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EMSL Report

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Research Highlights

Gold Apes Hydrogen. The Structure and Bonding in the Planar $B_7Au_2^-$ and B_7Au_2 Clusters

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Clusters are groups of a small number of atoms that often have chemical and physical properties that are different than the corresponding bulk materials. Understanding the underlying physical and structural reasons for these unique properties may allow for improved materials for electronics, sensors, and catalysis.

Pure boron clusters have received limited experimental attention in the literature during the past couple of decades. A major breakthrough has resulted from a series of recent joint experimental and theoretical studies that have established that all small boron clusters are planar or quasi-planar. These studies have shown that photoelectron spectroscopy in conjunction with accurate *ab initio* calculations is a powerful approach to elucidate the complex structures of atomic clusters. Furthermore, the theoretical analysis has yielded detailed information about the chemical bonding in the clusters and allowed the planarity of the boron clusters to be understood on the basis of π and σ aromaticity/antiaromaticity.

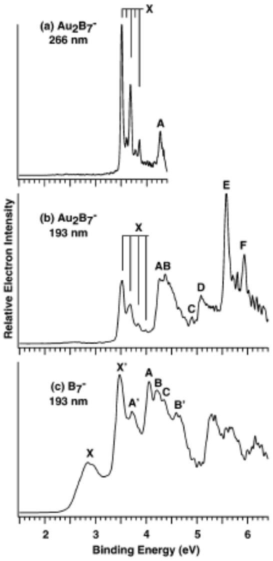


Figure 1. Photoelectron spectra of B_7Au_2 (a) 266 nm, (b) 193 nm, and of B_7- (c).

The $B_7Au_2^-$ anions were produced using a laser vaporization cluster source and the photoelectron spectra obtained using a magnetic bottle-type photoelectron spectrometer. The photoelectron spectra of $B_7Au_2^-$ at 266- and 193-nm photon energies are shown in Figure 1 and are compared with that of B_7^-. The photoelectron spectra of $B_7Au_2^-$ are substantially simpler and better resolved than those of B_7^-, despite its larger size. Most surprisingly, despite the addition of two heavy atoms, the ground-state transition (X) of $B_7Au_2^-$ is completely vibrationally resolved at 266 nm (Figure 1a) with the excitation of two vibrational modes, a low-frequency mode of 790 cm^{-1}, and a high-frequency mode of 1380 cm^{-1}. The vibrationally resolved ground-state transition yielded an accurate electron affinity of 3.52 eV for B_7Au_2.

Interestingly, the electron affinity of B_7Au_2 is very close to that of the elongated planar C_2V isomer for B_7 (3.44) corresponding to feature X′ in the spectrum of B_7^- (Figure 1c). Clearly, only one dominant isomer was present in the spectra of $B_7Au_2^-$. The observed $B_7Au_2^-$ cluster is likely to correspond to this isomer of B_7^- by adding two gold atoms to its two terminal B atoms similar to the ground-state structure of $B_7H_2^-$, as we expected.

To prove our hypothesis and confirm the observed $B_7Au_2^-$ structure, we performed quantum chemical calculations for a variety of $B_7Au_2^-$ structures. Figure 2 shows the global minimum and low-lying isomers of $B_7Au_2^-$. The good agreement between the experimental and theoretical vertical detachment energies confirmed the theoretical prediction of the global minimum structure VII for $B_7Au_2^-$, which is the same as that of $B_7H_2^-$.

The similarity in stability, structure, and bonding in the global minima of $B_7Au_2^-$ and $B_7H_2^-$ is analogous to the previous discovery of the gold/hydrogen analogy in silicon-gold clusters. Similar to the silicon-gold bond, which is highly covalent, we found that the boron-gold bonds in $B_7Au_2^-$ are also highly covalent with very little charge transfer from gold to boron. This is again due to the close electronegativity of boron and gold as a result of the strong relativistic effects in gold. This study demonstrates that the gold/hydrogen analogy may be a more general phenomenon and may exist in many species involving gold. The gold/hydrogen analogy will not only extend our understanding of the chemistry of gold, but will also be highly valuable in predicting the structures and bonding of many gold alloy clusters.

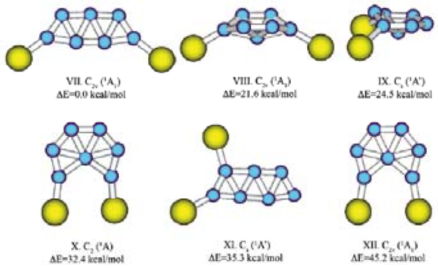
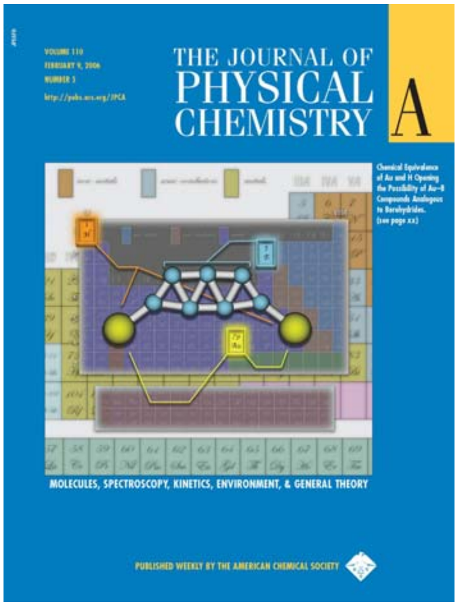


Figure 2. Global minima and low lying isomers of B_7Au_2.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Chemical Equivalence of Au and H Opening the Possibility of Au–B Compounds Analogous to Borohydrides. (see page xx)

MOLECULES, SPECTROSCOPY, KINETICS, ENVIRONMENT, & GENERAL THEORY

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Figure 3. Cover of the February 9, 2006, issue of *The Journal of Physical Chemistry A*.

This exciting research appears in a recent issue of *The Journal of Chemistry A* and is featured on the cover (Figure 3).

Citation

Zhai HJ, LS Wang, DY Zubarev, and AI Boldyrev. 2006. "Gold Apes Hydrogen. The Structure and Bonding in the Planar B_7Au_2- and B_7Au_2 Clusters." *Journal of Physical Chemistry A* 110(5):1689-1693.

NMR Structural Investigations of the Breast Cancer Susceptibility Protein, BRCA1

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BRCA1 is a complex protein that, when it malfunctions via mutations, can cause cancer. This research addresses how this protein interacts with other proteins in order to perform its various functions, including reducing the risk of breast and ovarian cancer.

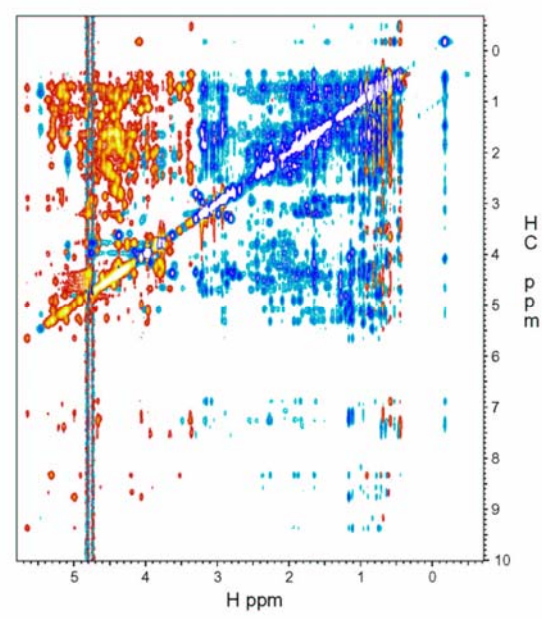

Figure 4. Two-dimensional projection of a three-dimensional Noesy-^{13}C-HSQC spectrum of unlabled ubiquitin bound to ^{15}N-^{13}C-labeled UbcH5c collected at 900 MHz.

Our work on the breast and ovarian cancer tumor suppressor protein, BRCA1, represents the convergence of two central research themes. The first relates to the importance of BRCA1 to a number of fundamental cellular processes, such as the cellular response to DNA damage, homologous recombination, and transcriptional regulation. Investigation of the function of BRCA1 in these pathways promises to yield insights into the role of BRCA1 in normal cellular development, and how loss of function results in the onset of breast and ovarian cancer. The second theme relates to mechanisms underlying ubiquitination. Protein ubiquitination provides a powerful regulatory mechanism for controlling pathways that include cell-cycle progression, transcriptional regulation, and responses to DNA damage. The importance of ubiquitin as a central biological process is underscored by the award of the 2004 Nobel Prize in Chemistry for research into the function of ubiquitination at the molecular level. It has recently been shown that BRCA1 can function as an E3-ubiquitin ligase. This activity is only observed when BRCA1 is complexed with a second protein called BARD1. Both BARD1 and BRCA1 have N-terminal RING-domains which mediate the interaction between the two proteins. Thus, work on BRCA1 allows us to integrate structural investigations on the role of BRCA1 in the development of breast and ovarian cancer as well as the study of the mechanisms of protein ubiquitination.

BRCA1 is a large and complicated protein which is undoubtedly comprised of a multiplicity of functional domains. A growing body of literature suggests that BRCA1 interacts with at least 30 different macromolecules to accomplish its diverse functional roles. Our structural work involves characterization of macromolecular complexes involving the N-terminal RING domain and the C-terminal BRCT domain of BRCA1. Much of our recent work at EMSL has focused on understanding the ubiquitination activity mediated by the BRCA1 RING domain. As E3-ligases, RING domains are thought to facilitate the specificity of ubiquitination reactions by forming a multiprotein complex, binding both a ubiquitin conjugating enzyme (E2) covalently activated with ubiquitin and specific proteins targeted for ubiquitination.

In addition, the BRCA1 RING domain mediates its interaction with BARD1. Cancer predisposing mutations found in the BRCA1 RING domain have been found to interfere with its ability to function as a ubiquitin ligase.

This system provides a unique opportunity for studying protein-protein interactions by nuclear magnetic resonance (NMR). It involves characterizing the structures and interactions among at least four different protein components: BRCA1, BARD1, an E2 (UbcH5c or UbcH7), and ubiquitin (Ub). The molecular weight of the fully assembled complexes approaches 60 kD. In previous years, we have been able to collect a great deal of data on the individual components of this system. During the last year, data collected on EMSL's 600-, 800-, and 900-MHz NMR spectrometers have allowed us to develop a model of the complex series of protein-protein interactions that are required to assemble an active BRCA1-dependent ubiqutin-ligase complex.

Recent work at EMSL allowed us to determine the structure of the noncovalent complex between UbcH5c and Ub. The high-field 800- and 900-MHz NMR spectrometers were critical to this effort and provided the necessary sensitivity and resolution (Figure 4) required to determine the solution structure of the 25-kD complex (Figure 5). Though a host of other structurally similar E2 exists, the ability to form a noncovalent complex with ubiquitin is unique to the UbcH5 family of ubiquitin-conjugation enzymes. Our structural work provided a foundation for investigating the mechanistic importance of this interaction. We were able to design a mutation, Serine 22 to Arginine (S22R), in UbcH5c that selectively abrogates the noncovalent binding of ubiquitin, leaving all other functions of UbcH5c intact. The integrity of the noncovalent ubiquitin binding interface is critical for the function of UbcH5c in ubiquitin transfer reactions. Though S22R-UbcH5c is capable of transferring a single ubiquitin to a target protein, it can no longer form poly-ubiquitin chains in BRCA1-directed ubiquitination reactions.

Figure 5. Structure of the noncovalent complex formed between UbcH5c and ubiquitin. Ubiquitin (red) binds to the exposed β–sheet region of UbcH5c (blue–green). The active site of UbcH5c is on the opposite side of the molecule.

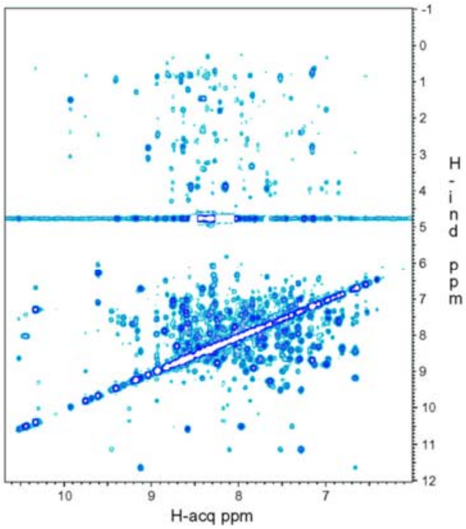

Figure 6. Two-dimensional projection of a three-dimensional Noesy-^{15}N HSQC spectrum of ^{2}H,^{13}C,^{15}N-labeled BRCT domain of BRCA1 in complex with an unlabeled domain of CtIP collected at 600 MHz. The molecular weight of the complex is ~35kD. Many of the peaks observed in the top half of the spectrum represent intermolecular interactions.

Part of the answer to this riddle is provided by our work on the activated UbcH5c~Ub covalent complex. UbcH5c carries activated ubiquitin via formation of a covalent thiolester bond between the active site cysteine of UbcH5c and the C-terminus of ubiqiutin. Formation of the activated UbcH5c~Ub complex in the context of S22R-UbcH5c allows us to investigate in molecular detail the structural changes caused by activation. This work is presently ongoing at EMSL. However, when we use wild-type UbcH5c, we find the presence of the noncovalent ubiquitin-binding site allows activated UbcH5c~Ub to self-assemble into higher molecular weight complexes. This ability to self-assemble is critical for the formation of poly-ubiquitin chains. Much of this work will be detailed in an upcoming publication of *Molecular Cell.*

The recent installation of cold probes on 600- and 800-MHz NMR spectrometers has allowed us to investigate other BRCA1 protein-protein complexes. The C-terminus of BRCA1 contains an ~225 residue BRCT domain that also contains a number of cancer-predisposing mutations. This domain specifically binds a phosphopeptide motif found in a number of nuclear proteins. One of these, CtIP (CtBP Interacting Protein) is of particular interest as its association with both CtBP, a ubiquitous transcriptional repressor, and BRCA1, a transcriptional regulator, is believed to play a crucial role in the tumor suppressor function of BRCA1.   As shown in Figure 6, we have been able to collect high-quality data on the BRCA1-CtIP complex, allowing investigation into the molecular details of this interaction.

Citations

Brzovic PS, J O'Keeffe, DE Christensen, DW Hoyt, and RE Klevit. 2006. “A Noncovalent Complex Between UbcH5c and Ub is Required for Processive BRCA1-Directed Poly-Ubiquitination Reactions.” *Molecular Cell* (in press).

Estimated IR and Phosphorescence Emission Fluxes for Specific Polycyclic Aromatic Hydrocarbons in the Red Rectangle

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(d) Centre d’Étude Spatiale des Rayonnements, CNRS and University Paul Sabatier, Toulouse, France

Calculated infrared spectra of polycyclic aromatic hydrocarbons were compared with available experimental infrared data to correctly identify spectroscopic components of the Red Rectangle Nebula (considered to be a Rosetta Stone for astrophysical processes).

Following tentative identification of the blue luminescence in the Red Rectangle Nebula by Vijh et al. 2004, Mulas and collaborators used EMSL’s computational chemistry software, NWChem, to compute absolute fluxes for the vibrational infrared emission of three small polycyclic aromatic hydrocarbons (Vijh et al. 2005). The calculated infrared spectra were compared with available observational data from the Infrared Space Observatory (see Figure 7 for spatial distribution). A subset of the emission bands are predicted to be observable using presently available facilities and can be used for an immediate, independent, discriminating test of their alleged presence in this well-known astronomical object.

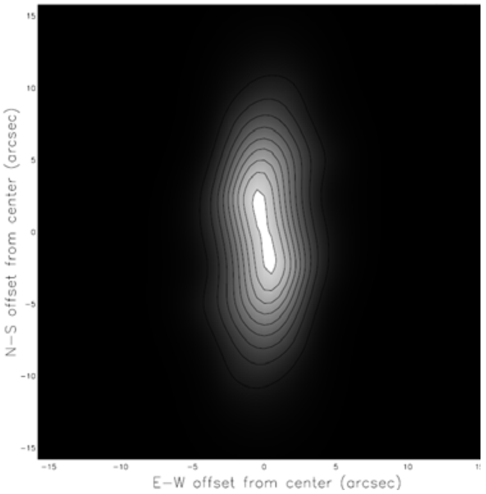

Figure 7. Spatial distribution of the blue luminescence surface brightness of the Red Rectangle Nebula, interpolated from the values given by Vijh et al. 2005. East is left, north is up, and contour lines are in 5% intervals.

Simulations of the photophysics of the candidate molecules were carried out using a Monte Carlo code, together with quantum-chemical calculations (NWChem and Octopus computer codes) for the relevant molecular parameters, and available laboratory measurements for the photoabsorption spectra and for the visible and infrared fluorescence quantum yields. This produced a quantitative prediction of the infrared and phosphorescence emission spectra for each given molecule, which must be related to the integrated blue luminescence attributed to this same molecule.

Citations

Mulas G, G Malloci, C Joblin, and D Toublanc. 2006. "Estimated IR and Phosphorescence Emission Fluxes for Specific Polycyclic Aromatic Hydrocarbons in the Red Rectangle." *Astronomy & Astrophysics* 446(2):537-549.

Vijh UP, AN Witt, and KD Gordon. 2004. "Discovery of Blue Luminescence in the Red Rectangle: Possible Fluorescence from Neutral Polycyclic Aromatic Hydrocarbon Molecules." *The Astrophysical Journal* 606:L65-L68.

Vijh UP, and AN Witt. 2005. "Small Polycyclic Aromatic Hydrocarbons in the Red Rectangle." *The Astrophysical Journal* 619:368-378.

Solution State Structure Determination of Silicate Oligomers by 29Si NMR Spectroscopy and Molecular Modeling

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Silica solution species are an important complexant for many toxic contaminants in the environment, including radionuclides. Establishing a fundamental understanding of all silica solution species allows better prediction of the fate and transport of contaminants in the environment.

Evidence for nine new solution-state silicate oligomers was discovered at EMSL using ^{29}Si nuclear magnetic resonance (NMR) homonuclear correlation experiments of ^{29}Si-enriched samples. In addition to enhancing signal sensitivity, the isotopic enrichment increases the probability of the ^{29}Si-^{29}Si two-bond scalar couplings that are necessary for the observation of internuclear correlations in two-dimensional experiments. The proposed assignments are validated by comparisons of experimental and simulated cross-peaks obtained with high-digital resolution. The internuclear connectivity indicated by the NMR data suggests that several of these oligomers can have multiple stereoisomers, including conformers and/or diastereomers. The stabilities of these oligomers and their possible stereoisomers have been investigated by electronic structure calculations.

Experimentally, the significant advancement made in this study was the use of a double-quantum filter (DQF) in collection of the two-dimensional ^{29}Si COSY (COrrelation SpectroscopY) measurements of isotopically enriched silicate solutions. This was essential to suppress the intense dispersive diagonal peaks of singlet lines, which obscure several cross-peaks and autocorrelation multiplets near the diagonal in the nonfiltered experiment (Figure 8).

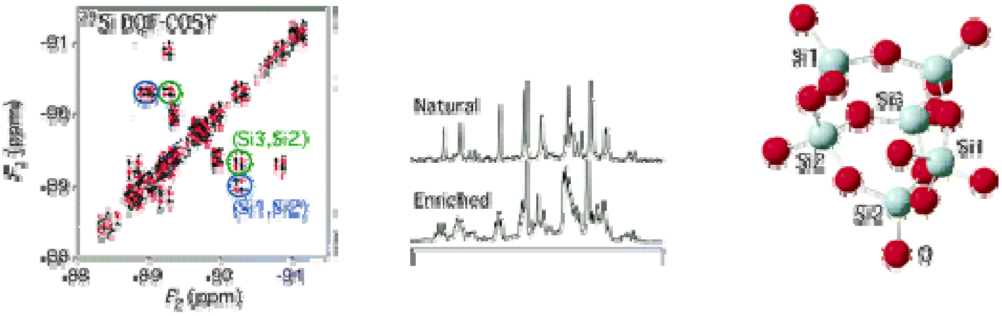

Figure 8. (Left) Two-dimensional ^{29}Si DQF-COSY spectrum of bicyclic hexamer, (center) comparison of one-dimensional ^{29}Si spectra natural and enriched abundance spectra, (right) energy-minimized trans bicyclic hexamer structure.

Computationally, analysis of the correlation experiments is that the newly detected oligomers contain only a small number of chemically inequivalent silicon sites, in most cases three or less. In addition, from the integrated one-dimensional peak intensities, it can be inferred that the new oligomers are comparable in concentration to the small oligomers discovered in the past. These observations imply that the new oligomers should have relatively simple, small, symmetric structures. From a survey of traditional ball-and-stick drawings of oligomer structures, it might appear that there are too few plausible candidate structures with NSi e 6 to support this conclusion, but such drawings fail to adequately represent the multiplicity of isomeric forms a silicate network can assume, especially when the potential chirality of Q3 and Q3t sites is considered. Computational models confirm that several oligomers have several stereoisomers that are stable energy minima, and thus are satisfactory structures. The chirality of certain silicon sites greatly expands the spectrum of geometries that a silicate network can have, both in solution-state species and in solid lattices. These diastereomers will have different NMR parameters, chemical properties, and structures, which suggest greater attention will be needed in future experimental and theoretical studies in the specification of silicate structures with the potential for configurational and conformational isomerism. This research is discussed in further detail in Cho et al. 2006.

Citation

Cho H, AR Felmy, R Craciun, JP Keenum, N Shah, and DA Dixon. 2006. "Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling." *Journal of the American Chemical Society* 128(7):2324-2335.

Geophysical Imaging of Stimulated Microbial Biomineralization

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Understanding how microorganisms influence the physical and chemical properties of the subsurface is hindered by our inability to observe microbial dynamics in real time and with high spatial resolution. Here, we investigate the use of noninvasive geophysical methods to monitor biomineralization at the laboratory scale during stimulated sulfate reduction under dynamic flow conditions. Geophysical data reflected the distribution of mineral precipitates and biomass over space and time, with temporal variations in the signals corresponding to changes in the aggregation state of the nanocrystalline sulfides. These results were correlated with data obtained by transmission and scanning electron microcopy. The results suggest the potential for using geophysical techniques to image certain subsurface biogeochemical processes, such as those accompanying the bioremediation of metal-contaminated aquifers.

The problem of groundwater contamination by acid-mine drainage, industrial sources, and government nuclear weapons programs has spawned interest in the ability of microorganisms to facilitate remediation through sequestration of metals in insoluble precipitates. High-resolution geophysical techniques have proven extremely useful at the field scale for estimating hydrogeological properties, providing information about subsurface environments. In this study, the sensitivity of two geophysical techniques, complex resistivity and acoustic wave propagation, is tested to the products of microbial biomineralization. The primary objective was to follow the reaction dynamics of a column-scale biostimulation experiment using conventional biogeochemical and mineralogical measurements, as well as noninvasive geophysical techniques. We tested the hypothesis that metal sequestration via microbe-induced sulfide precipitation creates physical property changes that directly alter the response of geophysical signals. We compared the temporal response of such signals against concomitant changes in fluid chemistry and microbial biomass to investigate if the geophysical responses are sensitive to the products of biomineralization. Finally, we validated our interpretation of the geophysical responses using electron microscopy techniques.

Sulfate-reducing bacterium *Desulfovibrio vulgaris* was used for monitoring of microbe-induced ZnS and FeS precipitation within saturated sand-packed columns. Acoustic wave measurements and saturated hydraulic conductivity measurement were done during the duration of the experiment. Columns were terminated after 78 days and analyzed for concentration of sediment-affixed metal sulfides and microbial biomass. Solution samples from the influent, effluent, and multiport samplers were analyzed for major dissolved components at 3- to 5-day intervals. Total dissolved zinc and iron was determined by inductively coupled plasma atomic emission spectroscopy. Lactate, acetate, and sulfate concentrations were determined by gradient elution ion chromatography. Solution pH was measured using a sulfide-tolerant electrode. Transmission and scanning electron microscopy were used for characterizing microbe-mineral associations and the crystal size and aggregation state, and they documented significant spatial variability in the abundance and distribution of cells and their associated mineral products. Transmission electron microscopy-based analysis of the precipitates revealed them to be a mixture of sphalerite (ZnS) and mackinawite (FeS), with an average crystal size of 3 nm (Figure 9). Scanning electron microscopy revealed grain coatings consisting of dense accumulations of sulfide-encrusted microbes.

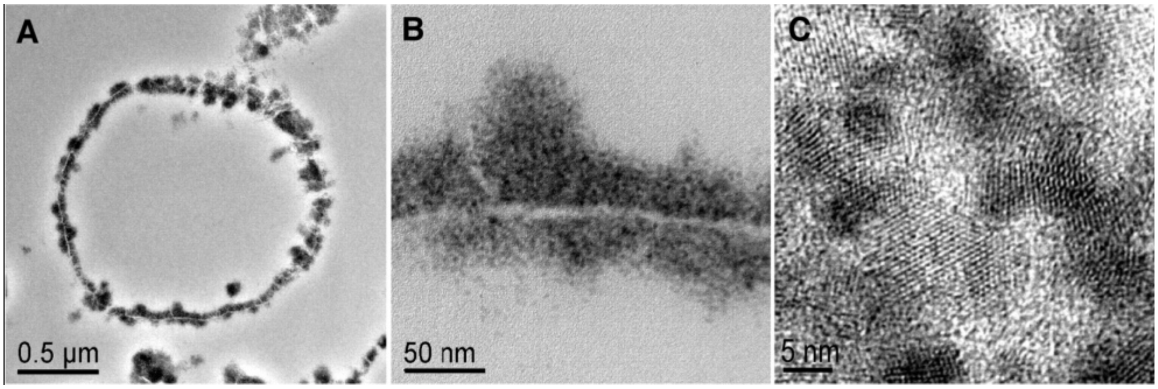

Figure 9. (A and B) Cross-sectional transmission electron microscopy images of a single *D. vulgaris* cell with membrane-bound ZnS and FeS precipitates. (C) High-resolution transmission electron microscopy revealed the nanocrystalline character of the precipitates with a typical particle size of 3 to 5 nm.

We have shown that the stimulation of sulfate-reducing microorganisms and the associated formation of insoluble metal sulfides create physical property changes that are directly detectable using geophysical techniques. We have resolved spatiotemporal changes in complex resistivity and acoustic wave propagation resulting from variations in the electric charge-carrying capacity and elastic moduli of precipitates and pore fluids. The changes persisted over time and were confined exclusively to those regions where metals were sequestered in insoluble precipitates. Temporal changes in the geophysical signals appear to offer insight into the aggregation state of the sulfides and may be indicative of pore-scale crystal growth and aging, with such a result having implications for the fate and transport of microbe-induced precipitates. Our laboratory results are relevant to the larger spatial scales of the natural environment where methods currently used for field-scale geophysical monitoring may be used in an analogous fashion. These results show the potential of using complex resistivity and acoustic wave techniques for remotely monitoring regions of contaminant sequestration via biomineralization and for evaluating the overall long-term stability of such precipitates.

A Soft X-ray Absorption Spectroscopy Study of Ceria Grown on $Al_2O_3(0001)$

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Both O 1s and Ce 3d x-ray absorption spectra show that ceria films with particle sizes of 3 nm and 7 nm are largely oxygen deficient. As a result, a significant amount of trivalent cerium ions are present in the ceria films, whereas the ceria film with a particle size of 38 nm is fairly stoichiometric CeO_2*. Furthermore, the* ^{18}O *intake measurements of ceria films show that the redox potential of* Ce^{3+}/Ce^{4+} *ions is flexible enough such that the nanocrystalline ceria is stable at room temperature and can be manipulated for specific applications, such as catalysis.*

Ceria-based oxides are being used as catalysts in many technological applications because of their unique redox properties. The overall performance of these oxides depends on particle size, structural characteristics, and chemical nonstoichiometry. Most applications for the ceria-based oxides are surface sensitive, and recent advances in nanotechnology enable fabrication of these oxides as nanostructures. These nanostructures can be used to reach a high surface-to-volume ratio, in addition to improved redox properties, related to oxygen vacancy generation. Therefore, a detailed scientific understanding of the growth and characterization of ceria nanostructures becomes necessary to determine viability of these materials for various applications. In this study, we investigated the oxidation state and local structure of ceria grown on $Al_2O_3(0001)$ single crystal surfaces with different particle sizes prior to and following oxygen intake using soft x-ray absorption spectroscopy.

The O 1s and Ce 3d x-ray absorption spectra of ceria films measured at Beamline 6.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory are shown in Figure 10. The prominent features in the O 1s spectra are a sharp pre-edge transition at 530 eV and an intense transition at 532.5 eV, which is superimposed on the edge jump, and a broad band centered at 536.9eV. The sharp pre-edge transition at 530 eV arises from the excitation of O 1s core electrons to 2p hole-states in the narrow 4f dominated bands resulting from strong Ce 4f and O 2p hybridization in the ground states of CeO_2. Similarly, the intense transition at 532.5 eV and the broad band at 536.9 eV are assigned to the transitions from O 1s to Ce $5d(e_g)$ and $5d(t_{2g})$ states, respectively, while the edge jump corresponds to transitions to empty continuum states. It can be noted from Figure 10a that the intensities of the transitions at 530 eV, 532.5 eV, and 536.9 eV in the O 1s spectra collected at both $\theta=0^o$ and $\theta=82.5^o$ increase with increasing the particle size of ceria films from 3 nm to 38 nm. This intensity increase for the transition at 530 eV amounts to ~19% and ~17% for the spectra recorded at $\theta=0^o$ and 82.5^o, respectively. For transitions at 532.5 eV and 536.9 eV, the intensity increase is 7% each for the spectra recorded at both $\theta=0^o$ and 82.5^o. In general, the electronic transitions in the x-ray absorption spectra occur from a selected atomic core level to unoccupied states and intensities of these transitions are directly related to the unoccupied density of states, which results from the chemical and electronic structures of a given chemical composition.

The x-ray diffraction and high-resolution transmission electron microscopy results show that the ceria annealed at 573 K and 723 K retain nanocrystalline phases, while the ceria annealed at 1173 K reveal characteristics of polycrystalline CeO_2. The intensity increase in the O 1s spectra suggests that the nanocrystalline ceria films with lower particle sizes are oxygen deficient, which leads to the formation of Ce^{3+} in the ceria films. With increasing annealing temperature, the oxygen-deficient nanocrystalline ceria films absorb oxygen from air, which facilitates the oxidation of Ce^{3+} to Ce^{4+} with increased bond formation leading to increased particle size and long-range ordering. Comparison of these O 1s spectra with the spectra from reference materials suggests that the pre-edge transition at 530 eV is originated from CeO_2, whereas the transitions at 532.5 eV and 536.9 eV can originate from oxide ions coordinated to both Ce^{3+} and Ce^{4+}. A moderate increase in intensity (~7%) for the transitions at 532.5 eV and 536.9 eV with increasing particle size of ceria films only suggests an increase of long-range ordering of the ceria film with annealing temperature, assuming that the fluorescence cross sections of oxide ions coordinated to Ce^{3+} and Ce^{4+} are the same. A drastic increase in intensity (19%) for the pre-edge transition at 530 eV shows the presence of Ce^{3+} in ceria film with lower particle size and it is being oxidized to Ce^{4+} in addition to increase of long-range ordering with increasing particle size of ceria films.

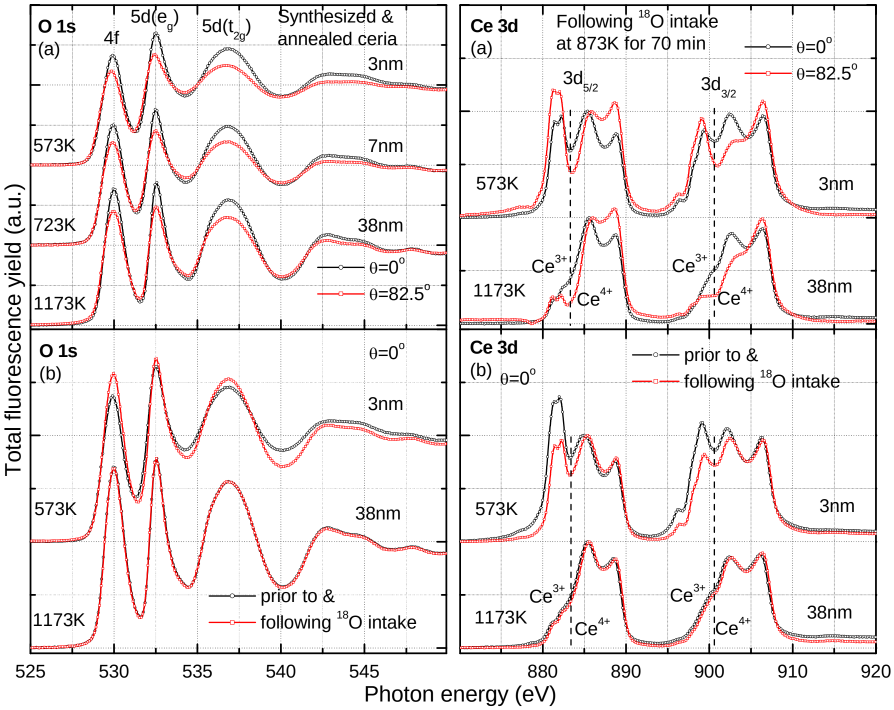

Figure 10. (a) Comparison of the normal (θ=0°) and grazing incidence (θ=82.5°) x-ray absorption spectra at O 1s and Ce 3d edges from ceria films on $Al_2O_3(0001)$ with particle sizes of 3 nm, 7 nm, and 38 nm. (b) The normal incidence (θ=0°) x-ray absorption spectra at O 1s and Ce 3d edges from ceria films on $Al_2O_3(0001)$ with particle sizes of 3 nm and 38 nm prior to and following ^{18}O intake by annealing the films in 4.0 x 10^{-6} Torr of $^{18}O_2$ at 873 K for 70 min.

Furthermore, the intensities for all transitions in the O 1s spectra collected at θ=82.5° are significantly reduced (14%) compared to the spectra at θ=0°, regardless of ceria particle size (Figure 10b). These ceria films do not show polarization dependence because of the lack of specific orientation; however, the probing depth at θ=0° is up to 300 nm, and it is restricted to only the near-surface region at θ=82.5°. Therefore, the difference between the spectra collected at θ=0° and θ=82.5° results from the variation of ceria surface from its bulk. A reduction in intensity for grazing incidence spectra suggests more oxygen deficiency and a lack of long-range ordering in the near-surface region compared to the bulk ceria film.

The O 1s x-ray absorption spectra collected at θ=0° from ceria films with a particle size of 3 nm show an increase in intensity for all transitions following ^{18}O intake. However, the increase in intensity for the transition at 530 eV is significant as this transition is characteristic of CeO_2 and is sensitive to oxygen deficiency. These results suggest that the ceria film with a particle size of 3 nm is oxygen deficient and takes more oxygen when subjected to annealing at high temperature in an oxygen atmosphere. In contrast, the spectra for the ceria film with a particle size of 38 nm prior to and following annealing the films in 4.0×10^{-6} Torr of $^{18}O_2$ at 873K for 70 minutes show no changes, suggesting that this ceria film is stoichiometric CeO_2.

In the Ce 3d x-ray absorption spectra collected at θ=0 and θ=82.5 from ceria films grown on $Al_2O_3(0001)$ with particle sizes of 3 nm, 7 nm, and 38nm, the transitions occur from the initial $3d^{10}4f^n$ state to the final states of the form $3d^94f^{n+1}$. Spin-orbit interaction splits the Ce 3d into $3d_{5/2}$ and $3d_{3/2}$ states separated by ~17.6 eV. The spectra reflect the oxidation states of Ce in ceria films with different particle size. Based on the spectra from reference materials, the transitions originating from Ce^{3+} and Ce^{4+} are separated with dashed lines in both the $3d_{5/2}$ and $3d_{3/2}$ edges of Ce. The energy separation between Ce^{3+} and Ce^{4+} in ceria films corresponds to ~3.0eV. The intensities of the transitions originating from Ce^{3+} relative to the intensities of the transitions originating from Ce^{4+} decrease for the spectra recorded at both $\theta=0^o$ and $\theta=82.5^o$ from ceria films with increasing particle size, suggesting that the relative concentrations of Ce^{3+} ions decrease. Furthermore, the relative intensities of the transitions originating from Ce^{3+} is larger for the spectra recorded at $\theta=82.5^o$ compared to the spectra recorded at $\theta=0^{,o}$ regardless of the particle size of the ceria film, suggesting that the relative concentrations of Ce^{3+} on the surface is larger than in the bulk of the ceria film with a specific particle size. Ceria on the surface is also more susceptible to reduction by x-ray, especially when the particle sizes are smaller, because of their larger surface area with no or reduced long-range ordering. These results are in good agreement with those obtained from O 1s spectra.

The intensities of the transitions originating from Ce^{3+} relative to the intensities of the transitions originating from Ce^{4+} are significantly reduced for the spectra recorded from ceria film with particle sizes of 3 nm following ^{18}O intake, compared to the spectra recorded prior to ^{18}O intake. These results suggest that the Ce^{3+} present in the ceria film with particle sizes of 3 nm prior to ^{18}O intake is oxidized to Ce^{4+} following ^{18}O intake. However, the spectra recorded from ceria film with particle sizes of 38 nm prior to and following ^{18}O intake show no changes, suggesting that this ceria film does not have significant concentrations of Ce^{3+}. These results are also consistent with those obtained from O 1s spectra.

Proteomic Characterization of a Macaque Flu Infection Model System

JM Jacobs,(a) MG Katze,(b) MA Gritsenko,(a) DG Camp II,(a) DL Diamond,(b) and RD Smith(a)

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This research involves characterization of a non-human primate model system to gain more insight into the proteins that are important in the progression of flu infections.

Initial proteomic characterization of the macaque flu infection model system used a bottom-up proteomics approach with the isolation of proteins from macaque lung tissue either infected (influenza) or mock-infected, followed by tryptic digestion to peptide form for sequence identification and relative quantitation using liquid chromatography coupled to tandem mass spectrometry analysis. Additionally, a cysteinyl-peptide enrichment step was performed at the peptide level, providing enhanced coverage of the macaque model proteome. The resulting high-quality data set of 14,100 peptides and 3,548 proteins identified in this preliminary study of the macaque model system is, to our knowledge, the first comprehensive proteomic survey performed for this model. Among the proteins detected are many candidates of particular interest based on previous clinical, pathological, and gene expression data, demonstrating the suitability of the non-human primate model for studying influenza virus pathogenesis. These include several well-known interferon-induced proteins as well as other non-cellular mediators of the innate immune response. This new macaque lung protein database creates the foundation for future research efforts aimed at applying comparative quantitative proteomics measurements to longitudinal studies of non-human primate models of influenza virus infection.

When comparing the differentially identified proteins between uninfected and influenza virus-infected lung tissue samples, consistent with previous observations demonstrating the establishment of an antiviral state in the lungs of influenza virus-infected macaques, we observed an apparent up-regulation of many proteins involved in the innate immune response. These included both interferon-induced proteins and non-cellular mediators of the innate immune response. We believe the findings reported clearly demonstrate the potential of proteomics for assisting in the determination of protein players and pathways affected by influenza virus infection.

Synthesis of Organically Templated Nanoporous Tin (II/IV) Phosphate for Radionuclide and Metal Sequestration

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(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Effective removal of heavy metals and pollutants from the environment will lead to a clean living environment. Nanoporous materials offer an efficient way of selectively sequestering many types of metals and radionuclides in a very small volume. The high-surface area of a nanoporous structure enhances mass transfer in sequestration applications and enables ions to be highly concentrated in a very small volume of material. Operations related to nuclear energy and weapons production have produced significant quantities of radioactive waste during the last half century that will be processed and buried in a deep geological repository at Yucca Mountain in Nevada. The current proposal is to include "getter materials" with this waste to sequester any radionuclides that might leach from the waste forms. Of particular interest are the long-lived actinide species (e.g., plutonium, americium, neptunium) and the anions (e.g., pertechnetate, iodide). Getter materials must be able to survive long-term exposure to elevated temperatures (>150°C) and moderately high radiation fluxes. The frailty of organic components towards radiolytic degradation precludes their use for either structure or function in the final getter material.

During the last decade, metal phosphates have been extensively studied for their potential use in catalysis, ion exchange, and phase separation. Since the first open-framework tin phosphates were prepared nearly 15 years ago, there has been interest in the structural flexibility of tin phosphates crystallizing in one-dimensional, three-dimensional, or layered structures. Open-framework tin phosphates have been prepared by direct precipitation and by incorporating organic amines into the crystal lattice. Surfactant-templated, open-framework tin phosphates have been reported using structure directing amine compounds including ethylenediamine, 1,6-diaminohexane, 1,2-diaminopropane, 1,8-diaminooctane, and 1,4-diaminobutane. Only recently, however, has a nanoporous tin (IV) phosphate been reported, and, to date, this is the only known report of a nanoporous tin phosphate. The cationic quaternary ammonium salt $CH_3(CH_2)_{15}N(CH_3)_3Br$ was used as the surfactant. The use of cetyltrimethylammonium bromide as surfactant resulted in surface areas of 230 m^2/g and pore sizes of 35-38 Å. Although the pore size was reduced from 39 to 35 Å, the structure was stable following calcination.

The goal of this study was to produce a similarly stable, mesoporous solid using tin (II) as the starting material to produce a material capable of sequestering redox-sensitive species, such as pertechnetate, neptunium, chromium, and iodide. The large pores afforded with quaternary ammonium surfactants and the high-surface area of nanoporous structures are valuable features for enhanced mass transfer in sequestration applications. This work summarizes efforts to make a nanoporous tin(II) phosphate phase. The synthesis method consists of preparing 200 mL of 6.87 mmol cetyltrimethylammonium chloride CH3(CH2)15N(CH3)3Cl, in deionized water. The solution is acidified with 0.626 mL of concentrated phosphoric acid. A concentrated solution of 15.22-g stannous chloride was dissolved in 100-mL hydrochloric acid. 2.5 mL of SnCl2/HCl solution was added with stirring at room temperature to the acidified surfactant. The solution stirred for 30 minutes at room temperature and was placed in an oven at 65°C for 48 to 72 hours. The synthetic material was collected via vacuum filtration using a 0.45-μm filter, washed with deionized water, and dried under ambient conditions. Chemical analysis of the synthetic material indicates the structure is composed of Sn:P:O with a ratio of 1:1:5.

Selected-area electron diffraction analysis of a typical tin phosphate (NP-SNPO1) illustrates a completely amorphous structure. Analyses with high-resolution transmission-electron microscopy revealed a spherical particle morphology approximately 150 nm across, with uniform pore distribution narrowly distributed around 2 nm. It was also observed that directly precipitated NP-SNPO materials, in addition to being thermally stable (500°C), are chemically stable over the entire pH range (pH = 0 to 14); therefore, tin will not leach into water during remediation operations (Figure 11).

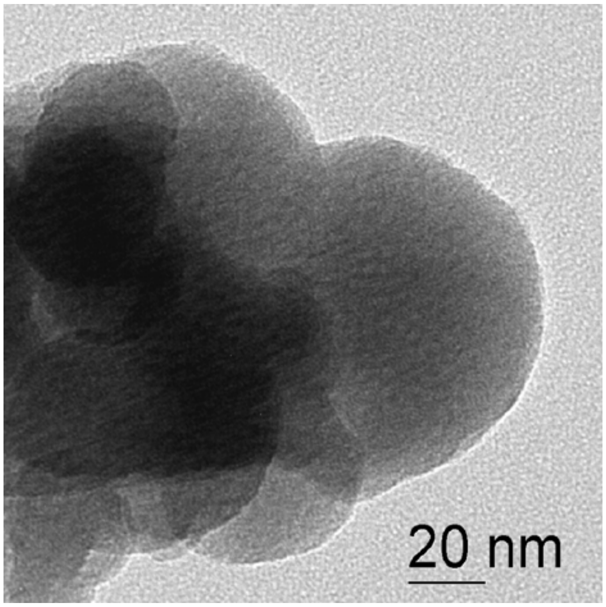

Figure 11. Calcination of the as-synthesized material at 500°C produced a material with a surface area of 262 m^2/g. The x-ray diffraction pattern of the surfactant-$SnPO_4$ and calcined $SnPO_4$ are shown above. The d spacing of the 100 plane in surfactant-$SnPO_4$ is 5.01 nm, whereas after calcination it was reduced to 4.62 nm. Subjecting the nanoporous $SnPO_4$ (NP-SnPO) to high temperatures during calcination has little impact on pore size.

Preliminary batch contact studies have been conducted to assess the effectiveness of NP-SnPO in sequestering redox-sensitive metals and radionuclides, technetium(VII), neptunium(V), thorium(IV), and a toxic metal, chromium(VI), from aqueous matrices. Equilibrium was achieved in less than an hour at a solution-to-solids ratio of 100, therefore a batch contact time of 2 hours was used to ensure that these values represent true equilibrium conditions. Under these conditions, the nanoporous, calcined tin (II) phosphate removed >95% of all contaminants investigated from solution. Distribution coefficients, Kd, are defined as a mass-weighted partition coefficient. Kd values were typically >10,000 in groundwater for the nanoporous tin (II) phosphate; whereas, Kd values for non-porous tin (II) phosphate was ~100. At a solution-to-solids ratio of 100, a Kd value of 10,000 indicates that at equilibrium there was 100 times as much contaminant in the nanoporous metal-phosphate phase as there was remaining in the supernantant solution.

Data obtained via x-ray absorption near edge spectra/extended x-ray absorption fine structure analysis clearly illustrate the sequestration of Tc(VII), Np(V), and Cr(VI) with NP-SNPO occurs through redox-coupled reactions with the target metals being reduced to their least soluble valence states, namely, Tc(IV), Np(IV), and Cr (III), with oxidation of tin in NP-SnPO. Although lacking spectroscopic data, we surmise that Th(IV) adsorption on NP-SnPO is due to Lewis acid-base interaction with PO4 groups.

These nanoporous tin (II) phosphates exhibited significant promise as sorbent materials for anionic and redox-sensitive metals and actinides. The detailed kinetic studies of these materials are planned for publication.

Effect of Pore Scale Heterogeneity in Transport

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While there is general agreement that pore-scale heterogeneity plays an important role in subsurface reaction and flow/transport processes, characterization efforts have typically focused on sediment properties on the scale of architectural elements while essentially neglecting fine-scale heterogeneity. Consequently, there is a lack of consensus on which microscopic geometrical properties are needed to predict the macroscopic transport properties required for field-scale model predictions.

This project has been focused on 1) identifying which microscopic geometrical properties are needed to predict direction-dependent macroscopic properties, 2) quantifying the effects of pore-scale heterogeneity on macroscopic transport properties, and 3) comparing the relative contributions of physical and geochemical heterogeneities to field-scale reactive transport. Resolution of the effects of multiscale heterogeneity on subsurface transport requires large simulations, typically ~10^5-10^7 grid cells. Progress in this research is dependent on a variety of computer simulation tools, most of which have been developed for use on massively parallel computers, such as EMSL's supercomputer.

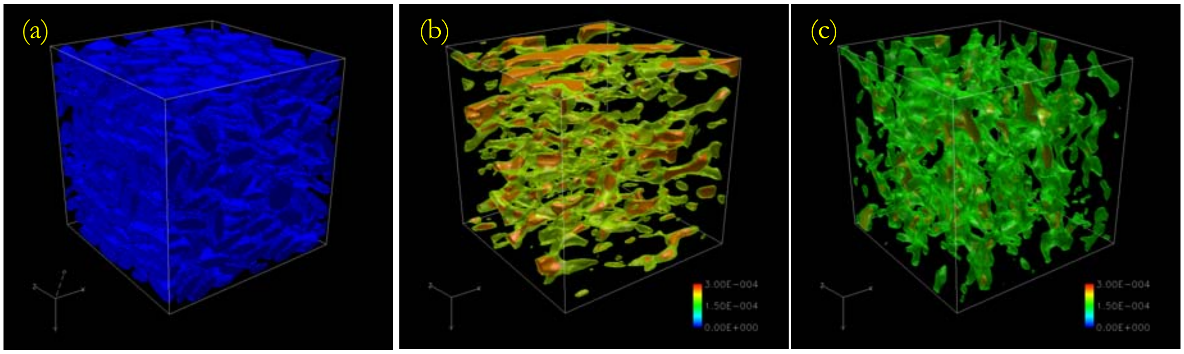

Figure 12. (a) Random particle pack with 3:1 aspect ratio and 0.58 porosity, (b) velocity distribution imposed by horizontal gradient, and (c) velocity distribution imposed by vertical gradient. Note the higher velocities in the horizontal flow case, indicated by yellow and red versus the green in the vertical flow case.

Ward and coworkers made use of a Lattice-Boltzmann model (Stewart et al. 2006, in press) and digital representations of porous media with different degrees of heterogeneity and particle aspect ratios (see Figure 12). The Lattice-Boltzmann flow simulation method can efficiently use massively parallel computers to resolve the effects of complex boundaries.

This work has led to the development of new constitutive theory for describing saturation-dependent anisotropy for porous media (Ward et al. 2006). The new theory has been incorporated into the PNNL STOMP (Subsurface Transport Over Multiple Phases) computer model and is already being used for the evaluation of remedial options for a variety of waste management areas at the Hanford Site and within the DOE complex.

Citations

Stewart ML, AL Ward, and DR Rector. “A Study of Pore Geometry Effects on Anisotropy in Hydraulic Permeability Using the Lattice-Boltzmann Method.” *Advances in Water Resources*, 29 (In Press).

Ward AL., ZF. Zhang, and GW Gee. 2006. “Upscaling Unsaturated Hydraulic Parameters for Flow Through Heterogeneous Anisotropic Sediments.” *Advances in Water Resources* 29(2):268-280.

Awards and Recognition

Research Highlighted on the Cover of the *Journal of Physical Chemistry A.* EMSL users Alexander Boldyrev, Lai-Sheng Wang, and Hua-Jin Zhai produced the $B_7Au_2^-$ mixed cluster and studied its electronic structure and chemical bonding using photoelectron spectroscopy and *ab initio* calculations. The research was featured on the cover of the February 9, 2006, issue of *Journal of Physical Chemistry A*.

Instrument Development Laboratory Staff Develop Remote Control Software for State-of-the-Art Confocal Microscope. EMSL Instrument Development Laboratory staff Derek Hopkins and Brian LaMarche, intern Anoop Mayampurath, and staff from PNNL’s Computational and Information Science Directorate and Fundamental Science Directorate have developed software to control a state-of-the-art confocal microscope in real time from a remote location. In a recent demonstration, live cell images were acquired and streamed across a 1-gigabit Ethernet connection at 15 and 30 frames per second. This capability will ultimately enable external researchers to use unique instruments found only at PNNL, as well as provide unique opportunities for real-time collaboration. Figure 13 shows the software in use.

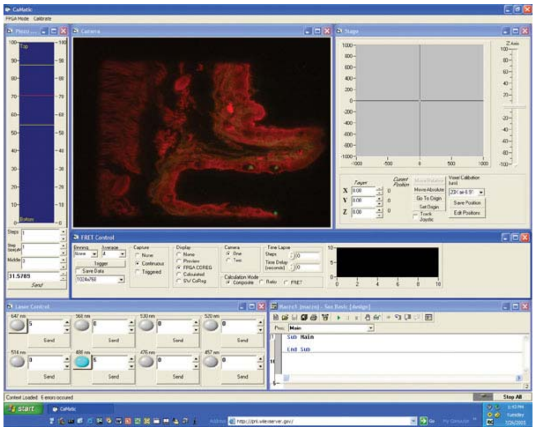

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Figure 13. Screen shot of software in use.

This development expands the potential reach of the EMSL user program by providing a framework for remote access of state-of-the-art instrumentation. The demonstration displayed the potential of remote control software tools to expand availability by enabling researchers around the world to remotely access instrumentation, limited only by the available bandwidth.

Current studies on cell physiology and reaction to stimuli usually are performed using cells cultured on two-dimensional surfaces. This geometry greatly simplifies the methodology used to observe and propagate cells; however, it places great constraints on how one can investigate intercellular communication and stress responses. The high-speed confocal microscope is a tool necessary to analyze cell signaling in a three-dimensional environment. It provides users the ability to look at cellular signaling, protein interactions, and cellular localization/translocation of signaling molecules, in real time and in living cells. These capabilities are being applied to research in cell, cancer, and radiation biology.

The microscope control software was based on the flexible Surf-O-Matic architecture developed initially at EMSL for surface science research. The application has controls for setting the laser wavelength and amplitude, three-axis stage positioning, and image capture settings, and allows the user to write Visual Basiclike scripts to automate all aspects of the application. This provides the unique capability to run highly configurable experiments unattended for long periods of time. The imaging portion of the software interfaces two Coreco PC-DIG capture cards capable of frame rates up to 30 frames per second. At full frame resolution, the software captures 15 frames per second—or 14.4-million pixels per second. Each frame captured is approximately 1.3 MB in size. Coupled with automated experiments running days on end while generating images at 15 fps, this system is capable of generating large amounts of data in a short time span. The software is also unique because it corrects for physical defects in the images (e.g. lens distortion) by using a distinctive image registration technique that allows a pixel-perfect match in real time.

Visitors and Users

Chemistry and Physics of Complex Systems Facility

- Olexandr Bondarchuk, University of Texas at Austin, Texas, worked on the study "Atomically Resolved Studies of Transition Metal Oxides."

- Luis Cuadra-Rodriguez, University of Colorado, Boulder, Colorado, worked on the study "Mechanisms of Organic Ions Released from Water Droplets."

- David Flaherty, University of Texas at Austin, Texas, worked on the study "Chemical Characterization of Arrays of TiO_2 Nanocolumns."

- Mary Gilles and Rebecca Hopkins, Lawrence Berkeley National Laboratory, Berkeley, California, gave the seminar "Using Scanning Transmission X-Ray Microscopy to Examine Black Carbon."

- Weigang Lu, University of New Orleans, New Orleans, Louisiana, worked on the study "Early Transition Metal Oxides as Catalysts."

- Katsumi Tanimura, Osaka University, Osaka, Japan, worked on the study "Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl."

- Zhenrong Zhang, University of Texas at Austin, Texas, worked on the study "Photochemistry of Halogenated Hydrocarbon on TiO_2(110) Surface."

Environmental Spectroscopy and Biogeochemistry Facility

- Tracy Bank and Phil Jardine, Oak Ridge National Laboratory, Oak Ridge, Tennessee, and EMSL researcher Ravi Kukkadapu carried out X-band continuous wave electron paramagnetic resonance and cryogenic Mossbauer studies of pristine and chemically modified sediments that were sterilized by gamma irradiation (20 kGy). The study addressed the effect of gamma irradiation on the oxidation states of iron, which exists both in clays and as iron oxides, and manganese minerals. Results of the study will help gain insights into the observed changes in the cation exchange capacity of the soil and its increased uptake of U(VI) sorption.

- As a collaborator of EMSL user Barry Bickmore, Brigham Young University, Provo, Utah, Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, ran Car-Parrinello density functional theory simulations of the structure of water using the PBE and revised PBE functionals. This work is part of their ongoing investigation of gibbsite edge surface structures.

- Stuart Bogatko, University of California, San Diego, La Jolla, California, visited EMSL on February 6-20 to collaborate with Eric J. Bylaska, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Marat Valiev. His research involves studying high-temperature (pressure) electrolyte solutions thought to facilitate metal ion transport in hydrothermal environments by using *ab initio* molecular dynamics (AIMD) methods. He is also developing a novel AIMD method that will be able to perform simulations two times larger than is now possible with existing AIMD methods. The EMSL supercomputer is being used to perform simulations for this research.

- Saumyaditya Bose, a graduate student from the laboratory of Michael Hochella, Jr. at Virginia Polytechnic Institute and State University, Blacksburg, Virginia, is working with scientists Brian Lower and Yuri Gorby from the Pacific Northwest National Laboratory, Richland, Washington, to examine the reduction kinetics of whole cell electron transfer by *Shewanella oneidensis* to synthetic hematite nanoparticles. As part of EMSL's Biogeochemistry Grand Challenge, the overall goal of this work is to understand the effects that surface area and electronic properties have on the reduction kinetics of hematite nanoparticles by *Shewanella oneidensis*.

- Baolin Deng, University of Missouri, Columbia, Missouri, along with Chongxuan Liu, Pacific Northwest National Laboratory, Richland, Washington, continued their collaboration to investigate arsenic removal from waste waters by clay or geotechnical membranes. Deng's group is designing and synthesizing the clay membranes and performing experiments to assess membrane filtration properties and membrane behavior mechanisms. Liu is developing a coupled model of electrodynamics and irreversible thermodynamics for simulation.

- Carrick Eggleston, University of Wyoming, Laramie, Wyoming, on sabbatical at the Swiss Federal Institute of Technology, Lausanne, Switzerland and Janos Vörös, ETH Zurich, Switzerland continued collaborations with Brian Lower and Liang Shi, Pacific Northwest National Laboratory, Richland, Washington. They are studying the adsorption properties of *Shewanella oneidensis* cytochromes, OmcA and MtrC, with metal-oxide surfaces using optical waveguide lightmode spectroscopy. This research is part of the EMSL Biogeochemistry Grand Challenge, which is aimed at elucidating the mechanism of Fe(III)- and Mn(IV)-oxide reduction by bacterial cytochromes and their associated complexes.

- Erica DiFilippo, University of Arizona, Tucson, Arizona, continued working with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Tom Wietsma. Her experimental flow and transport experiments were designed to investigate the amount of dense nonaqueous-phase liquid mass flux reduction as a function of source zone mass removal. This relationship will be useful in evaluating the benefit of partial source zone mass removal. The third flow cell experiment, focusing on removal of carbon tetrachloride from three residual zones, is currently in progress. A dual-energy gamma scanner is used to determine time-dependent saturations. Carbon tetrachlorid-dissolved samples were obtained from 19 locations and analyzed simultaneously.

- Jerry Gibbs, Virginia Polytechnic Institute, Blacksburg, Virginia, worked with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, to map electron density distributions in a suite of iron/copper sulfide minerals. The calculations have been completed and the work is in the manuscript preparation phase.

- Tim Magnuson, Idaho State University, Pocatello, Idaho, has started a collaboration with EMSL researcher Alice Dohnalkova to investigate processes leading to metal-transforming by bacteria from extreme environments. The Magnuson research group has isolated and studied a number of metal-metabolizing bacteria from a variety of terrestrial habitats. Among the isolates is an arsenic-reducing thermophile, Strain YeAs that produces a novel biogenic mineral, beta-realgar. The imaging and analytical methods coupled to the electron microscopy will be used for visualization of newly formed biominerals in association with microbes.

- Martin Schroth, Swiss Federal Institute of Technology, Zurich, Switzerland, collaborated with Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Tom Wietsma to develop experimental procedures to determine interfacial areas between water and nonaqueous phase liquids (NAPLs), such as carbon tetrachloride and trichloroethene. The novel procedures lead to interfacial areas estimates at various stages during the dissolution of entrapped NAPL in the subsurface. The new method produces interfacial area saturation relationships needed in numerical-subsurface flow and transport modeling. The column techniques were developed during his visit to EMSL in December. Tom Wietsma developed the analytical methods for the surfactant quantification in February. A series of column studies is planned for April and May. A paper outlined the basic science behind the experiments was recently published.

- During her 3-week visit to EMSL, Frannie Skomurski, University of Michigan, Ann Arbor, Michigan, continued her investigation with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washington, on Fe(II)-U(VI) electron transfer calculations. Frannie also worked with Eugene Ilton, Pacific Northwest National Laboratory, on the experimental design for x-ray photon spectroscopy measurements of U(VI) reduction at magnetite surfaces. A major task for this trip was to calibrate the rate of uranyl reduction during x-ray photon spectroscopy analysis in order to derive true concentrations of U(IV) on the surface.

- Matthew Wander, Stony Brook University, Stony Brook, New York continued work with Kevin Rosso, Pacific Northwest National Laboratory, Richland, Washigton, on his second manuscript on small polaron motion in Fe(OH)2, which is an analogue for green rusts.

- Nick Wigginton, Virginia Polytechnic Institute, Blacksburg, Virginia, visited EMSL for 4 weeks to continue his collaboration with Kevin Rosso and Brian Lower, Pacific Northwest National Laboratory, Richland, Washington, to examine the electron transfer properties of outer-membrane multi-heme cytochromes from the metal-reducing bacterium *Shewanella oneidensis*. Nick worked on the preparation and scanning tunnelling microscopy characterization of OmcA/MtrC complex thin films. They also worked on his manuscript describing tunneling spectroscopic modeling for deca-heme cytochromes. The team is finishing a study defining the electron transfer quantities that underpin the tunneling behavior of OmcA and MtrC cytochromes. This research is part of the EMSL Biogeochemistry Grand Challenge, which is aimed at elucidating the mechanism of Fe(III)- and Mn(IV)-oxide reduction by bacterial cytochromes and their associated complexes.

- Thomas Willingham and Charlie Werth, University of Illinois at Champaign-Urbana, Illinois, have started micromodel flow and transport studies under the guidance of Mart Oostrom, Pacific Northwest National Laboratory, Richland, Washington, and EMSL researcher Tom Wietsma. The EMSL Subsurface Flow and Transport Laboratory's ISCO pumps are used to evaluate the effects of porous media structure on reactive transport in groundwater. This phase of the testing procedures requires perfectly uniform fluid flow from two parallel injection streams. All initial tests have been completed successfully.

High-Field Magnetic Resonance Facility

- Garry Buchko, Michael Kennedy, and Shuisong Ni, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 600-MHz and 600-MHz Cryoprobe NMR spectrometers for the study "Structural Studies of a Novel Family of Manganese Uptake Proteins in Cyanothece Containing a Repeated Five-residues Domain." This study is part of EMSL' Membrane Biology Scientific Grand Challenge

- Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 800-, 750-, 600-, and 500-MHz NMR spectrometers for the study "Structural Genomics Collaborative Access Team (CAT)."

- Rachel Klevit and Peter Brzovic, University of Washington, Seattle, Washington, worked onsite and remotely using the 900-, 800-, and 600-MHz Cryoprobe NMR spectrometers for the study "NMR Structural Investigations of BRCA1."

- Andrew Lipton, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 900-, and 500-MHz NMR spectrometers for the studies "Correlation of Structure and Function of Zinc Metalloproteins via Solid-State NMR Methods" and "Investigation of the Role of Mg^{2+} in DNA Repair Proteins APE1, Pol, and FEN1."

- Kris Ooms and Kirk Feindel, University of Alberta, Edmonton, Alberta, Canada, worked onsite using the 900- and 750-MHz NMR spectrometers for the study "High-Field Solid-State Mn-55 NMR Spectroscopy of Manganese Pentacarbonyls."

- Joel Pounds, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 600-MHz Cryoprobe NMR spectrometer for the study "Identify Biomarkers for COPD (Chronic Obstructive Pulmonary Disease) in Humans using Metabonomic Analysis of Serum and Urine by NMR."

- Ponni Rajagopal, University of Washington, Seattle, Washington, worked remotely using the 900- and 800-MHz NMR spectrometers for the studies "Structural Investigation of a Molecular Chaperone" and "Structural Investigation of alphaB-Crystallin Core Domains."

- Raymond Reeves, Washington State University, Pullman, Washington, worked remotely using the 900- and 750 MHz NMR spectrometers for the study "Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function."

- Wendy Shaw and Eric Pierce, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 750-MHz NMR spectrometer for the study "Hydrogen Storage Materials."

- Paul Sideris and John Palumbo, State University of New York at Stony Brook, Stony Brook, New York, worked onsite using the 900-, 750-, and 500-MHz NMR spectrometers for the study "A Multinuclear MAS NMR Investigation of Environmentally Relevant Materials: Lanthanum Strontium Gallium Magnesium Oxide and Magnesium Aluminum Layered Double Hydroxides."

- Thomas Squier, Pacific Northwest National Laboratory, Richland, Washington, worked onsite using the 500-MHz NMR spectrometer for the study "Development of Multipurpose Tags and Affinity Reagents for Rapid Isolation and Visualization of Protein Complexes."

- Kevin Thorn, U.S. Geological Survey, Denver, Colorado, worked onsite using the 750-, 600-, and 500-MHz NMR spectrometers for the study "Analysis of Nitrogen in Humic Substances and Photochemical Degradation of TNT."

- Gabriele Varani, University of Washington, Seattle, Washington worked remotely using the 600-MHz Cryoprobe NMR spectrometer for the study "Structure of Telomerase RNA and Telomeric Proteins."

- Yunhuang Yang, Wayne State University, Detroit, Michigan, worked onsite and remotely using the 800-, and 600-MHz Cryoprobe NMR spectrometers for the study "Structural Studies of Lipid-Free Apolipoprotein A-1."

The following individuals sent samples to be run on the 800-, 750-, 600-, and 500-MHz cryoprobe NMR spectrometers in support of EMSL's Structural Genomics Collaborative Access Team, led by Michael Kennedy, Pacific Northwest National Laboratory, Richland, Washington:

- Cheryl Arrowsmith, University of Toronto, Toronto, Ontario, Canada

- Guy Montelione, Rutgers University, Piscataway, New Jersey.

High-Performance Mass Spectrometry Facility

- Steven Hallam, University of British Columbia, Vancouver, British Columbia, Canada, discussed the results from the collaborative work performed on his sea sediment samples. He also gave a presentation outlining the significance of the proteomic data gleaned from his samples and the impact on microbial communities work in general. He also discussed two potential manuscripts derived from the proteomic data with Mary Lipton, Pacific Northwest National Laboratory, Richland, Washington.

- Takane Kikuchi, Ohio State University, Columbus, Ohio, recently visited EMSL to learn proteomics sample preparation techniques. She gained hands-on knowledge of microbial sample preparation methods during her week-long stay. She will use these methods during preparation of samples of *Ehrlichia chaffeensis* and *Anaplasma phagocytophilum*, both of which are potentially fatal emerging zoonoses from the rickettsiae family. Following preparation of these samples, they will be sent to EMSL for mass spectrometric proteome analysis.

- Arzu Umar, Erasmus University Medical Center, Rotterdam, the Netherlands, is visiting EMSL with the goal of characterizing functional pathways that lead to clinical resistance to tamoxifen (anti-estrogen) treatment in breast cancer patients. To accomplish this, she is using laser microdissected tumor cells obtained from patients that were either responsive or non- responsive to tamoxifen treatment. Laser microdissection enables isolation of selected subpopulations of cells (such as tumor cells) thus, overcoming the issue of tissue heterogeneity. This process is, however, very time consuming and, as a consequence, only a few thousand cells (i.e., a few hundred nanograms of protein) can be realistically collected per tissue. Analysis of such minute amounts of sample by conventional proteomics tools is severely constrained by detection limits. Ultra-sensitive nanoliquid chromatography-Fourier transform ion cyclotron resonance mass spectrometry technology developed at EMSL is at the present the best option for performing comprehensive proteome analyses of laser microdissected cells. Protein profiles for the responsive and non-responsive laser microdissected cells were compared to detect response-specific proteins and enable better understanding of underlying mechanisms of tamoxifen-resistance. The identification of response-specific signature protein profiles that is currently being pursued holds great promise for better prediction of response and thus, development of a tailored patient treatment.

Interfacial and Nanoscale Science Facility

- Jiji Antony, University of Idaho, Moscow, Idaho, performed fundamental basic science studies that will benefit a whole range of applications involving nanoparticles in solution, including environmental remediation, corrosion, magnetic storage media, and heterogeneous catalysis.

- Madhusudan Kongara, Boise State University, Boise, Idaho, used the transmission electron microscopy laboratory to investigate the microstructural details of powder and thin film samples of oxide semiconductors SnO_2, TiO_2, and ZnO doped with magnetic impurities to produce magnetism.

- Yoon-mo Koo, Inha University, Nam-gu Incheon, Korea, studied immobilized enzymes for bioremediation and biosensing.

- Fumio Ohuchi, Koichi Takasaki, and Tomoyuki Miyassaka, University of Washington, Seattle, Washington, participated in an EMSL tour to learn about the facility and its capabilities.

Molecular Science Computing Facility

- Massimiliano Fatica, ClearSpeed Technology, San Jose, California, presented the seminar "An Overview of the ClearSpeed's CSX600 Chip," which covered chip architecture and programming models.

Molecular Science Computing Facility—New User Agreements with NWChem/Ecce

- Air Force Research Laboratory, Maui, Hawaii

- Beijing Normal University, Beijing, China

- Centre National de la Recherche Scientifique Toulouse, France

- Cleveland State University, Cleveland, Ohio
- College of William and Mary, Williamsburg, Virginia
- Ecole Normale Superieure de Lyon, Lyon, France
- Fritz-Haber Institut der Max-Planck-Gesellschaft, Berlin, Germany
- IBM, Rochester, Minnesota
- Kean University, Union, New Jersey
- Liverpool University, Liverpool, England
- Prairie View A&M University, Prairie View, Texas
- Purdue University, West Lafayette, Indiana
- Rudjer Boskovic Institute, Zagreb, Croatia
- Russian Academy of Science, Moscow, Russia
- Seoul National University, Seoul, Korea
- South China Normal University, Guangzhou, China
- Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dubendorf, Switzerland
- Tbilisi State University, Tbilisi, Georgia
- The Hong Kong Polytechnic University, Kowloon, Hong Kong
- The University of Hong Kong, Pok Fu Lam, Hong Kong
- Tufts University, Medford, Massachusetts
- U.S. Army Research Development and Engineering Command, Huntsville, Alabama
- Universidad Nacional Autonoma de Mexico, Mexico City, Mexico
- University of Alberta, Edmonton, Alberta, Canada
- University of British Columbia, Vancouver, British Columbia, Canada
- University of California, Berkeley, Berkeley, California
- University of Cincinnati, Cincinnati, Ohio

- University of Colorado at Denver, Denver, Colorado
- University of Crete, Crete, Greece
- University of Geneva, Geneva, Switzerland
- University of Kentucky, Lexington, Kentucky
- University of Nottingham, Nottingham, England
- University of Southern Queensland, Toowoomba, Australia
- University of Sydney, Sydney, Australia
- University of Toledo, Toledo, Ohio
- University of Warsaw, Warszawa, Poland
- University Rennes, Rennes Cedex, France
- University Rovira i Virgili, Tarragona, Spain

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Lu HP. 2006. "Exploring Single-Molecule Biophysical Chemistry." Presented by Peter Lu (Invited Speaker) at the University of Houston, Houston, Texas, on January 19, 2006, and at Bowling Green State University, Toledo, Ohio, on February 23, 2006.

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