbial Processes at Environmental Interfaces

Gordon E. Brown, Jr.[1,2], Anders Nilsson[2], Alfred M. Spormann[3], William P. Addiego[4], Karim Benzerara[5], Uwe Bergmann[2], Hendrik Bluhm[6], Bryan A. Brown[7], Georges Calas[5], Anne M. Chaka[8], Brent R. Constantz[9], Francois Farges[10], Scott E. Fendorf [1], Andrea L. Foster[11], Farid Juillot[5], Guillaume Morin[5], Satish C.B. Myneni[12], Lars G.M. Pettersson[13], Kevin M. Rosso[14], James J. Rytuba[11], Miquel Salmeron[15], Jennifer Saltzman[16], Michael Toney[2], Thomas P. Trainor[17], and Tae-Hyun Yoon[18]

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I. INTRODUCTION

The Stanford Environmental Molecular Science Institute (EMSI) was founded in September 2004 as a multidisciplinary, multi-investigator research, graduate training, and education/outreach program funded by the NSF Chemistry Division, with additional funding from the NSF Earth Sciences Division and the DOE Biological & Environmental Research Division through their Environmental Remediation Science Program. The Stanford EMSI team includes investigators from seven universities (Stanford University, University of Alaska-Fairbanks, Princeton University, University of Paris VI, University of Marne-la-Vallee, France, Hanyang University, Korea, and Stockholm University, Sweden), three national laboratories (Stanford Synchrotron Radiation Laboratory, Lawrence Berkeley National Laboratory, Pacific Northwest National Laboratory), two government agencies (National Institute of Standards & Technology and U.S. Geological Survey), and two technology companies (Corning, Inc. and Skeletal Kinetics). The main focus of the Stanford EMSI is on molecular and nano-scale chemical and microbiological interactions occurring at environmental interfaces (solid-water, solid-gas, microbial biofilm-solid) and how they affect contaminant sequestration, release, transport, and potential bioavailability. We also have major efforts underway on the structure of water and electrolyte solutions, the precipitation of biominerals by bacteria, the interaction of simple organic acids with mineral surfaces and of PAH's with black carbon, and the effect of various treatments on the structure and reactivity of activated alumina used as a catalyst support.

Chemical reactions governing the environment are dominated by those at environmental interfaces. The importance of such reactions is well summarized in a 1987 quotation from the late Werner Stumm **[1]**: *"Almost all of the problems associated with understanding the processes that control the composition of our environment concern interfaces, above all the interfaces of water with naturally occurring solids."* Mineral surface reactions play a dominant role in many geochemical processes, including mineral dissolution and precipitation, heterogeneous nucleation and growth of solids, pH buffering, cation and anion sorption and desorption, heterogeneous redox reactions, and heterogeneous catalytic reactions. These processes, in turn, affect (or control) chemical weathering of minerals and the development of soils, water quality, colloid stability, contaminant and nutrient sequestration and release, soil rheological properties, acid mine drainage, the respiratory cycle of many microorganisms, and the biogeochemical cycling of elements. The surfaces of aerosol mineral particles in the troposphere are also thought to play key roles in heterogeneous atmospheric chemistry, including the

Figure 1

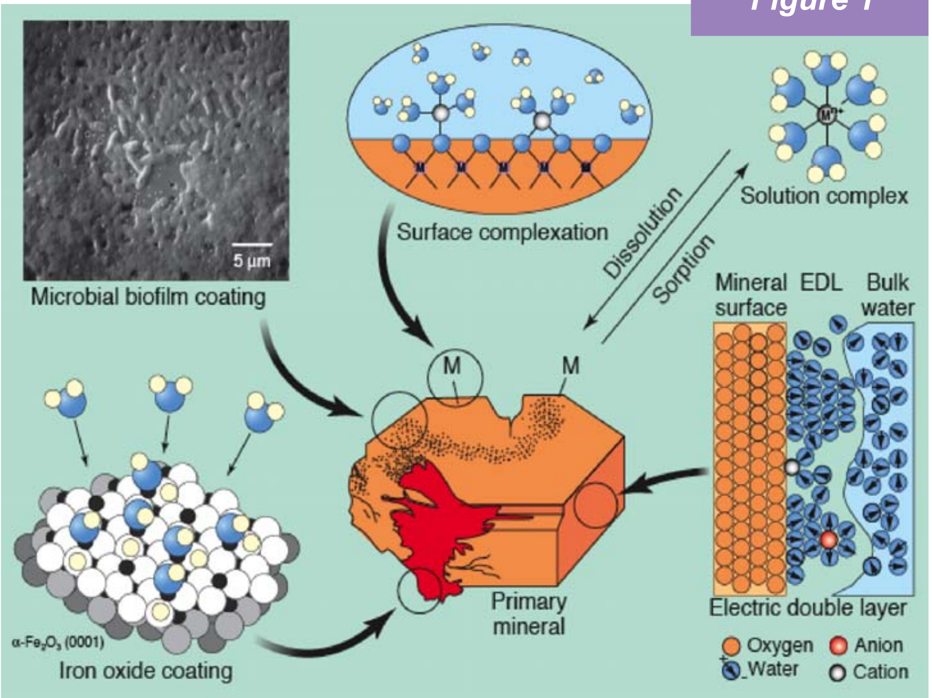


Figure 2

formation of cloud condensation nuclei and the conversion of nitrous oxide to nitrous acid, which affect climate and acid rain production, respectively.

Understanding the reactivity of mineral surfaces under environmental conditions is difficult. This is the case because most mineral particles at the Earth's surface or in the troposphere are in contact with a fluid phase (typically an aqueous solution), atmospheric or soil gas, organic matter, and/or biological organisms (**Fig. 1**) **[2]**. Not only are the structures and compositions of these interfaces poorly understood at a microscopic level, but it is also difficult to isolate the individual effects of aqueous solutions, gases, organic matter, and microbial organisms on mineral surface structure and reactivity. Another complicating factor is the presence of defects on mineral surfaces. Although it is thought that such defects may dominate interface reactivity, little is known about the nature and density of such features.

Over the past 40 years, UHV surface science studies have revealed a great deal about clean, compositionally and structurally homogeneous surfaces under controlled conditions **[3-6]**. However, such surfaces exist only in ultra-high vacuum, so the results of these studies are not generally applicable to "real" interfacial systems, *i.e.*, those in which surfaces are in contact with atmospheric gases, reactor gases and fluids in controlled catalytic reactions, aqueous solutions, organic matter, fungi, or microbial biofilms. Real surfaces have structures and reactivities that may be altered substantially by interactions with the environment. In addition, when liquid water is present, it is not likely that the geometric or electronic structures of surfaces will be the same as under UHV conditions, particularly for redox-sensitive surfaces or anhydrous bulk solids.

Mineral-liquid or mineral-gas interfaces under reactive conditions cannot be studied easily using standard UHV surface science methods. In order to overcome the "pressure gap" between *ex situ* UHV measurements and *in situ* measurements of surfaces at atmospheric pressure or in contact with a liquid, new approaches are required, some of which have only recently been introduced (*e.g.*, **[7]**). Because of the enormous complexity of environmental interfaces, no single experimental or theoretical approach is sufficient to characterize their geometric and electronic structures or compositions or to gain a fundamental understanding of their reactivities. Instead, a reductionist approach is required in which simplified model systems are studied using a variety of *ex situ* and *in situ* surface-sensitive methods coupled, where possible, with high level theoretical calculations of surface/interface structure, thermodynamics, and reactivity (see *e.g.*, **[8]**). Once the simplest model systems are understood, additional complexity can be introduced in a carefully controlled manner, with the ul-

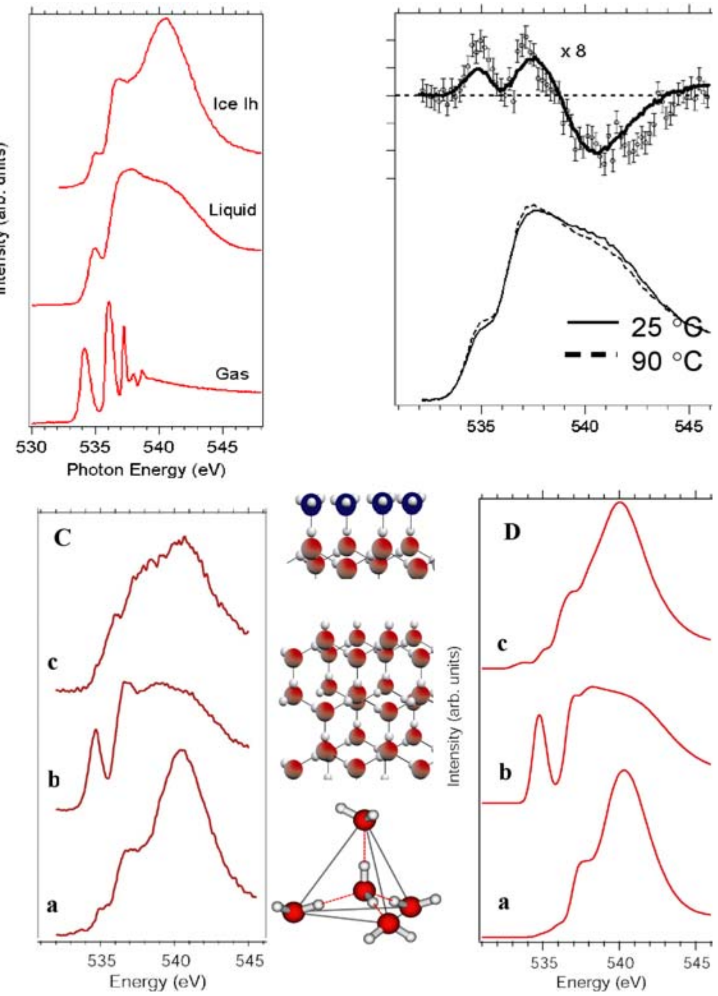


Figure 3

timate aim of approaching the complexity of real environmental interfaces. Initial characterization studies of simplified analogs of complex surfaces and interfaces usually include basic UHV surface science measurements, such as LEED and photoemission spectroscopy, on the clean surfaces prior to and following reaction with environmental species such as water and electrolyte solutions. However, these *ex situ* measurements must be followed by *in situ* measurements under reactive conditions in order to achieve as complete an understanding as possible of the complex interfaces under realistic conditions. A step toward this important goal involves utilization of differentially pumped sample chambers in which x-ray photoelectron, XANES, and x-ray emission spectroscopy can be carried out on a mineral surface with controlled amounts of water vapor present (see, *e.g.*, **[7,9]**). In addition, *in situ* x-ray spectroscopic of adsorbates at mineral-aqueous solution interfaces (see, *e.g.*, **[10]**) and x-ray scattering studies on mineral surfaces in contact with electrolyte solutions are required to provide molecular-level details about the modes in which sorbate ions bind at mineral-water interfaces and the structural and compositional differences between hydrated surfaces and their anhydrous or UHV analogs **[11]**. Beyond these fundamental studies of carefully controlled model systems, it is important to conduct parallel studies of molecular-level speciation and phase association of contaminant ions in real environmental samples in order to constrain the choice of model systems used in the reductionist approach (see, *e.g.*, **[12-16]**). Without such studies, unrealistic model systems may be chosen. Moreover, the model system studies are essential in unraveling the complexity of real environmental samples.

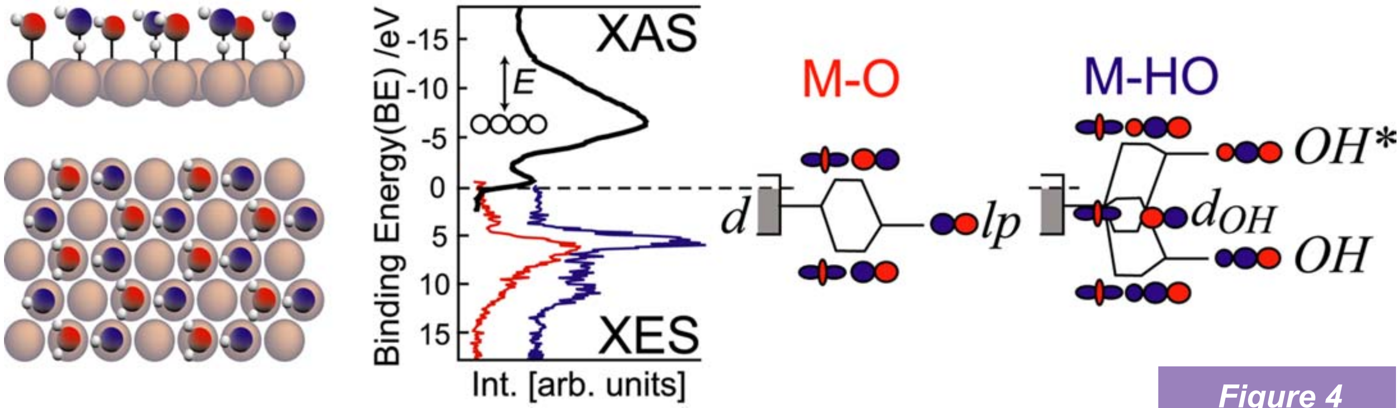


Figure 4

Consistent with a reductionist approach, the studies of the Stanford EMSI range from fundamental to applied. In the former, we utilize synchrotron radiation-based spectroscopic and scattering methods, coupled with quantum chemical modeling and scanning probe microscopy methods, to study a variety of properties and processes at solid-aqueous solution interfaces, including the structure of water, the structure of hydrated metal ions, the structure and reactivity of hydrated mineral surfaces, the structure of the electrical double layer, and the structure of adsorbed species at solid-water and solid-microbial biofilm interfaces. The Stanford EMSI also uses modern molecular genomic methods to study biofilm formation and the mechanisms of biofilm attachment to and detachment from mineral surfaces. Biofilms are microbial consortia that often form on mineral surfaces in natural environments when bacteria attach to surfaces and locally produce a highly hydrated film of extracellular polymers **[17-19]**. Such biofilms can alter the local Eh-pH conditions and can produce concentration gradients that may differ from those in the bulk environment. They may also alter the reactivity of a mineral surface by changing surface charge, blocking reactive surface sites, and providing functional groups (dominantly carboxyl, phosphoryl, and amino functional groups) to which metal ions bond preferentially relative to surface sites. Thus biofilm coatings, together with natural organic matter coatings (see, *e.g.*, **[20]**), create additional complexity at environmental interfaces that must be understood in order to develop a wholistic view of the chemical reactivity of mineral surfaces in nature. In the more applied studies, we use a combination of analytical methods, including synchrotron-based x-ray absorption fine structure spectroscopy, x-ray fluorescence imaging, scanning transmission x-ray microscopy, scanning electron microscopy, transmission electron microscopy, ICP-AES, and selective chemical extractions, to determine the molecular-level speciation of contaminant species and the association of these species (both heavy metals and organic species) with different solid phases in complex environmental samples.

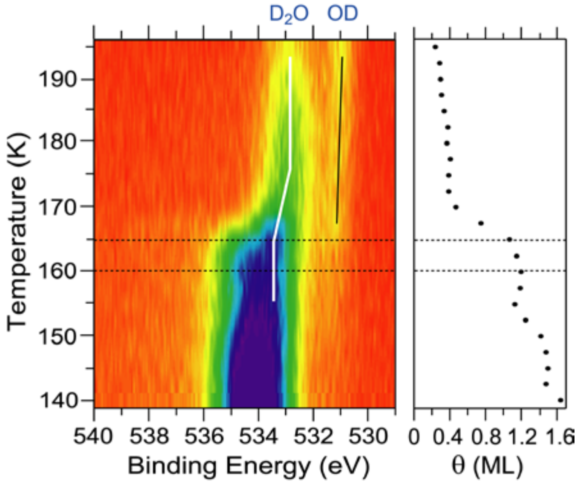


Figure 5

The overall goals of the Stanford EMSI are to (1) develop a quantitative molecular-level understanding of chemical and biological processes occurring at environmental interfaces and how they affect contaminant speciation, toxicity, mobility, and potential bioavailability; (2) explore how such interactions studied in the laboratory relate to the complexity found in natural environments; (3) provide platforms for new approaches to address environmental challenges involving contaminants; (4) recruit a diverse group of qualified graduate, undergraduate, and post-doctoral students; (5) create a stimulating multidisciplinary research/learning environment in which students and post-Ph.D. participants can tackle complex systems and questions relevant to problems in environmental chemistry, ranging from molecular to field scales; and (6) effectively disseminate our research results and approach to the broader public and to future generations of scientists, engineers, and policy makers and to engage K-12 science teachers in current topics in environmental chemistry.

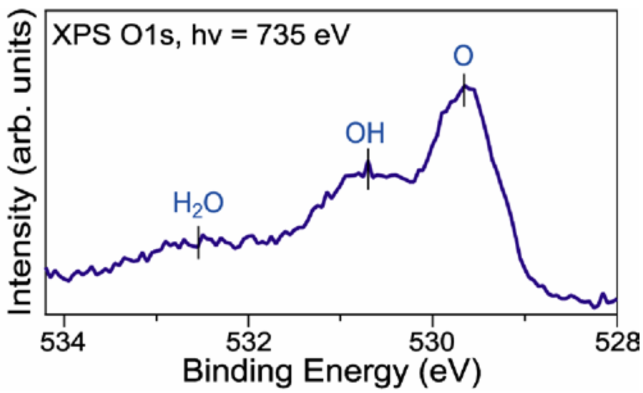
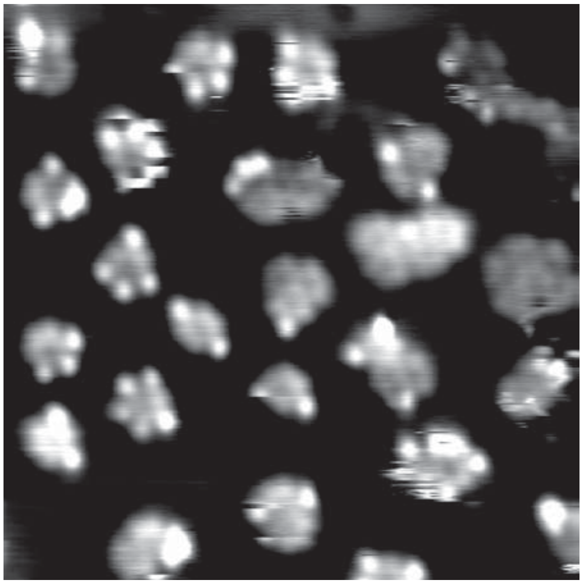


Figure 6

The activities of the Stanford EMSI can be broken down into ten research areas driven by ten teams, all of which have cross-links. They are (1) ***Team A: Interfacial Water*** [Anders Nilsson (SSRL – leader), Uwe Bergmann (SSRL), Hendrik Bluhm (LBNL), Kevin Rosso (PNNL), Miquel Salmeron (LBNL), and Michael Toney (SSRL)]; (2) ***Team B: Interaction of Water with Environmental Substrates*** [Salmeron (leader), Bluhm, Gordon Brown (Stanford University and SSRL), Anne Chaka (NIST), Satish Myneni (Princeton University), Nilsson, and Rosso]; ***Team C: Structure, Dynamics, and Reaction Mechanisms of Metal Complexes in Aqueous Solutions*** (Myneni (leader), Chaka, Francois Farges (University of Marne-la-Vallee, France), and Nilsson]; ***Team D: Structure and Reactivity of Hydrated Metal Oxide Surfaces*** [Tom Trainor (University of Alaska, Fairbanks – leader), Bluhm, Brown, Chaka, Rosso, Salmeron, and Toney]; ***Team E: Structure and Ion Distributions at Metal Oxide-Water Interfaces*** [Trainor and Brown (co-leaders), Bergmann, and Toney]; ***Team F: Sorption Processes at Solid-Aqueous, Microprobe-Aqueous, and Solid-Biofilm Interfaces, and Biomineralization*** [Brown (leader), Alfred Spormann (Stanford University), Farges, Scott Fendorf (Stanford University), Andrea Foster (U.S. Geological Survey), Myneni, Trainor, and Brent Constantz (Skeletal Kinetics); ***Team G: Theoretical Modeling of Solid-Aqueous Interfaces and Interfacial Reactions*** [Chaka (leader), Nilsson, Lars G.M. Pettersson (Stockholm University), and Rosso]; ***Team H: Dynamics in Biofilms at Solid-Aqueous Solution Interfaces, and Molecular Genomics and Biofilm Physiology*** [Spormann (leader), Brown, Fendorf, Foster, Myneni, and Rosso]; ***Team I: Environmental Applications*** [Fendorf and Brown (co-leaders), Georges Calas (University of Paris VI), Foster, Farid Juillot (University of Paris VII), Guillaume Morin (University of Paris VI), Myneni, James J. Rytuba (US Geological Survey), Spormann, and Trainor]; ***Team J: New Experimental Developments in Synchrotron Radiation-Based Spectroscopies and Micro-Imaging*** [Nilsson (leader), Bergmann, Bluhm, Farges, and Salmeron].

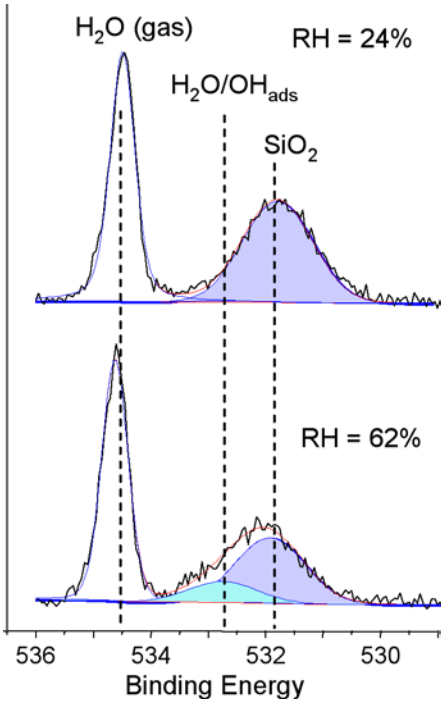
Figure 7



In addition to the research areas outlined above, the Stanford EMSI has a strong educational outreach effort led by Dr. Jennifer Saltzman, Educational Outreach Coordinator for the Stanford School of Earth Sciences and the Stanford EMSI, and Prof. Bryan Brown, Assistant Professor, Stanford School of Education and Stanford EMSI Educational Outreach Supervisor. A sampling of results from several of these research areas as well as education and outreach activities is presented below.

The first annual meeting of the Stanford EMSI was held at Stanford University of August 7-8, 2005 and was attended by about 50 SEMSI members, the seven members of the SEMSI External Advisory Committee, and several guests. The meeting consisted of 25 oral presentations and 15 poster presentations as well as break-out sessions of the various research teams listed above. A photograph of many of the attendees of the first SEMSI annual meeting is shown in **Figure 2**.

Figure 8



II. SUMMARY OF SELECTED RESEARCH RESULTS

A. Bulk and Interfacial Water (Nilsson, Pettersson *et al.*)

1. The structure of liquid water and aqueous solutions (Nilsson, Bergmann, Pettersson, Myneni *et al.*)

Water is key to our existence on planet Earth and is involved in many biological, chemical, environmental, geological, and physical processes. Although water is the most common molecular substance, it is also the most unusual with many peculiar properties such as an increased density upon melting, increased viscosity under pressure, a density maximum at 4°C, high surface tension, and many more. Another of the remarkable and invaluable properties of water is its ability to act as strong polar solvent, which makes it possible for ionic salts to be completely dissolved in it. Developing a fundamental understanding of the hydrogen bonding (H-bonding) network in water that gives rise to all of these unique properties is one of the most intriguing problems in chemical physics with many implications in environmental molecular science. This problem has been discussed intensively for over 100 years and has not yet been resolved. Due to the lack of detailed experimental information, many theoretical models exist, and in particular, results from theoretical molecular dynamics (MD) simulations have dominated the field over the last 20 years. In order to gain unique new information regarding the internal structure of the H-bonded network in water, it is essential to develop new techniques, both experimental and theoretical.

Figure 3A shows O K-edge spectra of water in its three forms of aggregation indicating that the electronic transitions in the condensed forms are significantly different from those in the gas phase. The gas phase spectrum exhibits well-separated peaks corresponding to O 1s excitations into the antibonding O-H $4a_1$ and $2b_1$ molecular orbitals at low energies (534 and 536 eV), and transitions into the Rydberg orbitals at high energies **[21,22]**. As water converts from the gas phase into the condensed phases, the spectrum broadens and shifts to higher energies. We note that the liquid spectum is somewhat in between the spectra from gas phase water and ice. The liquid water spectrum shows a strong pre-edge peak at 535 eV, a main-edge peak at 537.6 eV, and a post-edge peak around 540 eV **[21-23]**. These features reflect the 2p character of the unoccupied valence orbitals at the site of the oxygen atom of the water molecule. Through model experiments, i.e. tetrahedrally coordinated bulk ice and broken donating H-bonded structures at the ice surface, as well as density functional theory (DFT) calculations of XA spectra for clusters of water molecules, the spectral features could be related to specific molecular environments **[23]**. In particular, the weakly coordinated OH in molecules with asymmetric donating H-bonds gives rise to the strong pre-edge and main edge features observed for liquid water as well as for the ice surface, while the more strongly H-bonded OH contributes to the post-edge peak. The similarity of the ice surface and liquid water spectra and the comparison between the DFT calculated bond situations and experimental data suggest that liquid water consists mainly of water molecules with only one strong donating hydrogen bond (hydrogen bond on the hydrogen side), also denoted as single donor (SD) configuration. The other donated hydrogen bond is "broken" or "weak" due to either elongation or bending of the OH—O axis with a higher probability for bending in order to be consistent with radial distribution function (RDF) data obtained from neutron diffraction studies **[24]**. In tetrahedral configurations, as in ice, both OH groups are coordinated with neighboring water molecules and these are denoted double donor (DD). Thereby the intensity of the post-edge will be nearly twice as large compared with the SD configurations. In this sense part of the intensity of the post-edge is transferred to the pre-edge and main-edge upon breaking one donor bond forming SD from DD configurations. The investigation thus shows that most water molecules are in configurations with only two strong hydrogen bonds, which are connected via a three-dimensional weakly hydrogen bonded network [**23**]. This indicates a major discrepancy with molecular dynamics (MD) simulations, which suggest that most molecules are in local tetrahedral configurations not too different from ice **[25]**.

Figure 9

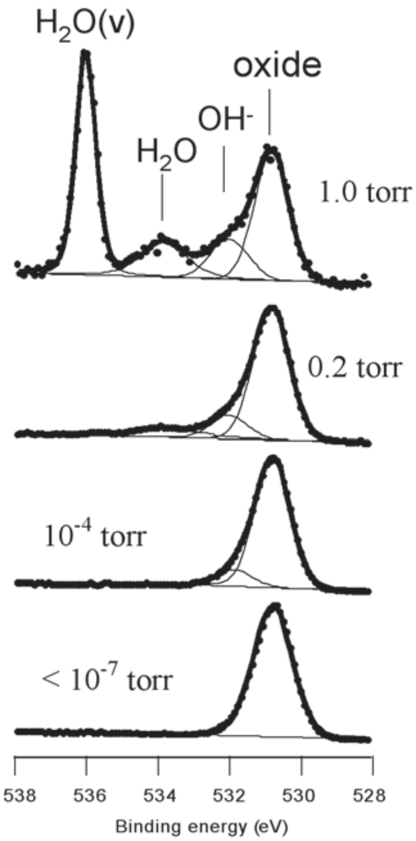


Figure 10

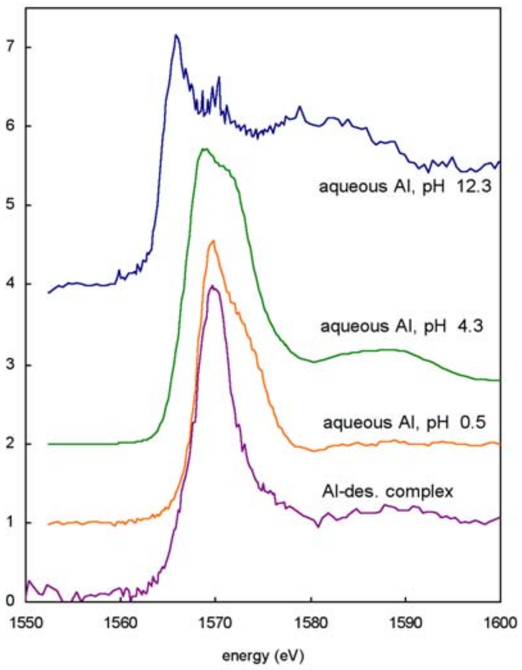


Figure 3B shows a comparison between XRS spectra of room temperature water (25˚C) and hot water (90˚C) **[21]**. Intensities in the pre and main-edge regions increase while post-edge intensities decrease upon heating. The changes are small compared to the changes observed between ice and the liquid indicating that room temperature and hot water have very similar local structures. Fig. 3B shows the difference spectra of 25˚C-water minus ice (solid curve) and 90˚C minus 25˚C-water (circles with error bars) **[21]**. The latter has been multiplied by a factor of 8 in order to match the intensities. The similarity of the curves, in particular the same isosbestic point at 538.8 eV, supports a two-component structure in terms of O-H coordination: Configurations with one uncoordinated or weakly H-bonded O-H group replace tetrahedral ones in the ice-liquid phase transition, and heating liquid water causes very similar types of changes, but of ~8 times smaller magnitude. A recent ultrafast IR pump and Raman probe study of water confirms this picture through the observation that there are two distinct subbands with clearly distinguishable dynamical behavior **[26]**. Furthermore, a reanalysis of older neutron diffraction data shows that a model with large concentrations of SD species is fully consistent with the present results **[27]**.

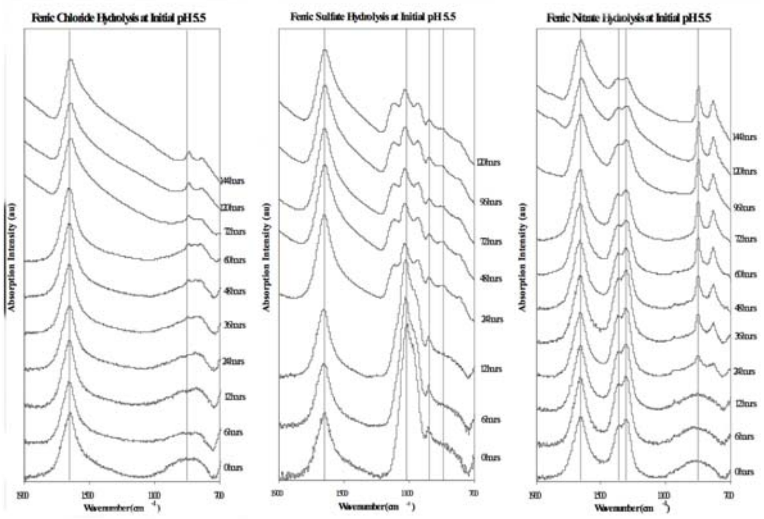
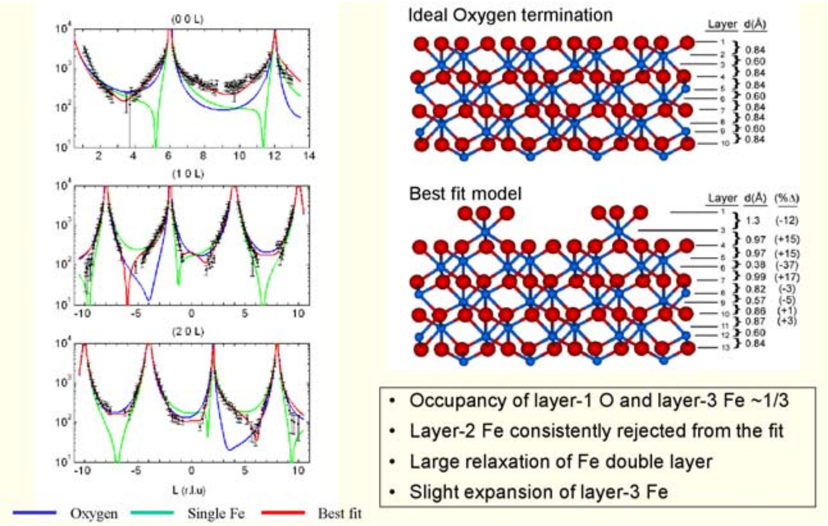


Figure 11

Figures 3C and **3D** show a comparison of experimental O K-edge XANES spectra and simulated O K-edge XANES spectra of bulk ice Ih, the ice Ih surface, and the NH_3-terminated first half bilayer of the ice Ih surface. The agreement between experiment and theory is quite good.

Figure 12



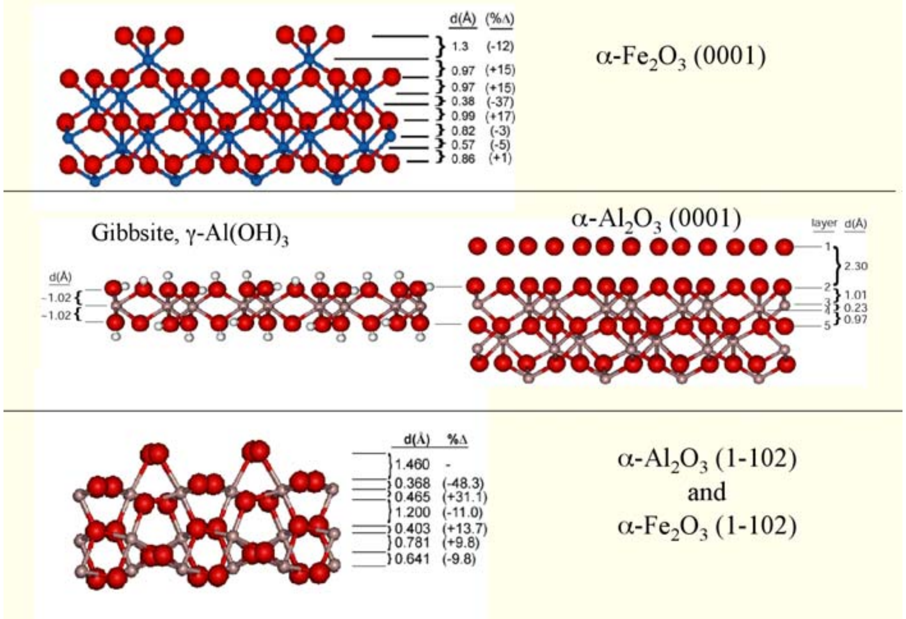
Our XAS study of the structure of water was the subject of a *Science Perspective* **[28]**, and it was also selected by *Science* for *Science Top Ten Breakthroughs* in 2004 **[29]** with the comment that "...*debate will likely rage through 2005.*" This paper was the 6th most cited paper in chemistry in 2005, having been cited more than 70 times in less than two years, and the debate has indeed begun. The conclusion of this study was challenged by another paper by Smith *et al.*, which was published in *Science* in October 2004 **[30]**. The Smith *et al.* study used temperature-dependent XAS from a liquid jet. Based on a Boltzmann distribution analysis similar to previous Raman studies, it was suggested that the conventional tetrahedral water structure model is consistent with the energetics derived from the large spectral changes. However, we have shown in a Technical Comment in *Science*, May 2005 **[31]**, that the Smith *et al.* study is inconsistent with expected spectral changes, based on new XRS data taken on the BioCat beamline at the APS, and it appears to be a victim of saturation effects providing experimental artifacts and that furthermore the spectral analysis was based on incorrect assumptions concerning spectral intensities.

2. Structure, bonding, and reactivity of water on metal surfaces (Nilsson, Pettersson *et al.*)

The structure, bonding, and chemical speciation of water on surfaces have far reaching implications for the fields of environmental molecular science, corrosion science, fuel cell technology, and electrochemistry. Molecularly thin water films adsorbed under ultra high vacuum (UHV) conditions on certain well-defined single crystal metal surfaces have served as well-defined model systems for our initial investigations. The water films have been studied by synchrotron-based soft x-ray spectroscopies: x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and x-ray emission spectroscopy (XES), in combination with density functional theory (DFT). XPS provides a quantitative tool sensitive to the chemical speciation of water; XAS is an element specific probe that provides information on orbital symmetry which is key to resolving the unoccupied electronic states; and XES provides an atom-specific symmetry-resolved orbital picture of the occupied valence electronic states. These spectroscopies are reliably modeled within DFT, and the spectroscopic modeling, therefore, constitutes a direct link between our experimental and theoretical studies of water adsorption.

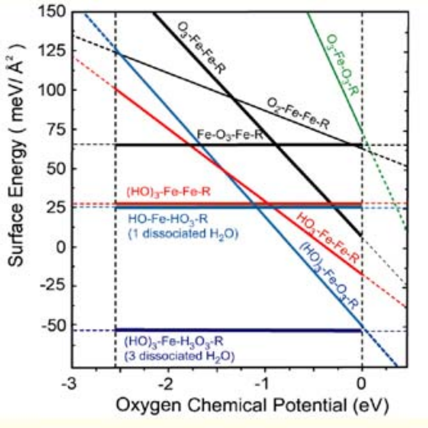
From our studies we have drawn novel conclusions about the structure of the water overlayer on metal surfaces and have arrived at an atom-specific orbital picture of water chemical bonding to the substrate. A general adsorption model for the completed first water layer at saturation coverage and temperatures slightly below 150 K, where non-dissociative wetting occurs, is found for the substrates Pt(111) **[32]**, Ru(001) **[33]**, and Cu(110) **[34]**. The model consists of alternating metal-oxygen (M-O) and metal-hydrogen (M-HO) bonding to water with only limited numbers of uncoordinated H-donor species (see **Figure 4**, above). As can be seen in **Figure 4**, the energetic position of the metal d-band center is a crucial component for understanding the chemical bonding of water to the substrate.

Figure 13



Water growth on Cu(111) and Cu(110) at temperatures below 150 K has been studied to gain insight into the underlying microscopic nature of wetting-nonwetting phenomena. Whereas the first water layer adsorbs in an orderly 2D-fashion on Cu(110) resulting in complete wetting of the substrate, on Cu(111) water (ice) growth occurs in a 3-D fashion. This clearly indicates that to understand this difference contributions to the chemical bonding other than the d-band model need to be considered in order to explain the larger adsorption strength of water on Cu(110) compared to Cu(111). The electrostatic contribution to the adsorption strength depends on the charge density modulation of the specific surface in question. In the case of Cu(110) the electrostatic contribution to the adsorption energy of water is large enough for complete wetting to occur.

For many surface chemical processes in the presence of water, atomic O and surface hydroxyl (OH) species are very important reactants and



- Calculated surface energies in equilibrium with water vapor.
- Predict lowest E stoichiometry and structure (relaxations) for direct comparison to expt.
- Best fit to CTR data based on linear combo of theory models:

~1/3 $(HO)_3$-Fe-H_3O_3-R

~2/3 $(HO)_3$-Fe-Fe-R

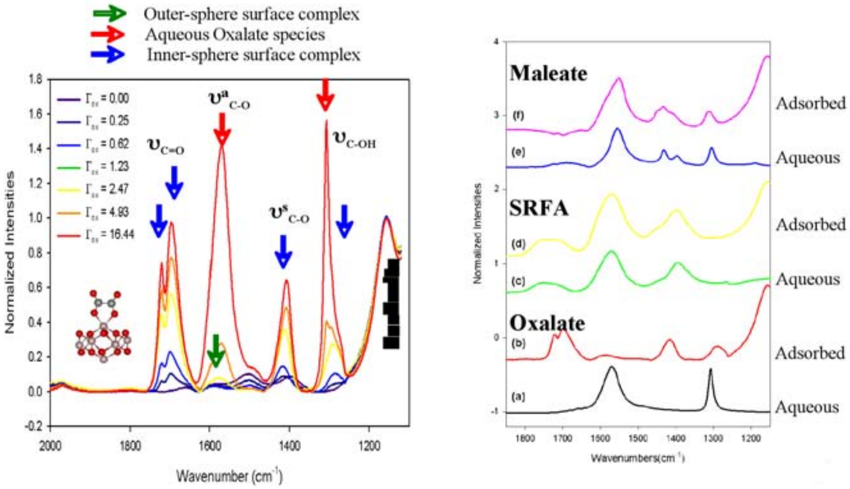
Figure 14

intermediates. The activation barriers towards water dissociation into OH (+ H) were studied and quantified utilizing XPS on the fairly reactive substrates Cu(110) **[34]** and Ru(001) **[33]** as well as on oxidized Pt(111). While water adsorbs molecularly intact on clean Pt(111) **[32]**, an oxidized Pt surface activates and splits adsorbed water even at low temperature. The results on water dissociation on Cu(110) and Ru(001) have resolved some recent controversies in the field of water surface chemistry.

Water adsorbs molecularly on Ru(001) at temperatures below 150 K **[33]**. We find that the D_2O monolayer desorbs molecularly intact giving rise to a water desorption-feature at about 185 K. However, for the H_2O monolayer, significant dissociation occurs in kinetic competition with desorption at temperatures above 150 K, giving rise to an extra desorption-feature at about 220 K originating from the recombinative desorption of water dissociation fragments. These results now explain previously reported anomalous isotope effects in the thermal desorption of the water isotopes on Ru(001). On Cu(110) the water adsorption and dissociation results share similarities with the H_2O/Ru(001) system **[32]**. The XPS results for water on Cu(110) are displayed in **Figure 5**, which shows a temperature-dependent study of water on Cu(110) in the 140 – 195 K range. Dissociation into hydroxyl (OD) is observed to occur in the 160 – 165 K range with an activation barrier of 0.53-0.56 eV.

Our studies of water adsorption on Cu(110) utilizing XPS have been expanded to encompass near ambient conditions at the MES beamline 11.0.2 at the Advanced Light Source (ALS), Berkeley. Our previous results on the water/Cu(110) system under UHV conditions offer a frame of reference. Initial water adsorption experiments on Cu(110) at pressures up to 1.5 Torr in the temperature range 270 - 470 K using synchrotron-based XPS have already been performed. The adsorption of water on Cu(110) has been studied at low temperatures (<160 K) using PES **[34]**. It was found that water adsorbs molecularly under those conditions. **Figure 6** shows an example in which a Cu(110) surface covered by a p(2x1) oxygen layer was exposed to 1 torr of water vapor at room temperature. The O1s PES spectrum shows three distinct peaks that originate from chemisorbed oxygen and newly formed hydroxyls and water at the Cu(110) surface. The spectrum in **Figure 6** implies that at least part of the water adsorbed at room temperature is adsorbing molecularly. We are currently investigating water adsorption on clean and oxygen-precovered surfaces in more detail.

Figure 15



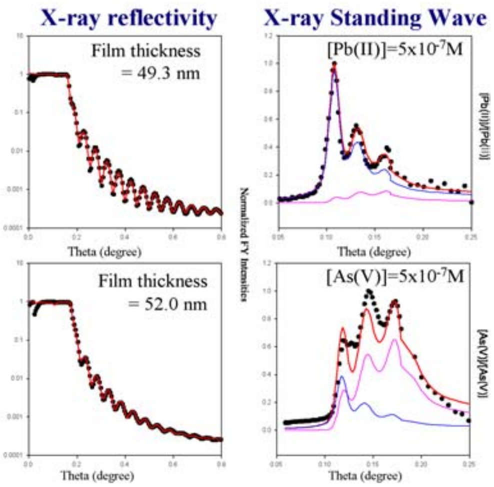


Figure 16

B. Interaction of Water with Environmental Substrates (Bluhm, Salmeron, Nilsson, Brown *et al.*)

1. Scanning tunneling microscopy (STM) studies (Salmeron *et al.*)

Using STM we have studied the adsorption of water on Ru(0001) at low temperature. We have observed the formation of 2-dimensional hexagonal water clusters that are epitaxially related to the Ru surface. At temperatures of 40 to 100 K the clusters grow in the form of a few side-sharing hexamers that appear to consist of undissociated water (**Fig. 7**). The limited size of the clusters calls for a model, already found to operate for Pd(111), where water molecules are fully H-bonded to other molecules in a planar geometry **[35]**. Bonding to the substrate Ru atoms is done via the O-lone pair p_z orbitals. The self-limiting size growth is a result of the extra H-bonds that cannot be accommodated inside the cluster and therefore terminate the growth by decorating the edges in dangling configuration. Heating to 130 K appears to be necessary to form larger 2-dimensional islands, with no sign of dissociation to OH+H_2O or other fragments. Interestingly the STM images show a dramatic change in the structure and contrast when the substrate is heated to 180 K. Dissociation is the most likely cause for the observed changes. We are currently investigating this possibility.

2. Ambient pressure photoemission spectroscopy studies of the interaction of water with metal oxide surfaces (Bluhm, Salmeron, Nilsson, Brown *et al.*)

The ambient pressure photoemission spectrometer at the Molecular Environmental Science beamline (11.0.2) at the Advanced Light Source in Berkeley allows one to investigate samples in gas atmospheres at pressure of up to 10 torr. Collaborative studies, within the Stanford EMSI of water adsorption under ambient conditions on such substrates as α-SiO_2, α-Fe_2O_3(0001), and MgO(100) are now in full progress at ALS-MES beamline 11.0.2. We have used this spectrometer to perform first experiments on water adsorption on α-SiO_2, which is a major component of silicate minerals and on α-Fe_2O_3 (0001), which is an important environmental substrate. Of special interest in these investigations are the structure and the properties of thin water layers under ambient conditions, *e.g.*, at temperatures from -50 to +100 °C and at water vapor pressures in the torr range.

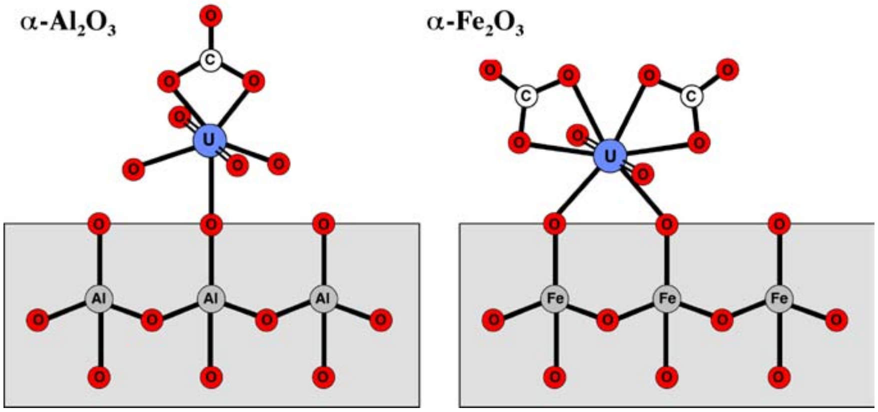


Figure 17

Figure 8 shows ambient pressure PES oxygen 1s spectra of an amorphous SiO_2 surface in the presence of water vapor at a pressure of 1.5 torr. Both gas phase water and surface peaks can be seen in the O1s spectra. The relative humidity (RH) at the sample surface was changed by changing the sample temperature. Adsorption of water at 24% RH is weak, since (besides the water vapor peak) only the SiO_2 O1s peak is present in the spectrum. When the sample temperature is lowered to -8°C (62 % RH) a new peak appears at a binding energy of 532.7 eV which is most likely due to adsorbed water. We will use these kinds of experiments to measure water adsorption isobars on various surfaces.

Figure 9 shows preliminary oxygen 1s XPS spectra of water on the surface of a highly polished natural sample of α-Fe_2O_3 (0001) (specular hematite from Brazil). At $pH_2O = 10^{-7}$ torr, only the lattice oxygen feature is evident (at ≈ 531eV). With increasing pH_2O, a surface OH feature appears at ≈ 532 eV, followed by a feature at ≈534 eV due to molecularly physisorbed water. The chemical shift of the oxygen 1s feature in water vapor is sufficiently large, relative to physisorbed water, that it is easily observed.

C. Structure of Metal Complexes in Aqueous Solutions (Myneni *et al.*)

1. Chemistry of Al- and Fe-hydroxide polymers in aqueous solutions and in precipitates

Hydroxylated species of iron and aluminum are the primary sorbents for different contaminants and nutrients and control their solubility and transport in many natural systems. The crystalline and amorphous varieties of the hydroxides and oxyhydroxides of these metals are also the dominant forms of Fe^{3+} and Al^{3+} in weathering environments. The hydrolysis of these metal cations leads to the rapid formation of aqueous polymers and insoluble gels, which convert to crystalline varieties slowly. This structural reorganization of gels can take months to years and is controlled by different environmental variables, such as temperature, pH, and the types and concentrations of co-ions and counter-ions. Although the chemistry of crystalline phases is well understood, the structural and chemical characteristics of the amorphous precursors to the crystalline phases are not. In this investigation, we are exploring the maturation of amorphous Al-, and Fe-hydroxide gels, and how the above-mentioned environmental variables modify the gel structure and their rates of transformation.

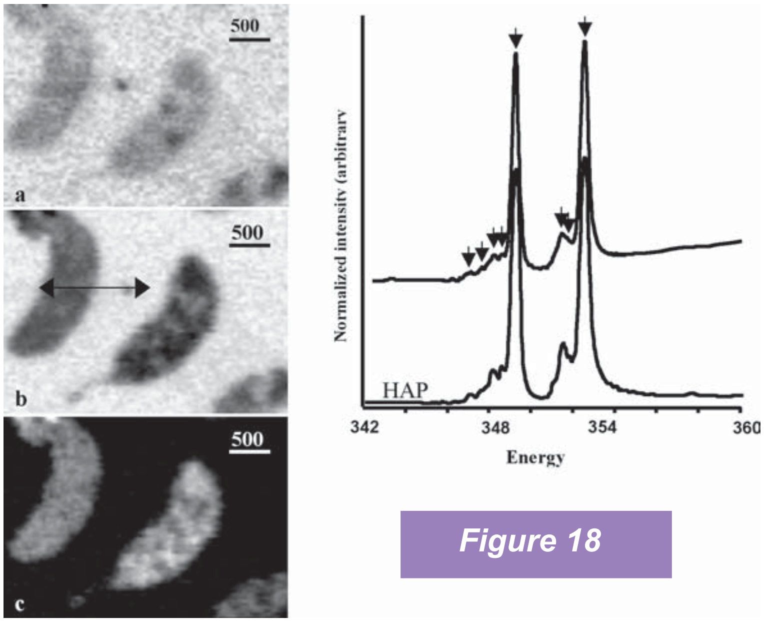


Figure 18

During the formation of aqueous hydroxyl polymers and gels from soluble monomers of hexa-aqua Al^{3+} and Fe^{3+}, water molecules from the coordination spheres of these metals are replaced gradually with stronger hydroxo and oxo bridges between different cationic polyhedra. The rates of formation of hydroxo and oxo bridges, the rate of exchange of water molecules from the coordination spheres of metals, and the rate at which the gels mature to produce crystalline phases are controlled by the presence of different ligands in the inner-solvation sphere of these metals and the H-bonding environments of the bridges. Thus the coordination environment of the bridging hydroxyls, which connect different metal polyhedra, holds the key to understanding the maturation of the gels and their reactivities.

We are using different techniques to evaluate the chemical state of these bridging hydroxyls, including (1) soft X-ray absorption spectroscopy at the O K-edge to probe the local coordination environment of linking oxygens and hydroxyls, (2) metal-EXAFS and X-ray scattering to probe the coordination environment of Fe- and Al-containing polyhedra, distortions in their geometries, and the long range order in the gels, and (3) infrared spectroscopy to probe the vibrational modes (stretching and bending vibrations) of hydroxyls coordinated to metals, and the lattice modes. A brief summary of some of our preliminary results is presented here.

Figure 19

a. Soft x-ray absorption spectroscopy studies of aqueous Al-species (Myneni *et al.*)

Aluminum speciation in aqueous solutions and in precipitates has been investigated by several researchers using NMR spectroscopy. These studies indicate that aqueous Al^{3+} exists in octahedral coordination with water molecules and/or hydroxyls in solutions of acidic and near neutral pH, and that the coordination of Al^{3+} changes to tetrahedral coordination by hydroxyls in alkaline solutions. Only recently, indirect evidence has pointed to the existence of penta- coordinated Al^{3+} at intermediate pH values **[36]**, but its short residence time prevented direct observation by NMR spectroscopy. In this investigation we have explored how Al coordination changes in aqueous solutions and in amorphous gels, and how different co-ions and counter-ions influence the structures of these phases.

Our group built a soft x-ray XAS end station to conduct studies on aqueous solutions, and we have used this end station to evaluate the coordination of Al^{3+} as a function of pH and the presence of different complexing ligands in aqueous solutions, and in different crystalline Al-containing phases (silicates, hydroxides, oxides). Previous experimental and theoretical studies indicate that the Al K-edge XANES spectrum exhibits electronic transitions from 1*s* to empty orbitals of Al 3*p* and 3*d* character.

Our soft x-ray XAS studies indicate that Al K-edge XANES spectra are highly sensitive to variations in the local coordination environment of Al (**Fig. 10**). The XANES spectrum of Al^{3+} complexed with desferrioxamine B (a hydroxamate siderophore) exhibits a sharp narrow transition (corresponding to electronic transitions from 1*s* to mixed Al 3*p*-O 2*p* orbitals), indicating that the mixing of Al 3*d* orbitals with O 2*p* orbitals is weak. When compared with this spectrum, the XANES spectrum of $Al(H_2O)_6^{3+}$ complex in water is much broader with a high energy shoulder, which indicates that the $Al(H_2O)_6^{3+}$ complex is highly distorted (**Fig. 10**). As the pH of this sample was increased, the absorption edge shifted to lower energy (the energy difference between the highest and lowest pH samples was over 3.5 eV). These spectral changes indicate that the coordination environment of the complex changes from octahedral to tetrahedral as the sample pH is increased, in agreement with the previous NMR observations. However, aqueous Al K-edge XANES spectra at intermediate pH values (4.0-9.5) were difficult to evaluate. The polymerization of Al^{3+} at these pH values resulted in the formation of precipitates or colloids of Al-hydroxide in addition to soluble Al-species, and the XANES spectra of these samples showed contributions from these different components. The absorption edges of these samples at intermediate pH values are in between the edge energies of tetrahedral and octahedral complexes discussed above (about 1.5 eV below the absorption edge of the octahedral $Al(H_2O)_6^{3+}$ complex). Recent theoretical studies attributed such spectral shifts to the presence of penta-coordinated Al in Al-EDTA complexes. Based on these theoretical studies, we hypothesize that our spectra may indicate a mixture of both octahedral and penta-coordinated Al species. Swaddle *et al.* **[36]** provide kinetic evidence for the existence of penta-coordinated Al-species in such solutions. We are exploring these results in detail to confirm this.

b. Infrared spectroscopy of amorphous Fe-oxyhydroxide precursors (Myneni *et al.*)

The initial phase of this study focused on evaluation of the vibrational spectroscopy of structural hydroxyls in synthetic crystalline Fe-oxyhydroxides, goethite (α-FeOOH), akaganeite (β-FeOOH.Cl), and lepidocrocite (γ-FeOOH). We used this information to interpret the nature of bridging hydroxyls in amorphous ferric polymers.

Infrared spectroscopic studies of different crystalline Fe-oxyhydroxide phases indicate that the bending vibrations of OH groups in minerals exhibiting tunnel-like structures (*e.g.*, goethite, akaganeite) are significantly different from minerals that exhibit sheet structures with cooperative H-bonding networks (*e.g.*, lepidocrocite). Although small variations in the energies of the OH band exist between minerals within each class, spectral differences between the two classes of Fe-oxyhydroxides are significant. For example, OH groups in goethite and lepidocrocite are H-bonded to bridging oxygen atoms and Cl^-, respectively, which results in small differences between OH stretching and bending vibrations. Conversely, the OH moieties in lepidocrocite form H-bonds to the OH groups in the adjacent layer, and thus exhibit significantly different spectral features. We used spectral differences between these different crystalline phases to identify the variations in coordination environments of OH in amorphous ferric gels, and their variation as gel maturation progresses.

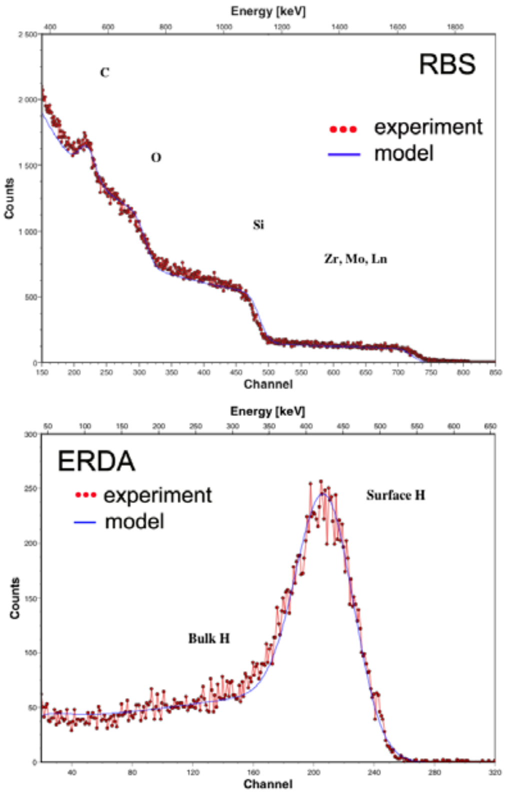


Figure 20

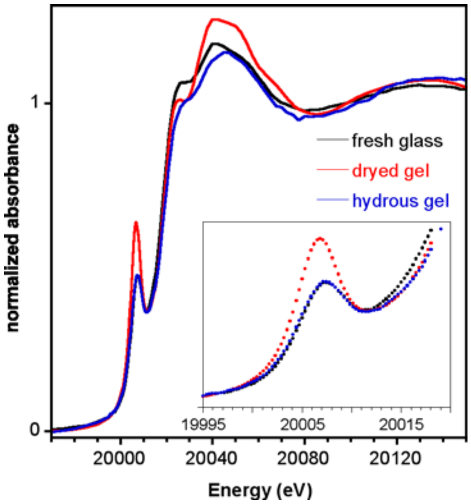


Figure 21

Freshly prepared gels from soluble ferric iron exhibits a broad band centered at 900 cm^{-1}, which remains the same or gradually changes to a doublet as the samples are aged at 90°C (**Fig. 11**). Appearance of this doublet is indicative of the formation of goethite, which was found to be the final stable mineral phase in all of our maturation studies. The rate of maturation was dependent on sample temperature and pH and the type of counter ions. Our studies show that conversion of amorphous gels to goethite is rapid in alkaline solutions in the presence of ions that do not form complexes with ferric iron (*e.g.*, NO_3^-). Although the rate of ripening was improved significantly in the presence of complexing ions (*e.g.*, Cl^- and SO_4^{2-}) in acidic solutions, it was significantly delayed in alkaline solutions. Similar changes were also found at 50°C, but the rates are much slower than those observed at 90°C.

The infrared spectra of the initial precipitates formed at different temperatures and in the presence of different ligands exhibit the same type of Fe-OH bending vibrations at ≈ 900 cm^{-1}. As mentioned earlier, only crystalline hydroxides with tunnel-like structures exhibit spectral features in this energy region. This may suggest that Fe(III) hydrolysis produces close-packed crystalline phases with tunnel-like structures that mature from precipitates with similar structural environments present in the early stages of gel formation. Although different chemical conditions alter the times at which they become well ordered, their local structural environments are perhaps similar. This information is significant in predicting the evolution of different crystalline Fe-oxyhydroxides and the cycling of different elements associated with them.

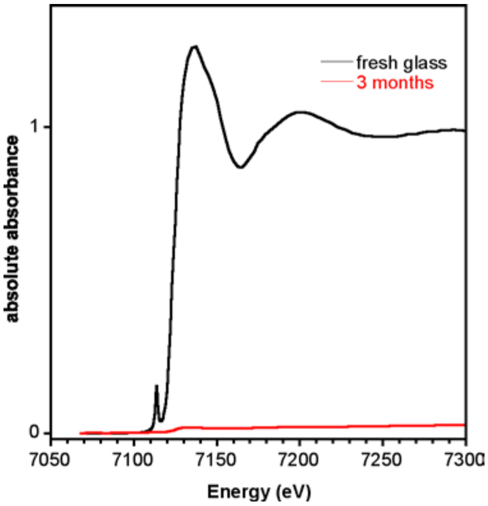
D. Structure and Reactivity of Hydrated Metal Oxide Surfaces (Trainor, Chaka, Brown *et al.*)

Surface diffraction methods allow for precise determination of the atomic structure of surfaces **[8,11,37,38]**. Because surface diffraction is a hard (high energy) x-ray technique, insulator surfaces can be studied under environmentally relevant PT conditions, including the presence of bulk liquid films (*in situ*) and structural analysis of buried interfaces within multilayer samples (*e.g.*, surface terminations with organic and inorganic coatings). A general observation based on surface studies by our group and others is that hydration or hydroxylation of metal-oxide surfaces results in terminations that differ substantially in structure and composition from simple stoichiometric cleavages of the bulk crystal. This has significant implications for understanding the reactivity of metal-oxide mineral phases under aquatic conditions, since the adsorption affinity of aqueous solutes, dissolution/growth rates, and surface charge properties are dictated by the composition and coordination environment of surface functional groups. One of our major goals is to understand the influence of hydration on surface structure. We can use the experimentally determined surface structures to test both simple coordination chemistry models and *ab initio* methods for predicting structure and reactivity of mineral fluid interface systems.

From a coordination chemistry perspective, two factors appear to be dominant in dictating the experimentally observed surface structures; (i) water reaction results in complete coordination shells of near surface metals, (ii) unfavorable polyhedral arrangements present in the bulk structure are diminished at the solid-solution interface, as evidenced by relaxation of metal-oxygen bond length distortions or removal of metal centers associated with unfavorable polyhedral linkages (c.f. results on α-Al_2O_3 (0001), (1-102) and α-Fe_2O_3 (0001), (1-102) surfaces – see **Figures 12 and 13**). The observed deviations of the surface structure from bulk terminations result in non-stoichiometric metal-oxygen ratios at the solid-aqueous solution interface. In our earlier work we had assumed that hydrogen ions serve to balance the charge associated with a non-stoichiometric model, and hydrogen positions were determined based on simple crystal chemical considerations (surface diffraction methods cannot identify the positions of H due to their weak scattering power). There is strong experimental evidence for the presence of hydrogen as surface hydroxyl groups based on previous photoemission spectroscopy **[39]**, vibrational spectroscopy **[40]**, and batch titrations **[41]**. However, we still lack a method for precise determination of the structural identity of surface hydroxyl groups, their spatial arrangement on a surface, and their influence on surface relaxation and reactivity.

We have approached this problem by combining our experimental results with first principles density functional theory (DFT) calculations. These calculations are done in collaboration with Anne Chaka's (EMSI Co-Investigator) group at NIST. The approach is to develop theoretical models for all plausible surface structures including variations in protonation state of surface metal-(hydr)oxide moieties and to calculate optimized structures for direct comparison with experimental results. This approach has allowed us to distinguish between surface hydroxyl topologies that cannot be directly discerned from the surface diffraction results. Our recent work on the a-Fe_2O_3 (0001) surface shows excellent agreement between the structures of best-fit experimental models and the lowest-energy theoretical models (**Fig. 14**) **[8]**. More recent work combining both theory and experiment on the α-Fe_2O_3 (1-102) surface is in preparation for publication, and again shows excellent agreement between these approaches. These results suggest that this combined theoretical/experimental approach will allow us to develop and test quantitative approaches for predicting complex hydroxylated surface structures. We are continuing work on a number of model systems to test this approach across a wide range of bulk oxide composition, structure and surface orientation (*e.g.*, recent experimental work on systems listed above). Of particular interest is extending our work to redox active substrates (*e.g.*, Fe_3O_4 is currently under study) and silicate minerals (planned experiments for later in 2006).

Figure 22



Other experimental efforts have focused on the study of binding affinities and interfacial distributions of metals on hydroxylated metal-oxide surfaces. These measurements combine surface diffraction, long-period XSW, and grazing-incidence x-ray absorption spectros-

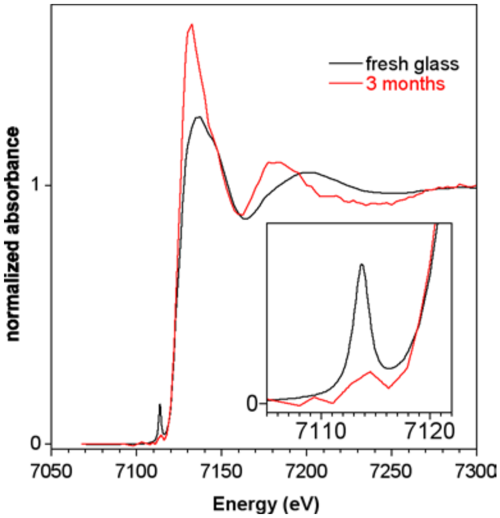


Figure 23

copy to investigate the binding mode (*e.g.*, sorbate and interfacial species local structure), oxidation state, and distribution of species at the solid-aqueous solution interface. Systems we are currently investigating include Pb, Cd, and As sorption on low-index faces of hydroxylated α-Fe_2O_3. These measurements will allow us to investigate quantitatively the structure-reactivity relationship of surfaces in which detailed models have been derived from the surface structure analysis discussed above.

While pursuing these studies we have continually improved our methods and infrastructure for data collection, analysis and computation. We have recently modified the surface diffraction analysis code (in collaboration with P. Eng of GSECARS, University of Chicago) to include a molecular group concept to aid analysis of sorbate binding structures. We have also recently modified the long-period XSW code to include electron density gradients across interfaces and multi-layer element distributions to improve the analysis of multi-layer systems and systems where surface leaching or film growth results in complex interfacial structure. We have also invested significant effort in the past several months to improving sample preparation and characterization and data collection methods. This effort has in part involved the development of in-house chemical-mechanical-polishing capabilities (in collaboration with P. Eng) and surface quality characterization by in-house atomic force microscopy analysis (at UAF). The development of these capabilities greatly enhances our throughput for generation of new surfaces and allows us to readily test the reproducibility of our results. Finally, with A. Chaka we have developed a strong collaboration with the Arctic Region Supercomputer Center at UAF and are well underway to utilizing their resources and expertise in the computational aspects of our work (see section F below).

E. Sorption Processes a Solid-Aqueous, Microbe-Aqueous, and Solid-Biofilm Interfaces and Biomineralization (Brown, Spormann, Yoon, Benzerara, Farges, Constantz *et al.*)

1. Sorption of organic acids at mineral-water interfaces (Brown, Yoon *et al.*)

We have completed a series of molecular-level studies of the interactions of several low molecular weight organic anions (oxalate, malate, maleate, citrate, pyromellitate) with aluminum oxide and aluminum oxyhydroxide surfaces **[42-46]**. Such anions are common in many natural settings due to their exudation by plant roots, production by fungi, and discharge by microorganisms. Their adsorption onto particle surfaces in soils and groundwater aquifers can have a significant impact on the interaction of aqueous heavy metal ions with these surfaces. In addition, they serve as simplified surrogates of more complex humic substances, thus are good starting points for more fundamental studies of the interaction of natural organic matter with mineral surfaces using a reductionist approach. In these studies we used a combination of ATR-FTIR spectroscopy, DFT geometry optimization and vibrational frequency calculations, organic anion uptake measurements, CD-MUSIC modeling of uptake data, Al dissolution measurements, and potentiometric titration measurements of surface charge as a function of pH and ionic strength. Examples of FTIR spectra we have taken on oxalate, maleate, and Suwannee River Fulvic Acid sorbed on boehmite are shown in **Figure 15**.

The following conclusions were reached for the *oxalate-boehmite* (g-AlOOH)-water and *oxalate-corundum* (α-Al_2O_3)-water systems **[42]**: (1) at pH 5.1, at least four different oxalate species were found at or near the boehmite/water interface for oxalate surface coverages (G_{ox}) ranging from 0.25 to 16.44 mmol/m^2; (2) at relatively low coverages ($G_{ox} < 2.47$), strongly adsorbed inner-sphere oxalate species (IR peaks at 1286, 1418, 1700, and 1720 cm^{-1}) replace weakly adsorbed carbonate species, and a small proportion of oxalate anions are adsorbed in an outer-sphere mode (IR peaks at 1314 and 1591 cm^{-1}); (3) with increasing oxalate concentration ($G_{ox} > 2.47$ mmol/m^2), the boehmite surface binding sites for inner-sphere adsorbed oxalate become saturated, and excess oxalate ions are present dominantly as aqueous species (IR peaks at 1309 and 1571 cm^{-1}); (4) oxalate-promoted dissolution of boehmite following inner-sphere oxalate adsorption becomes increasingly pronounced with increasing G_{ox} and results in an aqueous Al(III)-oxalate species, as indicated by shifted IR peaks (1286 to 1297 cm^{-1} and 1418 to 1408 cm^{-1}); (5) the similarity of adsorbed oxalate spectral features at pH 2.5 and 5.1 implies that the adsorption mechanism of aqueous HOx^- species involves loss of protons from this species during the ligand-exchange reaction. As a consequence, adsorbed inner-sphere oxalate and aqueous Al(III)-oxalate complexes formed at pH 2.5 have coordination geometries very similar to those formed at pH 5.1; (6) Among the models considered, calculated IR frequencies based on a bidentate side-on structure with a 5-membered ring agree best with the observed frequencies for boehmite/oxalate/water samples at G_{ox} = 0.25 to 16.44 mmol/m^2 and pH 2.5 and 5.1 and for a corundum/oxalate/water sample at G_{ox} = 1.4 mmol/m^2 and pH 5.1. Based on these results, we suggest that oxalate bonding on boehmite and corundum surfaces results in 5-coordinated rather than 4- or 6-coordinated Al surface sites; (7) Consistent with the ATR-FTIR findings, macroscopic adsorption data measured for oxalate concentrations of 0.125 – 2.50 mM can be generally well modeled with a single bidentate, inner-sphere oxalate complex using the charge distribution – multisite complexation (CD-MUSIC) model **[44]**. However, at intermediate oxalate concentrations (0.50 and 1.25 mM) and pH < 5, the extent of oxalate adsorption measured experimentally is found to fall significantly below that predicted by CD-MUSIC simulations. The latter finding is interpreted in terms of competition for oxalate from dissolved Al(III), the formation of which is promoted by the dissolution-enhancing properties of the adsorbed oxalate anion; (8) increasing concentrations of dissolved Al(III) in solution are found to significantly decrease the extent of oxalate adsorption on corundum under acidic pH conditions, presumably through promoting the formation of Al(III)-oxalate complexes with reduced affinities for the corundum surface compared with the uncomplexed oxalate anion; (9) increasing con-

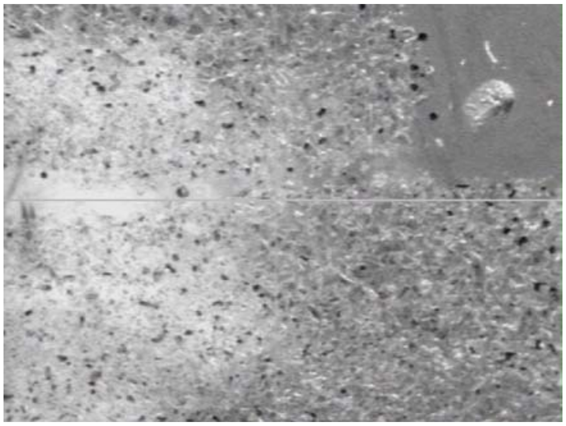


Figure 24

centrations of oxalate successively shift the electrokinetic isoelectric point (iep) and pH of the maximum shear yield stress (τ_{YMAX}) to more acidic conditions (a similar conclusion was reached for maleate and citrate interactions with corundum colloidal suspensions); (10) inner-spherically adsorbed oxalate and citrate can significantly charge-reverse the corundum-water interface, with the extent of charge reversal being related to the relative binding strengths of the oxalate and citrate anions; (11) oxalate (and maleate and citrate) generate steric barriers to inter-particle approach, leading to substantial reductions in the magnitude of τ_{YMAX} at low to intermediate anion concentrations; (12) At the highest anion concentrations investigated, increases in τ_{YMAX} were observed, and can be attributed to the formation of bridging Al(III)-organic surface precipitates, as suggested by *in situ* ATR-FTIR spectroscopic measurements of corundum-oxalate suspensions at high oxalate concentrations. The extent of precipitate formation is greatest for the corundum – oxalate system due to the strong dissolution-enhancing properties of the inner-spherically adsorbed oxalate anion (*i.e.*, its ability to generate enhanced concentrations of dissolved Al(III) which can then participate in precipitate formation).

The following conclusions were reached for the *maleate-corundum-water* system **[43]**: (1) *in situ* ATR-FTIR spectroscopic measurements indicate that maleate binds predominantly as an outer-sphere, fully deprotonated complex ($\int AlOH_2^+—Mal^{2-}$) at the corundum surface over the entire range of maleate concentrations (0.125 – 5.0 mM) and pH conditions (2-10) investigated; (2) consistent with the ATR-FTIR data, maleate macroscopic adsorption data can be modeled as a function of maleate concentration and pH using an extended constant capacitance approach and a single $\int AlOH_2^+—Mal^{2-}$ species; (3) outer-sphere adsorption of maleate is found to significantly reduce the protolytic dissolution rate of corundum under acidic conditions (pH < 5). A likely mechanism involves steric protection of dissolution-active surface sites, whereby strong outer-sphere interactions with maleate hinder attack on those surface sites by dissolution-promoting species.

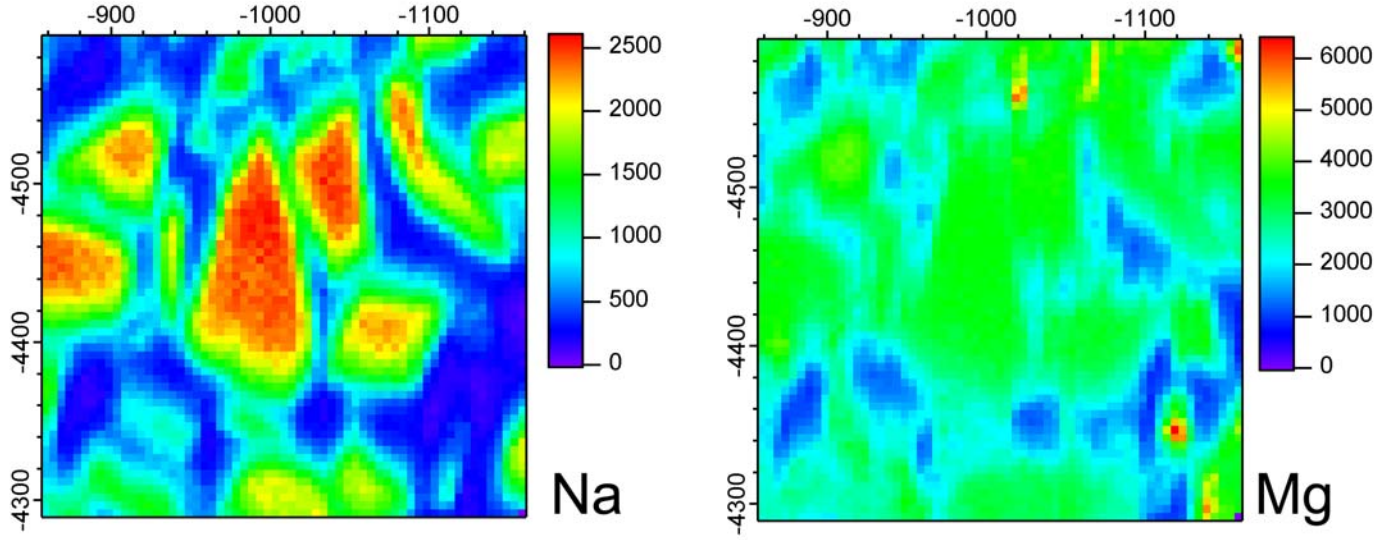
The following conclusions were reached for the *pyromellitate-corundum-water* system **[45]**: (1) the adsorption modes of pyromellitate on corundum are dominated by a fully deprotonated, outer-sphere pyromellitate species ($\equiv AlOH_2^+—Pyr^{4-}$) at pH ≥ 5.0; (2) at lower pH conditions, however, an additional protonated outer-sphere species ($\equiv AlOH_2^+—H_2Pyr^{2-}$) and an inner-sphere species are also evident; (3) in accordance with the ATR-FTIR findings, modeling of macroscopic pyromellitate adsorption data using an extended constant capacitance treatment was possible using two outer-sphere ($\equiv AlOH_2^+—Pyr^{4-}$ and $\equiv AlOH_2^+—H_2Pyr^{2-}$) and one inner-sphere ($\equiv AlPyr^{3-}$) adsorbed pyromellitate species; (4) the presence of adsorbed pyromellitate strongly inhibited the dissolution of corundum under acidic (pH < 5) conditions, consistent with our mechanism previously proposed for maleate adsorption on corundum [2] whereby outer-spherically adsorbed Pyr^{4-} species sterically protect dissolution-active surface sites from attack by dissolution-promoting species such as protons. A reduction in the protolytic dissolution rate of corundum results.

In addition to these studies of the interaction of LMW organic anions with Al-oxyhydroxide surfaces, we have also carried out detailed molecular-level studies of the interaction of natural humic (Suwannee River Fulvic Acid – SRFA) and fulvic (Pahokee Peak Humic Acid – PPHA) acids with the same surfaces **[47,48]**. The results of these studies are as follows: **(1)** at relatively high SRFA surface coverages (G_{SRFA}= 5.33 mmol m^{-2}), *in situ* ATR-FTIR spectral features of adsorbed SRFA are very similar to those measured for SRFA in solution at approximately 1-3 pH units higher. At sub-monolayer surface coverages (G_{SRFA}= 1.20 and 2.20 mmol m^{-2}), several new peaks and enhancements of the intensities of a number of existing peaks are observed. The latter spectral changes arise from several non-organic extrinsic species (*i.e.*, carbonate and adsorbed water, for alkaline solution conditions), partially protonated SRFA carboxyl functional groups (near-neutral pH conditions), and small quantities of inner-spherically adsorbed SRFA carboxyl groups and/or Al(III)-SRFA complexes (for acidic conditions)f. The spectra of PPHA adsorbed at boehmite/water interfaces also showed changes generally consistent with our observations for SRFA sorbed on boehmite. These observations confirm that SRFA and PPHA are predominantly adsorbed at the boehmite/water interface in an outer-sphere fashion, with minor inner-sphere adsorption complexes being formed only under quite acidic conditions; **(2)** these results suggest that the positively charged boehmite/water interface stabilizes SRFA and PPHA carboxyl functional groups against protonation at lower pH; (3) Measurements of the concentration of dissolved Al(III) ions in the absence and presence of SRFA showed that the boehmite dissolution process is clearly inhibited by the adsorption of SRFA, which is consistent with previous observations that outer-spherically adsorbed organic anions inhibit Al-(oxyhydr)oxide dissolution.

2. Trace element partitioning at polymer film-metal oxide interfaces (Brown, Yoon *et al.*)

The distributions of Pb(II) and $As(V)O_4^{3-}$ ions in the interfacial region between thin polyacrylic acid (PAA) coatings and α-Al_2O_3(0001), α-Al_2O_3(1-102), and α-Fe_2O_3(0001) single crystal substrates were studied using

Figure 25



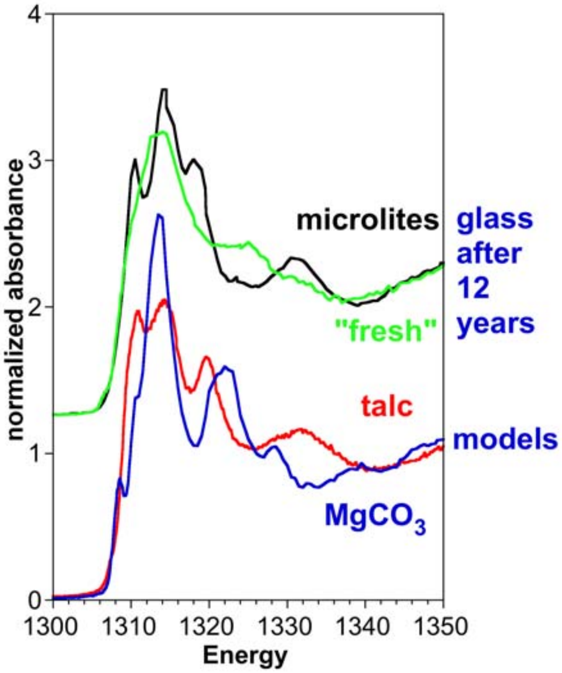


Figure 26

long-period x-ray standing wave fluorescent yield (XSW-FY) and x-ray reflectivity techniques **[49]**. The PAA film serves as a simplified analog of natural organic matter (NOM) coatings on mineral surfaces. Such coatings are often assumed to play an important role in the partitioning and speciation of trace heavy metals in soils and aquatic systems. The goal of this study was to evaluate this assumption in a carefully controlled model system. Synchrotron-based XSW-FY spectroscopy is one of the few methods that allows quantitative *in situ* studies of trace element partitioning at organic film-mineral or biofilm-mineral interfaces (see, *e.g.*, **[50,51]**). On the α-Al_2O_3 (1-102) surface, Pb(II) ions were found to preferentially bind to the PAA coating, even at sub-micromolar Pb(II) concentrations, and to partition increasingly onto the metal oxide surface as the Pb(II) concentration was increased ([Pb(II)] = 5×10^{-8} M to 2×10^{-5} M, pH = 4.5; 0.01 M NaCl background electrolyte) (**Fig. 16**). This observation suggests that the binding sites in the PAA coating out-compete those on the α-Al_2O_3 (1-102) surface for Pb(II) under these conditions. The As(V)O_4^{3-} oxoanion partitions preferentially to the α-Al_2O_3(1-102) surface for the As(V) concentrations examined (1×10^{-7} to 5×10^{-7} M, pH = 4.5; 0.01 M NaCl background electrolyte) (**Fig. 16**). Partitioning of Pb(II) (at 1×10^{-7} M and pH 4.5) was also examined at PAA/a-Al_2O_3(0001), and PAA/a-Fe_2O_3(0001) interfaces using XSW-FY measurements. Our results show that the PAA coating was the dominant sink for Pb(II) in all three samples; however, the relative order of reactivity of these metal oxide surfaces with respect to Pb(II) sorption is α-Fe_2O_3 (0001) > α-Al_2O_3 (1-102) > α-Al_2O_3 (0001). This order is consistent with that found in our previous studies of the PAA-free surfaces **[50]**. These XSW results strongly suggest that the characteristics of the organic film (*i.e.* binding affinity, type and density of binding sites) as well as metal oxide substrate reactivity are key factors determining the distribution and speciation of Pb(II) and As(V)O_4^{3-} at organic film/metal oxide interfaces.

3. CTR diffraction and grazing incidence XAFS study of U(VI) adsorption to α-Al_2O_3 and α-Fe_2O_3 (1-102) surfaces (Brown, Trainor *et al.*)

Evaluation of the long-term health risks of uranium contamination in soils, sediments, and groundwater requires a fundamental understanding of the various processes affecting subsurface transport of uranium, including adsorption processes at mineral/water interfaces. Although there have been a number of studies of the sorption of U(VI) on mineral surfaces using XAFS and luminescence spectroscopy methods (*e.g.*, **[10, 52-55]**), there is still some question about the mode of binding of U(VI) to mineral surfaces and thus how effectively it is sequestered in adsorption complexes on mineral surfaces. We have used a new approach involving a combination of crystal truncation rod (CTR) diffraction and grazing incidence EXAFS (GI-EXAFS) spectroscopy to determine the binding sites and surface complexation of U(VI) adsorbed on the (1-102) surfaces of α-Al_2O_3 and α-Fe_2O_3 **[56]**. The available binding sites on the (1-102) surfaces were constrained through bond valence and steric analyses. On both surfaces U(VI) forms uranyl-carbonato ternary complexes to surface oxygens that are singly coordinated to aluminum or iron. On the α-Al_2O_3 (1-102) surface, a monodentate complex results, whereas on the α-Fe_2O_3 (1-102) surface, the binding is bidentate to adjacent singly coordinated oxygen sites (*i.e.* binuclear) **(Fig. 17)**. Differences in protonation of the singly coordinated oxygen atoms, surface charging, U(VI) aqueous speciation, substrate structure, or the electronic structure of surface functional groups may be the cause of these differences in adsorption geometry. Both XPS and CTR diffraction reveal higher U(VI) surface coverages on the α-Fe_2O_3 (1-102) surface than on the α-Al_2O_3 (1-102) surface. This difference cannot be the result of differences in defect concentration alone as CTR diffraction is not sensitive to U(VI) sorbed to defect sites, implying that the α-Fe_2O_3- (1-102) surface has an intrinsically higher affinity for U(VI). The surface complexes observed in this study are different from the bidentate, mononuclear complexes typically derived for U(VI) on powdered aluminum- and iron-(oxyhydr)oxides and clay minerals using U L_{III}-edge EXAFS spectroscopy. However, the presence of monodentate, mononuclear and bidentate, binuclear complexes may have been overlooked in past EXAFS studies on such substrates, as these complexes have U-Al or U-Fe interatomic distances that are too large to be easily detected by EXAFS spectroscopy.

4. Arsenite sorption onto 2-line ferrihydrite, hematite, goethite, and lepidocrocite under anoxic conditions (Calas, Morin, Juillot, Brown *et al.*)

The modes of As(III) sorption onto hematite (Hm), 2-line ferrihydrite (Fh), goethite (Gt), and lepidocrocite (Lp) have been investigated under anoxic condition using extended X-ray absorption fine structure spectroscopy (EXAFS) **[57]**. The absence of oxygen was required to minimize As(III) oxidation due to Fenton reactions. EXAFS data indicate that As(III) forms similar inner-sphere surface complexes on 2-line ferrihydrite and hematite, but forms different types of surface complexes on gœthite and lepidocrocite. The dominant complex types on Fh and Hm are bidentate mononuclear edge-sharing (^2E) and bidentate binuclear corner-sharing (^2C), with As-Fe distances of 2.90 ± 0.05 Å and 3.35 ± 0.05 Å, respectively. In contrast, As(III) forms dominantly bidentate binuclear corner-sharing (^2C) sorption complexes on Gt and Lp [d(As-Fe) = 3.3-3.4 Å], with a minor amount of monodentate mononuclear corner-sharing (^1V) complexes [d(As-Fe) = 3.5-3.6 Å]. Bidentate mononuclear edge-sharing (^2E) complexes are virtually absent in Gt and Lp. These results help explain the differences in reactivity of Fe(III)-(oxyhydr)oxide surface sites.

5. Sequestration of Sr(II) by calcium oxalate (Brown, Farges *et al.*)

Calcium Oxalate (CaOx) is produced by 2/3 of all plant families and can comprise up to 80 weight percent of bulk plant tissue. CaOx can also be found in many surface environments, where oxalate is derived from plant and fungi excretions, and precipitates with Ca in soils. It is unclear how CaOx in plants and soils might interact with metals and possibly sequester them. We have examined the type(s) and strength of interactions between CaOx and Sr in a model system **[58]**. Uptake experiments were conducted to determine the extent of uptake, and extended X-ray absorption spectroscopy (EXAFS) was used to determine the mechanism and nature of Sr(II) uptake. Batch uptake experiments indicated that Sr uptake by CaOx is independent of pH, and corresponds to Ca release. Sr K-edge EXAFS revealed the presence of a Sr-oxalate mixed hydration phase. We conclude that Sr exchanges with Ca at the CaOx surface to form a Sr-oxalate coating. As Sr-oxalate is less soluble than CaOx, this could potentially be a significant factor in the biogeochemical cycling of Sr in surface environments where CaOx is present. The formation of Sr-oxalate in plants and soils could retard Sr movement in surface environments.

6. Scanning transmission x-ray microscopy (STXM) study of microbial calcification (Brown, Spormann, Constantz *et al.*)

Calcium phosphates and calcium carbonates are among the most prevalent minerals involved in microbial fossilization. Characterization of both the organic and mineral components in biomineralized samples is, however, usually difficult at the appropriate spatial resolution, i.e., at the submicrometer scale. Scanning Transmission X-ray Microscopy (STXM) was used to measure C K-edge, P L-edge, and Ca L-edge NEXAFS spectra of some calcium-containing minerals common in biomineralization processes and to study the experimental biomineralization by the model microorganism *Caulobacter crescentus* **[59]**. We have shown that the Ca $L_{2,3}$-edges for hydroxyapatite, calcite, vaterite, and aragonite are unique and can be used as probes to detect these different mineral phases. Using these results, we showed that *C. crescentus* cells, when cultured in the presence of high calcium concentration, precipitate carbonate hydroxyapatite (**Fig. 18**). In parallel, we detected proteins, polysaccharides, and nucleic acids in the mineralizing bacteria at the single-cell scale. Although the present study has not proven that a certain class of organic molecule is responsible for the formation of calcium phosphates in *C. crescentus*, it has been able to distinguish among several different biochemical compounds, including proteins, EPS, and DNA associated with hydroxyapatite biominerals in or on these cells. Proteins, polysaccharides, or lipids have been shown experimentally to be potential matrices for the precipitation of calcium-containing minerals (*e.g.*, **[60]**), but the relative importance of each class of molecules for calcification leading to carbonate or phosphate deposits is yet to be determined. The study of such deposits of suspected biogenic origin by STXM may help in determining which of these biomolecules are the most frequent ones associated with calcium carbonates and calcium phosphates in nature. Finally, we suggest that characterization of purported nanobacteria by STXM could help resolve the debate about whether they are calcified microorganisms or calcified macromolecules of a single type, such as proteins.

7. Reactivity of oxide glass surfaces (Farges, Brown *et al.*)

Oxide glasses react strongly with water because glasses are metastable phases formed from rapid quenching of high-temperature melts. In addition, nanoscale chemical heterogeneities between network formers (such as Si and Al) and modifiers (such as Na and Ca) facilitate percolation of protons, which enhances glass weathering. Because various types of glasses are used for urban and nuclear wastes, it is important to gain an improved understanding of chemical reactions at the glass/water interfaces at the molecular scale. We have used a combination of microscopies (scanning environmental), nano-SIMS, nuclear-based techniques (ERDA, PIXE, and RBS), and x-ray absorption techniques to investigate the reaction of freshly cleaved (under vacuum) glass (alumino and borosilicate) surfaces with aqueous solutions as a function of ionic strength, pH (1-12), and exposure times (1 day – 1 year). The weathered glass surface (**Fig. 19**) shows dissolution cracks and precipitates of various types (*e.g.*, clays, metal oxyhydroxides). Rutherford backscattering (RBS) and energy recoil detection analysis (ERDA) of these glass surfaces (**Fig. 20**) show depletion of heavy metals (*e.g.*, Zr, Mo, La, Th), which is correlated with the formation of a highly hydrous gel layer.

The chemical and mechanical stabilities of silicate glass over time are in large part related to its ability to resist weathering and bio-aggression. This research is particularly important for long-term waste repositories, as the glass must retain the toxic cations in confined storage for geologic time periods. Resistance to corrosion is also crucial for the preservation of historical heritage within the urban environment (including "massive" tourism sustainable development). The main focus of this research is to understand how aged glass surfaces react with aqueous solutions after periodic dry-wet seasons, urban pollution, and/or touristic flow. Most previous studies have focused on moderately aged glasses (1-2 years duration) or highly aged glasses (geological, > 10^6 years). However, these time frames are not ideal for understanding the durability of silicate glass over tens, hundreds, and thousands of years, which are the critical timescales for sustainability considerations.

In this work, we have focused first on actively weathered glasses ("soxhlet" confinement, 1 year, 90°, pH < 2). After such weathering, even REE's are leached from a borosilicate glass simulating new compositions used by the French nuclear agency. Leaching leaves mostly ferric iron and thorium in a silica-rich matrix (RBS, ERDA, PIXE and XANES data). Much less energetic weathering (12 years duration, PSI) results in a steady state rate of weathering after 3-4 years. Cracks are filled with precipitation products (ESEM; $CaMoO_4$) (**Figs. 19** and **21**). Corrosion cupules appear next, filled by a SiO_2-rich matrix depleted in most elements except Fe (**Fig. 22**) in the form of ferrihydrite (as obtained from XANES) (**Figs. 22** and **23**). Replacing Zn by Mg dramatically enhances the glass dissolution rate, and Mg-rich clays are formed (-XRF).

8. Use of historical glasses to assess the durability of glassy matrices (Farges, Brown et al.)

A variety of historical glasses were selected for durability studies, ranging in age from 3000 BC (Pharonic middle dynasty) to Gallo-Roman (2000 years old) to middle-ages (stained glasses from various cathedrals of France) and XIXth century (Sacré Coeur, Paris). We used a combination of macroscopic and μm-scale x-ray fluorescence and x-ray absorption

Figure 27

mapping to characterize the nature of the weathered glassy inclusions observed in various composites exposed to either sub-desertic (Egypt) or temperate climates (Gallo-Roman) **(Figs. 24-26)**. Analyses of the Na, K, Ca, Mn, Fe and Cu K-edge XANES show that a sodic birnessite and ferrihydrite coexist with other Cu-rich phases related to CuO. Also the antique glasses are oxidized compared to modern counterparts synthesized under various oxygen fugacities. In addition, some oxidized phases are formed by leaching of network modifiers, leaving a substrate enriched in network formers on which metals can slowly coprecipitate as various oxide-type rich phases.

Stained glass from the Strasbourg Cathedral (eastern France) (**Fig. 27**) shows corrosion rinds (**Fig. 28**), which are enriched in Fe and Mn oxyhydroxides compared with the bulk glass, as shown by Mn K-edge XANES spectra (**Fig. 29**). Such rinds contribute to the opacity of these historic glasses. An understanding of this corrosion is necessary for effective conservation efforts.

F. Theoretical Modeling of Solid-Aqueous Interfaces and Interfacial Reactions (Chaka, Rosso *et al.*)

1. DFT and *ab initio* thermodynamic studies of the structure and reactivity of metal oxide surfaces (Chaka *et al.*)

The structure and reactivity of metal oxide surfaces are extremely sensitive to the concentration of species at the interface. UHV studies have indicated that many of these changes do not occur gradually with an increase in gas pressure, but occur suddenly at threshold vapor concentrations. The technique of *ab initio* thermodynamics allows us to calculate surface energies as a function of gas pressures and aqueous concentrations of species, and thus predict the occurrence of thresholds that result in chemically distinct structures. This method has enabled us to understand the different domains that form on hematite as a function of oxygen or water vapor pressure in UHV and under aqueous conditions. We also show why the stoichiometric alumina and hematite (1-102) surfaces are not observed under aqueous conditions.

2. Theoretical analysis of the relationship between mineral dielectric properties and overlying water structure (Rosso *et al.*)

In collaboration with PNNL staff, we have begun incorporation of algorithms into our NWChem software for the calculation of the low and high frequency dielectric tensors using the Car-Parrinello electron density. When finished, we will be able to compute the dielectric properties at any location in our simulation cell at any time interval in a quantum molecular dynamics trajectory. This will put the SEMSI team into a position to rigorously develop this aspect of mineral/water interfacial chemistry for the first time and at an unprecedented level of theory.

3. Theoretical analysis of the electron transfer properties of magnetite surfaces and nanoparticles (Rosso *et al.*)

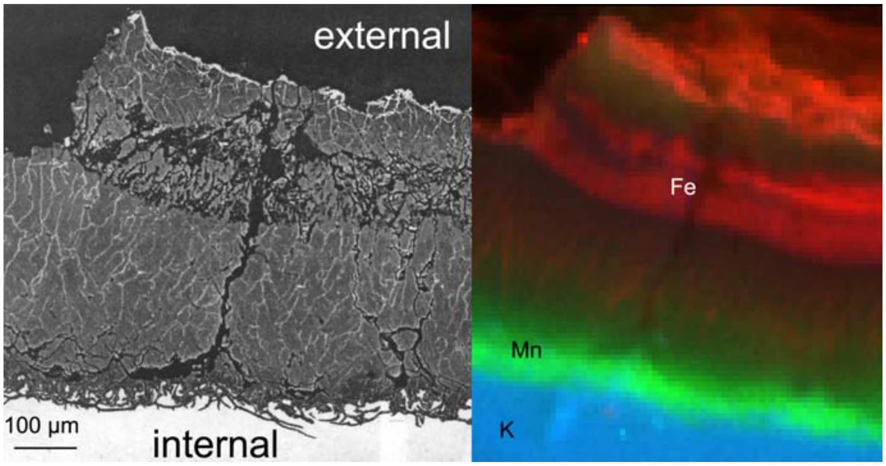
We are investigating the propensity of magnetite to serve as a natural reductant for the immobilization of U(VI) and Cr(VI). Quantum mechanical calculations are underway to address the atomic and electronic structure of magnetite nanoparticles. With Ph.D. student Frannie Skomurski, we are characterizing the atomic structure of magnetite (100) and (111) single crystal surfaces with STM, and mapping the reduction of U(VI) at these surfaces. With Ph.D. student Matthew Wander, we are examining theoretically the mechanisms of electron transfer in this system using quantum mechanical calculations. The calculations are aimed at computing the physical quantities that enter into Marcus' electron transfer model.

G. Dynamics of Biofilms at Solid-Aqueous Solution Interfaces, and Molecular Genomics and Biofilm Physiology (Spormann, Fendorf, Rosso, Brown *et al.*)

1. Metabolic interaction between the Fe(III) reducing bacterium *Shewanella oneidensis* and Fe-mineral surfaces (Spormann *et al.*)

This project encompasses the analysis of both structure and electron transferring capability of *Shewanella oneidensis* mineral surface biofilms. *S. oneidensis*, a facultative gamma proteobacterium is capable of respiring metals, specifically manganese (IV) and iron (III). Preliminary experiments in our laboratory have shown that *S. oneidensis* will attach to iron (III) containing minerals such as hematite and magnetite with affinity similar to a metabolically inert glass surface under aerobic conditions (**Fig. 30**). *S. oneidensis* is capable of growing thick biofilms on all three surfaces. However, when *S. oneidensis* is grown anaerobically on a hematite surface (with no other electron acceptor), the biofilm coverage is sparse with a mixed biofilm structure of single cells and small isolated mushrooms. (Biofilms were visualized through confocal laser scanning microscopy using a GFP-tagged strain in a flow cell system. In the anaerobic set up, cells were exposed to a DNA stain.) Clearly, biofilm development on the surface is dependent on a metabolic relationship between *S. oneidensis* and the surface. Furthermore, the availability of iron (III) plays a role in that biofilms grown on solid, insoluble iron (III) are quite different from those grown on a glass surface in the presence of soluble iron (III). Soluble iron (III) biofilms show development of a biofilm monolayer with the absence of mushroom structures. Timelines of biofilm development on soluble and insoluble iron (III) are currently being obtained.

Figure 28



2. Molecular mechanism of attachment of *Shewanella oneidensis* cells to mineral surfaces (Spormann *et al.*)

Biofilm stability is determined by two mutually exclusive processes: attachment of cells to and detachment from the biofilm matrix. Using *Shewanella oneidensis* MR-1, an environmentally versatile, Fe(III)- and Mn(IV)-mineral reducing microorganism, we identified *mxdA-D* as a new set of genes essential for formation of a three-dimensional biofilm **[62]**. Of these genes, *mxdA* encodes a putative cyclic-di-GMP-forming GGDEF protein and *mxdB* a membrane-associated glycosyl transferase. Both are essential for attachment, and the attachment-deficient phenotype of a *DmxdA* mutant could be rescued by overexpression of VCA0956, a GGDEF protein with cyclic-di-GMP-forming diguanylate cyclase activity.

In order to elucidate the connection between attachment and detachment, we focused on components controlling attachment of *S. oneidensis* cells to biofilms **[63]**. Based on the *S. oneidensis* genome sequence, no genes encoding enzymes for EPS biosynthesis with similarity to those in *Pseudomonas aeruginosa*, *E. coli*, or *Vibrio cholerae* are obvious. In a genetic analysis using Tn*5* mutagenesis coupled to a 96-well-based screen, we previously identified several mutants defective in biofilm formation. Among the mutants isolated were five with transposon insertions mapping to five independent positions of the gene cluster SO4180-4177, which we subsequently named, *mxdA-D* (for 'biofilm matrix deficient') because of the mutants' biofilm phenotype. Two insertions were found in *mxdA*, one in the promoter region of *mxdA*, one in the intergenic region between *mxdA* and *mxdB*, and one insertion in *mxdC*. Re-analysis of the amino acid sequences of these *orfs* revealed that MxdA is predicted to be a 462 amino acid protein containing a C-terminal region with weak homology to a GGDEF domain. MxdB is predicted to be a membrane-associated 403 amino acid protein with homology to glycosyl transferases of the family GT 2 type, MxdC is predicted to be a 351 amino acid membrane-associated protein with homology to efflux pump proteins. MxdD is oriented in the same direction as the previous genes, and is predicted to be a 118 amino acid membrane-associated protein without homology to any known protein. The MxdB amino acid sequence was 25% identical and 42% similar to that of AcsAB, the cellulose synthase of *G. xylinus*, over a range of 192 amino acids. The orientation and sequences of the *mxd* genes are highly similar and homologous, respectively, only to the *Vibrio parahaemolyticus* RIMD genes VPA0392-94.

In order to examine the function of these genes in biofilm formation, we constructed in-frame deletion mutants of all genes, and analyzed their phenotype in biofilms grown under hydrodynamic conditions. Deletion mutants of *mxdA*, *mxdB*, and *mxdC* exhibited strong defects in biofilm formation, and were severely impacted in developing a three-dimensional architecture.

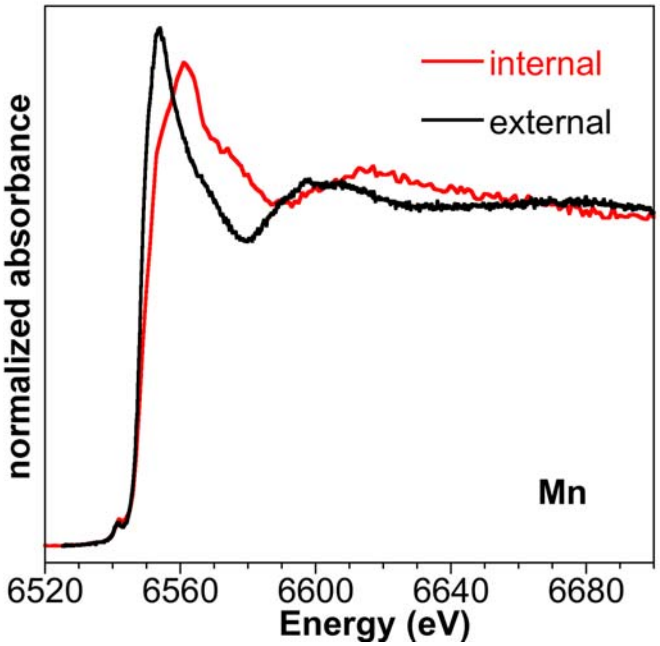


Figure 29

The initial adhesion of these mutants appeared to be similar to wild type. The mutant biofilms were arrested at the stage of a cell monolayer or few cell layers, and did not seem to progress from this stage even after 48h incubation. The most severe phenotype was visible in *DmxdA*. Quantification of biofilm biomass revealed that biofilms of *DmxdA*, *DmxdB*, and *DmxdC* carried between 84 and 94% less biomass than wild type biofilms after 48h. Deletion mutant *DmxdD* showed a delayed phenotype but progressed to a wild type-like architecture after 48h. The in-frame deletions of *mxdA* and *mxdB* could be complemented and the wild type biofilm phenotype restored both by expressing the wild type genes *in trans* or by 'knock-in' gene reconstructions. These data, together with the sequence analysis suggested that the *mxd* genes might encode for a gene cluster essential for biofilm matrix formation via EPS biosynthesis in *S. oneidensis*.

We examined the transcriptional organization of the *mxdA-D* genes using reverse transcriptase (RT) PCR. When RNA prepared from cells grown to late exponential phase in a lactate mineral medium (see Material and Methods) was used as template, RT-PCR products were obtained for primer pairs probing for a contiguous mRNA between *mxdA* and *mxdB*, and *mxdB* and *mxdC*. The reading frames of *mxdB* and *mxdC* are overlapping by one base and were therefore not probed. No RT-PCR product was observed from the primer pair combination SO4181 and *mxdA*. Preliminary transcriptional analysis revealed that *mxdA-D* mRNA is present in cells in late exponential and stationary, but not in early and mid exponential growth phase.

3. Experimental studies of the electron transfer properties of outer-membrane proteins of *Shewanella oneidensis* (Rosso, Lower, Toney, Hochella *et al.*)

We are using a variety of experimental probes to characterize the electron transfer properties of individual OmcA and MtrC proteins. These outer-membrane decaheme proteins from the bacterium *Shewanella oneidensis* MR1 are suspected of facilitating the reduction of Fe(III) and Mn (IV)-oxides at the cell-mineral interface. A key focus area is the characterization of pathways and mechanisms for the terminal electron transfer step. A scanning tunneling microscopy (STM) study of monolayer films of these proteins has been carried out **[64]**. STM images show that a self-assembled layer of detergent covers and protects densely packed cytochrome films immobilized by recombinant tetra-cysteine tags. X-ray photoelectron spectra confirm the presence of thiol bonds between cysteine residues and the Au(111) surface. Temporary application of high bias voltage to the film while imaging causes the detergent film to reorganize around the tip, opening a window for direct STM imaging of the cytochrome layer underneath. The STM apparent sizes of both OmcA and MtrC are 58 nanometers in diameter (**Fig. 31**) consistent with expectations from their molecular masses. Current-voltage tunneling spectra over individual cytochromes showed that OmcA and MtrC have significantly different abilities to mediate tunneling current, reflecting differences in their electronic structures. This interfacial tunneling data suggests that the two cytochromes may have different roles in mediating interfacial electron transfer. We are currently in the process of modeling the current-voltage tunneling spectra using three-component tunneling junction models (metal / redox-center / metal) based on modern electron transfer theory. The structures of these proteins are currently unknown. To gain insight into the height distribution of iron atoms in heme groups with respect to the surface plane for these proteins, we are performing x-ray standing wave measurements. The measurements will allow us to determine minimum distances of separation between heme iron atoms and the solid surface, which has direct implications for predicting rates of electron transfer between the protein and the surface.

4. Scanning probe studies of the electronic properties of outer-membranes of *Shewanella oneidensis* (Rosso, Gorby, Lower, Spormann, Brown *et al.*)

Scanning tunneling microscopy (STM) and current-sensing atomic force microscopy (CAFM) are being used to characterize the electrical conductance of outer-membranes of Shewanella oneidensis MR-1 isolated on hematite (aFe$_2$O$_3$). Cells are grown under anaerobic conditions using basal surfaces of naturally conductive tabular hematite single crystals as the terminal electron acceptor. After incubation, the crystals are rinsed and attached cells are carefully lysed chemically for the purpose of removing all but the most strongly bound cellular material. Ambient AFM showed that residual cellular 'footprint' material on the hematite surface possessed a narrow height distribution between 5-10 nm. The isolated membrane features, presumably with the terminal components of their electron transport chains intact at the interface with the mineral, are then mapped in terms of their ability to pass a tunneling current using both current-sensing atomic force microscopy and STM. Conductance contrast within the footprints was captured by CAFM and STM, and spectroscopic current-voltage curves for various tip positions were obtained. The electronic properties of the tunneling junction are being quantitatively characterized by analysis of the current-voltage spectroscopic curves.

5. Nanoscale Environments Associated with Bioweathering of a Mg-Fe-Pyroxene (Benzerara, Yoon, Brown *et al.*)

Microorganisms are believed to create microenvironments leading to reaction products not predictable from equilibrium thermodynamics and to unique biomineral morphologies. Unambiguous evidence for such environments is, however, rare in natural samples. We have used scanning transmission x-ray microscopy and spectromicroscopy at the sub-40-nm scale, coupled with transmission electron microscopy, to examine bioweathering products on a meteoritic Fe-Mg-orthopyroxene colonized by a filamentous microorganism **[65]**. Our measurements reveal an amorphous Al-rich layer beneath the microorganism, calcium carbonates of unique morphology intimately associated with polysaccharides adjacent to the microorganism, and regions surrounding the microorganism with different iron oxidation states (**Fig. 32**). Our results confirm the presence of different microenvironments at this microorganism-mineral interface and provide unique nanometer-scale views of microbially controlled pyroxene weathering products.

6. Nanoscale detection of organic signatures in carbonate microbialites (Benzerara, Brown *et al.*)

Microbialite deposits associated with microbial mat communities are thought to be evidence of some of the oldest life on Earth. Despite extensive studies of such deposits, little is known about the role of microorganisms in their formation. In addition, unambiguous criteria proving their biogenicity have yet to be established. In this study we have characterized modern calcareous microbialites from the alkaline Lake Van, Turkey, at the nanometer scale by combining X-ray and electron microscopies **[66]**. We describe a simple way to locate microorganisms entombed in calcium carbonate precipitates by probing aromatic functional groups and peptide bonds. Near Edge X-ray Absorption Fine Structure spectra at the C and N K-edges serve as unique signatures for microbes. Nanometer-sized aragonite crystals, which comprise the largest fraction of the microbialites, are embedded in an organic, likely polysaccharidic, matrix, which helps explain the sizes and shapes of the aragonite crystals. These crystals are surrounded by a 10-nm thick amorphous calcium carbonate layer containing organic molecules. These results question existing models of the role of microorganisms in carbonate precipitation and provide new biosignatures for these deposits.

7. Interaction of *Acidothiobacillus* sp. with pyrite surfaces (Brown, Fendorf, Spormann *et al.*)

This project was initiated as part of our NSF-CRAEMS grant, and it has been continued as part of our NSF-EMSI grant. In our earlier studies, we prepared pyrite (100) surfaces from natural single crystals and characterized them using surface science methods **[67-70]**. Following these characterization studies of the clean pyrite (100) surface and the surface after reaction with molecular O$_2$, water vapor, ambient air, and H$_2$O$_2$, we grew pure cultures of *Acidothiobacillus ferroxidans* and, in separate experiments, pure cultures of *Acidothiobacillus thiooxidans* on pyrite (100) surfaces and let them react with the surfaces for time periods up to 6 days; we also grew mixed cultures of both species on the same pyrite surface using the same experimental protocols. On the pyrite surfaces reacted with *A. ferrooxidans*, we found a coating of ferrihydrite (Fe(OH)$_3$) in a broad halo surrounding each bacterial cell; such coatings could potentially block reactive sites on the pyrite surface. No ferrihydrite was found on pyrite surfaces oxidized under abiotic conditions in our experiments. Immediately adjacent to each *A. ferrooxidans* cell was a rim of precipitates consisting of a mixture of goethite (α-FeOOH) and schwertmannite (Fe$_8$O$_8$(SO$_4$)(OH)$_6$). On pyrite surfaces reacted with *A. thiooxidans*, we found no such halos or biomineralization rims around the bacterial cells, and only minor amounts of elemental and oxidized sulfur on the pyrite surface. In the case of the mixed culture, we found hematite as the main surface precipitate on pyrite. In all cases, etch pits were observed on the pyrite surfaces following reaction with *Acidothiobacillus* sp., and they were typically located at some distance from the bacterial cells. This study

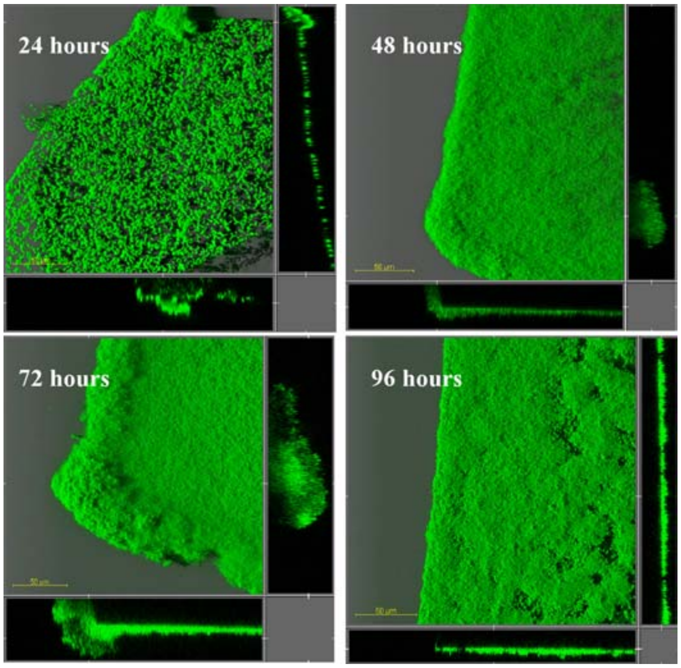
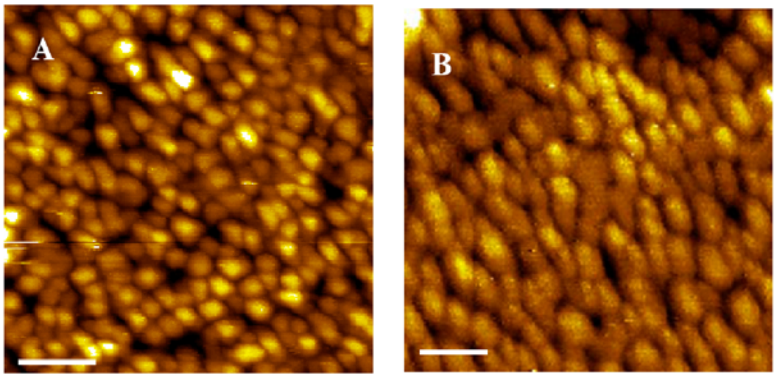


Figure 30

clearly shows that consortia of *A. ferrooxidans* and *A. thiooxidans* oxidize pyrite differently than abiotic oxidation or either organism in isolation.

In our continuing studies of these reactions, we have carried out detailed kinetic measurements and have found that the rates of microbially mediated pyrite oxidation are about 10 times greater than abiotic controls. This rate is much less than the 10^4 to 10^5 increases in rates proposed in older studies. We are currently preparing a manuscript for publication **[71]**.

Figure 31



8. Soft X-ray Spectromicroscopy Study of Chemical Heterogeneities in Iron Precipitates formed at or near Bacterial Cells (Yoon, Benzerara, Brown *et al.*)

The redox chemistry of iron is one of the major factors determining the geochemical cycling of various elements in the environment. Traditionally, the geochemical cycling of iron has been described in term of equilibrium thermodynamics in abiotic chemical system. However, it was also recently recognized that iron oxides formed in neutral-pH aqueous environments are frequently associated with microorganisms, indicating the importance of living organisms and their local environments in the geochemical cycling of iron species **[72]**. For example, Zachara *et al.* [73] proposed a conceptual model to explain the formation of biogenic secondary iron minerals, where the phases of secondary iron minerals were primarily determined by the biogenic Fe(II) supply rate as well as its total concentration at or near the microorganisms. Therefore, characterization of the nanometer-scale local environments of microorganisms, where the biogenic iron minerals are formed, is extremely important in understanding secondary iron biomineralization processes as well as the biogeochemical cycles of various other elements, including both pollutants and nutrients.

Synchrotron-based scanning transmission x-ray microscopy (STXM) is one of the few methods capable of characterizing sub-micron sized particles (> 30 nm in diameter) in the presence of water and/or under atmospheric conditions **[74].** In addition to the good spatial resolution, STXM also has a good chemical speciation capability through the K- and L-edge NEXAFS spectra of various elements (*e.g.*, carbon, calcium and iron), which are sensitive to chemical composition, oxidation state and coordination numbers of the element **[59,65]**.

In this study, soft x-ray spectromicroscopy was used to investigate chemical heterogeneities of iron-containing precipitates formed at or near *Shewanella putrefaciens* (strain CN32) cell surfaces. Spectromicroscopic measurements at the iron L_3- and carbon K- edges with 30 nm spatial resolution provide direct evidence for nanometer-scale chemical heterogeneities in biogenic iron oxide precipitates both temporally and spatially.

Soft X-ray spectromicroscopy experiments were performed on the bacterial reduction of ferrihydrite (coated on quartz) by *S. putrefaciens.* On day 4 of the batch culture experiments, as shown in **Figure 33** (STXM image at iron L_3-edge, 709.5 eV) and H2B (FE-SEM image), we found bacterial cells covered with numerous iron nanoparticles (20-100 nm in diameter), which probably resulted from (1) dissolution of ferrihydrite and reprecipitation on the bacterial cell surfaces and/or (2) dissemination of ferrihydrite into nanoparticles and adsorption on the bacterial cell surfaces. In addition to this imaging which showed iron nano particles, we also conducted Fe L_3 NEXAFS spectroscopy to identify the mineral phases of these iron nanoparticles. We observe only spectral features very similar to those of ferric iron-containing iron oxides (*e.g.*, ferrihydrite, goethite, and hematite) for most of the particles we examined (spectra not shown here). This observation of ferric oxide minerals on bacterial cell surfaces is consistent with Zachara's conceptual model of secondary iron biominerals formed under the condition of low Fe^{2+} supply rate and concentration **[73]**.

We also collected STXM images on the samples cultured for a longer time. **Figure 34A** shows STXM image of a heavily mineralized *S. putrefaciens* single cell after 8 days of culture with ferrihydrite coated quartz. Further processing of STXM images collected on this bacterial cell at the two different energies of the Fe L_3 edge (707.7 eV and 709.5 eV) produced iron maps at these energies (**Figs. 34B** and **34C**) with distinct contrast differences, which is indicative of the presence of heterogeneous iron precipitates formed on the surface of a single bacterial cell. For example, those regions marked as "b" and "d" in **Figures 34B** and **34C** have significant contrast differences; region "b" is much brighter in the iron map collected at 709.5 eV, while region "d" is brighter in the iron map collected at 707.7 eV. To spectroscopically confirm these visual differences in iron maps and to identify their mineral phases, we collected stacks of images for the same bacterial cell and extracted Fe L_3 NEXAFS spectra for four different regions ("a"-"d" in **Figs. 34B** and **34C**). These stack images are presented in **Figure 34D**. As we predicted from the visual comparison of the iron maps at two

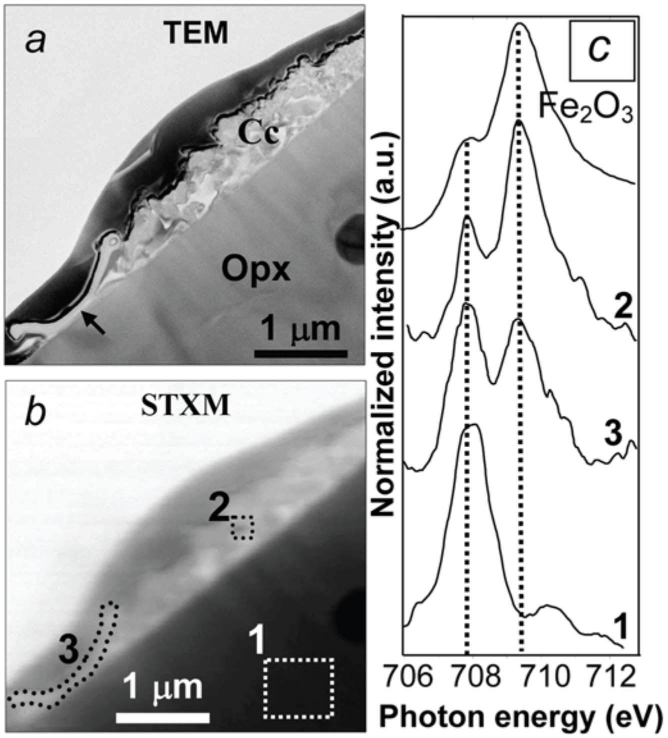


Figure 32

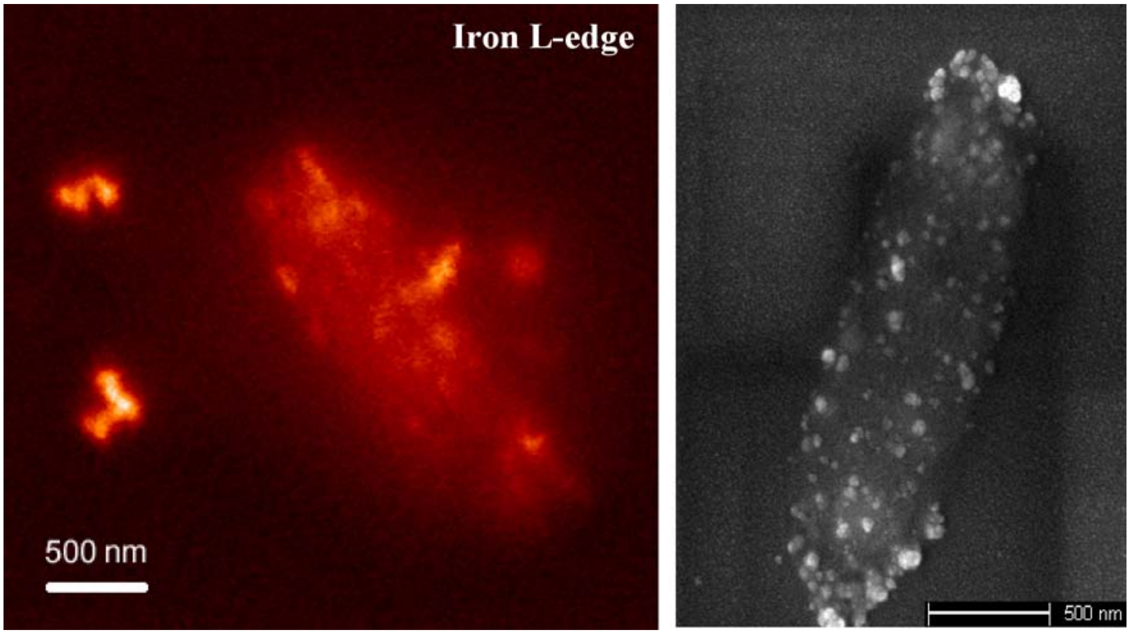


Figure 33

different energies, Fe L_3 NEXAFS spectra for these different regions show quite different spectral features. Spectra from regions "a" and "b" display features very similar to those of Fe(III)-containing iron oxides (*e.g.*, ferrihydrite, gorthite, and hematite), and we believe that Fe(III)-containing nanoparticles reprecipitated and/or adsorbed on the bacterial cell surfaces in these areas, as we observed in the previous sample of day 4. In addition, we also observed significant changes in the Fe L_3 NEXAFS spectra from regions "c" and "d", where the iron peak at the lower energy position (707.6 eV) becomes more intense. The spectra extracted from region "d" show a dominant peak at 707.6 eV, and this spectral feature is most similar with that of siderite in our Fe L_3 NEXAFS spectral database.

Therefore, we think that on the 8th day of the batch culture, the supply rate and local concentration of ferrous ion and carbonate ion in the vicinity of the cell wall increased and resulted in the formation of siderite-like iron precipitates on the bacterial cell wall, as previously suggested by Zachara *et al.* **[73]**.

In this spectromicroscopic study of iron biomineralization by *S. putrefaciens,* adsorption or reprecipitation of Fe(III)-containing nanoparticles (*e.g.*, ferrihydrite) was dominantly observed on *S. putrefaciens* cell surfaces at the early stages (day 4) of batch culture experiments, whereas extensive coverage of the *S. putrefaciens* cell by Fe(II)-containing minerals [*e.g.*, siderite ($FeCO_3$)] as well as Fe(III)-containing nanoparticles was observed on a single bacterial cell surface in later culture stages (day 8). These direct observations of temporal and spatial distributions of heterogeneous iron oxide precipitate formation on bacterial cell surfaces support a previous suggestion by Zachara *et al.* **[73]** on the importance of local nanoscale environments in determining the fate of secondary iron minerals.

H. Environmental Applications (Fendorf, Foster, Brown *et al.*)

1. Biogeochemical processes controlling dissolved concentrations of arsenic (Fendorf *et al.*)

Arsenic is a naturally occurring trace element that poses a human health risk when incorporated into food or drinking water supplies. At present, The World Health Organization's established maximum for arsenic in drinking water is 10 mg/L. Arsenic tainted drinking waters are unfortunately being experienced in many localities around the world and are particularly apparent within Asia. At the present time, more than 57 million people are being exposed to drinking water exceeding the World Health Organization's As limit in Bangladesh alone **[75]**. The natural and anthropogenic processes that lead to increased As concentrations in surface and ground water are highly variable and complex, with ion displacement, reduction of arsenic, and reductive dissolution of iron-(hydr)oxides all being possible desorption mechanisms.

We have initiated column experiments to observe the mobility of As(V) or As(III) adsorbed onto ferric substrates (*e.g.*, ferrihydrite) upon arsenic and/or iron reduction. We incorporated into our arsenic-ferrihydrite sand columns either *Sulfurosprillum barnesii* strain SES-3, a freshwater anaerobic bacterium that reduces both Fe(III) and As(V) through respiratory processes **[76,77]**, or *Bacillus benzoevorans* strain HT-1, a bacterium found in the digestive tract of hamsters that was recently observed to reduce As(V) to As(III) through respiratory processes **[78]** but is incapable of iron reduction. We observed that dissimilatory As(V) reduction promotes arsenic release, and that while Fe(III) reduction can facilitate As release, it may act to limit desorption by yielding Fe(II) concentrations sufficient to induce secondary sequestration of arsenic.

We initiated examination of bioreductive processes on arsenic mobilization by addressing transport within columns having arsenite loaded ferrihydrite coated quartz sand. Dissolved As in the effluent is highest immediately after initiation of flow, reaching a maximum concentration on day 2 and dropping off rapidly to < 5 μM by day 10. Iron concentrations in the effluent and pore waters increased with time; back-reaction with Fe(II) then further altered the iron mineralogy (darkening of sands). When arsenate (as opposed to arsenite) is adsorbed on ferrihydrite, both Fe(III) and As(V) reduction may transpire with *S. barnesii*. Despite changes in the initial arsenic species, and an additional redox reaction, similar elution trends of arsenic are observed. Reduction of As(V) to As(III) is evident in the effluent, and solution phase As is primarily As(III) after 2 d of flow. Reduction of Fe(III) to Fe(II) also occurred, with Fe(II) increasing in the eluent to nearly the same levels (~700 μM as observed in the As(III) loaded column. Re-adsorption of Fe(II) induced conversion of ferrihydrite to magnetite and goethite, as was evidenced by marked darkening of the sands within the first few days of the experiment.

In comparison to the ferrihydrite columns with S. barnesii, *the As(V)-loaded column with* B. benzoevorans *eluted moderate to high levels of As (initial arsenic loading of 482.7 mg Kg*$^{-1}$*) and only very minor amounts of Fe(II)—as expected based on the respiratory capabilities of this bacterium. Surprisingly, elution of As from the abiotic (sterile) columns is substantially greater than that observed in the columns with* S. barnesii, *but showed similar patterns as noted for* B. benzoevorans.

In summary, our initial studies reveal that the activity of Fe(III) and As(V) respiring bacteria have a pronounced influence on As(III) and As(V) desorption from ferrihydrite-coated sands and subsequent transport under advective flow. In the presence of As(V) and Fe(III) respiration, As release from ferrihydrite is most pronounced during the initial influx of waters containing labile carbon but quickly decrease once Fe(II) levels increase. Surprisingly, however, more arsenic [both as As(V) and As(III)] is released under advective flow in abiotic columns from ferrihydrite-sands over longer periods of time than in systems containing bacteria respiring on As(V) and Fe(III)—generation of Fe(II) in particular has a pronounced impact on As sequestration. Bacteria having the capacity to only respire on As(V), thus generating As(III), provide elution trends consistent with abiotic release of As from As(III) loaded columns.

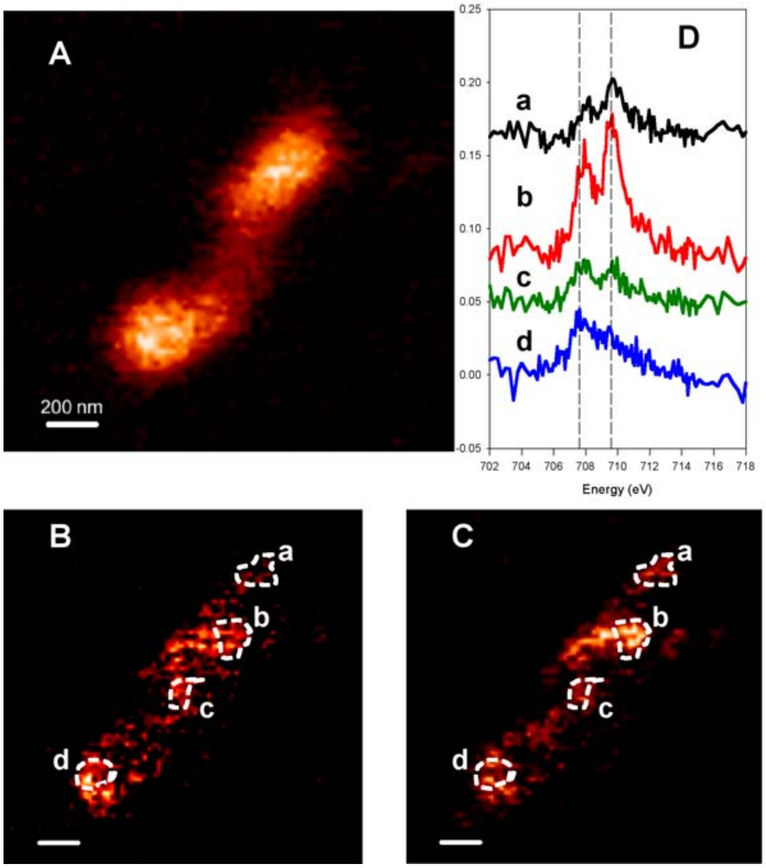
2. Role of organic acids in promoting colloidal transport of mercury from mine tailings (Brown, Rytuba *et al.*)

Inoperative Hg mines contaminate surrounding ecosystems via transport of dissolved and particle-associated species of mercury (Hg). Columns packed with Hg mine tailings were leached with organic acid solutions to simulate infiltration through the rooting zone of vegetated mine waste **[7]**. Specific issues addressed include (1) the physicochemical conditions under which Hg-bearing colloids may be mobilized, (2) the speciation of Hg in mobilized colloids, and (3) the extent of particle-associated versus solution-based Hg transport. For all organic concentrations investigated, particle-associated Hg was mobilized, with the onset of particulate Hg transport occurring later for lower organic acid concentrations. Chemical analyses of column effluent indicate that 98 weight-percent of Hg mobilized from the column was particulate. Hg speciation was determined using extended X-ray absorption fine structure spectroscopy and transmission electron microscopy, and indicated that HgS minerals dominate the Hg species in the mobilized particles. Hg adsorbed to colloids is another likely mode of transport due to the tailings' abundance of mineral phases to which Hg adsorbs. The results of this study suggest that transport of colloid-associated Hg from vegetated Hg mine tailings sites may contaminate hydrologically proximate aquatic environments due to the influence of organic acids produced by plants.

3. XAS evidence of As(V) association with iron oxyhydroxides in a contaminated soil at a former arsenical pesticide processing plant (Calas, Morin, Juillot, Brown *et al.*)

The molecular-level speciation of arsenic has been determined in a soil profile in the Massif Central near Auzon, France that was impacted by As-based pesticides **[80]**. We used a combination of conventional techniques (XRD, selective chemical extractions) with X-ray absorption spectroscopy (XAS) in this study. A thin layer of schultenite ($PbHAsO_4$), a lead arsenate commonly used as an insecticide until the middle of the 20th century, was found at 10 cm depth. Despite the occurrence of this As-bearing mineral, oxalate extraction indicated that arsenic was mainly released upon dissolution of amorphous iron oxides, suggesting a major association of arsenic with these phases within the soil profile. These results were confirmed by XAS analysis which indicate that arsenic occurs mainly as As(V) associated with amorphous iron(III) oxides as adsorbed species and co-precipitates. This study emphasizes the importance of iron oxides in restricting arsenic dispersal within soils following dissolution of primary As-bearing solids manufactured for use as pesticides and released into the soils.

Figure 34



I. New Experimental Developments in Synchrotron Radiation-Based Spectroscopies and Micro-Imaging (Nilsson, Bluhm, Salmeron, Brown *et al.*)

Significant progress has been made in commissioning and refining the Molecular Environmental Science beamline (BL 11.0.2) at the Advanced Light Source. This soft x-ray beam line covers the energy range from about 80 eV to 2000 eV and has an elliptically polarized undulator insertion device. BL 11.0.2 has two end stations, one devoted to scanning transmission x-ray microscopy **[81,82]**, and one devoted to wet photoemission spectroscopy and x-ray emission spectroscopy **[8]**. The former is used for spectromicroscopy studies of nanomaterials, microorganisms, biomineralization products, and weathering reaction products, as illustrated in sections **E6** and **G5**. The latter is used for photoemission spectroscopy studies of the interaction of water and other gas-phase and liquid molecules with solid surfaces. It is based on a differentially pumped, multi-stage UHV chamber that allows exposure of a solid surface to multi-torr gas pressures, and thus can be used for *in situ* studies of the interaction of solids with water, CO_2, and other molecules. We are currently using this beam station to examine the interaction of water with α-Fe_2O_3 single crystal surfaces using *in situ* photoemission spectroscopy for the first time. This beam station is also used for x-ray emission spectroscopy studies of adsorbates on surfaces using a specially designed x-ray emission spectrometer **[83,84]**.

In addition to these two state-of-the-art synchrotron-based facilities, in which the Stanford EMSI team has played a major role in terms of conception, fund raising, design, commissioning, and research, Anders Nilsson's group is also building a specialized high-pressure analytical chamber at the Stanford Synchrotron Radiation Laboratory that will allow IR spectroscopy, LEED, photoemission, and other surface science methods to be applied to surfaces and adsorbates on surfaces. The Stanford EMSI grant provided major funding for this analytical chamber, which will contribute significantly to bridging the pressure gap in surface science.

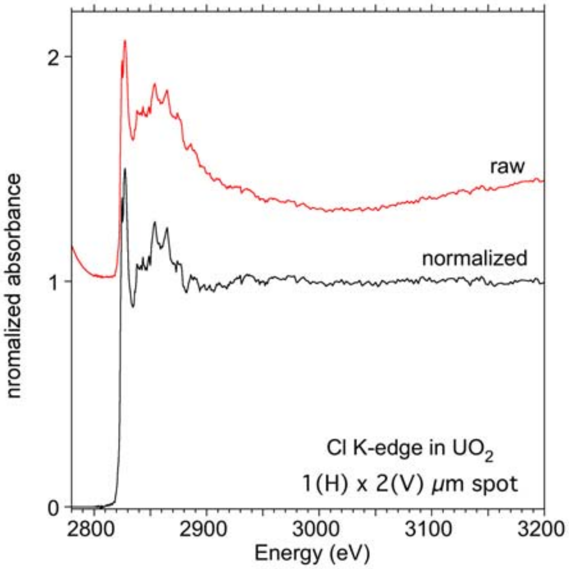


Figure 35

J. Computational Developments for Improving X-ray Absorption Fine Structure Spectroscopy Analysis (Farges, Brown *et al.*)

We have developed a series of approaches to improve the analysis of x-ray absorption fine structure spectra. We have introduced a new way to normalized "difficult" XAFS spectra that are severely distorted because of the use of micro-focused hard x-rays **(Fig. 35)**. In addition, we have implemented wavelet analysis of EXAFS and XANES spectra **(Fig. 36)**. Wavelets are superior to Fourier Transforms for distinguishing between real signals from spurious contributions. Wavelets also allow one to reduce the noise in the spectra in a robust manner, and this approach is used widely in remote sensing or information retrieval systems. We have also introduced bond valence analysis in EXAFS simulations calculated using either empirical or *ab-initio* molecular dynamics. From this combined approach, it is easier to verify that the modeled structure using MD methods is plausible or not. Using this approach we have been able to reject (in a few minutes of CPU time) some MD models that were later shown to be inconsistent with more sophisticated wide-angle x-ray scattering (WAXS). Finally, we have implemented Reverse Monte-Carlo refinements of XAFS spectra of metal ions adsorbed at mineral/water interfaces. Based on the code rmc-XAFS by Markus Winterer, we are able to provide mathematically plausible models of Au(III) ions at the goethite/water interface **[85]**. Although this model is not a true simulation of the actual surface, it provides information on strengths and limitations of EXAFS parameters derived by classical approaches. Use of these approaches can minimize over interpretation of EXAFS data in deriving the ways in which molecules absorb on a substrate.

III. EDUCATION AND OUTREACH ACTIVITIES

A. Education and Outreach Activities (Stanford University)

1. Stanford-Berkeley Summer School on Applications of Synchrotron Radiation (June 13 –18, 2005, held at SLAC).

We had over 60 applicants from the US and abroad for our 2005 summer school and accepted 43. The co-director of the summer school was Prof. Anders Nilsson (Stanford EMSI Co-PI) and Prof. David Attwood (X-ray Optics Division, LBNL). The instructors included Nilsson, Attwood, Gordon Brown (Stanford EMSI PI), Philip Bucksbaum (Professor, Stanford University and SSRL), Dan Dessau (Visiting Professor from the University of Iowa), Francois Farges (Consulting Professor at Stanford, Professor at the University of Marne-la-Vallee, France, and Stanford EMSI Member), Jo Stohr (Professor at SSRL and Deputy Director of SSRL), Mike Toney (Staff Scientist at SSRL and EMSI Member), and Tony Warwick (Staff Scientist at the ALS). (see **Fig. 36**)

2. SEMSI Summer Teachers Institute on Environmental Chemistry and Microbiology (August 1-3, 2005, Stanford Campus)

We offered a three-day course on "Mercury in the Environment" to a group of 15 high school science teachers from San Francisco Bay Area high schools (see **Fig. 41**). We targeted the advertisement to teachers who are interested in new science pedagogy. Bryan Brown has been active in working with high school science teachers in developing effective teaching methods, particularly in problems involving "the language of science". EMSI Participants in this new institute included Bryan Brown, Gordon Brown, Scott Fendorf, Andrea Foster (USGS), Adam Jew, Kihyun Ryoo, Jennifer Saltzman, Aaron Slowey, and Alfred Spormann.

3. SSRL Gateway Program (Summer 2005, SLAC)

This program is a partnership between SSRL and the University of Texas, El Paso, and is funded in part by the Office of Basic Energy Sciences at DOE. Its purpose is to bring Hispanic students from Texas El Paso to SSRL for experimental studies, including studies relevant to environmental molecular science. Anders Nilsson is the Director of the Gateway Program, and he plans to expand the program to local colleges and junior colleges in the San Francisco Bay Area that attract Hispanic students. We also plan to expand the emphasis of the Gateway Program on environmental chemistry by building a partnership between the Stanford EMSI and this program.

4. SLAC Summer Undergraduate Intern Program

This program is designed to bring in college students from around the U.S. for a summer research experience at SLAC. Several EMSI members will have summer interns as part of this program, which is funded by SLAC.

5. Stanford Summer Undergraduate Research Intern Program

This program internal to Stanford offers funding to Stanford students to participate in research projects at Stanford. Student funding is provided by Stanford University through the Office of the Dean of Undergraduate Studies. The Stanford EMSI hopes to attract several undergraduates from this program to work on EMSI-related projects this summer.

6. High School Student Intern Program

In partnership with local high schools in the Stanford Area, Stanford has a program to provide summer research experiences for high school students. The Stanford EMSI will mentor three high school students during Summer 2005.

7. Environmental Molecular Science Symposium, 230th American Chemical Society National Meeting (August 28-30, 2005, Washington, DC)

Members of the Stanford EMSI and their students and post-docs presented 14 of 55 oral presentations and two out of six poster presentations at this special symposium.

8. Science Journalist Workshops

Jennifer Saltzman, Gordon Brown, Anders Nilsson, and Alfred Spormann are investigating how to best design and offer short workshops for science journalists. We are talking with science journalists, the Northern California Science Writers Association, and the Knight Journalism Fellowship Program at Stanford, as well as other science writers' workshops. Our first workshop is planned for June 2006.

9. Environmental Courses at Stanford University Relevant to the Stanford EMSI

Gordon Brown continues to teach a 4-unit senior-level undergraduate course in Environmental Geochemistry each year. In addition, the Stanford EMSI introduced a graduate-level seminar series that meets weekly or bi-weekly for seminars and discussions of topics relevant to the Stanford EMSI. Scott Fendorf and Stanford colleague Prof. Christopher Francis offered for the first time during Winter and Spring quarters of 2005 a graduate level seminar series on Geomicrobiology & Microbial Geochemistry. Alfred Spormann offers a year-long graduate-level course on Environmental Microbiology each year. Spormann and Brown are offering a sophomore-level seminar course Spring quarter 2006 entitled "Environment and Human Health". A description of this course follows: This new Sophomore Seminar will explore the intricate interrelationship between the geosphere and the biosphere with an emphasis on how geological processes affect biological evolution and human health; how chemical, biological, and geological processes have altered the environment; and how anthropogenic activities affect the environment and human health. A student debate will be held in the second half of the quarter on a current environmental health issue such as how the Environmental Protection Agency sets the maximum contaminant level (MCL) for arsenic in drinking water, which was recently lowered from 50 parts per million (ppm) to 10 ppm. The seminar will be led by Gordon Brown (an environmental geochemist from the School of Earth Sciences), Alfred Spormann (a microbiologist from the School of Engineering), and Gary Ernst (an emeritus professor of Geological & Environmental Sciences and co-founder of the Stanford Earth Systems Program). Additional Stanford faculty members, including several from the School of Medicine, will participate in this interdisciplinary seminar. Several spaces are still available.

B. Education and Outreach Activities (University of Alaska, Fairbanks)

Outreach activities involve the incorporation of two post-docs and three graduate students into SEMSI research at PNNL (see below). The two post-docs are resident at PNNL. The three graduate students each are making extended visits to PNNL in 2005. As a consequence, SEMSI research will form a central theme in the Ph.D. dissertations of three individuals.

Our initial education and outreach efforts have focused on making graduate and undergraduate students aware of the critical role of interfacial chemical processes in the environmental chemistry of aquatic systems, and train students in the experimental and theoretical tools available for forefront research in this area. As part of this effort we established a new graduate course in Environmental Geochemistry (Chemistry 609/ Geology 631) during the Spring 05 semester. The material covered in the course focused heavily on the theoretical models and experimental methods used to understand the role of mineral-fluid interface processes on the chemistry of trace elements in soils and aquatic systems. The course utilized content from current literature and required that each student conduct a research project on a topic related to environmental geochemistry. Projects included density functional theory calculations of metal ion binding on metal-oxide surfaces and carboxylated polysaccharide materials, batch adsorption studies of metal ion partitioning to amorphous iron-hydroxide, particle size analysis of natural colloids, and x-ray diffraction analysis of soil clay compositions. The use of computational methods in the course was significantly aided by a visit from A. Chaka and C. Lo in Feb. 2005 in which we organized workshop for the CHEM 609 students on DFT methods. As part of this visit we also organized seminars on

Figure 36

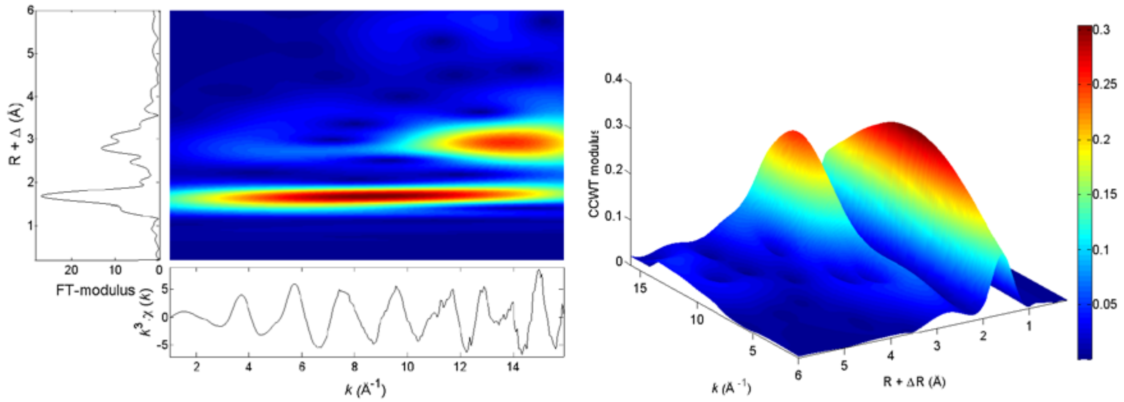


Figure 37

methods in interfacial chemistry research targeted at both faculty/staff and undergraduate audiences in Chemistry, Geology and the Arctic Region Supercomputing Center.

Another goal of our outreach and education work is to provide undergraduate students the opportunity to participate in research. Over the 2004-05 academic year Vanessa Ritchie worked in the Trainor lab on a number of projects related to characterization of metal oxide surfaces, their synthesis and reactivity. She continued a project over the summer of 2005 using ICP-MS and x-ray absorption spectroscopy techniques to characterize antimony speciation in natural water and sediment samples associated with the weathering of Stibnite (Sb_2S_3) rich mine waste from the Fairbanks, AK mining district and the Kantishna district of Denali National Park. In the future, we will attempt to establish a number of such projects, since these are an ideal and practical introduction into the methods used in environmental chemistry research and are likely to serve as a catalyst for generating interest in more advanced research topics that may be pursued as part of a graduate degree.

As part of our student training in advanced methods in environmental interface research, a number of UAF students have become involved in synchrotron-based research projects. To accelerate training in this area we anticipate that 2 UAF graduate students and 1 postdoctoral student will attend the Stanford-Berkeley Summer School on Synchrotron Radiation. During experimental time at SSRL over the summer of 2005, five UAF students (including an undergraduate student) participated in synchrotron-based experiments.

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V. Publications Based on Work Supported by the Stanford EMSI (Sept. 2004 - Feb. 2006)

A. Papers Published in Peer-Reviewed Journals

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