LBNL-103E

# Laboratory Directed Research and Development Program FY 2013

**June 2014**

# Report on
# Ernest Orlando Lawrence
# Berkeley National Laboratory

# Laboratory Directed Research and Development Program

## FY 2013


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# Table of Contents

# Introduction

The Ernest Orlando Lawrence Berkeley National Laboratory (Berkeley Lab or LBNL) is a multi-program national research facility operated by the University of California for the Department of Energy (DOE). As an integral element of DOE's National Laboratory System, Berkeley Lab supports DOE's missions in fundamental science, energy resources, and environmental quality. Berkeley Lab programs advance four distinct goals for DOE and the nation:

- To perform leading multidisciplinary research in the computing sciences, physical sciences, energy sciences, biosciences, and general sciences in a manner that ensures employee and public safety and protection of the environment.
- To develop and operate unique national experimental facilities for qualified investigators.
- To educate and train future generations of scientists and engineers to promote national science and education goals.
- To transfer knowledge and technological innovations and to foster productive relationships among Berkeley Lab's research programs, universities, and industry in order to promote national economic competitiveness.

Berkeley Lab's research and the Laboratory Directed Research and Development (LDRD) program support DOE's Strategic Themes that are codified in DOE's 2006 Strategic Plan (DOE/CF-0010), with a primary focus on Scientific Discovery and Innovation. For that strategic theme, the Fiscal Year (FY) 2013 LDRD projects support each one of the three goals through multiple strategies described in the plan. In addition, LDRD efforts support the four goals of Energy Security, the two goals of Environmental Responsibility, and Nuclear Security (unclassified fundamental research that supports stockpile safety and nonproliferation programs). Going forward in FY 2014, the LDRD program also supports the Goals codified in the new DOE Strategic Plan of May, 2011. The LDRD program also supports Office of Science strategic plans, including the 20-year Scientific Facilities Plan and the Office of Science Strategic Plan. The research also supports the strategic directions periodically under consideration and review by the Office of Science Program Offices, such as LDRD projects germane to new research facility concepts and new fundamental science directions.

Berkeley Lab LDRD program also play an important role in leveraging DOE capabilities for national needs. The fundamental scientific research and development conducted in the program advances the skills and technologies of importance to our Work For Others (WFO) sponsors. Among many directions, these include a broad range of health-related science and technology of interest to the National Institutes of Health, breast cancer and accelerator research supported by the Department of Defense, detector technologies that should be useful to the Department of Homeland Security, and particle detection that will be valuable to the Environmental Protection Agency.

The *Berkeley Lab Laboratory Directed Research and Development Program FY2013* report is compiled from annual reports submitted by principal investigators following the close of the fiscal year. This report describes the supported projects and summarizes their accomplishments. It constitutes a part of the LDRD program planning and documentation process that includes an annual planning cycle, project selection, implementation, and review.

The Berkeley Lab LDRD program is a critical tool for directing the Laboratory's forefront scientific research capabilities toward vital, excellent, and emerging scientific challenges. The program provides the resources for Berkeley Lab scientists to make rapid and significant contributions to critical national science and technology problems. The LDRD program also advances Berkeley Lab's core competencies, foundations, and scientific capability, and permits exploration of exciting new opportunities. All projects are work in forefront areas of science and technology. Areas eligible for support include the following:

- Advanced study of hypotheses, concepts, or innovative approaches to scientific or technical problems;
- Experiments and analyses directed toward "proof of principle" or early determination of the utility of new scientific ideas, technical concepts, or devices; and
- Conception and preliminary technical analyses of experimental facilities or devices.

The LDRD program supports Berkeley Lab's mission in many ways. First, because LDRD funds can be allocated within a relatively short time frame, Berkeley Lab researchers can support the mission of the Department of Energy (DOE) and serve the needs of the nation by quickly responding to forefront scientific problems. Second, LDRD enables Berkeley Lab to attract and retain highly qualified scientists and to support their efforts to carry out world-leading research. In addition, the LDRD program also supports new projects that involve graduate students and postdoctoral fellows, thus contributing to the education mission of Berkeley Lab.

Berkeley Lab has a formal process for allocating funds for the LDRD program. The process relies on individual scientific investigators and the scientific leadership of Berkeley Lab to identify opportunities that will contribute to scientific and institutional goals. The process is also designed to maintain compliance with DOE Orders, in particular DOE Order 413.2B Admin Chg 1 (dated January 31, 2011). From year to year, the distribution of funds among the scientific program areas changes. This flexibility optimizes Berkeley Lab's ability to respond to opportunities.

Berkeley Lab LDRD policy and program decisions are the responsibility of the Laboratory Director. The Director has assigned general programmatic oversight responsibility to the Deputy Laboratory Director, with administration and reporting on the LDRD program supported by that office. LDRD accounting procedures and financial management are consistent with the Laboratory's accounting principles and stipulations under the contract between the University of California and the Department of Energy, with accounting maintained through the Laboratory's Chief Financial Officer.

In FY2013, Berkeley Lab was authorized by DOE to establish a funding ceiling for the LDRD program of $23M including General & Administrative (G&A) overhead, which equated to ~3.0% of Berkeley Lab's FY2013 projected operating and capital equipment budgets. This funding level was provided to develop new scientific ideas and opportunities and allow the Berkeley Lab Director an opportunity to initiate new directions. Budget constraints limited available resources, however, so about $22.9M was expended for operating expenses.

In FY2013, scientists submitted 231 proposals, requesting about $49.5M in funding prior to assessing laboratory overhead. Ninety four projects were funded, with awards ranging from $36K to $720K. These projects with final costs are summarized with in the Table of Contents.

**Free Electron Laser Soft X-ray Self-Seeding**

Principal Investigator(s): Paul Emma (Marco Venturini since Oct. 2013)

*Project Description*

The goal is to demonstrate free electron laser (FEL) soft x-ray self-seeding (SXRSS) at the Linac Coherent Light Source (LCLS) by the end of 2013. This demonstration, enabling seeded FEL performance that would generate fully coherent, narrow bandwidth (~0.02%) soft x-ray beams, would have a significant impact on the science reach of many existing or future facilities around the world, such as LCLS/USA, SACLA/Japan, SwissFEL/Switzerland, XFEL/Germany, PALXFEL/Korea, etc. Hard x-ray Self-Seeding (HXRSS) was recently demonstrated at the LCLS, producing 40-50 times narrower FEL bandwidth (with respect to the nominal SASE spectrum), fully coherent, 1.5 Angstrom x-ray pulses. The techniques developed for HXRSS is, so far, only applicable to hard x-rays in the 8-9 keV region. However, a similar scheme, using diffraction grating in addition to mirrors and a weak magnetic chicane could generate soft x-rays. This scheme can be implemented and tested at the LCLS for a very reasonable effort, providing another dramatic improvement on 4th generation light source capabilities. LBNL has been charged with building and testing the grating, x-ray mirrors, their motion controls, and support systems, with SLAC building and testing the magnetic chicane, controls, and necessary diagnostics (2 intercepting beam screens).

*Accomplishments*

In FY 2012, the LBNL engineering team designed the optical systems, including the grating, the x-ray mirrors, their motion control and support systems. The optical assembly was started and successfully completed on schedule in FY 2013. In the meantime SLAC proceeded to build and test the new magnetic chicane, the vacuum chamber, the necessary controls, and diagnostics, setting the stage for installation and testing of the complete system. This was accomplished toward the last months of calendar year 2013. The first successful demonstration of self-seeding at 800eV photon energy was carried out on December 20, 2013. Further work aiming at refining the experiment will continue through 2014.

## Probing Point Defect Dynamics in Solids with Short Ion Beam Pulses

Principal investigator: Thomas Schenkel, Accelerator and Fusion Research Division
Co-PI: Andrew Minor, Materials Science Division and UC Berkeley

### Project Description:

Many properties of solids depend on the presence of defects. Defects can be engineered to tune desired properties, or defects can lead to materials failure. The understanding of defects dynamics in solids has to date been limited largely to "static" studies, where defects are first formed and the resulting changes in materials properties are probed much later. Simulations aim at capturing defect dynamics, but they are severely hampered by the lack of direct experimental validation. We have a unique short pulse (ns), intense ion beam capability available at LBNL and in the first year of this LDRD we used it to gain access to the dynamics of radiation induced defects in solids on a ~1 to 100 ns time scale. Advances in our fundamental understanding of defect dynamics will enable advanced materials development, e. g. for radiation tolerant high performance structural components in reactors and for materials with tailored defect properties e. g. for applications in energy conversion.

### Accomplishments:

In the first year of this LDRD we demonstrated reproducible formation of pulsed lithium ion beams (135 - 300 keV) with tunable pulse lengths of 15 to 600 ns, and carrying up to $2x10^{11}$ ions/pulse/cm$^2$. When ions from such a pulse impinge on single crystal silicon samples (our first target material of choice) lattice atoms can be dislodged and a cascade ensues, where many vacancies and interstials can be formed, followed by rapid cooling and recombination of defects. We probed the built-up and relaxation rates of defects during ion pulses by making use of the channeling effect. Ions can channel deeply into pristine crystals, but defects scatter ions out of channeling trajectories. We quantify the fraction of channeling ions *ex situ* by Secondary Ion Mass Spectrometry and *in situ* by time resolved measurements of ion transmission through silicon membranes. In situ ion transmission measurements allow us to track damage built-up with a time resolution of ~1 ns. Figure 1 shows the time trace of ions in a pulse after transmission through a membrane (red) and a reference trace without membrane (blue). The trace with membrane shows a rapidly damped peak of channeled ions. The decrease of the channeling peak occurs within ~100 ns in this example, indicating a characteristic lifetime for defect affecting channeling. In year 2, we will increase the time resolution, perform systematic measurements for a series of pulse and target conditions and compare our results to simulations.

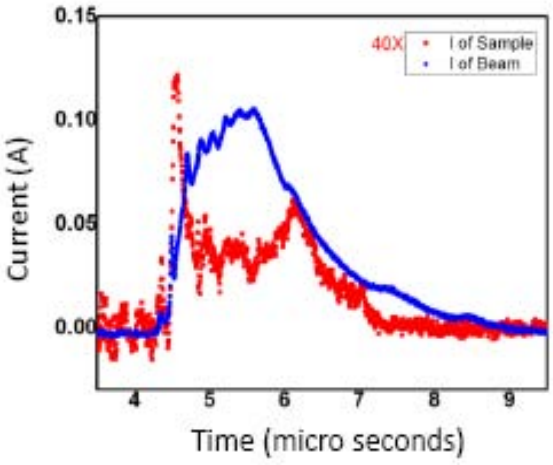


Fig. 1: Time resolved detection of lithium ion transmission through a silicon membrane (red) reveals lattice damage built up in the first 100 ns during a 600 ns long pulse, causing de-channeling of ions as compared to the pulse profile without the membrane (blue).

# Experimental Realization of a High-Harmonics-Seeded, Laser-Plasma-Accelerator Driven Free-Electron Laser

Principle Investigator: Jeroen VAN TILBORG

## Project Description

The purpose of this project is to experimentally realize soft X-rays (20-100 eV) seeding into a laser-plasma-accelerator (LPA) driven free-electron laser (FEL). The proposal contains two stages: (1) Construction and characterization of an ultra-short high-power seed source of soft X-rays through means of high harmonics generation (HHG) from a near-infrared laser. (2) Simulation study of the coupling of the seed pulses and LPA-based electron beams in the undulator to optimize FEL output flux, stability, and temporal coherence. The T-Rex laser at LOASIS is to be used to produce and deliver both the high-power HHG seed and the high-current electron beam into the THUNDER undulator. The proposed system will benefit the non-linear X-ray community and serve as a test-bed for seeded FELs.

## Accomplishments

During the 2012 & 2013 period, the main focus of the research was geared towards the characterization of the coherent seed pulses. This seed was generated through laser-driven high-harmonic generation (HHG) off a spooling tape surface, with the HHG generation mechanism in the so-called Coherent Wake Emission (CWE) regime. The spooling tape allowed us to obtain extensive parameter scans. Even and odd harmonics up to the 17th order were observed (up to 26 eV), with a beam divergence of 5-10 mrad (rms) and photon energy of 50-100 nJ in the 15th harmonic. New insight that was obtained includes:

(*) We studied the dependence of the surface roughness on CWE HHG beam divergence. To characterize the roughness, we measured the Power Spectra Density (PSD), which is a roughness function versus spatial frequency. This allowed us to isolate the relevant spatial scale over which roughness becomes critical to CWE production. At spatial scales less than the laser spotsize (<25 micron), we observed a clear correlation between divergence and PSD amplitude. This work was recently published [B. Shaw *et al*., J. Appl. Phys**114**, 043106 (2013)].

(*) We observed spectral broadening and blue-shifting of the individual harmonics when the laser intensity was increased. After comparison to a CWE model, and after extending the model to include a dynamically increasing front-surface plasma gradient length scale, agreement to the data was accomplished. This result was recently published [J. van Tilborg *et al*., Opt. Lett. **38**, 4026 (2013)], and highlights the potential gain in CWE HHG energy conversion if the plasma expansion is optimally controlled.

Our detailed analysis of the experimental results provides a path towards further improvement of the coherent CWE seed source: more photons within a smaller divergence are feasible with smoother tapes and plasma gradient expansion control. However, we performed FEL simulations that demonstrate that even at our current seed source parameters (2-3 MW in the 15th order, at 7 mrad divergence), significant seed-enhanced FEL lasing is achieved. The strong seed photon flux produced through CWE HHG more than compensates for the somewhat larger divergence of 7 mrad. With the LPA electron beam and coherent seed beam verified to be of sufficient quality, we are confident to move forward towards integration of these components towards the first LPA-driven seeded FEL.

**Magnetic-Field-Induced and Transient Quantum Phases in Correlated Materials**

Principal Investigators: Elke Arenholz and R. Ramesh

*Project Description*

The coupling of charge, orbital, lattice, and spin degrees of freedom in complex oxides gives rise to intriguing phenomena such as multiferroics, piezoelectricity, magnetostriction, photostriction, high temperature superconductivity, colossal magneto-resistance etc. A fundamental understanding of the physics behind these phenomena will be essential in order to develop the principles for directed materials design and synthesis to exploit the remarkable properties of these materials. This is an ambitious goal, with tremendous potential impact across diverse technology areas: from efficient energy transport, storage, and conversion, to low-power/high-speed information processing and communication, to high-density information storage, to materials and meso- and nanostructures with engineered thermal, mechanical, and electrical properties for specific applications.

We proposed developing resonant soft x-ray scattering (RSXS) into a powerful technique for the study of novel quantum phases and coupling phenomena occurring only at interfaces in layered and columnar heterostructures as well as near domain walls characterized by the abrupt reorientation of order parameters leading to unique properties in conductance, magnetism and structure.

*Accomplishments*

We have optimized our RSXS setup at ALS for experiments involving interfaces and domain walls in nano- and mesoscale heterostructures and successfully studied the following systems:

*+ Self-Organized Functional Multiscale Arrays*

Self-organized functional multiscale arrays in form of columns in a matrix can be synthesized by co-depositing a transition metal oxide with spinel structure and another with perovskite structure. On a suitable substrate the system self-assembles into spinel nano-columns embedded in a perovskite matrix. This approach uniquely allows the coupling of order parameters at the interfaces between columns and matrix. In suitable geometries constructive interference of soft x rays scattered at the interfaces between columns and matrix occurs providing otherwise inaccessible information about the interface electronic and magnetic structure.

+ *Superlattices With Novel Functionalities*

Similarly to the RSXS studies of nanoscale columns in a matrix, RSXS is uniquely sensitive to the interfacial electronic structure of layered oxide systems: Monitoring the photon energy dependence of the scattered intensity for $La_{0.7}Sr_{0.3}MnO_3$/ $La_{0.7}Sr_{0.3}CoO_3$ we observed a linear dichroism characteristic of interfacial orbital ordering.

+ *Periodic Domain Wall Arrays in Multiferroics*

Domain walls corresponding to a rotation of the ferroelectric polarization exist in $BiFeO_3$. It has been shown that domain walls are conductive and can carry an uncompensated magnetic moment pointing towards a unique electronic and magnetic structure in the domain walls as compared to the bulk. By carefully choosing the layer thickness, periodic domain arrays with evenly spaced domains separated by walls of only one type have been created by our team. These refined periodic arrays then served as a model diffraction lattice for soft x-rays. We observe a modulation of the scattered intensity for wave vectors corresponding to the domain width and a pronounced dichroism providing new insights into the electronic and magnetic structure of the domain walls.

The experiments address hotly debated questions in physics using unique instrumentation developed at ALS. ALS does not have a beamline optimized for RSXS experiments on quantum materials at this time. Building on the work conducted within the scope of this LDRD will allow ALS and ALS-II to establish a significant research effort in this field.

Studying the Emergence of Electronic Correlations with Time- and Momentum-Resolved RIXS
Principal Investigator: Yi-De Chuang

*Project Description*

The scope of this project is to develop the expertise, capability and capacity of resonant inelastic soft X-ray scattering spectroscopy (RIXS) at the Advanced Light Source. RIXS is a powerful technique for studying the dynamics of elementary excitations in strongly correlated materials (e.g. transition metal oxides, TMO), which exhibit the emergent properties such as high temperature superconductivity, colossal magnetoresistance, Mottness, multiferroicity …etc. Although there is a high resolution, low energy RIXS endstation (MERIXS) at the ALS, the delocalized core and intermediate states involved in the low photon energy RIXS process, and the reduced fluorescence over electron yield channels and limited momentum-transfer restrict studies on some of these exciting TMOs. To fill in the gap, the high energy RIXS instrumentation is critically needed at the ALS.

A modular momentum-resolved RIXS endstation (qRIXS) for soft X-rays is funded separately by DOE. However, the funding does not include support for the personnel to commission and develop scientific program with this instrumentation. Therefore, the first year LDRD is intended for hiring a postdoc to commence the commissioning effort of the qRIXS spectrographs.

This LDRD has the following co-PI, L.A. Wray (ALS), W. Yang (ALS) and Z. Hussain (ALS).

*Accomplishments*

Two postdocs are hired with 50% support each from this LDRD. The postdocs have been trained by the PI to be familiar with the design and operating principles of grating-based soft X-ray spectrographs. Part of the funding is used to build up the test stand for commissioning the spectrographs at BL6.3.2 of the ALS, and beamtime has been awarded. Two spectrographs are being assembled and will be ready for commissioning at the beamline by January 2014.

In the meantime, the postdocs are carrying out RIXS measurements on CuO, ruthenates, U-compounds at the MERIXS endstation to gain experience with RIXS data acquisition, analysis and interpretation. Their works have contributed to papers that are submitted to peer-review journals.

# Soft X-Ray Spectroscopy for In-situ Electronic Structure Study of Artificial Photosynthesis

Principal Investigator: Jinghua Guo

## Project Description

This proposal is to develop an in-situ photon-in/photon-out soft x-ray detection system for electronic structure study of artificial photosynthetic catalysts. Such development is crucial for studying the inorganic and organic catalysts, especially in the dilute aqueous systems. The goal is to extend the soft x-ray spectroscopy into the catalytic, environmental, and biological communities in order to understand the mechanism of the multi-electron catalytic reactions. Catalytic reactions such as water oxidation and generation are all multi-electron reactions, where several intermediate states are involved in the reaction cycle. Therefore, a holistic study of the entire course of the reaction, including the intermediate states of the catalytic cycle, holds the key for discovering novel efficient photocatalysts. The proposed effort will have the significant impact on the renewable and carbon-neutral energy technologies that require us to understand, predict, and ultimately control chemical reactivity, selectivity, and charge transfer at the electronic, atomic, and molecular levels. The resulting systems will serve the need from JCAP and broad general user community.

The hierarchy of goals in the approach to these systems in the soft x-ray energy range will be:

1) To detect the weak signal from dilute samples by using an efficient detection scheme that collects fluorescence signal from a large solid angle.

2) To mitigate the radiation damage by using a bending magnetic beamline (BL631) with fast scanning capability and very stable photon beam, and cooling and liquid flow cell will also be applied.

3) To record soft x-ray spectra from a flow sample cell to probe the intermediate states of catalytic reactions in time-scale (~$\mu$s to ms) in a dilute (≤1 mM) and wet environment.

The collaborators are Per-Anders Glans, Elke Arenholz, Catherine Jenkins, Zahid Hussain (ALS), Junko Yano, Vittal Yachandra, Heinz Frei (PBD, JCAP)

## Accomplishments

In the first year, we have designed and constructed an endstation for photon-in/photon-out soft x-ray spectroscopy on BL6.3.1. The postdoc, Debajeet Bora was hired for the LDRD project. The endstation was assembled offline for vacuum test, and installed on BL6.3.1 in August. It has been operated for JCAP's scientists and general users to carry out a number of XAS experiments.

The four elements Vortex detector has been installed on ISAAC chamber and commissioned for user operation. Two new in-situ cells have been designed and fabricated: static electrochemical liquid cell (successfully operated) and flow electrochemical liquid cell (successfully operated) for the study of the electronic structure of artificial photosynthetic catalysts and energy storage materials.

The automation of the sample control is under developing. We are starting to design a high throughput soft x-ray fluorescence spectrograph. The design of high throughput fluorescence detection system was completed, and optics (mirror, grating substrates and ruling) have been ordered with the JCAP funding.

A few possible efficient catalysts for photoelectrochemical water splitting reactions are to be measured. The results are expected to be crucial in design and control of photocatalysts.

New opportunities in Hard X-ray Tomography– High Temperature and Elemental Imaging

Principle Investigators: Alastair MacDowell(ALS), Stephano Marchesini (ALS), Jonathon Ajo-Franklin (ESD), Ho-YingHolman (ESD), Peter Nico (ESD), Eleanor Blakely (LSD), Al Thompson (LSD) Joe Gray (OHSU) , Peter Denes (LDEG), Rob Ritchie (MSD, UCB)

Project Description

We have identified two unique areas of instrument development involving the technique of hard x-ray 3 dimensional (3D) micro-tomographic imaging that can provide novel measurements relevant for the CC2.0 initiative. The 2 instruments are:-

1) A High Temperature micro-Tomography load cell that can image in 3D the condition of materials when under tension or compression in-situ at up to 2000$^{o}$C.

2) A novel 3D imaging detector with elemental specificity.

Accomplishments

The High Temperature micro-Tomography load cell has been designed, assembled and commissioned. A series of SiC composite materials made by Teledyne Inc. have been imaged while undergoing strain to failure at 1750C. Typical future applications of such materials include critical components in hyper sonic aircraft, space re-entry vehicles and high temperature high efficiency turbines for jet propulsion and power generation. The samples were imaged in 3D with a resolution of 1-2 micron at high temperature showing crack propagation in near real time. Understanding crack propagation allows one to design tougher materials. Work this year focused on the testing of ceramic composite materials under load and high temperatures in an oxidizing atmosphere by adapting the equipment to allow precision control of partial pressures of oxygen in the hot chamber. Other members of the Advanced Light Source User community have come forward to use the cell in a wide variety of disciplines. These include the study of heat shield ablation of space re-entry vehicles (NASA), cracking of hot magma under tension to investigate the explosive nature of some volcanoes (UCB), reinforced concrete under tension (UCB) and heating of oil shale (Earth Science Division, LBNL).

The 3D Elemental imaging camera is based on encoded aperture technology and is intended to image fluorescent x-rays (5-25KeV) from a sample irradiated by excitation x-rays. Coded apertures were constructed and elemental test samples imaged to demonstrate the novel re-construction algorithms developed. Spatial resolution for this preliminary detector was ~50um with a field of view ~ 6mm. Code was developed that utilized the energy detection capabilities of the commercial CCD detector. This allowed the instrument to be energy resolving and so could distinguish elements. Preliminary experiments indicate the instrument is limited to samples that are low absorbing in the x-ray regime. Images of contaminant metal distribution in wood char and Uranium contaminant distribution in mouse kidneys were obtained as initial demonstration examples.

Ultra-high Resolution Microscopy of Nano-Materials by Scanning X-ray Diffraction Microscopy
Principal Investigator(s): David A. Shapiro

Project Description

Scanning x-ray diffraction microscopy (x-ray ptychography) is a robust imaging method which can take full advantage of the high brightness of the ALS. The goal of this work is to demonstrate the application of this technique to difficult scientific problems in the material sciences. We will study several material systems using imaging endstations at the ALS. Using the STXM at beamline 11.0.2 we will utilize carbon edge spectroscopic signatures to visualize nanoscale phase segregation in copolymer blends. In particular, we aim to determine the molecular ordering of polymer chains at the interface of polymer phases. Then we will use iron edge spectroscopy to visualize the orientation of delithiated phases in LiFePO4 nanoparticles. Finally, we will use the nanosurveyor at beamline 9.0.1 to study the three dimensional morphology of calcium silicate hydrate based cements and porous polymers. The study of each of these mesoscale systems requires the ability to visualize 10 nm scale features embedded in a micron-scale matrix. There currently is no imaging technique with such capabilities.

Accomplishments

In the first six months of this project we have applied soft x-ray ptychography to the study of phase transformations in $LiFePO_4$ nano-particles and the three dimensional structure of calcium silicate hydrate. Ptychographic measurements on $LiFePO_4$ proceeded at ALS beamlines 5.3.2.1 and 11.0.2 where the presence of Li can be identified by the oxidation state of the Fe. Using x-ray ptychography we were able to visualize Lithium rich and Lithium poor domains in partially de-lithiated $LiFePO_4$ with an unprecedented spatial resolution of 4 nm. Our chemical mapping has elucidated new insight into the study of these domains. Specifically, we can unequivocally identify a correspondence between a linear structural defect and the boundary of the domain front. Through comparison with Z-contrast imaging we can conclude that the structural defect is a surface crack which reveals unreacted $LiFePO_4$ below the surface (Figure). This indicates that the delithiation reaction is solid state limited proceeding more rapidly along certain crystallographic directions and can guide the synthesis of higher performance battery materials.

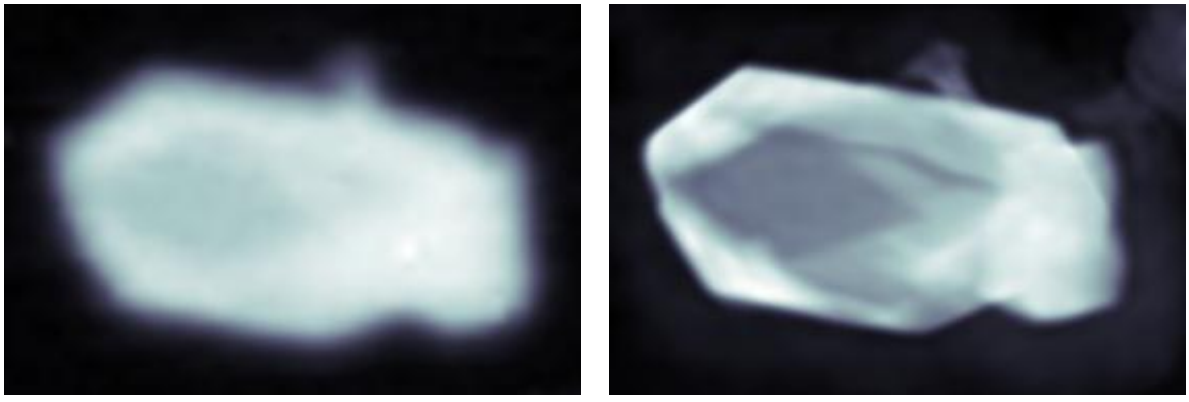

**Figure 1:** X-ray microscopy of $LiFePO_4$. (Left) Conventional scanning transmission image of partially de-lithiated $LiFePO_4$ with 25 nm spatial resolution. (Right) Ptychographic image of the same particle showing dramatically enhanced spatial resolution. The delithiated domain is shown in white and the field of view is 1 micrometer wide.

**Next Generation Gratings for X-ray Spectroscopy and Pulse Manipulation**

Principal Investigator: Dmitriy Voronov

*Project Description*

There is a great need in advanced diffraction gratings at the ALS and other synchrotron facilities. To provide high spectral resolution and high diffraction efficiency the gratings are required to have a variable line spacing (VSL), perfect blazed grooves, and smooth groove surface. For reflective zone plates elliptical lines are required to provide two dimensional focusing. Fabrication of such gratings with holographic recording and mechanical ruling is challenging. Due to limitations of conventional techniques one can only design gratings within a very limited set of variables. New approaches for fabrication of high quality grating in a cost effective manner should be found to make advanced diffraction gratings available.

This work aims development of a new grating fabrication process based on Direct Write Lithography (DWL) technique which is used in semiconductor industry for making high resolution MEMS structures, nanostructures, and consumer microelectronics. A grating pattern can be written by scanning a focused laser or electron beam over a substrate surface coated with a photoresist. The DWL technology will be used as a pattering technique for making diffraction gratings of arbitrary groove density variation and groove shape complexity. The best available DWL systems will be used for making grating prototypes which will be characterized in terms of groove position accuracy, imaging performances, and diffraction efficiency.

DWL process will be optimized and eventually combined with wet anisotropic etch technique for making highly efficient blazed gratings. Deposition of multilayer coatings on saw-tooth substrate will allow a new kind of x-ray gratings, Multilayer-coated Blazed gratings which will be a basis for a new generation of high resolution and high throughput x-ray instrumentation.

*Accomplishments*

1. A software tool for generating design of diffraction grating patterns including VLS gratings has been developed.
2. Photo-resist spin-coat process has been optimized for regular Si wafers and 5 mm thick substrates.
3. Optimization of exposure of resist-coated substrates with DWL66 and DWL2000 machines has been performed.
4. Reactive plasma etch process of patterned Si substrates has been optimized to provide good control of lamellar groove depth and smooth groove surface.
5. Wavefront measurements procedure for assessment of groove position accuracy has been developed.
6. A process of wet anisotropic etch of asymmetrically cut Si substrate has been improved to provide high quality blazed substrates.
7. Growth of a multilayer coating on saw-tooth substrates was investigated in details and optimized to provide highly conformal film growth.
8. This work is summarized in six additional publications and one invited talk this year. Two manuscripts have been prepared for publication.

## Grazing Incident Soft X-ray Scattering of Organic Photovoltaics

Principal Investigator(s): Cheng Wang, Alexander Hexemer, Howard Padmore, Yi Liu, Rachael Segalman, Jeff Kortright, Harald Ade, Thomas Russell

Project Description

The development of solution-processable organic electronic materials has enabled the use of low-cost deposition methods such as roll-to-roll print to make organic solar cells. The world record organic photovoltaics cells (OPVs) shave efficiency of more than 10% that is now reaching commercial viability. X-ray scattering methods have recently been widely used as high resolution, nondestructive probes for characterizing mesoscale structure of organic photovoltaics. The scattering represents a statistical average over a large sample area, therefore a great complementary to direct imaging techniques such as electron microscopy and scanning probe microscopy. X-ray scattering is the only research tool that allows high-throughput and in-situ characterization. It provides the capability to determine the fundamental connection between how organic electronic materials organize on small length scales during the device fabrication and how that translates into their operation in OPV device. This project is focusing on developing grazing incident soft x-ray scattering (GISoXS), a mesoscale structure probe, to study the OPV devices in the real device geometry and in-situ analysis during operation. GISoXS combines the conventional x-ray scattering with x-ray spectroscopy thus offers enhanced scattering contrast and chemical sensitivity by tuning x-ray photon energy close to the absorption edge of constituent materials. The goal is to develop a unique and powerful approach with this 3D mesoscale chemical structure probe that targets at high throughput realtime device characterization, which is currently unavailable with other techniques, therefore achieve better understanding of the correlation between nano-morphology and electronic structure for optimizing the OPV performance.

Accomplishments

During this LDRD, we have started the general method development of GISoXS with existing high performance OPV materials including polythiophene/fullerene and all polymer systems. Some of the results were published in high profile journals. Based on the existing scattering setup at BL11.0.1.2, we are optimizing the instrument to accommodate GISoXS experiment with the goal of high throughput operation as well as in-situ real device characterization with new materials. Thermal electric based sample environment has been developed and implemented for in-situ study of the effect of thermal treatment and solvent annealing during the device fabrication. Soft x-ray scattering data was collected as a function of incident angle, and photon energies, which should be selected to provide different depth information and resonant enhancement for the different polymer components at various timescale. A world first miniaturized in-situ Slot-die printing device was developed and in-situ SAXS/WAXS study were performed on OPV coating process. Customized instrumentation, established experimental protocol and advanced data analysis package is currently being developed for GISoXS that will be applied to a few applications on new OPV materials developed at LBNL. We anticipate it becoming a standard tool for high throughput organic thin film structure characterization, which will lead to faster discoveries of the best OPV materials for photovolatics and thereby contribute toward CC2.0's vision of reducing carbon emissions.

# Global Transcriptome, Deletome and Proteome Profiling of Yeast Exposed to Radioactive Metal Ions: A Tool to Distinguish Radiation Induced Damage from Chemical Toxicity

Principal Investigator: Rebecca Abergel

## Project Description

The goals of this project were to investigate the biological effects of exposure to lanthanides and actinides and to distinguish the chemical toxicity of the investigated metal ions from the radiation-induced damage due to their radioactive properties. Specific aims were to 1) investigate toxicity gene expression signaling pathways following exposure to selected *f*-elements and 2) elucidate the mechanisms of metal cellular uptake and deposition.

The consequence of exposure to radioactive and non-radioactive f-block metals was examined using a combined functional genomic, biochemical and spectroscopic approach on the powerful eukaryote model organism *Saccharomyces cerevisiae*. We anticipated the establishment of the metal-responsive transcriptomic and proteomic profiles following exposure to equi-toxic concentrations of the selected metal-ions. The identification of genes and proteins with altered expression upon actinide and lanthanide fission product exposure should permit the subsequent characterization of metal-protein complexes and the establishment of deletome genomic profiles.

## Accomplishments

The homozygous diploid *S. cerevisiae* strain BY4743 was used for viability/cytotoxicity assays, with metal ions from the whole series of lanthanides and selected actinides as contaminants. Equi-toxic concentrations of contaminants were established by monitoring cell growth and determining cell viability after metal exposure in YPD growth medium at 30°C over 24 hours. A pool containing thousands of different strains of yeast was then exposed to 1x, 0.5x, and 0.25x $EC_{20}$ concentrations of the whole series of lanthanides. DNA samples were purified and sequenced by Next-Gen Sequencing, in order to obtain the full map of the genetic pathways involved in the cellular response to *f*-element exposure.

Through toxicogenomic and proteomic analyses, we sought to identify metal-binding endogenous species and characterize the resulting complexes. While further analysis is needed to determine the key metal-binders, we have probed different techniques for spectroscopic characterization. The iron-transport protein transferrin (Tf) was used as a model species and its interactions with lanthanides and actinides were characterized by liquid chromatography, mass spectrometry, and UV-Visible and luminescence spectroscopy. Recognition of metallo-Tf complexes by the cognate cellular receptor TfR was then probed using these techniques, showing that metal complexation significantly affects the protein conformation, thereby enhancing or preventing passage through a cellular membrane and subsequent intracellular metal release. This secondary metal-recognition mechanism is selective among the *f*-block metals and could be used in the design of synthetic separation systems for *f*-elements. We will continue to explore the use of liquid chromatography coupled to mass spectrometry and luminescence spectroscopy to identify and characterize protein-metal species formed as a consequence of external exposure.

# Scientific Tools in Multi-Dimensional X-Ray Spectroscopy and Coherent Diffractive Imaging

Principal Investigator(s): A. Belkacem, R.W. Falcone, O. Gessner, S.R. Leone, C.W. McCurdy, D.M. Neumark, R.W. Schoenlein, Th. Weber

*Project Description*

The purpose of this project is to develop laboratory based test bed for next generation coherent diffractive imaging (CDI) methods and multi-color multi-dimensional x-ray spectroscopies with the goal of laying ground to lab-based experimental techniques that capture dynamical processes involving heterogeneous mixtures of complex samples. The experiments explore new routes to gain femtosecond time-resolved, atom specific information. The key idea for the coherent diffractive imaging is to take full advantage of the resonant and near-resonant interaction of soft x-ray radiation with the sample, i.e. to employ the atomic characteristics of the sample in order to gain information beyond the coherent superposition of elastically scattered photons. Multi color x-ray techniques make use of the major advances in high pulse-energy of high harmonic generation to probe multiple core and inner valence transitions within the same experiment, introducing atomic specificity to nonlinear spectroscopy techniques. These studies are carried out using two of the UXSL high harmonic sources. These include a moderate repetition rate high-intensity high-harmonic system, a high repetition rate moderate-intensity high-harmonic system. Each one of these systems has focused on a different aspect of the proposal

*Accomplishments*

Our most significant accomplishment has been to demonstrate the feasibility of ultrafast near-edge coherent diffractive imaging using a combination of a tabletop high-order harmonic generation (HHG) light source, an Extreme Ultraviolet (EUV) monochromator, and an imaging EUV detector. The spatial autocorrelation function of a micron-scale double pinhole in a 300 nm thick aluminum foil has been retrieved despite a dominant background signal from directly transmitted light across the entire range of detectable diffraction angles. The fringe visibility in the diffraction patterns, a direct measure of the achievable image contrast ranging from 0 (no contrast) to 1 (perfect contrast), was increased from 0 below 72 eV photon energy to $0.73 \pm 0.08$ in a differential near-edge measurement at the aluminum 2p inner-shell absorption edge. The proof-of-principle experiment demonstrates that the variations of XUV optical constants in the vicinity of an inner-shell absorption edge can be utilized to improve the chemical sensitivity and image reconstruction quality of laboratory-based ultrafast imaging experiments.

We also made major progress in multicolor multidimensional spectroscopy using a combination of photoelectron spectroscopy and fluorescence measurement as a signature of two-photon absorption by neon atoms and $CO_2$ molecules. Two separate coatings on the same face of a single focusing mirror with different multilayer structures that reflect the $17^{th}$ and $29^{th}$ harmonics respectively facilitate the critical spatial and temporal overlap between the two different XUV pulses. We showed that multicolor two-photon absorption in the extreme ultraviolet regime is routinely achievable in the 30-50 eV energy range at 1-kHz repetition rate. We observed significant fluorescence signal but are not yet able to attribute it uniquely to Coherent Raman scattering. We estimate from our measured two-photon absorption that a sizable fraction of the observed fluorescence is due to non-linear Coherent Raman.

## ASYMETRIC RESPONSES OF SYSTEMS FAR FROM EQUILIBRIUM

Principal Investigator: David Chandler

*Project Description*

We requested support for research toward developing general principles governing behaviors of systems driven far from equilibrium. It is abroad area of research. Here, we focus on one important aspect: asymmetric responses of glassy materials, where system responses reflect system preparation, even when that preparation was carried out long ago. Understanding such responses will enable design of synthetic nano-scale devices that exploit these asymmetric responses for energy storage and power strokes. Scientists have long exploited principles of equilibrium theory to design useful ordered and regular condensed phases. Regular solution theory used in the oil refining industry is an example. Nucleation theory used in the steel industry is another example. But no similarly fundamental understanding is yet available for kinetically trapped disordered solids and nanoclusters -- systems that emerge by driving liquid matter out of equilibrium. Further, there is currently little theoretical guidance for the wide possibilities of asymmetric responses in the behaviors of disordered and/or nano-structured solids, including design protocols for assembling these systems. Our planned research aimed at addressing some of this gap.

This research used methods of statistical mechanics, computer simulation and model building. The models were designed to capture the minimum information required to describe systems and behaviors of interest. Tests of approximations in this effort were made by comparing theory and experiment and by comparing theory and molecular simulation.

*Accomplishments*

We have developed a set of formulas that predict phase diagrams for glass-forming materials. These formulas derive from the space-time scaling of heterogeneous dynamics. Given the apparent complexity of the phenomena, its intrinsic irreversibility and multifaceted qualities, the universality and simplicity of our predictive formulas are especially remarkable. We have tested our understanding through successful applications of our formulas in treating calorimetric glass transitions in a number of materials.

Along with our general analytical treatment of glass transitions, we have also used our understanding to derive a procedure by which glassy materials can be successfully produced and then studied numerically. This is the “s-ensemble” method. The method proves successful even though the actual dynamics required to produce structural glass in the laboratory far exceed time scales accessible by straightforward molecular simulation. It is thus yet another advance made by our group for treating huge time-scale gaps with numerical computation, and it gives us the unprecedented ability to carry out molecular modeling of amorphous solids based upon rigorous physical principles.

Ultrafast X-ray Studies of Interfacial Charge Transfer Processes
Principal Investigator(s): Oliver Gessner, Hendrik Bluhm, Jinghua Guo, Miquel Salmeron

Project Description

The goal of this project is to develop time-domain X-ray spectroscopy techniques for *in situ* studies of charge transfer processes between a catalyst or electrode surface and adsorbed species on picosecond time scales. The project will establish the fundamental expertise for future ultrafast X-ray programs aimed at monitoring the time evolution of electronic states and chemical processes on ultrashort time scales and with the unique element specificity of X-ray transitions. The methods that will be developed will directly address the DOE grand challenge to understand and control energy-technology relevant systems at the level of electrons. Visible and ultraviolet laser ("pump") pulses will be used to electronically excite substrates and adsorbates, followed by X-ray interrogation ("probe") of valence electron configurations in the vicinity of specific target atoms at time delays varying from nanoseconds to picoseconds. In particular, *in situ* electrochemical cells and ambient-pressure photoelectron spectroscopy techniques that enable the interrogation of electrodes and adsorbed species using X-ray absorption (XAS) and X-ray photoelectron spectroscopy (XPS) while electric fields are applied, will be interfaced with laser-pump/X-ray probe schemes. The main objective of this project is to demonstrate and establish the ability to follow the temporal evolution of the electronic structure of adsorbates and substrate materials upon excitation to their lowest unoccupied molecular orbitals (LUMO) or conduction band levels, as a function of time in the femtosecond regime and under operando conditions.

Accomplishments

During the first year of funding the main focus of the project was to hire the personnel and create the technical infrastructure for the demanding experimental program, as well as to compete for beam time at several beamlines of the Advanced Light Source (ALS). An international search led to the hiring of a postdoctoral fellow with a unique combined expertise in both femtosecond laser-based time-domain experiments as well as X-ray based inner-shell spectroscopy studies. A mobile state-of-the-art high-power picosecond laser system has been installed and commissioned at the ALS. Proposals for experiments at three ALS beamlines were successful, resulting in beam time allocations at beamlines 6, 8, and 11. These beamlines and associated end stations will enable the implementation of time-domain *in situ* XAS (BL 6, 8) as well as time-domain ambient pressure XPS (BL 11) techniques. A multi-divisional monthly seminar series has been established to facilitate the efficient transfer of scientific and technical expertise between the groups participating in this project. In a first exploratory beam time at ALS BL 11 the picosecond laser system has been successfully synchronized with the ALS and a time- and position-sensitive XPS detector, paving the way for picosecond time-resolved XPS measurements on electrodes and adsorbates under ambient pressure conditions and with the unique surface-sensitivity of XPS. Beam times at BL 6 and BL 8 will extend the experimental capabilities toward time-resolved *in situ* XAS experiments that will access interfacial dynamics in working photoelectrochemical cells.

**Photo-switchable Metal Organic Frameworks for $CO_2$ Sequestration**

Principal Investigator(s): Mary Gilles

*Project Description*

Smart materials that combine high surface areas with the ability to undergo controlled nano- and macro scale structural changes offer creative approaches for $CO_2$ capture/release, sensors, and development of responsive materials. This project will construct metal-organic frameworks (MOFs) thin films containing chromophores that undergo reversible conformational and/or chemical changes upon photon absorption. We will utilize *in situ* soft X-ray spectroscopies to examine changes in physical properties (chemical bonding, oxidation states, and gas absorption) of the chromophores before and after photon (UV/Vis) absorption. The gas uptake of the MOFs before and after photo switching will be probed *in situ* by a variety of synchrotron based soft x-ray spectroscopies that examine bulk and interfacial properties.

*Accomplishments*

Metal organic framework thin films have been grown on $SiO_2$ and on self assembled monolayers on Au as a function of a wide variety of synthesis parameters. These films have been characterized using synchrotron based XRD, atomic force microscopy, scanning electron microscopy and ambient pressure photoelectron spectroscopy. The potential for x-ray induced damage has been explored and experimental protocols developed to minimize exposure. The gas uptake of CO an NO have been measured using in situ NEXAFS and XPS soft x-ray spectroscopies. At higher pressures, the uptake of NO on HKUST-1 was measured using a quartz crystal microbalance (QCM) system. The QCM technique was also used to examine CO uptake as a function of film thickness and film orientation. The enhanced role of x-ray reduced copper on the uptake of NO has been examined. Several chromophores were incorporated into the thin films. Experiments to detect changes in the structure due to light exposure have not yielded conclusive results. Experiments on effects on gas uptake are continuing. We have done extensive study on the growth of the thin films and are currently examining the kinetics of growth as well as how this changes at different film thickness.

**Mechanisms of Metal-Catalyzed Reactions within the Carbonic Anhydrase Matrix**

Principal Investigator(s): John Hartwig

*Project Description*

The emerging field of artificial metalloenzyme catalysis has largely grown without the support of mechanistic investigations of the catalytic systems of interest, despite the importance of such insight for the development of small-molecule transition metal catalysts. The purpose of this project is to develop methods for the rigorous analysis of transition-metal complexes and reactions within a protein matrix. In the literature, the most commonly reported artificial metalloenzyme system in one in which an organometallic complex is anchored to the active site or exterior of a protein, either via a covalent cysteine linkage or through a non-covalent interaction between the metal complex and the protein. An alternative method that we envision is the direct substitution of a new metal into a metalloprotein whose active site resembles a typical small molecule ligand. For example, the tri-histidine zinc-binding site in carbonic anhydrase (CA) bears resemblance to the known Tp and Timm ligand classes. Direct substitution of a transition metal into the active site of a protein has the potential to increase the influence of the primary and secondary coordination sphere of the active site over the selectivity of reactions occurring at the metal center. Thus, our initial goal is to develop methods to rigorously characterize the binding and stoichiometric reactivity of abiotic, noble metals within the active site of carbonic anhydrase.

*Accomplishments*

As supported by data collected from activity assays, ICP-OES, ESI-MS, UV-Vis spectroscopy, and $^{15}$N-$^{1}$H HSQC NMR spectroscopy, we have accomplished and characterized the selective binding of multiple rhodium precursors to the active site of CA, while avoiding metallation to the protein surface. Using ICP-OES and activity assays as preliminary indicators of Rh binding, we found that the Rh precursor structure, the equivalents of Rh, and the pH of the buffer were all factors that influenced the location and ratio of Rh binding. The precursors identified to have the best conversion were $[Rh(nbd)_2]BF_4$, Rh(COD)(acac), and $Rh(CO)_2(acac)$, which each reduced the recoverable native activity of the CA by at least 80%. Native nanospray ESI mass spectrometry was used to identify a discrete complex of CA, Rh, and a single norbornadiene ligand, formed upon the addition of 1 eq. of $[Rh(nbd)_2]BF_4$. To conclusively locate the site of Rh-binding, we have generated $^{15}$N-labeled carbonic anhydrase. One-bond $^{15}$N-$^{1}$H HSQC experiments allow an assessment of which histidines are bound to Rh and which are free. As shown in Figure 1, different occupancies of the active site are obtained by the reaction of apo carbonic anhydrase with different Rh precursors, and nearly full occupancy of the binding site is gained when just 1 equivalent of either $[Rh(nbd)_2]BF_4$ or $Rh(CO)_2(acac)$ is added. UV-Vis spectra also corroborate the formation of rhodium-protein complexes.

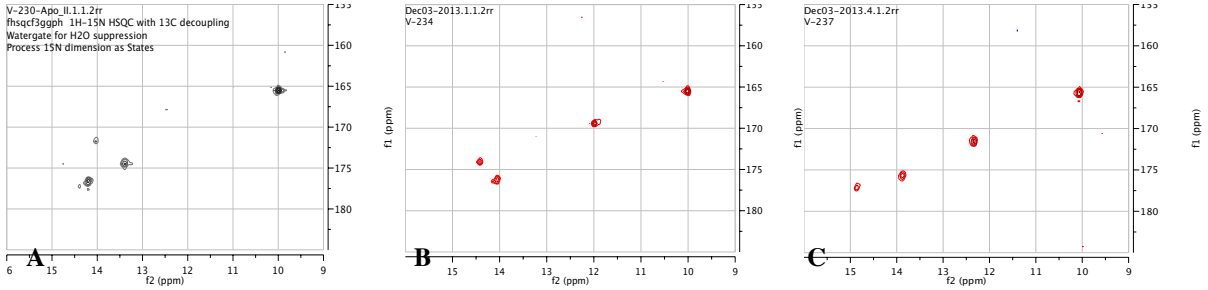


Figure 1. Histidine region of 1-bond $^{15}$N-$^{1}$H HSQC spectra of 3*His-CA (270uM CA, 50mM MES, pH =5.5) with and without Rh-adducts. F1 = $^{15}$N, F2 = $^{1}$H. δ1 Nitrogen signals of two active site and two buried histidine residues are observed. Fast N-H exchange excludes other residues. **A.** Apo 3*His. **B.** Apo-3*His + 1 eq. $[Rh(NBD)_2]BF_4$. **C.** Apo-3*His + 1 eq. $Rh(CO)_2(acac)$.

New Algorithms for Performing and Analyzing Large Scale Electronic Structure Calculations
Principal Investigator(s): Head-Gordon, Martin

*Project Description*

There are two synergistic purposes to this project. The first objective is to improve our ability to understand the physical factors that are responsible for intermolecular interactions. Electronic structure calculations are nowadays capable of calculating intermolecular interactions nearly as accurately as they can be measured. However such calculations by themselves do not provide any understanding of why the interactions have the magnitudes that they do. Methods for this purpose are called energy decomposition analyses (EDA). It is an important open challenge to design improved EDA's, which we take up in the first part of this project.

The second objective of the project is to develop new, more efficient numerical methods for solving the equations of electronic structure theory for molecular clusters (i.e. the same systems for which we are seeking new EDA's). There should be natural connections between new EDA tools, and the problem of computing those interactions more efficiently than has been hitherto possible. We believe the combination of improved EDA's for analysis together with lower-scaling (i.e. more computationally efficient) algorithms for calculating the interactions will be a potentially significant step forwards in quantum chemistry.

*Accomplishments*

Over the past year, our first significant accomplishment was defining and implementing approaches that yield well-defined lower and upper bounds to polarization in the overlapping regime. Our results show that the gap between upper and lower bounds for interesting model systems such as ion-molecule and hydrogen bonded dimers is small enough to be useful. This is exciting and encouraging, and formed the basis of the first publication reported during this year. Furthermore, unpublished results also suggested that the reduced basis used to describe polarization could also be employed for full electronic structure calculations including all interactions (i.e. not just polarization but also charge transfer) with nearly complete recovery of the exact energy. We are now exploring whether or not even tighter bounds are attainable, and how to adapt our procedure to yield the polarization term in what will be a new EDA.

We have also been investigating how to extend EDA's to wave function based correlation methods. Initial computational explorations have led to a very interesting discovery that is the basis for the second publication reported below. The electron-electron correlation energy is negative, and attractive dispersion interactions are entirely a correlation effect, so the contribution of correlation to intermolecular binding is commonly assumed to be negative, or binding in nature. However, there are many cases where the long-range correlation binding energy is positive, and therefore anti-binding, with certain geometries of the water dimer as a prominent example. The correlation anti-binding has its origin in the systematic overestimation of dipole moments by Hartree−Fock theory, leading to a reduction in the calculated electrostatic attraction upon inclusion of correlation. Thus, energy decomposition analyses that include correlation but do not correct mean field electrostatic terms are sub-optimal, especially those that describe all of the correlation energy as dispersion. Furthermore methods such as attenuated second order Møller-Plesset theory, which smoothly truncate long-range electron correlation effects to zero, can, paradoxically, have the correct long-range behavior for many intermolecular interactions. This result has major implications for the correct design of a correlated EDA, which we are currently exploring.

# ELECTROSTATIC NANOSCALE-MESOSCALE COUPLING TO DISCOVER DESIGN RULES FOR ENERGY MATERIALS

Principal Investigator: Teresa Head-Gordon

*Project Description*

The purpose of this project is to develop a powerful theoretical framework capable of discovering general design rules based on nanoscale properties of molecule shape and size, charge distributions, ionic strength, and concentration to influence the mechanism, percolation, morphology, and rates of assembly over mesoscale time and lengthscales. The ability to control for structure and dynamics of the assembly process is a fundamental problem that, if solved, will broadly impact basic energy science efforts in nanoscale patterning over mesoscale assemblies of block copolymer materials, polyelectrolyte organization at solid or liquid interfaces, forces governing multiphasic soft colloids, and growth of quantum dots in polydisperse colloidal medium. Fundamental design rules applied to complex and heterogeneous materials are important to DOE mission science that will enable next generation fuel cells, photovoltaics, and light emitting device technologies.

Coarse-graining (CG) and related multiscale methods can be highly beneficial to current interests in mesoscale design rules, i.e. how to control large-scale spatial organization or dynamical events by replacing the explicit potential and forces with an implicit influence of the missing degrees of freedom on the association dynamics of multiple nanoscale entities. Our CG approach, and our proposed extensions to genuine multiscale models, can be generically applied to any materials problem involving electrostatic nanoscale-mesoscale coupling. To accomplish this we have derived the first completely general analytical solution to the linearized Poisson Boltzmann equation (LPBE) for computing the screened electrostatic interaction between arbitrary numbers of nanoscale spheres of arbitrarily complex charge distributions, separated by arbitrary distance (i.e. concentration). This analytical solution in turn serves as the foundation for our semi-analytical LPBE solver for any nanoscale shape. The level of abstraction of the LPBE theory allows us to develop general design rules for controlling mesoscale outcomes, but with enough chemical detail to connect to molecular properties of shape, size, charge distributions, ionic strength, and concentration that can be directly tested and developed in the laboratory.

*Accomplishments*

We have extended the applicability of our LPBE solver, Poisson Boltzmann Semi-Analytical Method (PB-SAM), by deriving force and torque expressions that fully account for mutual polarization in both the zero and first order derivative of the surface charges, and have embedded them into a Brownian dynamics scheme to look at electrostatic-driven mesoscale assembly and kinetics (1). We demonstrated the capabilities of the PB-SAM approach by simulating the protein concentration effects on the biomolecular rate of association of barnase and barstar, under periodic boundary conditions and evaluated through mean first passage times. We applied PB-SAM to the pseudo-first order reaction rate conditions in which either barnase or barstar are in great excess relative to the other protein (124:1); this can be considered a specific case in which the PB-SAM approach can be applied to crowding conditions in which crowders are not inert but can form interactions with other molecules. The efficiency of our PBE solver is a completely new way to calculate rate constants within the LPBE framework and applied to very large systems with a level of unprecedented accuracy. We are now extending PB-SAM to improve polymer electrolyte membrane used in fuel cells, by improving selectivity for protons and reducing the electro-osmotic drag coefficient to overcome flooding that inhibits oxidation.

**Developing f-electron Soft X-ray Spectroscopy Simulation, Theory, and Experiment for Clean Energy Materials**

Principal Investigator(s): David K. Shuh, David Prendergast, and Andrew Canning

*Project Description*

The objectives of this project coupled experiment to the development of robust density functional theory (DFT)-based simulation tools for soft x-ray absorption spectroscopy (XAS) of f-electron systems and made these user-friendly methods available. Examples of where soft x-ray spectroscopy at the Advanced Light Source and the corresponding theory and simulation understandings have been used to design improved lanthanide (Ln) materials, were for energy applications such as photovoltaics, batteries and lighting, as well as to actinide (An) materials such as potential separations ligands and advanced materials for nuclear energy. Selected candidate materials identified through a materials design process have been synthesized and characterized, followed by soft XAS and comparison to theory/simulation. New DFT-based methods have been developed for understanding soft XAS of Ln and An materials. Theory capabilities coupled with experiments enabled the design of new f-electron materials and/or modification of existing materials related to clean energy technologies, that perform better and are more economically viable than existing materials. Coupled with simulation and theory, soft x-ray f-electron priorities were established for current and future ultrafast light sources.

*Accomplishments*

The combination of the existing DFT-based computational methodology for simulating the X-ray absorption spectra of low-Z ligand elements (such as carbon, nitrogen, oxygen) was augmented with a self-consistent procedure to evaluate on-site Hubbard-like localized electron correlation at an actinide atom (so-called DFT+U) and this successfully reproduced spectra at the N K-edge of BBP-$UO_2$ complexes. Contributions to the structural understanding of the non-planarity of BBP-$UO_2$ complexes were made using ground-state DFT calculations, which indicate that the effect is due to steric repulsion between ligands on opposite sides of the uranyl cation and not particularly due to electronic structure effects.

Several new actinide complexes that are potentially the first transuranic single molecule magnets were synthesized and structurally characterized prior to measurement of their detailed magnetic properties. These included Np and Pu monomers and dimers. Theoretical studies of these actinide-based molecular complexes with interesting magnetic properties were made using DFT+U, and electron counting rules established to explain switching from ferromagnetic to antiferromagnetic coupling in actinyl dimers via super-exchange through oxygen ligands.

Several novel porous framework (PAF) materials were synthesized, characterized, and their separation properties towards f-elements (lanthanides and actinides) determined. The electronic structure and morphologies of the PAF materials, both pristine and with sorbed f-elements, were determined by soft X-ray spectromicroscopy utilizing the ALS. The separation characteristics of the initial PAF materials for f-elements is excellent.

The Materials Project software has been used to predict new f-electron materials relevant to clean energy and advanced nuclear energy, in particular Eu materials. We have been looking for new oxide and nitride Eu systems with possible applications in energy efficient lighting. Using the structure predictor a new tetragonal structure for $EuO(NO_3)$ was found. First principles calculations have been performed to determine the properties and suitability for applications of some of the new materials.

**A Multi-Investigator Approach Towards Chemoenzymatic Catalysis**

Principal Investigator(s): F. Dean Toste, Kenneth N. Raymond, Robert G. Bergman

*Project Description*

We intend to develop processes that merge biological catalysts such as enzymes with soluble transition metal catalysts, offering opportunities to carry out reactions that would not be possible using either type of catalyst independently. Despite the potential for innovation encompassed by this approach, relatively few examples of chemoenzymatic catalysts exist. This is in part due to the fact that enzymatic and chemical catalysts often operate under drastically different conditions. Most notably, enzymatic catalysts tend to work best in aqueous environment, while many of our most powerful homogenous catalysts prefer organic solvents and require the exclusion of moisture. In this program we will investigate a novel approach towards this goal: chemical catalysts are transformed into 'nanozymes' by incorporation into a supramolecular assembly. As such they are able to mimic many of the features of enzymatic catalysts, including the ability to operate in aqueous environments.

Towards this goal, we propose to investigate reactive metal cations contained within water-soluble molecular tetrahedra as catalysts. More specifically, gold catalysts will be initially investigated. Like many cationic metal complexes, these catalysts have only modest stability and activity in aqueous solution and therefore, their application into chemoenzymatic processes requires stabilization of the catalysts towards water. We envision that this can be accomplished with an aqueous host-guest complex. We propose to combine theoretical studies with our experimental work, in order to provide a strong foundation for future catalyst development. As such, we believe that the concepts and insights developed in these studies can be applied to other reactive catalysts systems, with the ultimate goal of developing a tool-box of water-active homogenous catalysts that can be coupled with enzymatic processes.

*Accomplishments*

We showed that cationic phosphinegold(I) complexes are encapsulated by an anionic $Ga_4L_6$ tetrahedral host in water and employed as a catalyst (up to 67 turnovers) for the intramolecular hydroalkoxylation of allenes and that the catalytic activity of was *increased* 8.7 fold by encapsulation. We also deomstrated that the encapsulated gold(I) complex catalyzed the cycloisomerization of enynes, and by excluding water, produced a product different from that observed with the unencapsulated catalyst. This phenomenon was also more dramatically shown in the catalytic cyclization of monoterpenes.

Having established the viability of the encapsulated gold complexes as catalysts, we have examined their ability to operate in concert with enzymes. We reported the gold(I) complex encapsulated in a $Ga_4L_6$ tetrahedral supramolecular cluster was well-tolerated by the enzymes and in some cases show improved reactivity and selectivity relative to the free cationic guest. We infer that in these cases, encapsulation of organometallic complexes prevents diffusion of these complexes into the bulk solution, where it can interact unfavorably with biological catalysts.

The supramolecular host is a chiral assembly as a result of the three catecholates coordinated to a metal vertex in either a right ($\Delta$)- or a left ($\Lambda$)-handed helical fashion. Recently we have reported a strategy to introduce point chirality on the edge ligand using chiral amide linkages. We have demonstrated that the resulting chiral enantiopure assemblies are capable of catalyzing and controlling the selectivity in the intramolecular addition of alkenes to aldehydes.

# Oxidative Transformations of Organic Aerosol

Principal Investigators: Kevin R. Wilson and Allen Goldstein

## Project Description

Organic aerosols play critical roles in the radiative balance of the atmosphere with far ranging impacts on climate and human health. New molecule-based analytical approaches are required to achieve a fundamental description of the atmospheric oxidation of organic aerosols, which are comprised of thousands of individual molecular species. By combining synchrotron vacuum ultraviolet (VUV) photoionization mass spectrometry (MS) with gas chromatography (GC), a new experimental technique was developed, enabled by this LDRD, to probe the complex photochemical reaction pathways that transform organic aerosol. This approach provides a new way to construct molecule-based descriptions of the oxidation chemistry of multi-component organic aerosols and provide new data that is needed for accurately assessing the impact of particulate pollution on air quality, human health and climate. These measurements form the basis for improving parameterizations of organic aerosol chemistry in computer models in broad support of Carbon Cycle 2.0's goal of understanding, assessing and predicting the environmental impact of fossil energy use.

## Accomplishments

The viability of the proposed GC/VUV-MS technique was demonstrated for the analysis of diesel fuel—a prototypical environmental pollutant whose chemical complexity itself is a stringent test of any new analytical technique. Traditional GC electron impact ionization mass spectrometry or two dimensional GC analysis of diesel fuel can identify only a fraction of the molecular species in the fuel leaving a substantial amount of material as an "unresolved complex mixture" (UCM) composed primarily of hydrocarbons. The UCM, a common feature in urban organic aerosols and other environmental samples, has yet to be quantified or described molecularly and originates from the enormous number of possible aliphatic isomers with similar mass spectrometric signatures. The strong molecular ion peak in VUV mass spectra allows new molecular structures previously buried within UCM to be observed and assigned. Alkanes, cycloalkanes, bicycloalkanes, etc. can be resolved and quantified. Furthermore, within a specific alkane series, branched vs. linear isomers are clearly separated and quantified.

We have used this technique for the analysis of primary organic aerosol collected in the Caldecott tunnel (Berkeley, CA.). In this work, unprecedented chemical characterization of primary aerosol was achieved, with a mass closure of 80 ± 30 %. The primary combustion aerosol was characterized by number of carbon atoms ($N_C$), number of double bond equivalents ($N_{DBE}$) and degree of molecular branching. This in depth analysis revealed that lubricating oil is the dominant component of particulate pollution for both gasoline and diesel powered vehicles.

Cyclic alkanes constitute a large fraction of aliphatic hydrocarbon emissions originating from incomplete combustion of diesel fuel and motor oil. To examine the heterogeneous chemistry of this class of compounds, cholestane ($C_{27}H_{48}$) was used as a model system to examine the OH-initiated heterogeneous oxidation pathways using a photochemical flow tube reactor. Our analysis revealed that the first-generation functionalization products (cholestanones, cholestanals and cholestanols) account for up to 70% by mass of the total speciated compounds. 55% of the cholestanones/cholestanals are found to have the carbonyl group on the rings of the androstane skeleton; while 74% of cholestanols have the hydroxyl group on the rings. These results provided detailed insight into the oxidation chemistry of complex molecules at the isomer level, revealing new details about atmospheric oxidation mechanisms.

## An Optimization-based Strategy for Computational Design of Nanoporous Carbon-Zero Materials

Principal Investigator: Maciej Haranczyk

*Project Description*

Our goal is to create a computational framework that will allow the in silico design of metal organic framework (MOF) materials through a strategy based on structure optimization with respect to property. Efficient global optimum search algorithms will be utilized to efficiently navigate the space of possible structures. By performing this search on a broad space of MOFs, we thereby remove limitations on the search space encountered by currently utilized enumeration-based strategies. We plan to explore two approaches. In the first, we abstract molecular models of MOF building blocks as geometrical – or alchemical – building blocks, defined by a number of continuous parameters, which are optimized using gradient-based techniques. In the second, we perform the search in a discrete space of real molecular building blocks and employ Genetic Algorithm (GA)-based search techniques.

Although the proposed approaches are general and can be used to design a MOF material with almost any desired property, our work will focus on properties critical for gas separation and storage. We aim to enable design of materials for carbon capture and natural gas storage. Therefore properties of interest include high surface area, large pore diameters and adsorption properties of gas(es) of interest. Our framework for MOF design comprises three components: (i) MOF assembly module; (ii) rapid property estimation module(s); and (iii) structure optimization control module. The key aspect of each component is modularity: these components can be substituted or extended to include other building block representation schemes, property estimation modules, scoring functions and optimization/search algorithms.

*Accomplishments*

We have developed and deployed a prototype of the optimization-based MOF design approach. As a result we have successfully identified many previously unexplored materials whose internal gravimetric or volumetric surface areas (GSA or VSA) suggest they are promising candidates for gas storage. Moreover, specific design rules for achieving high GSA or VSA have been elucidated from this work. Additionally, we demonstrated the first ever framework to design materials that satisfy multiple objectives such as GSA or VSA.

Our findings were enabled by developing the necessary components of the approach. Our MOF structure assembly component – module (i) – allows for automatic assembly of MOFs from metal and organic building blocks (ligands). The latter are placed in 3D space and connected according to a predefined topology. In our prototype approach, MOF ligands are abstracted as space-filling geometrical shapes; this abstraction enables building blocks to be encoded by their geometric properties: ring radii, branch lengths etc.. Initialized with a random set of such properties; module (i) constructs the ligand and assembles the resulting MOF, and module (ii) computes its GSA/VSA. By this abstraction technique, ligands comprising neighboring positions in a high-dimensional geometric parameter space can be automatically identified, and the corresponding MOFs evaluated using the same procedure. Module (iii) can therefore utilize gradient-based optimization to automatically tune these properties. The optimized space-filling MOF designs serve as abstract blueprints, which can be translated into real chemistry, with the resulting frameworks illustrating that MOFs with higher GSA/VSA than the known benchmark materials can be achieved for a variety of topologies.

Next Generation Computing for X-ray Science
Principal Investigator(s) : Xiaoye Sherry Li

Project Description

The goal is to develop new high performance computing (HPC) algorithms, codes, and software tools for the analyses of X-ray scattering data collected at the ALS. In conjunction with the development of new physical principles for analyses of novel scattering data, this approach will provide state-of-the-art analysis capabilities for deducing the structure-function properties of energy-relevant materials that directly advance the goals of Carbon Cycle 2.0. The newly developed HPC tools will consequently lead to increased data analysis productivity and more intelligent design of experiments for rapid scientific discovery at the light sources.

We will develop the massively parallel GISAXS and Reverse Monte Carlo codes on the Cray XE6 at NERSC and Titan at OLCF. We anticipate several orders of magnitude speedups through hybrid parallelization and extensive code optimization. We will develop a user-friendly interface by leveraging the other software tools developed at LBNL, such as NERSC Web Toolkit (NEWT) and the LDRD project "SPOT Suite" for end-to-end solution for light source data.

Accomplishments

We developed a flexible massively parallel GISAXS simulation software HipGISAXS based on the Distorted Wave Born Approximation (DWBA). The software computes the diffraction pattern for any given superposition of custom shapes or morphologies in a user-defined region of the reciprocal space for all possible grazing incidence angles and sample rotations. This flexibility allows study of a wide variety of possible polymer topologies and assemblies embedded in a thin film or a multilayered structure. HipGISAXS is capable of computing GISAXS images for highly complex structures with high resolution. The single-node GPU code is 200x faster than the sequential code. The multi-GPU code achieved additional 900x speedup on 930 GPU nodes, and the multi-CPU code achieved over 4000x speedup on 6000 nodes.

We also developed a parallel inverse modeling code HipRMC for morphology recovery. This requires fitting of a large number of structural parameters using the raw scattering images generated in the experiments with different sample configurations. We use the Reverse Monte Carlo (RMC) method to iteratively obtain the structure that matches the experimental data. We parallelized this algorithm on both clusters of multicore CPUs and GPUs, and obtained 282x speedup using 256 CPU nodes and 222x speedup using 256 GPU nodes, and the GPU code is order of magnitude faster than the CPU version.

The end result is tremendous increase of analysis throughout: The forward simulation used to take 20 seconds per frame, now HipGISAXS takes merely 0.05 seconds. The old RMC Matlab code used to took 240 minutes per frame, now HipRMC takes 15 minutes for 100 frames. We released HipGISAXS software to the public in June 2013, which is gaining wide use among the scientists in the world. In October 2013, we held the first hands-on training session to teach the scientists how to use HipGISAXS. We will release HipRMC software in the near future.

# *Nyx*: The Lyman Alpha Forest Cosmology Simulator
## PI: Peter Nugent

### Project Description

In recent years astrophysics has undergone a renaissance, transforming from a data-starved to a data-driven science. A new generation of experiments including Planck, BOSS, DES, DESI & LSST will gather massive data sets that will provide more than an order of magnitude improvement in our understanding of cosmology and the evolution of the universe. Given that several of the next generation cosmology experiments are focused on baryon acoustic oscillation (BAO) measurements, the time is ripe to expand and channel the current expertise of LBNL's Computational Cosmology Center to tackle this promising area of research.

To properly simulate the observations from the DOE-led SDSS-III project BOSS and the proposed DESI surveys, we need a fair statistical representation of our universe. Our ultimate goal is to calculate absorption spectra caused by neutral hydrogen in the cosmological environment, with all the relevant physical processes. This requires more than 1000 trillion particles in a single run. At 100 bytes per particle we need $10^5$ TB RAM. Such memory-limited computations can be performed only on future Exascale systems. Our approach is to modify the Compressible ASTROphysics code – CASTRO – to perform these simulations. This new code is called *Nyx*, primordial goddess of the night. *Nyx* is a new, multi-dimensional, Eulerian AMR radiation-hydrodynamics code designed for astrophysical simulations.

### Accomplishments

In the past year this effort has seen an incredible push forward and some remarkable results. Due to the tremendous interest in BAO cosmology we have attracted a strong suite of collaborators from UC Berkeley, Heidelberg University and Brookhaven National Laboratory. During this time we have been able to improve the code for a wide variety of astrophysical calculations and to mine the output of our simulations for direct comparison to observation through a BoxLib reader in the *yt* software package which allows us to perform most, if not all, of the visualization and cosmology analysis for the data produced by *Nyx* (see http://yt-project.org). This effort has been essential in carrying out code comparisons as well as verification and validation of our cosmology simulations.

Nyx has been designed to efficiently utilize tens of thousands of processors; timings of the code this past year on up to almost 100,000 processors on NERSC's Hopper supercomputer. It show excellent weak scaling behavior. Validation of Nyx in pure dark matter runs and dark matter with adiabatic hydrodynamics has been presented in a paper in the *Astrophysical Journal*. Our next paper, just submitted, has studied resolution and convergence for simulations relavant for Lyman-$\alpha$ forest and has show how *Nyx* is currently the best code available for this research. Future papers will give greater detail on the implementation in Nyx of source terms, and will present results from simulations incorporating different heating and cooling mechanisms of the gas, as needed for increased fidelity in different applications. Scientific studies already underway with Nyx include studies of the Lyman-$\alpha$ with direct comparison to n-body codes. In addition, we plan to extend Nyx to allow for simulation of alternative cosmological models to $\Lambda$CDM, most interestingly dynamical dark energy and modifications of Einsteins gravity.

# High-Performance Parallel Graph-Analysis for Key Genomics Computations

Principal Investigator(s): Leonid Oliker

*Project Description*

Many of biological datasets, including genome assembly and protein clustering, can be conveniently modeled as large-scale graphs and analyzed using state-of-the-art bioinformatics graph algorithms. However, biologists face significant challenges in effectively leveraging supercomputers due to the complexity of parallelizing these classes of computations on distributed memory systems. The goal of this project is to deliver unprecedented computational capability to large-graph analytics for key bioinformatics applications, via the development and integration of flexible and high-performance parallel graph software packages.

Our work will target two specific high-level genomics computations, in the areas of genetic mapping, phylogenomics, allowing us to significantly advance the analysis capabilities in those areas while simultaneously driving the development of parallel graph and data analysis software. By collaborating closely with computational biologists at the Joint Genome Institute who are directly engaged in solving specific data-intensive problems, we will ensure relevance of new tools to state-of-the-science genomics problems. Furthermore, the flexibility of our software will enable the evolution of simulation capability, allowing domain scientists to easily tune parameters, switch between various algorithms, and use different graph representations with varying amounts of annotation data on edges and vertices.

*Accomplishments*

Our most significant accomplishment has focused on improving gene mapping efficiency and accuracy. High-throughput "next generation" genome sequencing technologies have out-paced Moore's law, producing a flood of inexpensive genetic information that is invaluable to research, ranging from the development of new and improved crops to understanding the genetic variation that underlies cancer. However, this flood of new information presents a fundamental new challenge to genetic mapping, the process of assembling genetic data, which is a core operation in genomics research. The current generation of genetic mapping tools were designed for the small data setting, and are now limited by the prohibitively slow clustering algorithms they employ in the genetic marker-clustering stage of automatic genetic map construction.

Our recent work presented a new approach to genetic mapping based on a fast new clustering algorithm. Our theoretical and empirical analysis shows that the algorithm can correctly recover linkage groups. Using real-world and synthetic data, we demonstrated that our approach is able to quickly process orders of magnitude more genetic markers than existing tools and that by exploiting domain knowledge, it is able to out-perform more generic approaches based on spectral clustering. Finally, we demonstrated that by scaling to the available sequence data we are able to improve the quality of genetic marker clusters, leading to a higher quality ultra-high-density genetic map that can be used to improve genome assemblies and map quantitative traits.

**Interlinkage of Cross-Disciplinary Mathematical Technologies**

Principal Investigator(s): J. Donatelli, M. Haranczyk, S. Marchesini, B. Preskill, R. Saye, D. Ushizima, J.A. Sethian

## Project Description

Applied and computational mathematics can steer discovery in the DOE facilities, providing advanced algorithms and computational methodologies to efficiently extract data, interpret results, and guide experiments. Given the high cost of these facilities, often in the tens and hundreds of millions of dollars, modest investments can create sophisticated state-of-the-art mathematics that will yield tremendous cost savings in terms of numbers of experiments, data extracted, and materials used. As examples, new mathematics will be instrumental in providing tools to reconstruct structure and properties from synchrotron light sources, direct the hunt for new materials for batteries and gas separation, and model and optimize steps in the production of biofuels. We have been building mathematical models, algorithms, and technologies to attack problems within LBNL and DOE that are brand-new, and require core advancements, with particular focus on (i) New Reconstruction Methods for the Advanced Light Source; (ii) Fast Throughput Screening in the Design of New Materials; (iii) Mechanical Modeling of Biological Cell Clusters; and (iv) Advanced Imaging Capabilities in Material Analysis.

## Accomplishments

Following on our FY12 work, we have accomplished the following:

In new reconstruction methods, we have focussed on nanocrystallography, grazing incidence small angle scattering (GISAXS), and ptychographic analysis. In x-ray nanocrystallography, we have built a new multi-step computational technique to solve the twinning ambiguity. We built an algorithmic framework to determine crystal size, incident photon flux density, and orientation in the presence of the indexing ambiguity. We showed that phase information can be computed from nanocrystallographic diffraction using an iterative phasing algorithm, without extra experimental requirements, atomicity assumptions, or knowledge of similar structures required by current phasing methods, and then tested the approach on simulated data with parameters and noise levels common in current experiments. In GISAXS, we build a high performance simulation code based on the discrete wave Born analysis, which is orders of magnitude faster than before. In ptychographic analysis, we have developed a new, fast reconstruction method, and begun moving the code to a high performance computing environment.

In biological modeling, we built a complete simulation of cell cluster dynamics, evolving under the combined effects of hydrodynamic, elastic, and geometric forces. We have been adding inelasticity and adhesion to the computational infrastructure.

In new materials design, we have built new optimization algorithms to assemble components to meet design objectives. As an example, we designed record-breaking high surface area materials.

In materials analysis, we have developed a new method for tracking multiphase interfaces in materials, including applications to grain metal boundaries, liquid and solid foams, and in semiconductor failures. We have applied these techniques to image segmentation for rebuilding 3D structure from materials sampled at the ALS using micro-tomography (beamline 8.3.2). We we were able to simultaneously separate three different phases in materials analysis for carbon sequestration studies.

We have been in involved talks with DOE about long-term support for mathematics in service of the DOE facilities.

**Modeling Subsurface Reactive Transport Processes From Mineral-to-Pore-to-Continuum**

Principal Investigator: David Trebotich

*Project Description*

The overall objective of this project is to develop new approaches for representing pore scale processes in Darcy continuum scale numerical models of subsurface reactive transport. We hypothesize that a quantitative, mechanistic understanding of coupled physical and chemical processes at the pore-and-grain scale is possible, and that such an understanding can form a rational basis for upscaling fluid dynamics and geochemical kinetics to field scale systems. By carefully understanding processes at the pore scale, the ultimate goal of this research is to bring such knowledge to bear on the macroscopic scale of a reservoir, which is the relevant scale for carbon sequestration and other important subsurface flow problems such as environmental remediation and storage of nuclear wastes.

The foundation for the multiscale approaches presented here is highly resolved pore scale simulation data. To this end, we have previously developed a high performance simulation capability, called Chombo-Crunch, that models pore scale reactive transport processes associated with carbon sequestration at unprecedented scales. With this capability we have been able to show the effect of pore scale flow on average geochemical reaction rates using straightforward volume averaging over the domain volume. In general, we would expect that volume averaging does not retain heterogeneity in the flow. However, volume averaging can be used *locally* where it is appropriate without reservation. The question is what is the 'local' scale relative to a representative elemental volume (REV) for the continuum Darcy model? It would be of no surprise to discover that highly resolved pore scale data were to violate Darcy assumptions and display non-Fickian behavior, which our preliminary results indicate.

*Accomplishments*

We have been able to establish high resolution pore scale simulation as a credible basis for upscaling. Our direct numerical upscaling approach is to resolve the entirety of a continuum scale domain with pore scale resolution and to use flux-weighted averaging together with finite volume techniques based on the discrete divergence theorem on a local volume to obtain upscaled parameters like permeability. As an example, we simulated steady-state flow and reactive transport in a 2D heterogeneous continuum domain of 1 meter in length packed with approximately 100,000 spheres. We distributed each subdivided box of $256^2$ grid cells of the domain on each of 16,384 cores using the NERSC Cray XE6, Hopper. The grid resolution was 7.6 microns. This domain decomposition produces the sweet spot for load balancing where each subdivided box in the domain corresponds to a local volume that can be correlated to a representative elemental volume (REV) of the continuum Darcy model. We will continue to explore the relationship between the local volume and a REV and ultimately demonstrate the necessity of representing pore scale processes in continuum scale models using direct numerical upscaling.

In addition, we are using high resolution pore scale data and direct numerical upscaling to guide and verify more selective approaches to upscaling. In these more formal multiscale methods we are relying on adaptive modeling and/or statistical characterization of the pore space to sample pore scale data. Examples include adaptive model refinement and information theory.

# TOWARDS AN END-TO-END SOLUTION FOR LIGHT SOURCE DATA

Craig E. Tull [1], Jack Deslippe [2], Alexander Hexemer [3], David Prendergast [5], Brian Tierney [4] (1- CRD, 2- NERSC, 3- ALS, 4- ESNet, 5- MSD)

*Project Description*

Recent improvements in detector resolution and speed and in source luminosity are yielding unprecedented data rates at BES's national light source and neutron source facilities These data rates exceed the capabilities of data analysis approaches and computing resources utilized in the past, and will continue to outpace Moore's law scaling for the foreseeable future. The national BES software landscape is largely ad-hoc and relies heavily on a limited number of experts to handle analysis. The result is that BES beamlines' efficiency and ability to address important scientific questions are diminished. Next Generation Light Source (NGLS) data volumes and the associated challenges will be orders of magnitude larger than seen today at the ALS. The growing consensus within light source scientific communities is that scientific insight and discovery at BES facilities are now being limited by computational and computing capabilities much more than by detector or accelerator technology.

We propose a systematic investigation and design of the light source analysis environment that can provide an end-to-end solution for data access, management, and analysis; will seamlessly integrate with simulation codes; and will present easy-to-use web interfaces with single sign-on tied to ALS users' unique identity. The result of the LDRD will be a functional prototype end-to-end solution for current ALS data, and will be designed to scale to NGLS data rates. This prototype will enable research and development in the critical areas of data intensive computing that need to be addressed to enable large scale photon science at the ALS, other BES national facilities, and eventually the NGLS.

*Accomplishments*

Real-time feedback to during ALS beamtime is a capability critically needed by many ALS beamline users, yet unobtainable for very large data sets. We have developed an integrated, real-time prototype of a system which automatically captures and suitcases metadata and experimental data at the beamline, transfers the dataset suitcase to NERSC, harvests the metadata and launches a suite of processes on NERSC machines, and delivers the results back to the beamline via a NEWT-enabled Science Data Gateway.

This SPOT Suite (https://spot.nersc.gov) has been in constant operation at ALS micro-tomography Beamline 8.3.2 since March 2013, and has processed 1,356 datasets (>16 TB) and launched 346,371 jobs on NERSC resources in realtime. These data are processed and the results delivered via the Science Data Gateway in ~2 hours. This is not as fast, nor are the results as good as achievable by an expert with comparable tools, but is much better than most of the users who produced these datasets could do without expert assistance from a beamline scientist -- something that is not feasible for 1,356 datasets.

We have adopted several standard micro-tomography codes to the HPC environment, and parallelized them for high throughput. Two reconstruction codes are run concurrently on each dataset and the results of both, along with intermediate data products are browsable and searchable within SPOT. Our goal for the second year is to test and improve the prototype for 3 time-resolved, in-situ experiments at BL 8.3.2 and to extend the workflow, data management, and metadata DB to 2 other ALS beamlines.

# QUANTITATIVE IMAGE ANALYSIS FOR COMPUTATIONAL MODELING

Principal Investigator(s): Daniela Ushizima

*Project Description*

Our goal is to build computational tools to support research groups within LBNL and DOE, focusing on algorithms to extract patterns, structure, and quantitative properties from digital images. This is a multidisciplinary effort, aimed at attending the demands from: a) the EFRC, and micro-tomographic images from the Earth Sciences, acquired at the Advanced Light Source Division, LBNL, and b) the LSD and Physical Sciences Oncology Center, and microscopy images, as those acquired at the LSD, LBNL. Important research challenges at these centers are: a) micro-CT of materials for pore scale investigations of multiphase flow, with applications to carbon sequestration and remediation of contaminated sites; b) images of cells for quantification of biological forces at the cellular scale that drive cancer, and microbial communities for addressing multimodal image representation, segmentation and visualization. Common problems of these centers involve: a) quantitative measurement, b) initialization of sophisticated numerical modeling, and c) providing check points for numerical simulations and corroboration of mathematical models with experimental data. Images represent 3D structures of materials and/or cells, sometimes dynamic, often massive and noisy, typically analyzed manually by domain experts, relying on strategic, but repetitive visual inspections of the experimental outcomes to identify patterns. Proposed tools will augment manual observation with automated systematic procedures.

*Accomplishments*

Our most significant accomplishment has been to develop a new library in OpenCL to perform image-processing operations inside the framework ImageJ/Fiji. Our algorithms can use either graphical cards or CPUs for computing image transformations, which are particularly useful when input image stacks are larger than 2 gigabytes. This package has been applied to both simulated intensity images and real FIB-SEM image stacks of breast cancer cells. We are hopeful that this method will be generally applicable to other domains, such as micro-CT, which will greatly aid our future goal of processing and analyzing all the images generated by beamline 8.3.2 at the Advanced Light Source.

We have also succeeded in expanding Quant-CT, a software package that can quickly and easily derive data for large image stacks of micro-CT. We have developed and applied this tool to investigate crack formation in silicon-carbite (SiC) composites for turbines. The goal here is to characterize how fibers break at high temperature, how meandering of fibers influence cracks, and how to differentiate macro-cracks to micro-cracks. We are now testing if additional processing can enable necessary predictions to design materials that will crash gradually as opposed to undergo catastrophic crash.

## COMPUTATIONAL APPROACHES TO UNDERSTANDING ULTRAFAST SCIENCE

Principal Investigator(s): Alexander Kemper, Chao Yang

*Project Description*

During the past few decades, great advances have been made in the field of experimental time domain spectroscopy. With ever shorter laser pulses we have developed the capability of observing the motion of electrons and atoms as they move at their natural time scales. For the first time, it is possible to resolve the unbinding of the collective motion of electrons, such as the switching of single ferromagnetic or ferroelectric domains. At shorter time scales, one can see how electrons move relative to the lattice motion. As a consequence, one can look at the individual processes that bind up the degrees of freedom (charge, spin, orbital, and lattice) that form the basis of emergence. As we have so few tools that can explicitly do this unraveling, any insight that one can achieve from a theory perspective would have tremendous impact on our understanding of many fields of study, such as materials' novel phases (discussed here), but also femtochemistry, which looks at the breaking of chemical bonds, or studies of biological systems that depend upon the nature of charge transfer at metallic sites. The goal of our research is to provide the theoretical basis for understanding the experiments performed, with as few approximations as is possible.

*Accomplishments*

Among others, we successfully studied both the time-dependent electronic momentum distribution and the time-resolved photoemission response. The time-dependent momentum distribution is what could be measured in a pump-probe Compton scattering experiment. In our paper, we propose to use this novel technique to identify characteristic oscillation modes that appear when the electrons are driven into the unoccupied sector of momentum space and decay back towards their equilibrium positions. We showed that depending on the specific location in momentum space, the mode frequencies are directly related to the electronic band energy. Therefore the technique could potentially be used to map out the part of the electronic structure that is invisible to usual equilibrium techniques such as equilibrium photoemission spectroscopy.

In our second publication on this project, we demonstrated another fingerprint of electron-phonon coupling in the time domain, namely its implications for binding-energy resolved relaxation times. These relaxation times can be directly connected with a hallmark quantity of quantum many-body theory, namely the electronic self-energy, which contains information about scattering rates and the importance of various decoherence processes in a solid. In equilibrium, there is no direct way of reliably extracting these scattering rates and connecting them to the strength of the electron-phonon coupling in a unique way, which is why there is a strong variance of possible electron-phonon coupling strengths for instance for cuprate high-temperature superconductors in the literature. Out of equilibrium, the problem has so far been treated only on a phenomenological level assuming some time-dependent quasi-equilibrium of electrons and phonons. In our work, we show how a full nonequilbrium approach treats the problem without any such artificial assumptions and at the same time leads to a deeper understanding of the underlying physics and to richer results.

# Numerical Algorithms and Mathematical Software Tools for Computational Material Science and Chemistry

Principal Investigator(s): Lin Lin and Chao Yang

*Project Description*

The goals of this project are to develop efficient and reliable numerical algorithms and mathematical software tools for computational material sciences and chemistry. Such tools are becoming increasingly important in the design of new materials for harvesting alternative energy and the development of efficient catalyst to separate greenhouse gas from fossil plants. We aim at developing novel, efficient and reliable numerical algorithms and mathematical software tools for electronic structure theory. We particularly focus on the Kohn-Sham density functional theory (KSDFT), which is the most widely, used electronic structure theory for both molecules and condensed matter systems. We also pursue studies beyond standard KSDFT. We develop efficient algorithms for strongly correlated systems, as well as Dirac-Kohn-Sham density functional theory for systems with strong relativistic effect.

*Accomplishments*

We developed efficient numerical algorithms to accelerate the self-consistent field iterations (SCF) for KSDFT, particularly for large scale inhomogeneous metallic systems. The number of iterations can increase rapidly with the system size and makes the large scale electronic structure calculation prohibitively expensive. We developed an efficient preconditioner called the elliptic preconditioner for accelerating the SCF iteration. The computational cost of the elliptic preconditioner is much cheaper than existing techniques, and can efficiently accelerate the SCF iteration when standard SCF iteration techniques would take a large number of steps to converge.

For strongly correlated systems, it has been suggested that the many-body Coulomb repulsive energy of strictly correlated electrons (SCE) provides direct information on the exact exchange-correlation functional in the strong interaction limit. However, existing techniques for computing the SCE state are restricted to spherical atoms and 1D systems, and are not applicable even to the simplest molecules. We developed a nested optimization approach based on the duality principle. The method allows a general treatment of strictly correlated electrons for systems including atoms and small molecules.

The four component Dirac-Kohn-Sham equations require the computation of a large number of interior eigenvalues for a large linear system. Existing approaches rely on discretizing the Dirac-Kohn-Sham equations using a small basis set such as the Gaussian basis set, and solve the resulting linear eigenvalue problem as a dense linear eigenvalue problem. We developed the first efficient iterative method, called the LOBPCG-F method, for solving the fully relativistic Dirac-Kohn-Sham equations. The LOBPCG-F method is easy to implement, and is robust and efficient in studying the relativistic effect in systems containing heavy elements, using a large basis set such as planewaves.

# DEFINING AN ECOSYSTEM TO SUPPORT DATA-INTENSIVE SCIENCE

**Shane Canon**

*Project Description*

Scientists are struggling with a tsunami of data across multiple scientific domains. Emerging sensor networks, more capable instruments, and ever increasing simulation scales are generating data at a rate that exceeds our ability to effectively manage, curate, analyze, and share it. This data overload directly impacts our ability to address problems of scientific and national significance, including problems related to climate, energy, and scientific competitiveness. Unlike the hardware, algorithm and software models that currently exist for modeling and simulation, there is no complete ecosystem around data-intensive scientific computing.

This project explores the needs of data intensive computational scientists and the role that many new, potentially disruptive, technologies can play in accelerating discovery. This requires direct engagement with a broad class of scientists to understand their workflows, algorithms, current challenges, and future needs.

*Accomplishments*

We have explored the needs of data intensive computational scientists and the role that many new, potentially disruptive, technologies can play in accelerating discovery. We have directly engaged with a broad class of scientists to understand their workflows, their current challenges, and their future needs. In addition, we have worked extensively with two data-intensive communities: the Joint Genome Institute (JGI) and Advanced Light Source (ALS). These deep engagements offered an opportunity to build up key success stories that will serve as a model for future applications. The engagements also demonstrated the importance of creating strong partnerships between the application scientists and computer scientists with expertise in data.

We have explored new technologies, both hardware and software based, that will likely play a role in the data-intensive computing ecosystem. Specifically, we evaluated the use of NAND FLASH, the Hadoop software ecosystem, and NoSQL technologies. NAND flash is ubiquitous in today's consumer devices such as phones and cameras and, compared to a regular spinning disk, flash has a large latency advantage for both read and write operations. Therefore, for example, it has very attractive performance characteristics for database operations. Hadoop, the open source implementation of MapReduce, provides a framework for composing and managing highly asynchronous computations that rely on large amounts of data. Cloud applications are increasingly using schema-less (also referred to as Not Only SQL or NoSQL) data stores--which enables the capture of semi-structured data and supports flexible attribute-based searches. NoSQL databases address many of the needs of a data store for storing irregular, less structured, and evolving data schemas. Hadoop and NoSQL databases are extensively used for Web 2.0 data and promise to be critical components of a software data ecosystem. However, our studies show that these tools have some challenges for use in scientific applications and are currently not sufficient for supporting the next-generation data-intensive ecosystem in support of science. Finally, we identified gaps in tools for data management and analyses at scale that are required by next-generation scientific simulations and experiment facilities.

Next Generation Bioimaging
Principal Investigator: David Skinner

*Project Description*

Exponential data scaling in bioimaging, combined with the data fusion demands of increasingly multi-modal imaging approaches, require R&D in computational bioimaging solutions which extend the ways in which scientists can leverage image based data. Bioimaging is leaving an era of images-as-results and entering an era where results come in the form of biological models built on massive gigapixel images and vast image collections. These models require scalable *analysis, integration,* and *dissemination* of image data delivered from advanced bioimaging instrumentation. In Big Data bioimaging, images are the feedstock not the end result of the instruments we use to observe biological systems. The NGBI (NextGen Bioimaging) LDRD prototypes Big Data bioimaging methods in the context of biofilms, also known as microbial communities (Auer) as well as the Protein Atlas fluorescence microscopy project (Sudar). Biofilms are of high importance to the Department of Energy, due to their dominance of microbial lifestyle and their significance in microbial mediated processes. Protein expression and its spatial localizations studied by high-throughput automation promise a detailed understanding the proteome. NGBI is co-designing a modular web-based computing and data strategy with these two projects and a plan to extend this capability to other projects in Big Data bioimaging.

*Year 1 Accomplishments*

- Deployed NGBI gateway infrastructure and service to 35 LBL and UCSF scientists. The gateway has been popular with Auer and Sudar contacts as well as 22 others who have adopted the web-based approach for electron and fluorescence microscopy workflows.
- Large scale analysis: Volume of 40 microns by 40 microns by 100 microns containing ~10,000 bacteria and metal deposits was segmented automatically, allowing quantification of metal deposited by a microbial community. (Auer)
- Benchtop integration: Protein Atlas is integrated at the scope, custom interface. (Sudar)
- Complex systems: eukaryotic tissues, accurate montaging 2D high-res images & 3D image stacks. ~ *Gigapixel image dataset (800,000px by 600,000px) ~50GB*
- Parallel computing: XXXJC (what's the largest scale thing we've done?)
- Talk and Poster submitted to Keystone Symposium: Big Data in Biology.

**Developing a mechanistic high-latitude biological soil carbon and nitrogen cycle module for site, regional and global land models.**

Principal Investigator: Nicholas Bouskill

**Project description:**

This LDRD integrates existing ESD expertise in ecosystem modeling and environmental microbiology to develop a modeling capability for the carbon (C) and nitrogen (N) cycle in high-latitude soils. High-latitude permafrost soils underlie approximately 26 % of terrestrial ecosystems and have the potential to significantly impact the future balance of Earth's C and N cycles. Several models suggest that up to 90 % of the near-surface Arctic permafrost could thaw by 2100 affecting the structure and function of the microbial communities that mediate the majority of biological C and N cycling. These thermal, hydrological, geochemical and biological changes could lead to substantial increases in atmospheric $CO_2$, $CH_4$ and $N_2O$. The efflux magnitudes of these gases from thawing permafrost are largely dependent on complex feedbacks centering on the *in situ* diversity of C- and N-cycling microorganisms, the availability of N, and the physical changes that occur as permafrost thaws. Therefore, the development of a framework for simulating the emergence of microbial community structure based on a few physiological and genomic traits is a critical first step towards predicting how microbial communities will respond to the geochemical, thermal and hydrological changes accompanying permafrost thaw. A further outcome of understanding community emergence is the accurate prediction of rates (e.g., decomposition or $N_2O$ production) that is a consequence of the emergence of particular microbial communities.

**Accomplishments:**

Research over this part year has focused on one of the main goals of this LDRD, the integration of microbial trait-based modeling into microbial ecology field experiments. This approach broadens the tools available to explain field results, address current hypotheses and develop new ones. To this end we collaborated with researchers from the University of Lyon and Stanford University to apply our modeling approach to a long-term ecosystem experiment examining the response of nitrite-oxidizing bacteria (NOB) to multi-factorial global change scenarios. We parameterized the model using trait-values taken from the field and evaluated whether responses observed in the field, in terms of changes in community composition and N-cycling rates, to perturbation (i.e., warming, N-addition, moisture change) could be reproduced and explained by the model. We were extremely successful in reproducing field results and demonstrating the hitherto unappreciated importance of a mixotrophic NOB (i.e., an NOB demonstrating both autotrophic and heterotrophic strategies).

This framework is being further developed to represent the more complex aspects of heterotrophic respiration. Heterotrophs are responsible for the vast majority of C-cycling in soils and the decomposition of organic matter to $CO_2$. Our approach accounts for the more complex cellular thermodynamic balance of coupling different electron donors and acceptors and physiological trade-offs that determine the growth of biomass. This model will also simulate denitrifying bacteria, providing us with the capacity to represent the nitrogen cycle across scales.

**Integrative Mapping of Soil Heterogeneity at the Microbial Scale**

Principal Investigator(s): PI: Eoin Brodie; Co-PIs: Peter Nico, Janet Jansson, Hoi-Ying Holman, Margaret Torn, Jonathan Ajo-Franklin, Bill Moses, Jim O'Neil, Manfred Auer, Trent Northen, Tanja Woyke, Susannah Tringe and Dylan Chivian

*Project Description*

The aim of the project is to develop a predictive understanding of soil biochemistry by determining how μm-scale physics, chemistry and biology interact to control C and N biogeochemical cycles in soil. Most of our current knowledge of soil biogeochemistry is based on bulk analyses, and fine scale spatial (nm-μm) microbial interactions are often overlooked. Soils provide many valuable ecosystem services from carbon sequestration to food production. Studying soil physical, chemical and biological heterogeneity at a scale relevant to microbes will improve our understanding of the factors that regulate microbial activity in soils.

We aim to discover a set of universal interactions between microbial functions, soil chemistry and physical properties that are deterministic on biochemical cycles. We are currently focusing on $CH_4$ and $NH_3$ oxidation in soils which are important contributors to C and N fluxes in many ecosystems yet are poorly understood due to their spatial heterogeneity. This project integrates different methods and technologies to characterize biochemically active $CH_4$ and $NH_3$ oxidation "hot-spots" and to develop models to determine factors governing microbial activity in soils.

*Accomplishments*

Our most significant accomplishment to date is the development of an experimental work flow for multi-modal characterization of microbial functional distribution in soils. To detect activity hot-spots in the soils we used short-lived $^{11}C$-$CH_4$ at tracer concentrations to demonstrate real-time methane oxidation along a soil column initially using Radio Phosphor Storage imaging. We also established sterile conditions to sort individual aggregates (1mm to 50μm) from soils. The surface chemical composition of each aggregate has been resolved non-destructively via Fourier Transform Infrared (FTIR) spectroscopy equipped with an ATR (Attenuated Total Reflectance) prism. Based on FTIR spectra aggregates were clustered into groups and further analyzed via X-ray micro/nano-computed tomography (sCMT) and metagenomics. We have developed methods for DNA extraction and sequencing of individual aggregates which enables us to study their microbial metabolic potential and relate that to their physical and chemical components. To our knowledge, to date this is the only successful soil metagenomics study that has been performed at μ-scale and certainly the only attempt to relate metabolic potential to aggregate scale chemical composition. We have tested this experimental work flow on several contrasting soils (Alaskan tundra, Californian grassland and Midwestern Prairie) and successfully analyzed their biogeochemical properties.

We are in the process of integrating these workflow components to address questions of microbial functional partitioning across soil compartments and are beginning to use these observations to inform new trait-based reactive transport models to predict microbial activity and fitness under dynamic environmental conditions. To test these predictions we will manipulate conditions (pH, moisture, redox state, temperature etc.) and monitor changes in aggregate biogeochemical and biological properties. We hypothesize this approach will provide realistic parameters for in-situ microbial kinetics and improve existing models. We expect these data sets will also advance our understanding of microbial fitness, competition and activity at the scale at which microbes interact with their environment.

# High-throughput Isolation and Functional Screening (HIFS) of Microbes Relevant to Today's Carbon Cycling and Bioenergy Needs

PI: Romy Chakraborty

Project description:

The goal of this project is to unravel structural and functional diversity of microbial communities by developing a high-throughput technology that enables rapid isolation and cultivation of microbes based on their metabolic function. We are taking an innovative approach to overcome the bottlenecks that exist in studying 'unculturable' microbes. Microbial isolates provide information about microbial communities and metabolisms that cannot be obtained directly from genomic- dependent efforts alone. We are developing a rapid high-throughput phenotypic screen and isolation tool that will integrate several time-consuming batch culture-based techniques and yield high number of microbial isolates from any environment. This technique will then be employed to elucidate the cultivable microbial community dwelling in the rhizosphere of Switchgrass with a special emphasis on the microbes capable of 'fixing' nitrogen. Plants rely heavily on nitrogen-fixing bacteria living in the rhizosphere to provide them with a form of nitrogen they can assimilate. We will determine the effect of climate change (elevated temperature and elevated salinity) on the rhizobial microbial population of Switchgrass and Tobacco and study the ability of these microbes to survive environmental fluctuations.

Accomplishment:

The high-throughput technique was employed for three diverse environmental samples (soil, groundwater, ocean water) to determine whether a broad range of bacteria could be obtained and cultivated using this approach. We were successful in obtaining several hundred strains from these diverse environments with very diverse metabolisms. From rhizoplane, rhizosphere, meristem and roots of Switchgrass and Tobacco plants (considered as potential energy crops for bioenergy production), we isolated close to one hundred bacterial strains with representatives from Alphaproteobacteria, Gammaproteobacteria, Actinobacteria, Bacteriodetes and Bacilli. These isolations were achieved with very small amounts of starting sample, at a fraction of cost and increased throughput of traditional isolation methods. We performed phenotypic characterization of some of these strains, and majority of the rhizosphere isolates analyzed grew best with simple sugars (glucose, fructose, sucrose) and small organic acids (lactate, succinate, fumarate). From among these isolates, we identified those that were capable of fixing molecular nitrogen, as confirmed by PCR amplification targeting *nif* H gene, and those strains that enhance root growth. We further investigated the response of the isolated strains to conditions of elevated temperature and salinity, two common abiotic stresses found on marginal lands, which are also consequences of climate change. These changing conditions do have an affect on growth of the microbes and would also likely affect their rate of nitrogen fixation. $N_2$-fixing isolates tested showed decreased growth with increased salinity/osmolarity. Most strains grew optimally at 25°C, and showed decreased growth rate with temperatures over 32°C. Thus, the survival and beneficial metabolisms of these strains could be significantly effected in the event of climate change induced increasing temperatures and osmolarity.

# TROPICAL FOREST ECOSYSTEMS UNDER A CHANGING CLIMATE

Jeffrey Chambers (PI)

*Project Description*

Increasing levels of atmospheric $CO_2$ from anthropogenic activities is causing the Earth's climate system to warm resulting in costly societal impacts. However, ~50% of our $CO_2$ emissions are removed from the atmosphere by vegetation and ocean processes, with old growth tropical forests estimated to account for ~50% of the total terrestrial carbon sink. In addition to these direct effects of rising atmospheric $CO_2$ on net atmospheric carbon exchange, changing precipitation patterns and elevated surface temperatures are expected to cause a reduction in the terrestrial sink through vegetation mortality, primarily in tropical forests. Elevated disturbance regimes in tropical forests will result in shifting tree species composition, and commensurate shifts in the atmospheric exchange of mass and energy. This LDRD project will improve representation of these important processes in Earth system models (ESMs), leading to improved climate change predictions for the 21st Century, and is focused on the following three questions:

**Q1**: What are the key uncertainties associated with the old-growth tropical forest carbon sink and how can we improve model treatment of these processes?

**Q2**: How do land models currently treat drought-induced mortality, and what structures are required to improve forest response to altered precipitation patterns?

***Q3***: How will shifts in gap-phase dynamics and community composition under elevated disturbance regimes act to amplify climate system feedbacks?

To address these questions we will build on our existing Berkeley Lab expertise, including (*i*) extensive research activities with the Community Land Model (CLM) and DOE's Earth system modeling (ESM) efforts, (*ii*) new hires with expertise in ecosystem demography modeling, and (*iii*) the PI's 20 years of tropical forest ecosystem field research experience.

*Accomplishments*

This LDRD project started in May 2013. A postdoctoral researcher with extensive experience with ecosystem demography modeling was hired in June (R. Knox), and initial progress has been made addressing questions Q1 and Q3. This includes a sensitivity analysis of a version of the Ecosystem Demography model (ED2; co-developed by R. Knox) to rising atmospheric $CO_2$, and a comparison of that $CO_2$ response to extensive field data from the Central Amazon. The field data includes growth rates and species IDs for over 6000 trees on a 10 ha plot re-inventoried every two years since 1996, providing robust benchmarking for ED2 predictions over this same time interval (Q1). Most of the modeling and analytical work for this first LDRD activity has been accomplished, and a manuscript is in preparation. The ED2 model is also being evaluated with respect to adding a spatial dimension to the patch size of disturbances, which will enable improved simulation of forest carbon cycle responses following disturbances (Q3). In addition, a model development plan is being finalized for integrating ED2 functionality into the larger CLM framework, which will allow evaluation of our LDRD research questions in an ESM environment.

Isotopic Probe of Ion Migration Processes in Li-ion Batteries

John N. Christensen (ESD)
Ian C. Bourg (ESD
Vincent S. Battaglia (EETD)

**Project Description**

Despite the ubiquity of Li-ion batteries, they are not considered a mature technology and the basic science underlying their function is still a matter of intense research. Developments in Li-ion battery and related technologies are driven by the need to produce higher capacity, efficient discharge, and quicker recharge, while maintaining favorable weight/volume ratios, geometric flexibility, long lifetimes, safety and reliability. The migration of ions across the electrochemical system is a key process that affects the energy efficiency, capacity and voltage output of Li-ion batteries. However, the phenomena that determine ion migration rates for processes such as transport through the bulk electrolyte, through the solid-electrolyte interface (SEI), and into the intercalation space of electrodes are still poorly understood. Fractionation of isotopes by kinetic processes provides detailed insight into the pathways and rate-limiting steps of organic chemical reactions and metal aquatic geochemical reactions. Our goal in our research is to take advantage of kinetic isotopic fractionation (specifically isotopic fractionation of $^{6}$Li and $^{7}$Li) to advance the understanding of Li ion transport processes in batteries, and ultimately provide a predictive capability of ion mobility so that materials may be selected to optimize the performance of ion-based batteries.

We take a two-prong approach in our research: (1) laboratory experiments with battery materials (i.e. electrolytes and Li salts) and (2) computer intensive molecular dynamic simulations of ion migration.

**Accomplishments**

We have conducted a series of experiments to measure the isotopic fractionation of Li ions by diffusion through an electrolyte (propylene carbonate (PC)). In these experiments, small volume bulbs containing a solution of Li-bis(oxalato)borate in PC are immersed in a large volume of pure PC that acts as a sink for Li that diffuses from the bulb. These experiments are run for long periods of time, up to several months, in order to magnify isotopic effects. We found that the diffusivity of Li ions in PC is about 4 times faster than published values, but in accord with recent work involving Li diffusion in a similar electrolyte by a different group at LBNL. More significantly, we found a small negative isotopic fractionation, -0.3±0.1 ‰, attending Li diffusion. The small magnitude of the isotopic effect is consistent with strong solvation of Li by PC. The surprising result is that $^{7}$Li appears to diffuse faster then $^{6}$Li. At this stage we speculate that this may be due to quantum mechanical effects, or to a mass dependent effect on ion-pairing.

In the molecular dynamics (MD) simulation component of our study, we tested existing inter-atomic potential models for ethylene carbonate (EC) (a battery electrolyte similar to propylene carbonate (PC), but more extensively studied at the molecular scale). We identified a simulation methodology that gives reasonable predictions of the density and viscosity of pure EC electrolyte. We also developed a methodology for simultaneously predicting the diffusion coefficient and electromigration velocity of lithium ions, and we tested this methodology for Li+ in LiCl aqueous solutions. Molecular dynamics (MD) simulations of $LiPF_6$ in ethylene carbonate (EC) electrolyte are ongoing to determine the influence of Li isotopic mass on the diffusion coefficient and electromigration velocity of lithium.

Effect of Secondary Mineral Coatings on Biogeochemical Processes
Principal Investigator: James A. Davis

Project Description

The goal of the project is to establish a fundamental understanding of how secondary mineral grain coatings affect the rates and equilibria of biogeochemical processes occurring in porous media. We are conducting some of the first investigations that combine controlled reactive experiments with nanoscale characterization of natural and synthetic grain coatings.

Many important reactive phenomena that affect the environmental transport of contaminants occur at the mineral-water interface, including sorption, dissolution, and redox reactions. Fundamental knowledge of these phenomena are primarily based on observations with ideal mineral-water systems, in particular, studies of molecular scale reactions on single crystal faces or macroscopic observations of reactions with pure minerals. However, there is little knowledge of the impact of secondary mineral coatings on reaction rates and equilibria in aquifer sediments. Secondary mineral coatings usually contain multiple phases that depend on local biogeochemistry. The layered structures and variable compositions of the coating regime are important in the development of conceptual models for reactive contaminant transport, because coatings provide reactants, reactive surfaces, and diffusion barriers that may govern process kinetics. New experiments devoted to this topic are needed to advance interpretations of geochemical processes in environmental systems. The research will improve our understanding of how mineral-water interfacial processes affect field scale behaviors of consequence to DOE.

Accomplishments

Progress in 2013 included the completion of laboratory experiments determining the dissolution rates of a crushed and sieved aluminosilicate mineral, bytownite, (formula $K_{0.01}Na_{0.23}Ca_{0.77}Al_{1.75}Si_{2.25}O_8$) in various solutions and the influence of secondary mineral coatings on the dissolution rate.

The research demonstrated the following: 1) coatings on the native bytownite were quickly dissolved when the mineral was suspended in a KCl solution that was undersaturated with respect to bytownite solubility, 2) bytownite dissolution rate (moles/$m^2$/sec) increased significantly in KCl solution as the pH was decreased in an acidic pH range, 3) bytownite dissolution rate was also increased significantly by the addition of $Na_2H_2EDTA$ (EDTA = ethylenediaminetetraacetic acid), and 4) bytownite dissolution was less dependent on pH in the presence of the EDTA ligand.

The research demonstrates that EDTA could be an excellent additive to inject with $CO_2$ during carbon sequestration projects. The EDTA serves as a catalyst that can increase the dissolution rates of aluminosilicate minerals even at the acidic pH values found in waters mixed with the $CO_2$ phase. The enhanced dissolution of silicates is important because the cations dissolved can eventually precipitate as carbonate mineral phases as the $CO_2$ phase dissolves in groundwater, thus sequestering the carbon in the subsurface in a more stable form that will not be transported or leak through caprocks. Although some of the dissolved cations will be initially complexed with EDTA and advected with groundwater away from the injection borehole, metal exchange reactions eventually convert the EDTA aqueous speciation to Fe(III)- and Al-EDTA complexes, thus releasing any dissolved Ca(II), Mg(II), and Fe(II) to be precipitated as carbonate mineral phases.

**CyanoAlkanes:**
**Engineering Cyanobacteria for Phototrophic Production of Advanced Biofuels**
**Principal Investigator: Christer Jansson**

**Project Description:** Photosynthetic organisms, like plants, algae and cyanobacteria, offer the potential to convert sunlight and $CO_2$ directly to transportation fuels, bypassing the need for biomass deconstruction. Cyanobacteria are Gram-negative bacteria and well suited for synthetic biology and metabolic engineering approaches for phototrophic production of various desirable biomolecules, including high-density liquid biofuels such as alkanes and isoprenoids. Many cyanobacteria also thrive in high $CO_2$ levels such as those in flue gas from coal-fired power plants. The main objective of the CyanoAlkane LDRD project is to develop a strong platform for photosynthetic conversion of point-source $CO_2$ to advanced biofuels using freshwater and marine cyanobacteria.

**Accomplishments:** We have produced more than 40 engineered strains of the cyanobacterium *Synechocystis* 6803 (*S*. 6803) with enhanced accumulation of alkanes (Alk+ strains), and of fatty acids (FAs; FA+ strains) as precursors for alkane and FA methylester biosynthesis, and with increased capacity for uptake and assimilation of $CO_2$ (CCM+ strains). By constructing an artificial operon with the fatty acyl-ACP reductase (*FAR*) and fatty aldehyde decarbonylase (*FAD*) genes, constituting the alkane biosynthetic pathway downstream of fatty acid synthesis, we demonstrated a five-fold increase in the endogenous accumulation of alkanes (heptadecanes) in *S*. 6803. We also showed that the artificial *FAR-FAD* operon could direct biosynthesis of heptadecanes and other alkanes in a non-cyanobacterial microorganism. Together with Cheryl Kerfeld and the GEBA-Cyano project at JGI, we have demonstrated the potential for production of a wide array of alkanes by combining *FAR* and *FAD* genes from different cyanobacteria.

To enhance the uptake of $CO_2$ in conjunction with increased carbon sink, we have endowed *S*. 6803 strains with extra copies of the BicA and SbtA bicarbonate ($HCO_3^-$) transporters. Such CCM+ strains demonstrate an augmented uptake of $CO_2$ and enhanced photosynthetic electron transport. In the absence of an increased carbon sink demand, the CCM+ strains demonstrate a massive production of exopolysaccharide substances (EPS), probably as a sign of overflow metabolism. When we engineered BicA to uncouple it from the regulatory switch that turns off the transporter at high $CO_2$ levels, the production of EPS increased even further and the cells suffered from lack of insufficient carbon sink. It is our intent to redirect the carbon flux to alkane biosynthesis in *S*. 6803 strains by combining the CCM+ and Alk+ traits.

Together with Hoi-Ying Holman, we have established synchrotron radiation Fourier transform IR (SR-FTIR) spectromicroscopy as a high-throughput diagnostic tool for real-time, single-cell metabolic analysis of genetically engineered cyanobacteria. SR-FTIR data showed accumulation of functional groups in agreement with the GC/MS/NMR results. Multivariate analysis of FTIR spectra revealed that the different strains were phenotypically segregated, but that the stochasticity in the populations gave rise to a high degree of cell heterogeneity within the population for each strain. We also used SR-FTIR to determine the deposition of EPS on the outer cell surface and also detected EPS released from the cells into the surrounding medium.

**Using Experiments and Numerical Models to Examine Ecosystem and Land Management Interactions with Atmosphere and Climate**

Principal Investigator(s): Lara M. Kueppers

*Project Description*

The overarching aim of the proposed research is to improve understanding of the degree to which ecological and land management processes influence the physical Earth system and feedback to climate change. The specific goals of the current proposal are aimed at evaluating and improving models of land-atmosphere interactions and climate change field experiments intended to reveal ecosystem responses to climate change.

Land surface models are used to represent the properties of vegetation and soils that influence weather and climate through their effects on energy, water and greenhouse gas fluxes. Until recently, land management and cropping systems have not been represented well by these models even though crop growth and management practices have potentially large impacts on many aspects of weather and climate. We are using ground based and satellite observations, including from the ARM site and Ameriflux network towers in agricultural regions to validate and improve a coupled atmosphere-land surface model, WRF-CLM. Such model improvements will improve predictions of weather and climate in agricultural regions, and in regions undergoing changing land management. Initial efforts focused on biogeophysics will lay the groundwork for evaluation and improvement of modeled greenhouse gas fluxes.

Climate change experiments are used to quantify vegetation responses to altered climate states, and mechanisms underlying the responses. Infrared heating is increasingly used to manipulate temperatures. This method has rarely been evaluated in terms of its effects on winter and early spring conditions, nor have comparisons been drawn across multiple sites with the same treatment implementation. We are using data from existing experiments in the Rocky Mountains to examine snowpack and soil responses to the climate manipulations.

*Accomplishments*

A key accomplishment in FY13 has been completing simulations and analysis of WRF-CLM for the continental U.S. using a modified version of the model that includes both irrigation and dynamic crop growth. The comparison to observations using Ameriflux and SGP data, as well as satellite data, revealed excess downward solar radiation mid-continent that coincides at least partially with a dry-soil bias, together contributing to a high temperature bias. Our analysis suggests that the coupled model is not simulating adequate cloud formation. However, by introducing dynamic crop growth and irrigation into the model, the biases were reduced somewhat, highlighting the importance of crop leaf area and soil water content to quantities like evapotranspiration, albedo, and sensible heat flux. A paper describing the model and evaluation is drafted and will be submitted within a month. A companion paper that specifically quantifies the effect of irrigation on heat waves has also been presented at the American Geophysical Union Fall Meeting (December 2013), and will also be submitted in the coming weeks.

In collaboration with Noah Molotch (University of Colorado, Boulder) we evaluated the effects of experimental heating on snow accumulation and melt. Molotch's student ran a snowpack model that agreed remarkably well with observed dynamics, allowing us to use it to infer heater effects on energy and water fluxes between the snow and atmosphere. A paper was submitted to *Journal of Hydrometerology* in FY13, and is now in revision for *Ecohydrology*. We also obtained gap-filled microclimate data from multiple warming experiments in anticipation of growing season analyses.

Interactions among Cloud Processes, Convection, and Climate Change
Principal Investigator: David Romps

## Project Description

Clouds have a significant effect on earth's heat budget. Clouds provide a powerful feedback on climate change, and they have remained the largest uncertainty for almost twenty years in the the study of earth's climate sensitivity. The goal of this project is to characterize the response of atmospheric convection to different states of the large-scale environment. In particular, this project aims to measure the vertical velocities of convecting clouds using stereo photography. For deep convection, there is very little existing data on these vertical velocities, especially over the tropical oceans.

## Accomplishments

In FY13, we have made progress towards extending ground-based stereo photogrammetry of clouds to oceanic settings, where there are often none of the landmarks used in traditional camera calibration. A potential application of these methods is the routine measurement of deep-convective vertical velocities over the tropical ocean. In an initial test of this technique, the method is tested with two off-the-shelf digital cameras situated about one kilometer apart facing Biscayne Bay in Miami. The precision of the stereo reconstruction is studied theoretically, and the accuracy of the reconstructions is validated against lidar and radiosondes.

We have successfully demonstrated that the stereo cameras are able to accurately reconstruct a histogram of cloud-base heights from a single image pair, a task that requires tens of minutes of observation from a cloud lidar. The stereo cameras are also able to accurately reconstruct horizontal winds in cloud layers with a temporal resolution in the range of 30 seconds to 5 minutes, compared to once every 12 hours for a typical radiosonde launch site. With these initial successes, the stage is set to begin measuring convective vertical velocities using these methods.

**Testing Soil Carbon Sequestration Through Gypsum Treatment**

Principal Investigators: Young-Soo Han and Tetsu K. Tokunaga

## Project Description

The purpose of this study is to understand the effectiveness of a proposed method to control adverse effects of increased atmospheric concentrations of $CO_2$ by decreasing rates of $CO_2$ emitted from soils through microbial respiration. Soils comprise the third largest global carbon pool, are readily accessible, and hence are potentially economical managed for C storage. This study is investigating a new strategy for increasing C retention in slightly alkaline soils through addition of calcium sulfates. These moderately soluble amendments can reduce microbial respiration, accelerate calcite ($CaCO_3$) precipitation, and promote soil organic carbon (SOC) complexation on mineral surfaces, but rates of these processes need to understood.

Moderate elevation of soil water osmotic potential from $CaSO_4$ dissolution can slow down rates of microbial decomposition of SOC. Increased $Ca^{2+}$ concentrations in soils with pH > 8 (often found in arid and semi-arid regions), can accelerate calcite precipitation. Calcium also promotes SOC binding onto mineral surfaces, thus diminishes leaching losses of SOC. Flue gas desulfurization gypsum (FGDG, $CaSO_4 \cdot 2H_2O$), a byproduct of exhaust gas desulfurization in coal-fired power plants, is an inexpensive source of calcium. The effects of $CaSO_4$ addition are being tested in laboratory soil columns with and without calcium sulfate-amended layers, and in greenhouse soil columns planted with switchgrass, a biofuel crop. The distributions of carbon in columns have been monitored in gaseous, aqueous and solid phases to understand the effect of adding $Ca^{2+}$ on C distribution in soils. A relatively high fraction of $^{13}C$-labeled bicarbonate has been injected in one column to differentiate the newly precipitated calcite from native soil calcite.

## Accomplishments

Our main accomplishments have been (1) the identification of conditions in which inorganic and organic carbon sequestration is practical in semi-arid and arid soils, (2) development of a method for measuring the total carbon balance in unsaturated soil columns, and (3) the quantification of different pathways for soil C sequestration in response to $CaSO_4$ amendments. Our results from laboratory column experiments demonstrate that additions of $CaSO_4$ promote soil C sequestration through suppressing microbial respiration to the extent of ~200 g per $m^2$ soil per m of supplied water, and promoting calcite precipitation at similar rates.

The newer studies conducted in the greenhouse on $CaSO_4$ treatments in soils planted with switchgrass are essential for understanding the C mass balance in more complete systems with soil $CO_2$ generated through respiration from both plant roots and the soil microbial community. These greenhouse experiments showed that the $CaSO_4$ treatments did not adversely affect biomass yield (~600 g dry biomass/$m^2$/harvest) at the higher irrigation rate (50 cm/year), but substantially reduced recoverable biomass under the more water-limited conditions (irrigation rate = 20 cm/year). These results provide information for evaluating land use practices for increased soil C sequestration under semi-arid region biofuel crop production.

## Nanoparticles-Stabilized Supercritical $CO_2$ Foams: Developing Novel Material for $CO_2$-Enhanced Oil Recovery

Principal Investigator: Jiamin Wan

*Project Description*

The initial motivation of this project is to develop a new surfactant that is viable, lower cost and more environmentally benign than the existing $CO_2$-compatable synthetic surfactants as a substitute for generating $CO_2$-foam in enhanced oil recovery (EOR). As the project developed quickly, we have expanded the potential application to the area of hydraulic fracturing (HF), using the $CO_2$-foam as an alternative frac-fluid to replace common water-based frac-fluids.

Although $CO_2$ has been used as a displacement fluid for EOR, it remains inefficient because of its low viscosity and high mobility that cause injected $CO_2$ to bypass oil and limits oil displacement efficiency. Surfactant-stabilized $CO_2$-foams have been found effective for increasing $CO_2$ viscosity, but the high costs (compare to oil prices) and the concerns over their potentially negative environment impacts have limited their commercial applications. Developing cost effective and greener $CO_2$-compatable surfactants has been an outstanding challenge in $CO_2$-EOR. Moreover, in HF, the currently used water-based frac-fluids (FF) cause "water block", that severely limits gas production. Additionally, the treatment of the retrieved wastewater is an environmental and economical burden. Developing techniques of using waterless or less-water frac fluids currently is a top priority for safe and economical energy recovery. $CO_2$-foam can become viable alternative frac-fluids if the cost issue is resolved. Motivated by these important needs, the objectives/tasks of this project include: to identify best raw materials for alternative surfactants; to develop the low-cost extraction technique for industry mass production of this surfactant; to optimize recipes to generate $CO_2$-foams with controllable viscosity; to test foam viability in EOR; and to test foam viability in HF.

*Accomplishments*

We discovered a CO2-compatable natural biogenic surfactant (NBS) contained in the Earth's abundant organic-rich sediments that is capable of generating and stabilizing $CO_2$ foams (LBNL Invention Disclosure, # IB-3242). We have developed a preliminary method (proprietary) to produce the NBS. The NBS performs as an effective surfactant, significantly reducing interfacial tensions between the air-water and the supercritical (sc) $CO_2$-water interfaces. The NBS is capable of generating and stabilizing dense sc$CO_2$-in-water foams containing $CO_2$ at up to 80 volume% with controllable effective viscosities up to 40 cP, three orders of magnitude higher than that of pure $CO_2$ at the same pressure and temperature.

To further testing the $CO_2$-foams performance in EOR and HF, we need to design and build high pressure and temperature facilities to simulate the deep subsurface reservoir conditions. To do so, we have recently contacted several gas/oil companies asking for funding support, and the responses are generally positive. We are currently continue collecting the basic date that the industries are looking for.

## SUPERCONDUCTOR UNDULATORS FOR LIGHT SOURCES

Principal Investigator(s): Soren Prestemon

*Project Description*

The purpose of this project is to develop the technology of superconducting undulators for light source applications. The primary goals include a) development of measurement system capable of accurate determination of trajectory wander, b) development of a tuning concept capable of reducing trajectory wander to within tolerance specifications, and c) design and fabrication of a $Nb_3Sn$ undulator demonstrating predicted performance of the technology.

In support of these goals, a significant amount of analysis is needed to develop a tolerance budget for fabrication and assembly, and to bound the amplitude of corrections required of the tuning method. Furthermore, testing of the undulator and of the tuning concept requires a test cryostat, which is also commissioned as part of this LDRD.

*Accomplishments*

Significant progress has been made on all fronts. A summary of accomplishments include:

a) The magnetic measurement system has been fully tested on the SLAC ECHO undulator, a permanent-magnet undulator with a period of 20mm, identical to that of the superconducting undulator prototype under development in this LDRD. Our system is based on the well-established pulsed-wire technique, but incorporating significant innovations that enhance the quality of the measurements. Most importantly, we have developed a mathematical treatment of the measured data that compensates for dispersion generated by the finite radius of the wire. The measurements have been compared with accurate Hall probe measurements taken by SLAC, and demonstrate excellent agreement of first and second-integrals. Unlike the Hall probe method, the pulsed wire technique is directly applicable to the small-bore, cryogenic environment of the superconducting undulator.

b) The test cryostat fabrication has been completed and the cryostat is currently under commissioning. The cryostat accommodates powering of the main coils as well as the end correction coils and the tuning system.

c) The core elements of a tuning concept have been developed and tested. The method applies single-turn superconducting loops an each pole of the undulator. During the tuning process, the current in each loop can be forced to be either 0 or $I_0$; all powered loops are in series, i.e. at the same (tunable) current $I_0$. The number and locations of the loops are free parameters during the tuning process. Detailed Monte Carlo simulations have shown that the tuning concept will bring the trajectory wander well within specification for light source applications with a modest number of active powered loops.

d) The detailed design of a $Nb_3Sn$ prototype with period 20mm has been developed. Fabrication of major undulator components has been completed. The design includes optimized ends as well as end correction coils that compensate for nonlinearities arising from varying iron saturation during energization.

**Saving lives with low-energy medical devices**

Principal Investigator(s): Shashi Buluswar

*Project Description*

The purpose of this project is to produce a suite of low-cost, energy-efficient medical devices for treating low-income patients in developing countries. The specific devices targeted with these funds are: a solar-powered vaccine refrigerator (for delivering temperature-sensitive vaccines to vulnerable populations which do not have access to proper clinics, to refrigeration, or even electricity), and an ultra-low-cost infant warmer to keep premature and low-birth-weight babies from exposure to hypothermia (which is one of the leading causes of neonatal deaths in low-income populations).

The project aims to develop, field-test, and where necessary, acquire approval from the World Health Organization (WHO) or other standard-setting body.

*Accomplishments*

To date, we have developed working prototypes of both technologies

- The vaccine fridge currently exceeds the WHO parameters for holdover time, i.e., the time for which it needs to hold the required 2-8$^{o}$C, in ambient temperature of 43$^{o}$C. We will be sending it for WHO approval by March, 2014, and expect to have approval within two months after that.
- The infant warmer is currently being evaluated by Harvard/Boston Children's Hospital, and by the Ministry of Health in Rwanda

We expect both technologies to be deployed, and have measurable impact towards saving children's lives, but the end of 2014.

# Generative Design Methods for Integration of Energy and Sustainability in Early-Stage Architectural Design

Principal Investigator: Luisa Caldas

*Project Description*

LBNL and UC Berlekey's Department of Architecture share a common interest in fostering the integration of energy and sustainability concerns from the conceptual stage of the architectural design process. This integration, to be first developed in an academic environment, aims to apply cutting edge simulation approaches with the optimization challenges of current architectural professional practice. Ultimately, the methods and tools developed both at LBNL and UC Berkeley, will help to further transform the use of state-of-the-art energy simulation tools among the architectural community.

Early-stage, conceptual architectural design has suffered radical changes in recent years due to development on powerful modeling tools that allow fast parametric modeling of complex building geometries, rapid-prototyping of 3D models, and links to diverse performance simulation tools. With parametric design progressively becoming an adopted method for early-stage conceptual design, both in academic and professional environments, the main questions to be addressed in this project are twofold:

1) - Information exchange between the most commonly used design tools in the architecture community, and reliable energy modeling tools such as EnergyPlus and Radiance.

2) - Use of Generative Design Methods to introduce performance-based optimization into architectural design, expanding upon parametric modeling capabilities. These approaches can be applied both to whole-building design, building envelope and urban design scales.

This project aims to explore the implementation of Generative Design Methods, in the context of shading systems design optimization, and a prototype development of a link between Rhino/Grasshopper and EnergyPlus for energy optimization goals.

*Accomplishments*

The LDRD research presented below was developed during the summer months at LBNL. For the first research question, the main accomplishments were:

1.1) Review of state-of-the-art practices, both in architectural (academic and professional) and energy simulations realms.

1.2) Initial review of BIM-to-BEM and other CAD-based platforms that include LBNL-generated simulation software (Energy Plus and Radiance), their capabilities for transferring BIM and CAD models into energy models, and potential for including optimization into the design process.

For the second research question, the main accomplishments were:

2.1) Initial development of design methods to support the deployment of reliable energy simulation tools in current early-stage design architectural practice. This was done mostly in the Rhino/Grasshopper platform, and using Radiance/Daysim simulation engines. Major obstacles were identified regarding the potential for integration of Rhino/Grasshopper with EnergyPlus, in part due to the serious limitations that EnergyPlus displays in dealing with complex building geometries. This aspect is currently being addressed in a new task related to Complex Building Geometries.

2.2) Exploration of methods for parametric design, different energy and daylighting metrics able to successfully guide design evolution, based on evaluation of performance through simulations with EnergyPlus and Radiance, and optimization methods and variables.

**Sodium Ion Batteries for Grid Storage Applications**

Principal Investigator: Marca M. Doeff

*Project Description*

The goals of this project were 1) to develop a dual intercalation battery based on sodium using aqueous electrolytes and 2) to investigate titanates as potential anode materials for sodium ion batteries with either aqueous or organic electrolytes. These goals were chosen with the specific purpose of enabling devices intended for cost and resource-sensitive applications such as large-scale energy storage (grid applications). Other benefits include the potential development of alternatives to lithium ion batteries for vehicular applications in case of lithium supply insecurity, a matter of increasing concern to the battery community.

Sodium ion batteries operate on a similar principle as that of the better-known lithium ion analogs; alkali metal cations shuttle between two host electrodes, which undergo reductive insertion at differing potentials. Sodium does not, however, insert into graphite, the most common negative electrode used for lithium ion systems; therefore, a suitable anode material must be found. Ternary titanates were targeted for this purpose, because they often exhibit ion exchange properties that imply high mobility for univalent cations including sodium. Additionally, they can be synthesized from cheap and abundant precursor materials, making them attractive as anode materials for sodium ion batteries. Because many structures are available and the structure affects the voltage profile, it is theoretically possible to tailor the electrode to the type of battery (aqueous or organic electrolyte).

*Accomplishments*

During this project, we successfully cycled 1V aqueous cells with $NaTi_2(PO_4)_3$ anodes and $NaFePO_4F$ cathodes at a pH of 8.6. We also identified two classes of sodium titanate anodes suitable for use in secondary cells with organic electrolytes; however, the discharge potentials of these materials are too low for use with aqueous electrolytes. The first anode material is derived from "sodium nonatitanate", a hydrothermally prepared compound used for nuclear waste clean-up, due to its affinity for $Sr^{2+}$ cations. Sodium nonatitanate is structurally identical to $NaTiO_6(OH)\cdot 2H_2O$, a layered precursor used for making $TiO_2$ nanorods. The material can be irreversibly dehydrated and deprotonated at 600ºC without changes to its gross structural features, and undergoes reversible lithium and sodium intercalation processes at about 0.5V *vs.* $Li^+/Li$ or $Na^+/Na$. This is the subject of our provisional patent filed March 8, 2013 (U.S. Patent Application Ser. No: 61/775,172). The second class of materials is based on lepidocrocite-type titanates, which have corrugated layered structures. The potassium-containing starting materials are preferably converted to sodium or lithium-containing analogs by ion-exchange processes prior to use in electrochemical cells. The average potentials of insertion of lithium and sodium are slightly higher than that of the analogous processes in the sodium nonatitanate-derived anode materials, with good reversibility. This class of materials is the subject of a Record of Invention (2013-148).

**Guiding LBNL low-carbon technology development with life-cycle energy and impacts analyses**

Principal Investigator: Jeffery Greenblatt

*Project Description*

This LDRD helped achieve LBNL's Carbon Cycle 2.0 vision by developing and applying new analytical capabilities and collaboration frameworks to bridge gaps between basic, applied, and analysis research at LBNL. The project assisted researchers in complementary, cross-divisional LDRDs to analyze the environmental (especially carbon cycle), human health and other impacts of their technology, and when possible, improve their net benefit and viability in the marketplace. We have established a unique approach where energy impact scientists work hand-in-hand with basic and applied research scientists to better inform and expedite the transition from laboratory research to the marketplace. Core capabilities include a suite of analytic tools for life-cycle assessment (LCA) of environmental impacts, air quality and human health impact assessment, geographic information system (GIS)-based analysis, scenario development, economic modeling, and uncertainty and variability analysis.

*Accomplishments*

Windows: 1. We published a paper describing our analysis of the potential heating/cooling savings from dynamic electrochromic nanocrystal window films for a range of near-infrared transmittance levels across 16 U.S. climate regions. This directly led to new funding from DOE's Advanced Research Projects Agency – Energy (ARPA-e); see below. 2. We published a paper quantifying the light-harvesting potential of dynamic prismatic optical element window coatings to enhance daylighting energy savings.

Biomass: We submitted a paper with the Joint Genome Institute reporting on a "fuzzy" GIS-based multi-criteria evaluation of agave production as a bioenergy feedstock in the U.S.

$CO_2$ Capture and Sequestration (CCS): We completed the first spatial and temporal life cycle analysis of $CO_2$ utilization pathways, and further developed our life cycle assessment of brine recycling from geologic sequestration in the United States.

Artificial Photosynthesis: We published a net energy analysis for an artificial photosynthesis-based hydrogen cell, working with Joint Center for Artificial Photosynthesis (JCAP) researchers. This directly led to follow-on funding from JCAP; see below.

Autonomous Vehicles: We developed and submitted for publication an energy and greenhouse gas analysis of the impacts of autonomous light-duty vehicles in the U.S.; the paper was rejected so we are rewriting for resubmission.

Health Wedges: We became coauthors (with external colleagues) on a paper analyzing the health benefits of several carbon mitigation strategies for the U.S. using "wedge" analysis.

Funding leveraged on capabilities developed in this LDRD totals $3.3M and includes: $2.1M from DOE's ARPA-e, $400k from DOE's Advanced Manufacturing Office, $253k from California Energy Commission, $170k from Google, $150k from DOE's Policy and International Affairs Office, $100k from JCAP, $100k (as two grants) from California Air Resources Board, and $45k from DOE's Energy Efficiency and Renewable Energy Office.

# A Balloon-Borne Platform for Measuring Vertically Resolved Concentrations of Black Carbon in the Troposphere

Principal Investigator(s): Odelle Hadley and Thomas Kirchstetter

*Project Description*

The purpose of this project is to develop a method to measure how aerosol particles are vertically distributed in the atmosphere, which in turn will clarify how air pollution influences climate. The project focuses on measuring sunlight-absorbing black carbon particles. Black carbon particles are emitted during combustion of fossil and biomass fuels. A recent comprehensive study concludes that black carbon emissions warm the climate and are the second most important human emissions in terms of climate forcing in the present-day atmosphere. Only the greenhouse gas carbon dioxide is estimated to have a greater climate forcing. The climate effects of black carbon particles depend on their vertical distribution in the atmosphere. However, vertically resolved BC concentrations have scarcely been measured.

This project will develop a balloon-borne platform for routine vertical profiling of black carbon, akin to radiosondes and ozone sondes that routinely measure the vertical distributions of meteorological variables and ozone. It will test, modify, and integrate several technologies into a payload to be lifted through the atmosphere by a balloon. The payload will include a) radio communication, data logging, telemetry, and tracking capabilities for payload retrieval, b) an instrument that measures black carbon concentration, and c) relative humidity, temperature, and altitude sensors. Once developed, instrumented balloons will be launched periodically in California in an attempt to quantify temporal variation in the vertical distribution of black carbon in the atmosphere. This type of data may be useful in distinguishing between locally emitted air pollution aerosols and aerosols transported long distances over the Pacific Ocean.

*Accomplishments*

The most significant accomplishment has been twelve successful launch and recovery missions of an instrumented payload. The payload included a new instrument that, in collaboration with its manufacturer, was modified for increased stability and measurement sensitivity required for this project. At a predetermined altitude, the payload's onboard computer releases the balloon, a parachute deploys, and the payload descends back to the Earth's surface. Transmitters incorporated into the instrument payload relay its location to a ground operator's laptop throughout the flight, allowing the payload to be recovered after each mission.

We have repeatedly demonstrated the ability to predict the rise rate, flight path, and recovery location of the instrumented payload. The data collected thus far indicated the presence of black carbon at high altitudes and above clouds, where radiative forcing is amplified. These observations support prior evidence of long-range transport of pollutants over the Pacific Ocean and support the notion that air pollution layers above the planetary boundary layer, in addition to locally emitted air pollution, may contribute to climate change.

We are in the process of conducting laboratory experiments to evaluate the black carbon sensor's sensitivity to changes in relative humidity in order to increase our confidence in measured black carbon concentrations.

# STICK-ON ELECTRICTY METERS: LOW INSTALLED COST BUILDING SUB-METERS FOR COMMERCIAL AND INDUSTRIAL ENERGY EFFICIENCY

Principal Investigator: Steven Lanzisera

*Project Description*

Research shows that electricity sub-metering can lead to a 10%-30% reduction in electricity use in commercial buildings, and it is likely these savings are available in residential and industrial facilities too. The cost to install available electricity metering technology is very high resulting in virtually no market penetration and an inability to achieve the available savings. We aim to demonstrate the core technologies needed for electricity metering technology that has one-tenth the installed cost of today's solutions. This new solution will provide sufficient accuracy and time resolution to enabling the retro- and continuous commissioning as well as distributed resource grid integration activities needed for a low carbon society.

The core technologies behind power meter are voltage and current measurement, and we will demonstrate non-contact measurement of both quantities. A suite of sensors will be installed on the surface of circuit breakers in electrical panels, and this installation can be done with minimal training and without an electrician. The sensors will measure the magnetic and electric fields passing through the face of the breaker thousands of times per second, and a set of inverse electromagnetic algorithms will estimate voltage and current in real-time. Each sensor unit will accurately estimate power under a variety of conditions and also compensate for external error sources automatically and without user driven calibration.

*Accomplishments*

Our most significant accomplishment is the successful demonstration of accurate voltage, current, and power measurement using a combination of commercially available sensors, custom electronics, and custom electromagnetic and statistical auto-calibration algorithms. The proof-of-concept sensor unit demonstrates that electric field can be reliably used to estimate voltage and magnetic fields of sufficient strength are available for current measurement in a variety of situations. We also demonstrated our first algorithms capable of providing critical calibration coefficients without user interaction when whole building power data are available.

We have also successfully demonstrated that spatially resolved magnetic field vector fields can be resolved using available sensor technology, and these vector fields are useful for key aspects of advanced auto-calibration algorithms that require no reference information. These vector fields allow for the identification of breaker topology and time varying interfering signals. Using electromagnetic finite element analysis and laboratory measurements, we have been able to identify and quantify error source characteristics that are needed for autonomous auto-calibration.

We are currently applying these results to the design of new sensors and auto-calibration algorithms. The new sensors use a combination of commercially available components and CMOS multi-axis magnetic field sensors. The new algorithms utilize newly identified statistical properties of the primary and interfering signals as well as new inverse electromagnetic analysis techniques.

# CREATING THE VEHICLE-TO-GRID SIMULATION (V2G-SIM) PLATFORM FOR PREDICTING THE IMPACT AND OPTIMALLY INTEGRATING PLUG-IN ELECTRIC VEHICLES ON THE ELECTRICITY GRID

Principal Investigator(s): Dr. Samveg Saxena

*Project Description*

Vehicle-grid integration (VGI) can simultaneously transform the electricity market and the automotive market. For the automotive market, VGI can: 1) allow vehicles to meet all corporate average fuel economy (CAFE) requirements and increasingly stringent emissions regulations, 2) move harmful vehicle emissions away from densely populated areas, and 3) provide revenue to offset the capital cost of vehicle electrification. For the electricity market, VGI can: 4) provide a distributed and growing source of grid energy storage, 5) provide better renewables integration, 6) provide a rapidly ramping resource for many electricity markets, and 7) encourage consumers to more closely scrutinize their home electricity bills just like with gasoline prices. Despite these benefits, the widespread deployment of VGI faces many uncertainties and barriers within both the electricity market and the automotive market. This LDRD project is creating the vehicle-to-grid simulation (V2G-Sim) platform to provide systematic quantitative methods to develop solutions to the electricity market and automotive market barriers to VGI.

This LDRD is developing two versions of V2G-Sim, 1) V2G-Sim Analysis, and 2) V2G-Sim Operations. The V2G-Sim Analysis model couples sub-models for: a) driver behavior, b) automated generation of trip-specific drive cycles (velocity-time profiles), c) vehicle powertrain models of energy usage during a trip, d) vehicle charging, and e) vehicle response to managed charging or V2G algorithms. V2G-Sim Analysis predicts the behavior for individual vehicles/drivers, and then aggregates individual vehicle profiles to generate grid impacts predictions for large numbers of plug-in vehicles (PEVs). With these coupled sub-models, V2G-Sim Analysis provides a platform for scenario analysis of PEV deployment for transmission and distribution infrastructure planning, impacts analysis from various PEV managed charging or V2G algorithms, design of market and pricing structures, etc. V2G-Sim Operations builds upon V2G-Sim Analysis to provide temporally- and spatially-resolved forecasting of PEV charging demands and V2G opportunities allowing an aggregator or integrator to bid PEV services (such as demand response, renewables integration, regulation, etc.) onto an electricity market and operate an electricity grid having many PEVs as a resource within the grid while ensuring each vehicle is sufficiently charged when it needs to be.

*Accomplishments*

V2G-Sim LDRD funding was confirmed in July 2013. The project accomplishments between approximately July 15, 2013 to September 30, 2013 were:

1. The requirements upon V2G-Sim for automotive and electricity markets were identified.
2. The methodological structure for V2G-Sim Analysis was created, the set of coupled sub-models were conceived, and preliminary code for V2G-Sim Analysis was created and tested.
3. The methodological structure for V2G-Sim Operations was created, and the preliminary code of V2G-Sim Operations was created and tested.
4. The COMSOL multi-physics platform, and the “battery and fuel cells” simulation package within COMSOL was purchased to evaluate if the pre-packaged battery kinetics models will provide the functionality that V2G-Sim requires.

# INTEGRATED ASSESSMENT CAPABILITY FOR SUSTAINABLE WATER-ENERGY CO-MANAGEMENT

Principal Investigator(s): Michael D. Sohn, William D. Collins

*Project Description*

An underappreciated aspect of climate change is how uncertainty about expected changes affects climate mitigation and adaptation measures. In the past, energy and water planners counted on a relatively stable assessment of climate, infrastructure and policy baselines. With climate change, planners face new uncertainties and forecasts of greater variability. Infrastructure plans must be revised which might include a new peripheral canal or a more decentralized electricity grid, mitigation measures might be considered, such as incorporating biofuels and improved batteries, and the valuation of water, as a product or as an energy commodity, must be reconsidered. However, the various uses of water are managed through separate processes, and the impact of management objectives for one can result in sub-optimal practices for the other, and will be exacerbated with predictions of greater year-to-year climate variability. Without a coordinated analysis capability, the ability to predict the effectiveness of climate mitigation, adaptation measures, or setting the value of water and energy is severely limited.

In this LDRD, we develop a computation tool and analysis framework for linked climate-water-energy co-simulation. The LDRD's resulting research will lay the foundation for an overall regional-scale integrated assessment capability. We will (1) develop analysis tools and software to estimate the cost of consuming water to produce energy, and the cost of consuming energy to produce water at regional spatial scales, and decade and multi-decade temporal scales, (2) develop analytical tools to specify the performance requirements of climate models for the aforementioned water-energy capability, (3) develop uncertainty analysis algorithms to map the tradespace between model unknowns (climate, water, & energy), and (4) demonstrate the resulting tools and software by analyzing the effects of climate uncertainty on water-energy management for the American River basin and Sacramento urban region of California.

*Accomplishments*

We have developed a new model for simulating joint water-energy interactions. In the first year of the LDRD, we linked two widely used regional planning models (WEAP and LEAP) and applied it to demonstrate the impact of climate variability on water and electricity in an urban area. The work has resulted in a journal paper submitted to *Applied Energy*. The paper is the first to report on the full integration of basin-scale models that include forecasting of demand and supply of water and energy for residential, commercial, industrial, and agricultural sector users. We apply the integrated model to study water-energy problems facing the Sacramento-American River basin. Historically, this area has seen dry and hot spells that have resulted in water and electricity demand spikes precisely when regional power production—hydro and thermal—are the most constrained. In the paper, we show the relative sensitivity of water and energy supply and demand to temperature and precipitation, to illustrate the functionality of the linked water-energy models. The results suggest that this region could sustain moderate changes in climate variability without large disruption to electricity or water systems.

FY13 LDRD: The Design and Evaluation of an Inexpensive, Fuel-Efficient and Super Low-Emissions Biomass Cookstove
Principal Investigator: Yungang, Wang

*Project Description*

The overall purpose of this LDRD project (in its first year in FY13) is to design and fabricate a useful, inexpensive, efficient, clean biomass burning cookstove that can be built and maintained within the economic and resource limitations of the poorest 2.7 billion people on the planet, exemplified by the populations of refugee camps in Darfur and rural Ethiopia. This project will make progress towards the Department of Energy (DOE) objectives of a high efficiency biomass stove emitting 90% less smoke that leads to adverse health impacts and climate change.

This project envisages building on the current Berkeley-Darfur Stove (BDS) model ("V14") with addition of a small self-powered fan to induce turbulence in the combustion zone. A cutting edge technology device will be introduced to generate electricity to power the small fan. We will design one such stove prototype. This technology will not compromise the usability of the stove, and may generate enough excess electricity to meet additional needs such as charging LED lights, charging cell phones, and radios off-grid. These combined advantages could enhance the adoption of the improved biomass cookstove globally.

*Accomplishments*

Our team has completed 18 Water Boiling Tests (WBT) on BDS-V14 and TSF to quantify the energy efficiency and emissions. Multiple tests are necessary to obtain good quality useful data owing to inherent variability in stove experiments. We used the highly time- and size-resolved particle counters (10 nm to 10,000 nm at 1 Hz) to capture the substantial variability in measurements of biomass stove emissions. Such results have not been presented earlier in the current literature. These measurements have also allowed us to understand the temporal evolution of baseline-stove emissions more accurately during various phases from initial ignition to full combustion to flame extinguishing at end of the cooking cycle.

We also performed a series of forced air experiments on BDS V14. Low velocity air was injected into the stove using a hand-held antistatic hot-air gun. Emissions reductions were analyzed qualitatively for a variety of air injection techniques and then quantitatively for injected air temperatures of different temperatures at the top of the firebox. Substantial reduction of BD was observed across a range of temperatures. These results show significant promise for an inexpensive, commercially-viable and super low-emission cookstove.

We are in the process of developing multiple stove prototypes that exploit these initial observations. A "Turbo Stove" prototype was designed and built. This prototype allows for injection of variable temperature air at a variety of flow rates and at six different locations. We aim to "fail quickly and inexpensively" to reach a winning stove architecture.

## URBAN SCALE ENERGY GRID MODELING

Principal Investigators: Michael Wetter, Tianzhen Hong

*Project Description*

The purpose of this research is to build and apply to test problems a computational platform for the design, retrofit and operation of urban energy grids that include electrical systems, district heating and cooling systems, and centralized and distributed energy storage. The need for this research arises because an integration of renewable energy beyond 30% poses dynamic challenges on the generation, storage and transmission of energy that are not well understood. Such a platform is also needed to assess economic benefits for the integration of co-generation plants that generate combined heating, cooling and power at the district level in order to decrease the carbon footprint of energy generation.

To address this need, this project will create a flexible computational R&D platform that allows expanding energy and policy analysis from buildings to district energy systems. Questions that this platform enables to address include where to place energy generation and storage, how to set the price structure, how to trade-off incentives for energy-efficiency versus incentives to add generation or storage capacity at buildings, how to integrate waste heat utilization to reduce the carbon footprint of district energy systems and how to upgrade the electricity grid to integrate an increasing fraction of renewable energy while ensuring grid reliability and power quality.

*Accomplishments*

Significant accomplishments have been made in multi-physics modeling and in algorithms for composing models of cyber-physical systems.

Regarding multi-physics modeling, we created a reusable library for alternating and direct current electrical systems in Modelica, an equation-based object-oriented library for modeling of dynamic engineered systems. These models can be connected to thermal models of buildings at multiple fidelities. To support integration of electrical systems with multi-fidelity building models, we allow three approaches: first, detailed whole building energy models can be exported from the DOE-developed whole building energy simulation program EnergyPlus in a standardized simulator-exchange format called Functional Mockup Interface. For this approach, we developed software that allows exporting EnergyPlus in this format, which then can be imported in a variety of software as a so-called Functional Mockup Unit which serves as a standardized gateway to the EnergyPlus simulator. Second, we created an algorithm that extracts from data series a reduced order model that may be linked with the electrical system models in order to reduce computing costs. Third, we allow existing native Modelica models of buildings to be linked to the electrical system models. We have applied the reduced order models to the development of a battery controller whose control objective is to stabilize voltage swells and sags in an electrical distribution network.

Regarding the composition of models for cyber-physical systems, we developed an algorithm that allows a deterministic composition of Functional Mockup Units for co-simulation. We developed conditions for the design of such Functional Mockup Units and for the master algorithm, which orchestrates the execution of these units. We also proposed an extension to the Functional Mockup Interface standard that enables deterministic execution for a much broader class of models.

# A Novel Nanoscale Chemical Analysis System for Low-Cost Solar Materials

Principal Investigator: Vasileia Zormpa

*Project Description*

Direct chemical imaging of elemental content and impurities with extreme spatial and depth resolution and specificity is required to understand, predict and minimize processes that adversely affect the macroscale properties of solar and other energy systems. A fundamental lack of key analytical techniques capable of providing this information leaves a pressing need for the development of next-generation nanoscale chemical imaging tools. The objective of this project is to develop a novel ultrafast laser spectroscopy technique based on a two near-field nanoprobe scheme which will overcome current limitations and meet the requirements of a versatile chemical imaging system for detecting and chemically mapping defects in solar energy systems and other energy materials.

This project will develop a sensitive femtosecond laser chemical imaging system in which both material excitation and signal detection occurs in the optical near-field vicinity. This chemical imaging system aims to enable a fundamental understanding of the properties and functionality of new solar material systems at spatio-temporal scales that were previously unattainable.

*Accomplishments*

In the first year we have established a proof of concept, demonstrated successful detection of femtosecond laser induced Fluorescence and Rayleigh scattering, and proceeded with optimization of the near-field excitation and detection processes as a way to improve sensitivity and resolution. Both ultraviolet and visible femtosecond laser pulses were coupled to the near-field excitation probe to obtain chemical signatures of different model material systems including nanoparticles, crystalline, and amorphous materials. The appropriate conditions for the distance between the two probes as well as the optimal combination of probe diameters were assessed with the goal of maximizing emission efficiency while maintaining spatially confined material sampling.

We further demonstrated chemical imaging across selected areas by simultaneously scanning both near-field probes (maintained at the same distance from each other) across the sample. Large variations in the chemical signatures across interfaces of materials were also shown, especially in samples with different optical properties. Near-field Rayleigh signal intensities were also studied as a function of different inter-probe distances (ranging from a few microns to contact) to find that a significant signal enhancement is achieved for smaller distances. The intensity decay with distance further underlines the importance of detecting signals in the near-field vicinity as a way to achieve high sensitivity, high resolution chemical imaging.

Development of biosensors for high-throughput functional screening of biosynthetic pathways
Principal Investigator(s): Samuel Deutsch, Rex Malmstrom

*Project Description*

The purpose of this project is to engineer highly sensitive and selective biosensors for a diverse set of target chemicals as a way to provide a high-throughput functional screening method for molecule production in microbial cells. Advances in DNA synthesis and combinatorial DNA assembly allow the construction of tens of thousands of pathway variants by varying both the gene content as well as the expression levels of the pathway components, a technique commonly referred to as pathway refactoring. However, a lack of sufficiently sensitive, selective, and scalable technologies to measure chemical production presents a major bottleneck that limits our ability to fully exploit large-scale synthesis efforts.

We will develop biosensor systems for target molecules of interest, by modifying the specificity of natural transcriptional repressors that mediate transcription of downstream genes in the presence of a ligand. Using synthetic biology approaches we will: (i) put GFP under the control of promoters regulated by the repressor, such that fluorescence is observed only in the presence of the ligand, and (ii) generate mutational libraries within the ligand-binding domains of such repressors so as to alter their ligand specificity. We will then screen for response of the repressors to a molecule of interest (measured by fluorescence levels) using fluorescence activated cell sorting (FACS). We will generate mutational libraries for 3-4 transcriptional repressors and screen for activation in the presence of target molecules including C6 and C15 alkanes and styrene all molecules of DOE relevance.

*Accomplishments*

During the first year of this proposal we developed a Miseq based sequencing method and analysis pipeline to determine transcriptional repressor library complexity both prior to selection and at different stages of positive and negative selection. The method was validated using a high complexity AraC mutational library that was previously used to identify biosensors for Mevalonate and Triacetic acid lactone. We observed interesting patterns of molecular evolution throughout the different stages of selection, which will help guide the design of future biosensors. We expect to publish this data once the analysis is completed.

We engineered two novel biosensors based on the BmoR and AlkS regulon. In the case of BmoR, response to target ligands (C5-C6 alkanes) was very low so it was not pursued further. For AlkS we observed up to 10X activation in the presence of multiple ligands and have so far tested response to C6-C10 alkanes as well as dicyclopropylketone (DCPK) and observed good sensitivity (10 uM) and dynamic range. We are currently testing this biosensor in the context of a previously characterized alkane producer strain that will be refactored and screened with the goal of maximizing alkane production.

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Revolutionizing genome sequencing of unculturable microorganisms: Development of a high-throughput pipeline for targeted single-cell genome amplification
PI: Rex Malmstrom

*Project Description*: Microbial communities represent one of the largest reservoirs of genetic and biochemical diversity on the planet, and genome sequencing represents one of the most powerful tools for accessing this reservoir. However, the vast majority of microbes cannot be cultured in the laboratory, making genome sequencing impossible using traditional approaches. Single-cell whole genome amplification (WGA) allows us to bypass the culturing bottleneck by generating large quantities of DNA from only one cell. Our goal is to develop a high-throughput pipeline for generating high-quality sequencing libraries from single cells. The pipeline will also enable rapid pre-screening for cells encoding genes of interest. Briefly, the system will encapsulate millions of individual cells into sub-nanoliter-size droplets using a custom microfluidic device. These droplets will serve as microscopic reaction vessels for performing massively-parallel single-cell WGA. Droplets containing genes (and thus genomes) of interest will be rapidly identified with molecular probes and separated using fluorescence activated cell sorting prior to full genome sequencing. Realization of this technology requires the transition of bench top chemistries to the nanoliter scale, with a primary focus on developing an effective cell lysis/DNA amplification cocktail compatible with microdroplet generation. This single-cell genomics pipeline will represent a major advancement in our ability sequence microbial genomes. The system will be integrated into the Joint Genome Institute's operational portfolio where it will be available as a unique resource for DOE researchers as well as the broader scientific community.

*Accomplishments*: For several years there has been a strong desire in the scientific community to improve genome amplification from individual cells using microdroplets, yet technological limitations have prevented realization of this desire. With LDRD funding we have developed new strategies that overcome these key technological hurdles. For example, we have:

- Designed and assembled a custom microfluidic device for generating microdroplets
- Developed novel chemistry for one-step cell lysis and DNA amplification inside of droplets
- Identified suitable agents and extraction procedures that enable recovery of intact droplets
- Upgraded FACS hardware and operation procedures for screening and sorting microdroplets

With the system we developed we were able to demonstrate single cell encapsulation, lysis, and DNA amplification. Individual droplets containing single-cell amplicons have also been sorted and sequenced, although the bias in genome recovery is greater than we hoped. We are currently working on new methods to reduce bias and improve genome recovery.

# COMPUTATIONAL, DATA MANAGEMENT AND ANALYSIS METHODS FOR THE STUDY OF A RAPIDLY EXPANDING GENOME AND METAGENOME SEQUENCE DATA SPACE

***Principal Investigator(s): Konstantinos Mavrommatis (Joint Genome Institute)***

## *Project Description*

The significant drop in the cost of sequencing with next generation technology platforms, such as Illumina HiSeq, has resulted in an exponential growth of new genome sequence datasets. However, due to the computational cost, performing comparative analysis involving a rapidly growing number of genomes and metagenomes is becoming an increasingly complex challenge. The computational, data management, and analytical challenges can be addressed by applying the pangenome construct on groups of genomes. A pangenome consists of the core part of a species (i.e. the genes present in all of the sequenced strains or of all samples of a microbial community) and the variable part (the genes present in some but not all of the strains or samples). From a data management perspective, pangenomes offer an efficient framework for handling the rapidly growing number of sequenced genomes while their analysis will help reveal genotypic and phenotypic properties across species, and track the evolution of member genomes in.

## *Accomplishments*

This fiscal year, significant progress was made on characterizing and applying ANI (Average Nucleotide Identity), a measure of genomic distance, to more than 15,000 bacterial and archaeal genomes. Understanding ANI and AF (Alignment Fraction, the average fraction of a genome that aligns to another) are important in order to determine the extent and type of similarity between a group of genomes that qualify to form a single pangenome. We have identified that AF and ANI values of 0.6 and 96.5, respectively, are lower bounds on such values for genome pairs belonging to the same species. Upon computing pairwise ANIs for approximately 83 Million pairs of genomes, we found anomalies in the species names for almost 50% of existing microbial species represented by at least two sequenced genomes. The analysis at this scale also uncovered evolutionary dynamics, revealing that 17.8% of the aforementioned species either exist in genetic continuums or are in a state of speciation. Genomes clustered based on complete linkage at minimum AF and ANI cutoffs of 0.6 and 96.5, respectively, were used to generate 1,029 seed groups for the formation of pangenomes using the pipeline described in the previous year's technical report. Of these, 11 pangenomes covering 10 species were generated with 7 of the 11 undergoing rigorous manual curation to feedback into the pangenome generation pipeline for results more representative of evolution. Currently, the pipeline for generation of pangenomes is in a well-developed state, is deployed on NERSC computational systems, and includes a visualization tool that was developed in the past 2 years to browse pangenomes in IMG (https://img.jgi-doe.gov). It is deployed to automatically generate the 1,029 pangenomes. The next step is to include the aforementioned pipeline in the context of IMG, which is a large system for comparative analysis.

**Function-Based Approaches for Distant-Acting Enhancer Discovery**

Principal Investigator: Len Pennacchio

*Project Description*

The purpose of this project is to develop methodologies to better screen the human and
mouse genomes for gene regulatory sequences residing in the 98% of the genome that is noncoding. Such data will provide important functional data on the location of these elusive sequences and aid in annotation the human genome. As whole human genome sequencing is poised to be a routine capability in the clinic, this foundation is essential to link human variation to human disease.

We will develop an unbiased, high-throughput functional assay for identifying and characterizing enhancer gene regulatory elements. These methods will pair pluripotent cell reporter assays and flow cytometry with recent advances in DNA sequencing to allow the parallel functional screening of hundreds to tens of thousands of DNA sequences for enhancer activity. These methods are expected to have a considerable impact on our understanding of transcriptional regulation by allowing for the identification of enhancers that have been thus far intractable to genome-scale identification.

*Accomplishments*

Over the course of the past 15 months, we have successfully developed proof of principle for an end-to-end system to screen for gene regulatory sequences in an unbiased manner. This work is currently undergoing peer review at *Nature Methods*, and an additional small project resulting from this work has been reported in *Biology Open*. Briefly, we have shown that we can clone hundreds to thousands of random sequences into a precise location in the mouse genome that is linked to a reporter gene, which is activated when sequences are behaving as enhancers. The targeted cells can be flow sorted to isolate those cells that are actively expressing the reporter gene, and the sequences responsible for this reporter expression can be identified through DNA sequencing. To date, we have used this method to test the embryonic stem cell enhancer activity of more than 0.5Megabases of mouse or human genomic sequence in 1kilobase increments.

To apply this method to a broader range of cell types, a major aim of this proposal, we have coupled the ES cell reporter assays we developed with *in vitro* differentiation and showed that we can accurately identify enhancers active in cardiac and neuronal cell populations. By comparing enhancers active at a specific locus in ES cells to those sites active in cardiomyocytes, we were able to observe the dynamic changes in regulatory architecture during cellular differentiation that likely mimic processes that occurring during mammalian heart development.

Over the last year, we have been exploring whether cutting-edge genome editing technologies can allow us to scale this method to assay an even larger number of putative enhancers in a single experiment. We have preliminary evidence showing that specific gene-mediated genome engineering methods indeed lead to higher rates of genome integration of enhancer test sequences, a major bottleneck in increasing the scale of this assay. Ongoing efforts are aimed at optimizing these engineering methods to further scale the technology to screen larger regions of the genome to better understand the rules of gene regulation.

# A Homology Independent, Computationally Efficient Method For New Enzyme Discovery.

Principal Investigator(s): Zhong Wang, Ph.D.

*Project Description*

The success of cellulosic biofuels and artificial photosynthesis both rely on the discovery of efficient enzymes and bioprocesses they are involved. The rapid pace in microbial genome sequencing, especially deep metagenome sequencing, has enabled rapid identification of millions of genes without cultivation, thereby providing a large pool for identifying new enzymes with desirable biochemical traits. Homology search with millions of genes against a rapid growing database, however, becomes increasingly impractical due to its computational burden.

To overcome the limitation, we developed a homology independent approach that is computationally efficient for new enzyme identification. The resulting software, "Buchner", achieves not only comparable sensitivity for proteins with linear homology, but also near linear computational performance with the growth in both queries and databases. This approach is based on the assumption that discriminative sequence features can be exploited to facilitate the prediction of new enzymes and new protein families without expensive multiple alignments procedures in BLAST or HMM.

*Accomplishments*

We systematically tested Buchner for the computing efficiency and accuracy in new enzyme prediction and the ability to identify new protein families. Starting from a subset of 1000 families having at least 1000 members from the Pfam-A database, we divided 20% of families as "new" and 80% as known protein families, and used 80% samples of known families as the training set and the rest 20% as the testing set. Frequencies of amino acid dimers with distance 0-5 were used as feature vectors. We adapted and optimized a learning algorithm based on L1-regularized logistic regression using LIBLINEAR C/C++ library to reduce memory consumption and maximize parallel processing.

In collaboration with NERSC (National Energy Research Scientific Computing Center), we could successfully learn 1.5 billion elements of training data in 20 minutes with less than 5GB memory requirement per process (average 480MB) using 800 processes. The average prediction accuracy among 800 families tested was 97.33%, and the time elapsed to calculate 160K records of the testing set were less than 3 minutes. For the specificity test, we examined 200K "new" sequences using learned classifiers and found that they are not likely—less than 5% chance—to be assigned into wrong families even with a liberal threshold that assigns a sequence to a family if it has 50% or greater membership probability to the family, suggesting that our method is robust to false positives while maintaining high sensitivity. Lastly, we applied genetic k-means algorithm to the sequences from "new" families and successfully assigned 70% of them correctly to the families they come from.

In conclusion, Buchner represents a computationally efficient and accurate protein function prediction method scalable to millions of genes.

# DEVELOPING EPIGENOMIC TECHNOLOGIES TO INTERROGATE GENOME FUNCTIONS RELEVANT FOR ENVIRONMENT AND BIOENERGY

Principal Investigator(s): Chia-Lin Wei

*Project Description*

The purpose of this project is to develop an array of whole genome sequencing based technologies that enable comprehensive characterization of epigenomes at fine resolution from organisms important for JGI's science and DOE mission. Coupling with JGI's state-of-the-art high throughput sequencing capability and integrated reference genome resources; we will decipher the distributions, dynamics and impacts of epigenome regulatory networks and high order architectures. We propose to apply them to profile functional genomes of relevant DOE flagship organisms or biofuel biosynthetic pathways and offer them to global JGI user community. The proposed plan also includes setting up data processing pipeline to provide users with the data and tools ready for biological interpretation and validation.

We will develop ChIP-Seq mapping of core histone modifications and variants, Methyl-Seq mapping of DNA methylation, FAIRE (formaldehyde assisted isolation of regulatory elements), DNase hypersensitivity mapping chromatin accessibility and ChIA-PET (chromatin interaction analysis through pair-end ditag) mapping of three dimensional (3D) chromatin architectures. After establishing this method, we will apply to profile functional genomes of relevant DOE flagship organisms or biofuel biosynthetic pathways. This data can reveal complex interplay between environment influence and genetic regulations. These data will be used together with gene expression information and metabolomics profiling to allow the system-wide analysis of lipid biosynthetic pathways in microalgae and their controls.

*Accomplishments*

We employed the analysis to interrogate the genetic pathways maximizing the production of lipids and their precursor TAG in microalgae. We were able to specifically and reproducibly profile histone modifications and DNA methylation across the *C. reinhardtii* genome. We established the concept that changes in histone modification of promoters may even be more sensitive and specific than expression profiling for detecting the key regulators. Combined with expression profiling, we identified key transcriptional regulators of lipid metabolism in *C. reinhardtii* and revealed the dynamic transcriptional components of the regulatory pathways responsible for TAG biogenesis and accumulation with high temporal resolution. Our results suggest the complex interplay between multiple cellular components in unicellular green algae and provide a robust framework to enable system-wide genetic manipulation in algae biodiesel regulation. With this result, a manuscript titled as "Uncovering Lipid Trigger in *C. reinhardtii* Suggesting Potential Biofuel Applications" is under preparation and plan to submit this fiscal year. An invention disclosure titled "Agents enhance the production of biofuel precursors in microalgae" was filed in Feb, 2013. A proposal named "EPICON: A Systems Biology Approach to Decipher EPIgenetic CONtrol of Lipid Production in Microalgae" responding in Science Focus Area (SFA) funding opportunity in the area of Genomic Science: Biofuels was submitted Dec, 2013.

**Integrated Imaging of Microbial Community Response to External Threats**

Manfred Auer, Musahid Ahmed, Bruce Cohen, Trent Northen

*Project Description*

The purpose of this project is to study model microbial community structure and metabolism (*Myxococcus xanthus* and *Bacillus subtilis*) using the tools of secondary ion mass spectrometry (SIMS), Nanospray Desorption Electrospray Ionization (nanoDESI) mass spectrometry, Correlative Light and Electron Microscopy (CLEM) and Fluorescence Live Cell Tracking (FLCT) microscopy, as well as high-resolution Transmission Electron Microcopy (TEM) Focused Ion Beam Scanning Electron Microscopy (FIB/SEM). While each of these techniques provides valuable information as a stand-alone technology we seek in this LDRD to integrate these different compositional, positional and architectural approaches and thus to develop a workflow by which multi-modal information can be acquired from a single sample. From a microbiology point of view we try to understand whether and how the community responds to an external threat in a localized, regional or global manner. Territorial disputes between bacterial species are common in most habitats, and are of great interest to a large number of DOE-relevant topics such as bioremediation, carbon cycling and lignocellulose degradation.

*Accomplishments*

We have developed the novel techniques of correlative ambient environment nanoDESI ion/fluorescence microscopy imaging, as well as correlative fluorescence microscopy/electron microscopy imaging and large area 2D and large volume 3D electron microscopy imaging, respectively, which has allowed us to study the interaction of different species microbial communities. We have identified mass signatures specific for *M. xanthus* DZ2 and *B. subtilis* 3610, and were able to distinguish the different species morphologically using TEM imaging. Liquid Chromatography Mass Spectrometry (LC/MS) has revealed the presence of antimicrobial small molecules (secondary metabolites) in *M. xanthus*, which are likely delivered by the abundantly present outer membrane vesicles (OMVs). We have also found by TEM imaging unexpectedly large quantities of OMVs and extracellularly secreted membranes that reside in the zone between hostile bacterial communities. Furthermore, TEM and FIB/SEM revealed the capability of *Myxococcus xanthus* to build exopolysaccharide (EPS)-based microchannels, that are essential for effective surface colonization.

While the project to date has been focused on optimizing each of the technologies in their own right, for this current fiscal year the focus lies on further integrating the information gathered about these systems by overlaying the multiscale, multimodal information obtained from the different techniques onto one another, and thus to obtain a comprehensive understanding of the microbial community response(s) to external threats/competitors, and therefore to answer the fundamental biological question of what precisely happens in a microbial community/biofilm when bacteria are faced with a competitor/external threat.

Effects of low dose radiation on communities of epithelial cells as a function of age
Principal Investigator(s): Mark LaBarge

Project Description

The purpose of this project is to determine how gamma radiation exposure impacts the cell fate decision process and rudimentary tissue-level organization in a normal human bilayered epithelium. This was a continuation of my FY2011 start-up/proposal, in which we were developing the functional cell screening technology platforms to study cell-radiation interactions in the contexts of microenvironment and tissue-level organization. Specifically we are developing assays to determine the functional effects of low dose radiation (LDR) on normal human mammary epithelial cell (HMEC) physiology as a function of patient age. To do so we are utilizing a unique and well-characterized resource of over 47 finite-life span HMEC strains, derived from women aged 16 to 91 years, together with three cutting-edge functional assay platforms, which enable measurement of responses to combinatorial microenvironments, to elastic modulus, and measurement of the ability to self-organize into epithelial bilayered tissues. It is particularly important to understand the effects of LDR (defined as ≤10cGy at a rate of ≤0.1cGy/day) on patients already in higher-risk categories for diseases, and age is the greatest risk factor for all solid cancers; 75% of new breast cancer diagnoses are made in women over 50 years old.

Accomplishments

We significantly changed our understanding of the processes and mechanisms by which human mammary epithelia maintain normal organization, and we have established a putative screening system for identifying environmental toxins (e.g. chemicals, radiation) and pharmaceuticals that can alter tissue-level organization. Prior to this work, our entire understanding of self-organization into a cohesive tissue was based on experiments with pond-dwelling organisms and engineered cell lines that suggested differential cohesive forces directed hierarchical nesting of different cell types in a tissue. Utilizing our quantitative microwell system with primary normal HMEC we have proven that the outer tumor suppressive myoepithelial layer forms dominant cell-ECM adhesive interactions, then the inner layer of luminal epithelial cells organize nested structures according to classical differential cell-cell cohesive forces. Interestingly genetic knockdown of multiple integrins in myoeps did not disrupt organization, only disruption of focal adhesion node proteins caused disruption of organization. This is interesting because last period we reported that post-menopausal HMEC myoeps were defective in their ability to self-organize, and we find no age-related changes in integrin repertoire; thus we suspect that focal adhesion signaling nodes are modified with aging. Concordant with that hypothesis, we developed a set technology that enabled single cell measurement of microenvironment-mediated signaling activation. We determined that young HMEC exhibit distinct signaling responses to different ECM, whereas post-menopausal cells were relatively unresponsive to different ECM. In young HMEC, the different ECM established distinct levels of permissible activation of the ERK and AKT pathways by growth factors, whereas in older cells growth factor-mediated activation of the pathways were wildly uncontrolled. Based on previous work in the Bissell lab that demonstrated bidirectional cross-modulation of integrins and growth factor pathways in mammary epithelia, I suspect that age-related changes in growth factor regulation are the key to explaining impaired self-organizing activity in post-menopausal HMEC.

These data are being used to pursue new funding from NCI, NIEHS, and will be used in support of research for the DOE Low Dose Program. Convergent with the biological sciences strategic plan these assays represent a novel and sensitive means to measure effects of environmental perturbagens on high-order tissue architectures.

## 4D DYNAMICS OF EPIGENOME REGULATION IN RESPONSE TO ENVIRONMENTAL CHALLENGES

Principal Investigator: Serafin Colmenares

*Project Description*

The goal of this project is to generate a comprehensive, integrated understanding of how common environmental challenges impact 4D dynamics of epigenome regulation, as well as the persistence of these changes across cellular and organismal generations. We will focus on the fruitfly *Drosophila melanogaster*, a powerful model system that allows us to elucidate components and mechanisms in cultured cells, tissues and organisms. Ultimately, we will use these tools and approaches to investigate how environmental epigenomics impacts human health. We will identify changes in chromatin dynamics and epigenetic modifications induced by three environmental factors known to negatively impact biological systems and human health: radiation, hyperthermia, and bisphenol A (BPA). Radiation triggers extensive chromatin reorganization important for DNA repair, including global heterochromatin expansion and relocalization of damaged sites to the euchromatic space. Hyperthermia simultaneously reduces global transcription, mobilizes heterochromatin proteins, and induces trans-generational transcriptional deregulation in Drosophila. Finally, the estrogen mimic BPA, a common component of plastics, is implicated in birth defects, cancer, and the induction of the H3K27 methyltransferase Enhancer of Zeste (EZH2) which is critical for Polycomb group-mediated gene silencing, developmental patterning, and trans-chromosomal interactions.

Through this project, we plan to generate a more comprehensive and detailed understanding of the spectrum of epigenetic changes in response to these environmental challenges, and their impact on cells and organisms. Successful completion of this study will provide 'proof of principle' of our ability to comprehensively analyze the interplay between the environment, the epigenome, and fundamental cell and organismal functions.

*Accomplishments*

We have successfully developed a high-quality ChIPSeq library protocol and ChIPSeq data analysis pipeline to pursue the goals of this project. So far, we have completed ChIPs of 4 histone modifications from Kc cells before and after acute ionizing radiation, and data processing of these results are ongoing. We have also completed ChIPSeq of H3K27Me3 from Kc cells treated with BPA, and discovered increased enrichment of H3K27Me3 at developmental genes that are known EZH2 targets. This suggests that BPA-induced increases in H3K27Me3 levels only occur at normal genome substrates of EZH2. Subsequent experiments treating flies with BPA at various developmental stages showed higher lethality rates in larval and pupal stages among females but not males. Future studies will focus on BPA effects on developmental programming in female larval and pupal tissues.

We have also further characterized immediate and delayed chromatin changes in Drosophila cells after heat shock by measuring protein levels of various chromatin components. Specifically, we found early loss of histone H2A ubiquitination and RNA Pol II phosphorylation after heat shock, and later increases in condensin and cohesin levels. We are currently investigating how these various chromatin changes are linked to heterochromatin mobilization and to each other using knockdown experiments and to determine whether the changes in protein levels are coupled to altered subnuclear localization. ChIP of HP1a and other heterochromatin components after heat shock are ongoing. Based on this progress, we expect to accomplish our projected aims for this calendar year, and acquire several interesting stories for publication in the near future.

Modeling Desert Soil Crust Microbial Community Responses To Pulsed Climate Events.
Principal Investigator(s). Trent Northen

Project Description

The overall goal of this project has been to use a tractable environmental soil microbial community, desert biological soil crusts (BSCs), to provide fundamental insights into bacterial carbon cycling and changes in community structure occurring in response to important environmental parameters, focusing on rainfall and temperature. Thus pioneering approaches are helping to unravel key mechanistic and dynamic aspects of the biogeochemical carbon (C) cycling in soils. This includes characterizing and modeling the dynamic responses of the soils primary producer *Microcoleus vaginatus*, the metabolites release by this bacterium and investigating possible microbial foodwebs based on these released metabolites. This program is an example of 'team science' and uses integrated biogeochemical, microbiological, genomic, metabolomic and computational approaches to define alterations in carbon cycling and community structure in response to wetting.

Accomplishments:

To elucidate the key events involved in soil carbon cycling in response to wetting events we performed a 'wet-up'experiment of a BSC and followed the response of the communities primary producer, the cyanobacterium, *Microcoleus vaginatus, in situ* using a whole-genome transcriptional time-course that included two diel cycles. From this we developed a conceptual model of the *Microcoleus vaginatus* desiccation cycle and showed that signaling genes were among the few that were transiently induced immediately upon wetting and have now purified 7 of the corresponding signaling proteins to determine their genomic targets.

We have developed and used a novel stable-isotope metabolomics approach to investigate the metabolic flux of *Microcoleus vaginatus* and found that this slow-growing organism has high metabolic flux through pathways related to desiccation response and biopolymer production. Using these observations, we have built a manually curated flux-balance model that predicts $CO_2$ flux during light and dark reactions. Metabolic profiling has shown that it releases a wide range of metabolites, including novel betaines and oligo-saccharides, potentially cross-feeding other soil bacteria. To examine possible foodwebs we made isolate libraries and selected 6 diverse and potentially important organisms for cross-feeding experiments. Metabolic profiling of spent media revealed heterotrophs use only a subset of these released metabolites.

To assess the potential interplay of BSC microbial communities and desert surface temperature, we sampled a gradient of BSC development with increasing pigmentation (decreasing albedo) and performed a wet-up experiment with 16S rRNA profiling. We found that there is a clear shift in the microbial community with increasing scytonemin (dark pigment) and the surface temperature of the sample. Excitingly, we have found the same replacement of *Microcoleus vaginatus* by *Microcoleus steenstrupii* that has been reported to be occurring across the western US is found as a result of changes in temperature. We also find that successional stages of crust maturity and wetting were both significant factors in explaining the variance of the phylogenetic distances, suggesting that BSC dynamics occurs across multiple temporal scales.

**Development of Protein Localization Atlases at Multiple Scales in Eukaryotes**

Principal Investigators: Damir Sudar and Gary Karpen

*Project Description*

The purpose of this project is to develop efficient gene product tagging, automated image acquisition using multiple modalities, visualization-supported image and image-derived data analysis tools, and to integrate these into a high-throughput pipeline to build protein localization atlases, starting with the fruit fly Drosophila. A proliferation of genome and transcriptome sequence data has produced comprehensive annotations of the genes, mRNAs and inferred proteins for many different eukaryotic organisms. We now have a new challenge: comprehensive determination of gene and protein functions. Among the most direct clues to the function of an uncharacterized gene are the spatial, temporal and subcellular expression patterns of protein products, and the interactions that a protein makes with other proteins or nucleic acid sequences. Our initial goal is a Drosophila Protein Atlas (DPA) – a comprehensive and quantitative map of subcellular protein localization in tissues and cells in *Drosophila melanogaster,* a key model organism for which we locally have extensive tools and expertise. About 75% of human disease genes have a homolog in the ~14k protein-coding fly genes but have unknown biochemical functions. Thus, the DPA will have enormous value for understanding animal proteomes, including mice and humans.

*Accomplishments*

In the first performance year, we have made significant progress in a number of critical areas and we assembled the preparation, acquisition, and analysis pipeline. The multi-disciplinary team uses a co-design methodology to ensure close coordination between the biologists, imaging scientists, and computational scientists throughout the development process. Specific accomplishments in first performance year:

1) Gene selection method established based on yeast and human orthologs and Drosophila Protein Interaction Map database.
2) High-throughput gene picking and plate preparation protocols implemented.
3) Cell line S2R+ selected and culture/transfection/plating protocols optimized.
4) Initial 72 genes processed through pipeline. 81% good localization. Localized manually to 19 different cellular compartments.
5) Semi-automated imaging protocols using wide-field fluorescence and confocal microscopy established and optimized. Automated imaging protocols and infrastructure under development.
6) Image database established based on OMERO. Contains thousands of annotated images.
7) Automated image analysis algorithms for image segmentation, feature extraction, and classification developed and deployed.
8) Automated classification accurately assigns patterns to 11 sub-cellular compartments – further optimization is under development
9) Image database, sample tracking database, image analysis, classification, and visualization software deployed on NERSC resources through close collaboration with David Skinner's Next-Generation BioImaging LDRD project.

With these capabilities in place or in final development stages, the project has started its 2nd performance year processing the next set of 96 genes to test the pipeline and the localization accuracy of a set of genes with previously unknown function and performing co-localization experiments of interacting proteins.

**Enabling Structural Systems Biology at NGLS**

PIs: John A. Tainer and Greg L. Hura

*Project Description*

The doubling of biological sequence data every 9 months far exceeds the two-year doubling rates for computer speed and data storage that transformed the world. To harness this biological data effectively will require technology to define the macromolecular machines controlling cell biology. Yet, the available tools to characterize the action of macromolecular assemblies are hugely inadequate for meaningful integration into LBNL biological multiscale efforts. To understand the function of complex macromolecular machines there are key dimensions to consider: spatial organization, time, and chemical environment. With current techniques, characterizing this large data space is proving impossible. The rate of data collection and analysis is far outpaced by the identification of new targets and important dimensions remain largely uncharacterized. Importantly, the next generation light source (NGLS) is predicted to deliver 36 trillion pulses per hour, with a human cell containing approximately a trillion macromolecules. Thus if each pulse were able to provide structural information on a biological macromolecule, the data scales would match NGLS capabilities. Employing the enormous NGLS advance to efficiently harnessing biological data is precisely what our LDRD enables.

*Accomplishments*

We developed and applied novel tools to understate DNA Mismatch repair machinery which involves many components, manipulates long stretches of DNA and utilizes transient or meta-stable states that are biologically important but challenging to characterize. The initiator of mismatch repair (MMR), MutS or MutS homologues (MSH2, MSH3, and MSH6), is itself a complex macromolecule with multiple known functionalities including DNA binding, DNA substrate recognition, ATP hydrolysis and binding of downstream partners in MMR. Adding to the contexts of interest are the implication of tens of human disease mutations in MSH2, MSH3 and MSH6. Through applying our high throughput approach we are building a global conformational comparison map of MutS under the varied conditions of interest[1].

In concert we are also following the conformation of long stretches of DNA as MMR repair proceeds by labelling the ends of DNA with gold nanocrystals[2]. Utilizing SAXS with gold nanocrystal labels we have demonstrated that mispair-containing DNAs were bent more by MutS than complementary DNAs, did not promote tetramer formation, and allowed MutS conversion to a sliding clamp conformation that eliminated the DNA bends. Addition of second responder MutL did not stabilize the MutS-bent forms of DNA. Thus, DNA distortion is only involved at the earliest mispair recognition steps of MMR: MutL does not trap bent DNA conformations suggesting migrating MutL or MutS-MutL complexes as a conserved feature of MMR. The complimentary approaches which provides global perspectives of MutS conformation with high throughput SAXS and DNA conformation with gold labels connect the macromolecular structure to the biology they enable.

**Project Title** X-RAY SPECTROSCOPY OF ELECTRIFIED INTERFACES
Principal Investigator(s): Balsara, Nitash; Salmeron, Miquel; Prendergast, David

*Project Description*

Lithium-sulfur batteries have theoretical capacities that are a factor of five larger than that of conventional lithium ion batteries. Unfortunately, polysulfides that are the products of sulfur redox chemistry, diffuse out of the electrode and severely limit the cycle life of these batteries. A necessity to the development of more efficient lithium-sulfur batteries is an understanding of the redox pathways through which lithium polysulfides ($Li_2S_x$, $2 \leq x \leq 8$) are formed. Spectroelectrochemical studies of these reaction pathways have been complicated by difficulties faced in spectral peak identification. As a result of reversible disproportionation reactions, lithium polysulfide intermediates exhibit coexisting equilibria in solution, making it difficult to obtain spectral standards and interpret spectral data obtained during electrochemical experiments. Thus, development of experimental techniques that can both differentiate $Li_2S_x$ molecules with different values of 'x' has become an important focus of Li-S battery research. We proposed to use a combination of X-ray absorption spectroscopy and first principles calculations to probe the formation of polysulfide species at electrified sulfur electrodes.

*Accomplishments*

We have demonstrated the use of X-ray absorption spectroscopy (XAS) as a tool for differentiating $Li_2S_x$ species. XAS at the sulfur K-edge was used to probe the state of $Li_2S_x$ molecules dissolved in thin films of poly(ethylene oxide) (PEO) and a linear block copolymer of poly(styrene)-poly(ethylene oxide) (SEO). In our mixtures, only the average value of x, $x_{av}$, is specified; the actual number of $Li_2S_x$ species in the mixtures is unknown. Principal component analysis was used to interpret spectral data without any assumption or knowledge of coexisting equilibria between polysulfide species. Our results indicates that mixtures with $x_{av}$ = 2, 4, 6, 8 are primarily one or two component mixtures. The $x_{av}$ = 2 and 6 mixtures primarily contain products of disproportionation reactions while $x_{av}$ = 4 and 8 mixtures appear to contain a single molecular species.

Interpretation of experimental XAS spectra is commonly achieved by fingerprinting to known standards. To date, there have been relatively few XAS studies of lithium polysulfides, and no reference spectra of the pure, dissolved lithium polysulfide. As a result, fingerprinting is accomplished by referencing solid lithium standards, or by using sodium crystalline analogs when no lithium solids are available. In this work, we provide the XAS spectra of pure lithium polysulfide molecules dissolved in tetraglyme (an oligomeric version of the electrolyte used in the experiments) from first principles calculations and offer clear interpretations of the spectral features. Our calculations show the feasibility of using XAS to detect the pure polysulfide species, and to differentiate between chains of different length. In particular, the ratio of the pre-edge XAS intensity to the main edge intensity is a smooth and monotonic function of polysulfide chain length.

Two publications summarizing the results of our work thus far will be submitted next week. The work formed the basis of a successful proposal to the BATT program.

Ultrafast Spin and Magnetization Dynamics in Nanoscale Magnetic Structures
Principal Investigator: Jeffrey Bokor

*Project Description*

One purpose of this project was the creation of new capabilities at the PEEM3 beamline at the ALS for pump-probe time-resolved studies of magnetization dynamics on the ~100 ps time scale, with a view towards laying the foundation for sub-ps time scale study of spin dynamics at the NGLS. One goal is to study the dynamics of closely coupled, interacting nanomagnets following full switching to the hard axis. This fundamental study lays the groundwork for a new way of processing information at ultra-low energy dissipation. A second goal was to characterize the switching dynamics of a ferromagnetic layer coupled to the multiferroic material bismuth ferrite (BFO) in order to understand the detailed nature of the electric field control of magnetism in this complex oxide material. Finally, the phenomenon of ultrafast magnetization dynamics triggered by femtosecond laser excitation will be generalized to investigate the creation of nonequilibrium electron distributions in magnetic materials by purely electrical hot electron injection across Schottky barriers. This overall effort, in turn, was intended to lead to a program at NGLS to study fascinating open questions in ultrafast magnetization dynamics in magnetic and ferroelectric materials triggered by excitation of nonequilibrium electronic states using both laser and direct electrical excitation.

*Accomplishments*

The initial effort in this project was devoted to the design, construction, and testing of the high speed circuit to be incorporated into the PEEM-3 sample holder, and the laser system and electronics that are used to trigger and synchronize the current pulse to the synchrotron x-ray pulse. This instrumentation was successfully built and commissioned during this year. Our most significant accomplishment has been to use this capability to study and characterize dynamics of linear chains of dipole-coupled single-domain nanomagnets. We observed deterministic propagation of discrete signals along these chains and showed that the switching proceeds at speeds on the order of just over 100 ps per nanomagnets, which corresponds well with modelling based on the Landau-Lifschitz-Gilbert equation. We also observed significant influence of thermal fluctuations as well as non-uniformities in the fabrication of individual nanomagnets. Both of these effects lead to frustration of the coherent propagation of the magnetic switching along the chain. These fundamental results are of considerable significance to the design of magnetic information processing systems.

Our effort to characterize the switching dynamics of BFO has not been successful so far. The pump-probe technique is one in which the dynamics of the system are repetitively triggered at a 3 MHz rate and the image is averaged over approximately $10^8$ cycles for each value of time-delay. This requires that the dynamical process is highly reproducible over perhaps $10^9$ cycles. However, we discovered that the electric field controlled switching in BFO/CoFe exchange coupled interfaces degrades after a much smaller number of cycles. The origin of the degradation is under investigation, but is suspected to be related to oxygen segregation at the interface.

Finally, we have installed a new femtosecond laser system and set up a time-resolved magneto-optic Kerr effect apparatus for initial studies of ultrafast magnetization dynamics. We are now in the process of fabricating suitable magnetic materials samples in collaboration with colleagues in the materials science division.

**Electron Microscopy With Vortex Beams Carrying Orbital Angular Momentum**

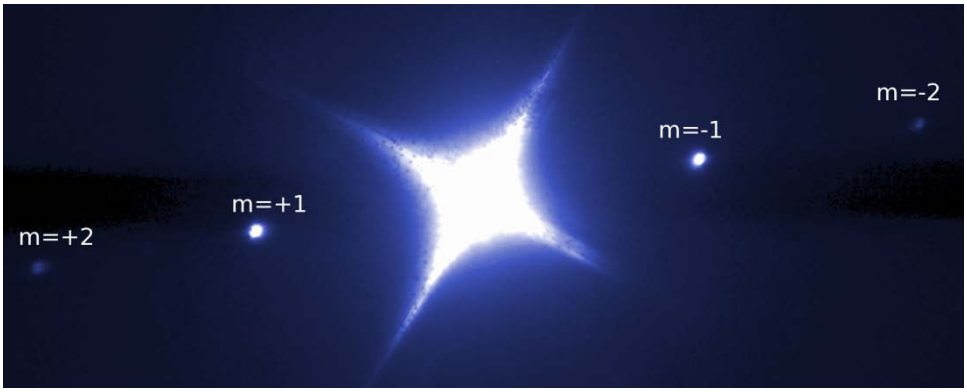
*Ben McMorran, Peter Ercius, Martin Linck, Stefano Cabrini, Andreas Schmid*

## Project Description

Materials directly involved in the Earth's carbon energy cycle are predominantly composed of light elements – "soft mater" such as biological tissue, macromolecules and polymers. Soft matter is difficult to analyze by transmission electron microscopy (TEM) because light elements do not efficiently scatter electron and none of the conventional methods of producing atomic resolution images for detailed studies of soft matter. A novel class of electron beams with quantized orbital angular momentum (OAM) has recently been demonstrated by several research groups. These beams, composed of free electrons with helical wavefunctions, are analogous to widely used optical vortices in beams of light. Utilizing recent advancements in nanofabrication methods, we are creating special diffraction gratings for electrons, which enable us to adopt coherent wavefront engineering techniques from light optics to prepare electron OAM beams. In an electron microscope, these beams can be used to illuminate a sample, revealing new dichroism and phase contrast signals that can provide more information about the sample's structure or magnetic properties. This development of spiral phase electron microscopy (SPEM) allows us to enhance capabilities for (a) imaging atomic magnetic moments and (b) enhancing contrast and resolution in soft matter imaging.

## Accomplishments

In year two of this LDRD, we further improved the fabrication techniques that were initially developed in phase I. Work at the University of Oregon produced significantly improved electron diffractive optical elements (holograms) with 80 μm diameters, which were installed in a basic scanning transmission electron microscope (STEM) and an advanced aberration corrected STEM (TEAM I) at NCEM. Custom condenser aperture assemblies were used to insert the apertures into the probe forming lens of the STEM and produced diffracted probes with atomic-scale dimensions. Images of the focused probes with single units of positive and negative OAM and the central beam were successfully demonstrated as seen in the figure. Each probe was spaced from the other probes to allow imaging with one probe without interference from the other probes. In such a configuration, the three main probes (-1m, 0m, +1m) were used to image several different types of samples to confirm the capabilities of the three probes. Thinly polished silicon (Si) and strontium titinate (STO) materials were used to prove the atomic dimensions of the projected probes. The next phase of the project will be to generate magnetic contrast at atomic resolution in Ni nanoparticles or other magnetic materials.



# Template Assisted Assembly of Monodisperse Discotic Phases as Highly Tunable Electronic Materials

Principal Investigator(s): Felix Fischer

## Project Description

The increasing importance of functional materials based on organic molecules for applications in electronics/computing, miniaturization of sensory devices, and energy production is well recognized. While the structure of these materials can conveniently be fine tuned at the molecular level many of the relevant electronic properties such as the charge carrier mobility, the absorption profile, and the exciton diffusion length directly depend on quantum-mechanical boundary conditions imposed by the random assembly of nanometer scale domains. A central challenge in the field of organic electronic materials is the control of the structure of nanometer size domains with atomic precision. We herein explore the potential of using template assisted self-assembly to control the formation of unambiguously defined monodisperse discotic phases. From the study of these supramolecular model systems both in solution and in OPVs/OFETs we seek to uncover structure-performance relationships and new assembly strategies that improve the performance of bulk organic electronic devices.

The use of template assisted self-assembly of discotic materials will allow for an unprecedented control of stacking order in all three special dimensions. The resulting functional materials are essentially monodisperse, providing for a highly reproducible performance and sensitivity. We seek to explore structure-function relationships that will provide the tools to rationally design desired photo– and electrophysical properties into organic materials. The highly modular solution-based synthesis provides for the facile introduction of diversity and meets the requirements for swift scale-up of the production of promising materials.

## Accomplishments

Our most significant accomplishment has been the development of a synthetic strategy that can be used to direct the self-assembly of discotic chromophores into columnar arrays ranging in length between 1-3 nm. Our approach takes advantage of π-π stacking interactions to assemble the discotic materials inside a covalently linked molecular cage. This strategy allows for the asymmetric functionalization of both ends of the discotic stack required for the highly ordered assembly into larger well-defined hierarchical structures.

We have also been able to introduce anchoring groups into the periphery of the host structure that direct the deposition of the discotic columns onto solid supports. Preliminary results of monolayers on atomically flat surfaces have been studied using atomic force microscopy (AFM). Efforts to extend our solution based self-assembly strategy towards extended 2D structure on surfaces has been limited by the competing molecule-molecule and surface-molecule interactions.

In order to overcome these limitations we modified our template assembly strategy to rely on a controlled living polymerization reaction that yields structurally well-defined supramolecular foldamers. The primary sequence of monomers in the block copolymer chain defines the π-π stacking length along the helical backbone.

We have succeeded in developing a new molybdenum based catalyst that is capable of polymerizing strained alkyne monomers in a controlled living ring-opening metathesis polymerization to yield highly regular block copolymers with exceptionally low polydispersity.

**Attosecond XUV Condensed-Matter Science: Electronic Wavefunction Coherence and Correlated Dynamics**

Principal Investigators: Robert A. Kaindl and Zahid Hussain

*Project Description*

The LDRD seeds a new research effort to directly probe attosecond coherence and electronic dynamics in solids. On such extremely short times, the effect of visible and IR light waves on the material can be directly observed with sub-cycle resolution, yielding a measure of the time-dependent perturbation and evolving coherence. Using extreme ultraviolet (XUV) attosecond pulses, we can apply photoelectron spectroscopy to access the dynamics of transient electronic states. Such studies can provide insight into a host of condensed matter processes, including charge transfer dynamics, quantum kinetics, high-field transport, and correlation timescales. By developing unique attosecond condensed-matter instrumentation, we provide the means to investigate coherent condensed-matter processes on the shortest timescales.

In solids, the eV-scale electronic excitations are fundamentally linked to an ultrafast dynamics of the electron wave functions evolving on the attosecond time scale. Our approach employs a customized scheme that combines few-cycle optical light fields, attosecond XUV pulses, and momentum-resolved photoelectron spectroscopy. In this project we take advantage of a laser-based source of attosecond XUV pulses to develop a unique attosecond condensed-matter UHV chamber and associated timing interferometer. This instrumentation can be applied to novel types of experiments to access the attosecond and few-fs coherent dynamics of electronic wavefunctions, non-equilibrium electronic structure, or field-induced carrier acceleration.

*Accomplishments*

In this LDRD, a unique setup was designed and commissioned for attosecond investigations of condensed-matter electronic dynamics. For the experiments, the attosecond timing and sample enviroment are split into separate customized vacuum chambers. This allows for true solid-state dynamics on clean sample surfaces to be observed by providing the critical UHV vacuum conditions around $10^{-10}$ Torr. Moreover, we successfully demonstrated differential pumping in four stages to overcome the pressure difference of 12 orders of magnitude between the gas-based high-harmonic source and the UHV sample environment. A load-lock for quick sample transfer and 4-axis UHV manipulator were implemented and applied to first experiments. In our scheme, the sub-cycle time delay between the attosecond XUV pulses around 95 eV and the infrared streak fields is enabled via a piezo-controlled optical interferometer.

With the setup completed, attosecond pulse trains were generated and their harmonic structure spectrally characterized with a discrete XUV grating spectrometer equipped with a X-ray CCD camera. With this, we observed photoemission from solid-state surfaces after focusing the attosecond pulses onto thin-film targets. Photoemission was detected with a hemispherical electron analyzer, which was carefully characerized for energy/momentum resolved studies, alongside a time-of-flight capability. A fiber-based $f$-2$f$ interferometer was implemented to successfully obtain long-term stabilization of the carrier-envelope phase of the few-cycle driving pulses, critical for attosecond generation and field streaking to access solid-state dynamics. Nanoscale antennas were fabricated for initial studies. This unique experimental setup along with first experiments provides the critical step for seeding a new research direction to investigate attosecond coherent electron dynamics in nanoscale and correlated materials.

## Search and Synthesis of the Next Generation of Topological Insulators

Principal Investigator: James Analytis

*Project Description*

The objective of this project is to develop a deeper understanding of exotic topological states emerging in strongly spin-orbit coupled materials. Our focus in this LDRD was to make new materials which combined topological properties with strongly correlated properties. We have focused on classical topological materials, specifically Bi2Se3 and Rashba materials, like BiTeI and BiTeCl. Our specific interest is in breaking time reversal symmetry in these materials by doping magnetic defects in an effort to take advantage of the spin-momentum locking of the Rashba state. Specifically we want to drive the magnetic sub-system to the quantum limit in high magnetic fields.

*Accomplishments*

Our focus in FY13 was to establish the Analytis lab's synthesis facilties. In FY13 we completed construction of the lab, installed 4 box furnaces, 4 tube furnaces, an inert-gas glove box, a functioning glass bench for sealing materials. In this time we have managed to make Bi2Se3 for our ARPES collaborators, and BiTeI/BiTeCl magnetically doped with Fe for our own experiments. We are presently in the process of testing our new materials in high magnetic fields.

# Exploiting Nanowire Surface States for Solar-Spectrum-Matched Plasmon-Enhanced Water Splitting

Principal Investigator(s): P.J. Schuck

Project Description:

Photogenerated fuels are an essential part of our nation's future energy portfolio. Within this context, direct photo-electrochemical (PEC) water splitting is being widely pursued through various technologies, all searching for novel materials with optoelectronic properties that both match the solar spectrum and provide appropriate over-potentials for driving electrochemical processes. These contradictory requirements make the search incredibly challenging, and so far there are no clear winning technologies. Current methods of water splitting mostly utilize large bandgap materials that absorb a fraction of the solar spectrum, rendering them inefficient for large-scale solar fuel production. This work describes a completely new approach based on semiconductor mid-gap surface (and defect) states, which provide greater solar spectrum overlap, efficient voltage offsets, and play a vital role in charge transfer at the liquid interface. Here, we integrate plasmonic nanoparticles and III-Nitride nanowire cavity structures to enhance mid-gap state absorption and overcome many of the current difficulties in water splitting. This solution, if successful, will significantly advance and alter the solar fuel generation landscape by greatly enhancing the rate and efficiency of direct photon-to-fuel conversion.

Accomplishments:

This year, we systematically investigated the properties of a number of different GaN nanowires and films, ultimately identifying a material system that exhibited high external quantum efficiency (EQE) and significant plasmon-enhanced photocurrent generation when excited with sub-bandgap light. Specific accomplishments included: 1) the PEC characterization of GaN nanowires and films, both with and without plasmonic nanostructure integration; (2) the study of the effects of In doping; and (3) the quantification of the plasmonic enhancement of gas production with metal-semiconductor structures using external quantum efficiency (EQE) as our metric. In this work at the Lawrence Berkeley National Laboratory, we have recently demonstrated the highest EQE, 51%, for GaN photocatalyst, which is much higher than other semiconductor photocatalysts. This has led to us successfully obtain $250,000 in external funding from the Research Corporation as part of a collaboration involving colleagues at the University of Utah.

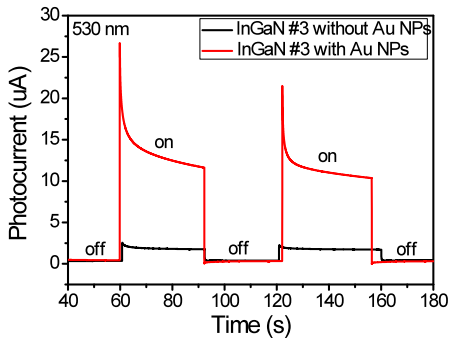



**Figure 1.** Photocurrent of InGaN #3 with and without Au nanoparticles at zero bias voltage irradiated with 530 nm green light.

| Sample # | Photocurrent (μA) | EQE (%) |
|---|---|---|
| **InGaN #1** | 118 | 51 |
| **InGaN #2** | 74 | 32 |
| **InGaN #3** | 49 | 21 |
| **GaN (301)** | 86 | 37 |

Structure of Solvation Shells at Electrode Surfaces

Principle Investigator: P. James Schuck

Project Description:

Predicting electrochemical reactions at real electrodes has proven difficult since our understanding of the liquid side of the solid-liquid interface—the electric double layer or EDL—is very crude. Our ultimate goal is to make *in situ* measurements of EDL composition, electric field, molecular orientation, and solvation structure of $Li^+$ ions in electrolytes used for Li-ion batteries. Such comprehensive information does not exist for any EDL, nor is there a validated theory to predict it. The difficulty of making measurements in the EDL is its extreme thinness—typically only about 1 nm. In order to be able to use FTIR to probe the EDL we used 2 techniques to reduce the volume of material interrogated. First, we used a ZnSe ATR crystal so that our FTIR signal came from the electrolyte volume within about 1 μm from the electrode surface, which was a thin gold coating on the crystal. Thus, only about $10^{-3}$ of the volume interrogated by the ATR (1 nm/1 μm) comes from the EDL. Second, we modulated the voltage on the electrode. The voltage modulation only affects the structure of the EDL, so the differences between spectra taken at high and low voltages come exclusively from the EDL. Since our signal to noise ratio is about 10,000, the signals from the EDL can be obtained with a signal to noise ratio of about 10.

Accomplishments:

The first step was to find an infrared feature that characterizes the concentration and bonding structure of Li ions in electrolyte. This was accomplished by spectra such as shown in Figure 1, which shows how the pure solvent spectrum (blue) is perturbed by the presence of $Li^+$. We found that the perturbation's intensity is directly proportional to the $Li^+$ concentration. We then took FTIR spectra as a function of voltage on the gold electrode. We expect that as the electrode becomes more positively charged, the $Li^+$ concentration in the EDL will be reduced, leading to smaller perturbation features.

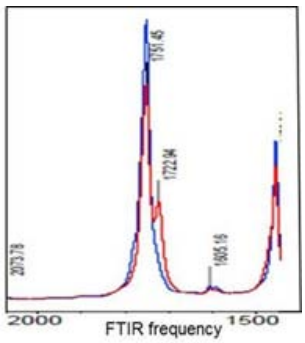
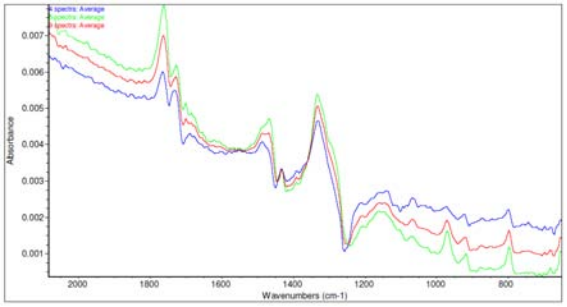



Figure 2 shows sample difference spectra taken with high and low voltages on the gold electrode. Each feature represents a *change* in the perturbation of a solvent spectrum by $Li^+$ due to changes in the EDL $Li^+$ concentration. Because the absorbances of the IR features are ~1, the difference spectra are on the order of $10^{-3}$, as expected. We are presently analyzing these spectra to determine details of the $Li^+$ solvation structures and the orientations of solvent molecules with respect to the surface, all as functions of surface voltage.




This work has led to a proposal that is part of the renewal proposal for the University of Texas EFRC, Understanding Charge Separation and Transfer in Energy Materials.

**Exciton Visualization and Engineering in Organic Materials for Energy Conversion**
Principal Investigator(s): **Alexander Weber-Bargioni, BiWu Ma, Jeffrey Neaton, Naomi Ginsberg**

*Project Description*
Our goal is to develop an understanding of excitons and other excited states in photoactive materials with high spatiotemporal resolution, which will lead to breakthroughs in many energy conversion technologies. For example, molecular photovoltaics are promising for solar energy conversion because they are cheap, lightweight, and flexible, and because their properties can be easily tuned via organic synthesis. However, OPVs suffer from low efficiencies. Space- and time-resolved understanding of excited states in these materials will lead to higher efficiencies. Despite more than two decades of past work, the transport and spectroscopic properties of organic materials in photovoltaics - and the nature and dynamics of their excitations - continue to be debated. A major challenge is the lack of knowledge of the interplay between morphology and excited states of these organic semiconductors.
For this LDRD we had proposed to develop and combine new approaches to synthesis, theory, and spectroscopy to, for the first time, spatially map, with nm-resolution, the evolution of excitons - as a function of molecular morphology - in well-defined tailored organic materials as a function of time. We suggested the use of state-of-the-art, materials-specific excited-state theory to interpret the exciton dynamics, study the microscopic origins of their dissociation and degradation processes, and, ultimately, predict molecular moieties and morphologies leading to robust and efficient energy conversion materials.

*Accomplishments*
Our most significant accomplishment has been to develop Localized Excitation Photo Current Microscopy (LEPCEM), which enables the direct measurement of exciton transport through organic materials, which we are currently writing summarizing in a manuscript that we will send to nature photonics (encouraged by the editor of nature photonics).

We hired two postdoctoral fellows, Dr. Mauro Melli starting on the LDRD project in November 2012 and Dr. Jiye Lee, starting in February 2013. Dr. Mauro Melli has developed Localized Excitation Photocurrent Microscopy, while Dr. Jiye Lee is developing a Field Effect Transistors with a spatially varying gate bias to direct exciton diffusion via a laterally varying E-field gradient, measured via LEPCEM. Furthermore, in we developed (lead by Dr. Ma) organic semiconductor materials that can be doped, whereby the exciton binding energy can be controlled. Prof. Ginsberg has established the instrumentation to study the exciton dynamics for the here-proposed work and Dr. Neaton developed a framework based on density functional theory (DFT) able to predict accurate excited-state energetics for static bulk solids, surfaces, and interfaces, working towards establishing the ability to simulate the dynamic component to exiton diffusion throughout a material.

In the last year we will converge these techniques to characterize fully the spatio temporal characteristics of excitons in a) Rubrene absorption layers since it is an ideal model system due to the large scale crystallinity, making the theoretical calculations represent the experimental measured environment; and b) Perovskite light harvesting materials since this new material class shows record power conversion efficiencies, while the light conversion mechanism – specifically the exciton properties are not understood at all.

# RATIONAL DESIGN APPROACH TO THE FORMATION OF HYBRID FRAMEWORK MATERIALS

Principal Investigator: Omar Yaghi

*Project Description*

The purpose of this project is the development of the building block approach for the rational design and synthesis of metal-organic frameworks, MOFs. MOFs are composed of inorganic secondary building units, SBUs, and organic linkers. Through careful selection of the organic linker and the inorganic SBU, the properties of the MOFs can be optimized. The formation of a desired inorganic SBU still remains as a synthetic challenge for the preparation of new MOFs with the desired structural features.

Previously, we were successful in the isolation of several molecular analogues of various inorganic SBUs. Among them, it was included a zirconium based SBU, with chemical formula $Zr_6O_4(OH)_4(-CO_2)_{12}$. This SBU is important because it has been shown that MOFs based on this zirconium SBU have great chemical and thermal stability. Thus, during this year we have focused our efforts on the obtaining of new MOFs with the same zirconium SBU. To achieve this goal, we have explored the synthetic conditions that led to the formation of this zirconium cluster in presence of organic linkers with various connectivity numbers. Furthermore, we have evaluated how the number of organic linkers connected to the cluster, (i.e. coordination number) can be tuned and controlled by the addition of modulating agents, resulting in a large structural variety.

*Accomplishments*

We have been successful in the preparation of a series of six MOFs based on the aforementioned zirconium-based SBU. Through control on the synthetic conditions by the addition of a modulating agent, we are now able to control the coordination number of the resulting SBU, without changing its basic conformation or number of metal elements. The most commonly found coordination number for this SBU is twelve, and there are some few examples of MOFs where this SBU shows coordination number eight. We have found that the addition of different amounts of formic acid during the MOF synthesis provides control on the coordinating features of the resulting SBU. In addition, the use of the modulating agent has proved to be important for the MOF crystal growing process. Indeed, the new MOFs have been obtained in the form of single-crystals, allowing their structural elucidation to be carried out with single-crystal x-ray diffraction techniques.

The structural analysis demonstrates the formation of SBUs with coordination numbers of 12, 10, 8, and 6. The variation on the coordination number is achieved by the coordination of formate ligands to the zirconium atoms, partially replacing the carboxylate groups that belong to the organic linkers. Thus, we have prepared two new MOFs, MOF-805 and MOF-806, with **fcu** topology by combining 12-coordinated SBUs with linear and ditopic linkers. Four new MOFs, (MOF-812, MOF-802, MOF-841, and MOF-808) with other topologies (**ith**, **bct**, **flu**, and **spn**) were produced by combining analogous SBUs of different coordination number (12, 10, 8, and 6) and organic linkers of different geometry (tetrahedral, bent ditopic, tetrahedral, and tritopic, respectively). Members of this series of MOFs exhibit permanent porosity. For example, MOF-808 has a BET surface area of 2060 $m^2\ g^{-1}$. These results significantly expand the number of available MOFs structures based on the important zirconium-based SBU, and show the way to the obtaining of new materials.

**Lattice QCD Codes by Discretizing Time and Space: FY2013 (Final Year)**

Investigators: Wick Haxton (lead), Volker Koch, Sergey Syritsyn, Andre Walker-Loud NSD

**Project Description:** This LDRD project is focused on developing a lattice QCD capability in the Nuclear Science Division, with particular emphasis on Standard-Model problems connected with weak interactions, fundamental symmetries, and astrophysics. Our program includes strategies for utilizing lattice QCD output as input into effective theory treatments of light nuclei, so that properties of light nuclei can be predicted from lattice results for two-nucleon systems, with known systematic errors. Our initiative is based on the "CalLat" partnership with Lawrence Livermore National Laboratory and Nvidia. Project goals include

- Solving problems important to our understanding of weak interactions, including Standard Model sources and hadronic parity and time-reversal violation.
- Advancing lattice QCD methods for petascale machines, including LLNL's Sequoia;
- Positioning our LBNL group to compete in SciDAC3 and other new funding initiatives.

This was the final year of this three year project. The LDRD funding helped us support two outstanding young researchers in lattice QCD through September, 2013: Andre Walker-Loud, a key member of the NPLQCD group who is leading efforts to calculate properties of two-nucleon systems, and Sergey Syritsyn, who previously helped lead the MIT group's efforts on computing nucleon properties and form factors. Andre, who began as an LBL postdoc and converted to a project scientist, recently left LBL to become an assistant professor at William and Mary. Sergey left in September, 2012, to join the Brookhaven National Laboratory Nuclear Theory group, his second postdoctoral position.

**Accomplishments:** Walker-Loud and collaborators developed methods to explore the role of strangeness in nuclei and in nuclear matter. They made initial estimates, using lattice QCD, of the strength of the hyperon-nucleon interaction. It is expected that in neutron star interiors, where the nuclear matter density may reach four times that of ordinary nuclei, hyperons and other aspects of strangeness may play an important role. Thus this effort is an important step toward using lattice QCD to predict aspects of the nuclear matter equation of state that are not directly accessible to experiment. Junakar and Walker-Loud also estimated the scalar strange content of the nucleon. This matrix element is important to theories of dark matter in which the coupling to the nucleus is proportional to the current quark mass: the strange quark can then play an important role, even though the strange quark content of the nucleon is low.

Similarly, Syritisyn and his LSD Collaboration partners evaluated the form factors for certain classes of composite dark matter that arise in technicolor theories. As these theories are strongly interacting, lattice techniques can be applied, just as in QCD, to make nonperturbative estimates of relevant matrix elements. This work has direct connections to that of Haxton, who with collaborators recently described the most general dark matter interaction using Galilean-invariant effective field theory. Some of the new operators they identified arise in technicolor dark matter theories.

# Explosive Astrophysics using High Performance Computing

Principle Investigator: Daniel Kasen

## Project Description

The purpose of this project is to better understand the conditions leading to the creation of the elements in extreme astrophysical environments. Our approach is to use advanced simulation codes on high performance computing systems to model the dynamics, nucleosynthesis, and the radiative transport of supernova explosions. Our end-to-end calculations will allow us to predict the composition, velocity and geometry of the ejecta, and thereby derive spectral signatures that are directly comparable to observational data. In this way, we will test our understanding of the conditions in explosive astrophysical environments and identify the important observable indicators of the nuclear physics occurring within.

We model the dynamics and radiation transport of explosions using a variety of codes. The smoothed particle hydrodynamics code SNSPH is used to model the dynamics of compact object mergers. In addition, we use the grid based adaptive mesh refinement hydrodynamics code CASTRO to model detonations. The radiation transport problems is addressed primarily using the SEDONA code, a Monte Carlo transport code which includes modern acceleration and variation reduction techniques.

## Accomplishments

We have primarily studied two different classes of astrophysical explosions: thermonuclear SNe arising from the merger of two white dwarfs, and radioactive transients from the merger of two neutron stars. Our studies of white dwarf mergers simulated the tidal disruption of the two stars, the nucleosynthesis and energetics of the detonation, and the observable spectra and light curves. We found that the luminosity of the resulting SNe depended both on the masses of the white dwarfs and the orientation of the system. The models resembled observations of a diverse range of Type~Ia SNe, from those of normal brightness to the most extreme luminosity events. The debris from the ejecta also displayed strong asymmetries.

Our studies of neutron star mergers have focused on the observable transients -- called kilonavae -- powered by radioactive heavy elements ejected in the event. The heavy elements are produced by rapid neutron capture (r-process) that occurs as neutron star material becomes unbound and undergoes decompression. We modeled the optical properties of r-process elements and showed that their opacity was ~100 times higher than previously thought. As a result, we found that the radiation from these events was emitted primarily in the infrared. Our studies led observers to follow up gamma-ray bursts with infrared facilities, leading to the first claimed discovery of a kilonovae. Comparison of these observations to our models allowed an estimate of the mass of the r-process material ejected. If the identification is correct, this is the first time that we have directly observed and quantified the synthesis of heavy r-process nuclei in the Universe.

**Initial CNNS Measurements at the Spallation Neutron Source at ORNL**

Spencer Klein

*Project Description*

The purpose of this effort is to measure the neutron backgrounds at the Oak Ridge Spallation Neutron Source (SNS) that are relevant for a first measurement of coherent neutrino-nucleon scattering (CNNS). CNNS is one of the last unobserved processes in the standard model of particle physics; in it, a neutrino scatters elastically from a target nucleus, which then recoils, but remains intact. The scattering is coherent, so the cross-section per nucleus scales as the atomic number, A, squared. By exploiting CNNS, one can build reasonably sized (5-10 kg) neutrino detectors. However, the nuclear recoil energy is small, usually less than ~ 50 keV. Since this is nuclear recoil, the ionization signal is smaller, typically 1-10 keV electron equivalent (keVee).

Two recent developments bring the observation of CNNS within easy reach. The first is the establishment of the SNS; its 1.2 MW proton beam leads to significant neutrino production, and the short pulses (600 nsec wide, at 60 Hz) allow timing cuts to reduce the non-accelerator backgrounds. The second is the development of low-noise point-contact germanium detectors; these detectors have low noise levels (65-200 eV typically), allowing them to be operated with thresholds below 1 keVee – well matched to a measurement of CNNS at the SNS.

The major background issue for a CNNS measurement at the SNS is due to beam-related backgrounds; these neutrons may interact in a germanium detector, mimicking a CNNS interaction. This LDRD provided funding for us to bring a point-contact germanium detector to the SNS, and measure the effect of SNS background neutrons on the detector.

*Accomplishments*

With this LDRD, we developed a movable data acquisition system for an existing Canberra BEGe (broad energy range germanium) detector, calibrated the detector at LBNL, moved the system to Oak Ridge, and took initial background measurements at a candidate site ("Beam Line 13a") at the SNS.

The data acquisition system digitized the signal from the BEGe preamplifier with a Struck 16-bit 100 Megasamples/s digitizer VME card. The digitizer included a field programmable gate array which implemented a trapezoidal filter to optimize the germanium energy resolution. This on-line filter was critical since triggering at an energy threshold below 1 keVee requires good trigger energy resolution. Otherwise, electronic noise fluctuations will swamp the trigger.

The system was initially calibrated at LBNL, and then shipped to the SNS. At the SNS, we set it up in a location about 20 m from the target, chosen to provide synergistic measurements with two neutron detectors: a neutron scatter camera from Sandia NL, and a liquid scintillator array from Oak Ridge. We initially observed significant electronic noise associated with the accelerator. We added some RF shielding, with considerable, but not complete success. We then took data with a slightly elevated threshold (a little over 1 keVee), and slightly degraded energy resolution. We observed a significant beam-related background: 4% of the triggers fell into a -1 μs + 3 μs window with respect to the beam; during that interval, this corresponds to 170 times the ambient background. A fraction of the background came with a larger delay, sometimes more than 100 μs. In contrast, there was no sign of any 'early' signal, from neutrons produced in upstream interactions. The energy spectra of the in-time background appeared similar to the ambient background, but we did observe a possible neutron-induced excitation of iron-56.

# Probing the Partonic Structure of Protons and Nuclei with Isolated Photons at the LHC

Constantin Loizides

*Project Description*

The goal of this LDRD is to formulate and carry out a systematic program for precise photon measurements with the ALICE detector at the LHC with sufficient precision to impact PDF measurements in an interesting kinematic regime.
In proton-proton collisions at center-of-mass energies at 7 TeV, cross section measurements of isolated photons will allow one to constrain the gluon distribution at small x with large leverage of the momentum transfer in the proton.

In particular, the following points will be addressed:
a) Simulation of the physics capabilities of ALICE' setup for 2011;
b) Development of the reconstruction code for photons using the shower shape in the kinematic range of about 10-30 GeV/c, where the main background, two-photon decays from neutral mesons, can still be distinguished in the calorimeter;
c) Development of alternative reconstruction algorithms outside of or complementary to the applicable region of the shower shape method;
d) Investigation of new isolation strategies using modern jet finders;
e) Investigation if further theoretical development for competitive results on PDFs is needed.

*Accomplishments*

The most significant accomplishments are the measurements of the raw isolated photon spectra, and their purity and efficiency, in proton-proton collisions at 7 TeV, using the shower shape approach. The isolation criteria have been obtained with a data-driven method using a template derived from neutral meson production in jets, as well as detailed simulations using generated events with PYTHIA that were reconstructed using similar (realistic) detector conditions as for the data. For these events also the simulation of the L0 trigger has been implemented.
The systematic uncertainty is dominated by the comparison of the above mentioned approaches. Further details regarding the background that arises from pileup events have been addressed. The results have been compared to calculations with JETPHOX and at higher energy also to those from the CMS and ATLAS collaborations, and found to be consistent in all cases. The measurement will be published in 2014. New analyses of proton-proton collisions at difference center-of-mass collision energies, and in proton-lead collisions have been started based on the experience of the one performed in the context of the LDRD.

# PROBING DYNAMICS OF ELECTRON TRANSFER FOR MICROBIAL-BASED ENERGY INTERCONVERSION

Principal Investigator(s): Caroline Ajo-Franklin (Lead), Matthew B. Francis, Naomi S. Ginsberg

*Project Description*

To achieve the optimal conversion of $CO_2$ and electricity into fuels via electrosynthesis, the inward electron transfer (ET) rate must be improved beyond what is known in naturally-occurring complexes. Yet, the current dearth of information about the mechanism ET dynamics from electrodes to multi-heme cytochromes *c* prevents rational attempts to redesign these proteins. Thus, the purpose of this project is to address the critical knowledge gaps that currently prevent the redesign of redox proteins that can directly transfer electrons to an electrode. The proteins known to accomplish interfacial ET are extremely complex, containing 10 hemes per protein, and thus are beyond the canonical approaches for single redox factor-containing proteins. As a result of our initial progress in this program, we are now in a position to combine recent innovations in synthetic and bioconjugation chemistry, synthetic biology and cyt *c* expression, and time-resolved optical spectroscopy to allow the first detailed electrochemical characterization of these complex protein species.

We will use MtrF and MtrA from *Shewenella oneidensis* MR-1 to develop the synthetic and optoelectronic tools required to determine the spatiotemporal dynamics of interfacial electron transfer. MtrF is a membrane associated protein that is the only structurally characterized biomolecule known to carry out interfacial ET. MtrA is a decaheme protein that is soluble and thus more tractable for various bioconjugation chemistries. While it is known from cyclic voltammetry that electrons are transferred from MtrF to an anode on the ms timescale [6], there is currently no information available to provide a deeper mechanistic understanding of this pathway. By measuring the rates of ET between the hypothesized entry point, connected to an anode, and each of three different putative exit points in MtrF, we seek to establish a quantitative, molecular-level understanding of interfacial electron transfer. The techniques can first be developed using MtrA and then applied to MtrF. These point-to-point rates will ultimately be used to inform protein re-engineering efforts to build simpler versions of extracellular ET pathways for more rapid microbial conversion of $CO_2$ and electricity into fuels.

*Accomplishments*

Our most significant accomplishment has been to develop methods to heterologously express MtrF at the highest levels reported to date. We have optimized expression by using a high throughput approach to screen multiple strains and various expression conditions and check for production of cytochrome *c* proteins. Having identified a candidate strain and condition, we find that the expression scales up to obtain ~10-20 mg of cytochrome *c* expressing cells from a liter of culture.

We have also developed methods of expressing these heme containing proteins anaerobically, without the need for an additional plasmid. This accomplishment gives us the flexibility to use another plasmid for incorporation of unnatural amino acids. Incorporation of unnatural amino acids allows us to perform bioconjugation chemistry at precise locations in the protein to properly test kinetics of electron transfer to and from the heme cofactors.

We are in the process of purifying MtrF and MtrA using various affinity tags for easy isolation.

**Functional Genomic Encyclopedia of Bacteria and Archaea: Evidence-Based Annotation of the Microbial Tree of Life**

Principal Investigator(s): (Adam Deutschbauer, Matthew Blow, James Bristow, Adam Arkin)

*Project Description*

The purpose of this project is to bridge the gap between microbial genome sequencing and genome characterization. Specifically, we aim to develop a flexible, rapid, and inexpensive platform to assay phenotypes, map promoters and gene models with RNAseq, and predict gene function using high-throughput transposon mutagenesis in bacteria and archaea. After establishing this pipeline, we aim to apply it to ~40 diverse microorganisms and use the resulting data to annotate gene function across the microbial tree of life using functional and comparative genomics. Lastly, we will expand the toolbox of the JGI and offer next-generation microbial characterization to the greater user community to meet DOE missions in energy, environment, and biomanufacturing.

*Accomplishments*

Our most significant accomplishment has been the development of a flexible and inexpensive method for assaying the phenotypes of thousands of genes in parallel using transposon mutagenesis and DNA barcode sequencing. The key to the approach is the introduction of random DNA barcodes into the transposon. A mutant library for a given microbe is characterized a single time using the time-consuming and expensive TnSeq protocol. All subsequent assays to measure mutant fitness for thousands of genes in parallel only require the quantification of the DNA barcodes, a simple and inexpensive assay termed BarSeq. We have applied this technique to 8 bacteria and generated over 1000 whole-genome mutant fitness profiles, representing ~3 million gene fitness measurements. We are beginning to use these data to predict gene function in diverse species using correlations in mutant fitness across hundreds of diverse growth conditions. With the random DNA barcode method developed, we are now applying this technique to additional, diverse microorganisms relevant to biofuel production, bioremediation, and nutrient cycling.

Additionally, we have established a robust pipeline for generating 5’ RNAseq, stranded RNAseq, and small RNAseq datasets to map promoters, identify small RNAs, and correct gene models. In FY14, we will integrate the RNAseq data with the mutant fitness data to assign phenotypes and putative function for small RNAs and other previously unannotated genes. Lastly, we will begin to explore the storage, visualization, and analysis of the phenotype, mutant fitness, and RNAseq data in KBase.

**Principles of Context-Controlled Standardized Biological Parts for Predictable and Rapid Assembly of New Biological Functions**

Principal Investigator(s): Nathan J. Hillson, Vivek K. Mutalik

## Project Description

Genetically engineered microorganisms have enormous near-term potential for the synthesis of fuels, commodity and specialty chemicals, and materials from a variety of sugar sources (*e.g.*, cellulose, starch, and sucrose) or sunlight/CO2. Unfortunately, to date, engineering organisms has been a time consuming, costly, and unpredictable endeavor due to the lack of well characterized biological components that can be readily assembled to create the metabolic pathways and genetic control systems. Another key challenge involved in reliable engineering of microorganism is having the library of parts, promoters, UTRs, properly coded genes, and terminators that are designed to work together and their operation predictable in different contexts. Each part has some dependence on its genetic context whether the part is assembled in a plasmid or in the genome. In addition, the growth and physiology of the cell in different environmental conditions will also impact the part operation.

Using a library of standard biological parts from in-house projects, we are developing a starting basis set of expression control systems that can be made predictable even as host-background and environmental conditions vary. At the heart of the approach is use of a standard design for composition and characterization of genetic parts called the Expression Operating Unit (EOU). The EOU provides a common context in which multigene operon systems can be designed such that it reduces the interference from cellular elements outside the immediate context of the EOU.

## Accomplishments

To demonstrate the functional composition of genetic parts within EOU, we used standard constitutive or inducible promoters, bicistronic designs (BCD), and specific mRNA target cleaving CRISPR elements driving the expression of genes in operon designs coding for mRFP and GFP fluorescent proteins. These elements were assembled in a medium copy plasmid and assayed for fluorescence in DH10B *Escherichia coli* grown in minimal media. We observed that, although individual expression cassettes made up of constitutive promoter-BCD-gene-terminator yield reliable expression across different genetic contexts, their assembly in operon systems exhibit cellular growth defects and unpredictable fluorescence outputs. To overcome the toxicity issues and unreliable functional compositions, we designed a series of full factorial combinatorial operon designs that included: replacing the constitutive promoters with inducible promoters (so that transcription rate can be controlled), sequence-independent parts (to reduce recombination artifacts), the absense of CRISPR elements (that may impact transcript stability and/or cause growth defects), changing vector copy numbers (to reduce cellular burden), and assembling the two-gene systems as two independent EOUs. We observed that, by using BCDs in operon designs, gene order determines the reliability of expression, and parts are impacted by genetic context. Instead, using tandem individual cistron designs (each within an EOU) produced very reliable gene expression.

We extended these design insights to engineer two distinct metabolic pathways in *E. coli*: combinatorial assembly of: 1) *pdc* and *adhB* genes in the ethanol pathway and 2) MevK and PMK genes in the isopentenol pathway, in operon and (separately) cistron-based designs. These experiments demonstrated that production titers impacted cellular physiology and nutrient levels, and further optimization is needed before analyzing the composition rules for the parts.

**SINBAD: Simultaneous INverse Beam Anomalous Diffraction**

Principal Investigator(s): James M Holton

*Project Description*

By splitting the beam from an x-ray free electron laser (XFEL) in two and bouncing each beam around to meet one another simultaneously at the sample position from exactly 180 degrees apart, we will enable a robust solution to the phase problem in macromolecular crystallography (MX) that requires only the natively-present elements of biological matter: sulfur and phosphorus. This new camera geometry will simultaneously solve the problems of radiation damage, attenuation corrections, background scattering, non-isomorphism and partiality that currently limit anomalous phasing at XFELs to only one or two extremely favorable cases. If successful, SINBAD will be a transformative breakthrough for the MX field and a compelling justification for NGLS.

This LDRD was conceived as a pilot project to investigate the four most critical potential problems with the design: 1) extracting anomalous difference data from stills, 2) using $\Delta F/F$ instead of $\Delta F$ itself for phase determination, 3) stability of back-scattered reflections, 4) availability of monochromator crystals that can bounce a 2.5 keV x-ray beam at near-90 degree angles without significant losses.

*Accomplishments*

Overall progress on the goals proposed for year 1 has been better than anticipated. To test Goal 1) the spindle axis at ALS 8.3.1 had to be precisely re-aligned, but this went very smoothly and data to test the accuracy of anomalous differences from "pseudo-SINBAD" stills has been collected. Software that can process these data, however, is still forthcoming as convincing standard MX packages to integrate without a Lorentz factor has proved difficult. We are therefore writing our own spot-integration code that is specific to stills.

Work towards Goal 2) has revealed that non-isomorphism between samples is going to be a significant problem for SINBAD and indeed for current XFEL MX work, and even conventional MX where multiple crystals must be used. Further investigation into non-isomorphism, however, revelaed the surprising insight that it may be entirely due to the humidity surrounding the protein samples, and we expect control of humidity throughout the sample handling process will dramatically improve isomorphism. Year 2 will focus extensively on this topic.

For Goal 3, we experimented with directly measuring the 11,1,1 reflection from crystalline germanium, which required a photodiode detector to be positioned just above the incoming beam pipe. Measuring this rocking curve, we found that it agreed very well with theory, and we also confirmed that the bandpass of the monochromator at ALS 8.3.1 can be made as low as 0.11 eV using the Si(333) reflection, an excellent situation for evaluating potential SINBAD monochromator crystals.

For Goal 4) we were surprised to find the dynamical theory of x-ray diffraction substantially lacking for softer x-rays where anomalous scattering effects can be significant. However, it was clear that optimal "bouncer" crystals for SINBAD, and also for self-seeding soft x-ray monochromators should be of high atomic number and with large unit cells. To test this hypothesis, we purchased small examples of Pt(111) and Ir(111) single crystals. Currently, we are working out robust procedures for measuring the rocking width of these crystals and expect to develop optimum polishing and etching techniques for them in year 2.

# OPTIMIZING PLANT-MICROBE INTERACTIONS FOR SUSTAINABLE SUPPLY OF NITROGEN FOR BIOENERGY CROPS

Principal Investigator(s):
Dominique Loque, Romy Chakraborty, Gary Andersen, Trent Northen, Manfred Auer and Musa Ahmed

*Project Description*

Nitrogen (N) is an essential component of proteins and consequently a key element for life and cell development. Mineral N is often limited for plants, which consequently reduces plant growth and biomass yield. While this practice has been partly responsible for the 'green revolution,' it has come at high environmental and economic costs. Today, the N fertilizer industry consumes more than 20% of the total energy used by petrochemical industries, number that keep growing since the demand is still expending. Furthermore, the addition of fertilizers to overcome N limitation is highly undesirable as that destabilizes the native ecosystems and adds carcinogenic compounds into the environment. In natural ecosystems, plants have developed strong relationships with microbes to cope with the low availability of essential nutrients such as N. For example, plant rhizospheres contain N2-fixing bacteria that are able to fix atmospheric N2 without the requirement of forming symbiotic association with a host-plant, however several of them depend on plant root exudates for carbon supply. Furthermore, endophytic bacteria colonizing root, stem and leaves of plants with N2-fixing function have been identified in several plants.

The aim of this project is to optimize interactions between plants and N2-fixing endophytic or FN2F bacterial communities to provide adequate amounts of assimilable N to host-crops. This would reduce fertilizer consumption and carbon footprint of feedstock production, and greatly improve the sustainability of biomass production. In order to tackle this challenging project, we created a team of scientists with different expertise to address multiple aspects such as the identification and characterization of native and culturable N2-fixing bacteria, screening preferred organic carbon sources and signaling molecules released by plants using metabolomics, and finally by engineering plants to produce customized root exudates under N limiting conditions.

*Accomplishments*

We first established a method to enrich culturable endophitic and rhizospheric bacteria, which were subsequently used to isolate culturable free $N_2$ fixing bacteria. Several samples derived from different plant organs (roots, stems and leaves) from different species (tobacco, switchgrass and Brachypodium) grown on soil under different N regimes were screened and only few $N_2$ fixing bacteria candidates that harbor NifH gene were isolated.

We established a hydroponic culture system to grow tobacco, switchgrass and Brachypodium plants to collect root exudates that are currently used for metabolomics profiling. More importantly, the hydroponic culture system facilitates the harvest of large quantities of exudates, which are used to feed isolated bacteria strains.

Finally as proof of concept to enrich root exudates with target organic acid compounds under N limiting condition, we generated some transgenic *Arabidopsis* engineered with N-dependent metabolic pathways to enhance malate or citrate content in root exudate under N limiting conditions.

We are currently optimizing metabolomics profiling techniques, characterizing engineered plants and isolated bacteria, and re-introducing isolated and tagged bacteria to swichgrass, tobacco and engineered plants.

## SYNCHROTRON X-RAY FOOTPRINTING

Principal Investigator(s): Corie Ralston, Musa Ahmed

*Project Description*

The goal of this project is to establish a high-throughput x-ray footprinting program at the Advanced Light Source. X-ray footprinting (XF) is a technique that allows determination of protein structure and dynamics in the solution state at the resolution of a single amino acid. It is a natural extension to standard structural biology techniques such as crystallography in that it can be used to map specific protein interactions in large complexes in solution, and allows for probing of dynamic interactions on millisecond timescales. The methodology of data collection, buffer calibration, and mass spectrometry analysis for the method has been previously developed and used very successfully at the National Synchrotron Light Source (NSLS) over the last few years. The establishment of an x-ray footprinting program at the ALS serves two purposes: 1) it allows continued support of projects currently underway at the NSLS beamline X28C (the only XF beamline in the country) during the commissioning of a new XF beamline at the NSLS-II, and 2) it further develops and extends the technique of XF into the sub-millisecond time regime.

*Accomplishments*

Significant progress toward developing a footprinting program at the ALS has been made with the first year of LDRD funding. Experimental feasibility was established: Radiolytic degradation of a fluorophore in standard buffer was analyzed at four ALS beamlines as a function of exposure to generate dose-response curves for each beamline, establishing the relative exposure times necessary to ensure modification in the linear regime. Beamline 5.3.1, a white-light beamline with a focusing mirror, produced the best results, in fact demonstrating that footprinting could be conducted in the microsecond domain, representing a significant extension of the technique. After determination of dose response curves, experimental protocols for x-ray exposure, protease digestion, de-salting, and LC/MS of proteins for footprinting experiments were established. Footprinting data was collected on a standard protein, Cytochrome-C, on beamlines 5.3.1 and 3.2.1. Analysis of the mass spectrometry results clearly showed that oxidation of residues match expected rates from the literature, and a paper delineating the establishment of a footprinting program at the ALS has been submitted.

Another significant accomplishment was the successful application of the technique to three important protein systems: a MegaDalton chaperonin protein, a 10kDa hexameric protein in complex with other proteins involved in microsome shell formation, and a 35kDA photosensitive protein system. In addition to demonstrating the utility of the technique for a wide range of protein sizes and complexes, each experiment gave information on protein structure that had been unobtainable using other standard structural biology methods.

In order to continue development of the technique, we have 1) obtained permission from the ALS to commission a fully dedicated XF beamline at the ALS using a previously decommissioned beamline, 2) established an MOU with the NSLS to support NSLS XF users from Sept 2014 through Feb 2016 using beamlines 5.3.1 and 3.2.1 at the ALS, and 3) submitted an R01 application to the NIH in June, 2013, seeking three years of support for the XF program.

**Computational Methods for X-ray Free-Electron Laser Studies of Solar Energy Converting Biocomplexes**

Principal Investigators: Nicholas Sauter, Ralf Grosse-Kunstleve, Petrus Zwart, Vittal Yachandra, Junko Yano, Paul Adams, Cheryl Kerfeld, Chao Yang, Stefano Marchesini

*Project Description*

The purpose of this project is to understand light-induced water splitting in green plants, algae and cyanobacteria; organisms that are responsible for producing most of the oxygen in the atmosphere. An important application of this knowledge will be in the design of future fuel production schemes based on artificial photosynthesis. The splitting of water, creating oxygen and hydrogen, is accomplished by the protein complex photosystem II, which contains a catalytic center containing four manganese atoms. To drive the reaction to completion, four sunlight photons sequentially oxidize the Mn atoms after which the catalyst returns to the reduced state. Traditional methods for studying structure and function, such as X-ray crystallography, have been hampered by the high sensitivity of the Mn center to probing X-rays, which reduce the metal atoms.

We have an unprecedented opportunity to map out the detailed reaction mechanism using X-ray free-electron laser (XFEL) experiments at the Linac Coherent Light Source (LCLS). In the experimental design, photosystem II crystals will be driven through the redox cycle with an optical laser. X-ray probe pulses at LCLS are short enough (50 fs) that all observations can be made before reduction and other damage processes occur. As the probe pulses are extremely intense, the sample becomes fully ionized after the observations are recorded; therefore, a continuous stream of new crystals must be delivered to complete the full data set. Atomic structure of the protein will be determined by X-ray diffraction, and the electronic state of the Mn atoms will be measured by X-ray emission and absorption spectroscopy. The experimental team is a collaboration between many groups at different institutions. This LDRD is specifically targeted at developing the requisite computational methods to interpret the data. Main challenges are the data size (~100 TB) along with novel detector and optical designs.

*Accomplishments*

The project was awarded two LCLS X-ray beamtime allocations for FY2013 and additional experimental time for FY2014. The team demonstrated that XFEL-based metal L-edge absorption spectra can be used to probe the oxidation state of model compounds, using a completely new spectrometer design. We also collaborated with investigators at Brookhaven National Lab to develop an acoustic-droplet delivery system for serial crystallography experiments, which will be orders of magnitude more efficient in terms of sample use. We continued to develop computational techniques for processing both spectroscopic and diffraction data, and released our software (*cctbx.xfel*) publicly for general use with LCLS crystallography experiments. We analyzed 114 TB of photosystem II data in real time, utilizing a 7.5 Gb/sec ESnet link to transfer data to NERSC for processing with a 1000-core Linux cluster.

We demonstrated that the 50 fs X-ray pulse is short enough to observe damage-free photosystem II in both the dark and first illuminated states. Simultaneous X-ray crystallography and X-ray emission spectroscopy experiments show that crystals are intact not only with respect to the protein structure, but also with regard to the electronic structure of the highly radiation-sensitive catalytic Mn cluster, opening new directions for future dynamics studies.

**Feasibility and Development of Fluctuation Xray Scattering at the NGLS**

Principal Investigator(s): Petrus H. Zwart

*Project Description*

X-ray solution scattering is a routine biophysical technique used to determine structure and dynamics of macromolecules in solution. When solution scattering data is interpreted, often with the aid of known atomic models, an improved understanding of the macromolecule's biological function and properties emerges. The main challenge associated with solution scattering data is the intrinsic lack of information that can be obtained from solution scattering curves. By performing the solution scattering experiment at the femtosecond time scale by using a free-electron laser, a technique known as fluctuation X-ray scattering, the information content of the data can be significantly enhanced, leading to fewer ambiguities in derived structural models and a better understanding of the associated biology. Whereas the development of fluctuation scattering at free electron lasers has been targeted primarily to obtain the shape of macromolecules, its scope and uses should be seen as an extension of classic solution scattering.

*Accomplishments*

Over the last year, a number of important advances have been made. First of all, we have demonstrated experimental feasibility of fluctuation scattering at the LCLS on biological nanoparticles. Associated with this accomplishment, is a significant gain in experience in the processing of experimental fluctuation scattering data. The development of novel data reduction routines in a high-performance-computing environment, have allowed us to produce a 3D model derived from experimental fluctuation scattering of a biological nanoparticle.

The second accomplishment is a new route for generating model data, using Graphical Processor Units. These highly parallel computational workhorses speed up model-data calculations significantly and will ultimately be used in model-based refinement against experimental data.

The third accomplishment of this research program are new theoretical insights obtained in the nature of fluctuation scattering data. By using analytical techniques, we have demonstrated Guinier-like relations that can be used to characterize and validate experimental datasets. Other results obtained are basic statistical properties of fluctuation scattering data that will ultimately lead to a maximum likelihood formalism in FXS structure determination.

In conclusions, we have made significant advances in the development of theoretical and experimental methods for fluctuation scattering.

**Higher Performance CCDs for Next Generation Dark Energy Experiments**

Principal Investigator(s): Christopher Bebek

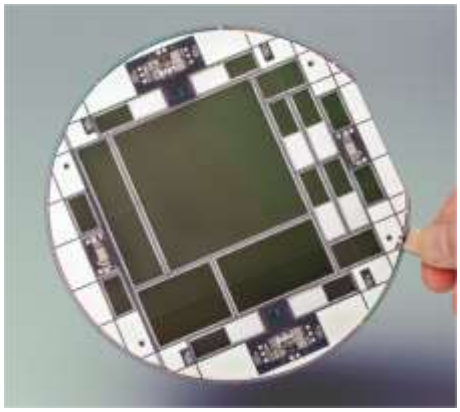
*Project Description*

The goals of this project are to develop advanced charge-coupled devices (CCDs) for use in the next generation of Dark Energy experiments that are now in the planning stages. CCDs developed at LBNL are presently in use in two existing Dark Energy experiments, the Dark Energy Survey, and the Baryon Oscillation Spectroscopic Survey. Future projects such as the Dark Energy Spectroscopic Survey and the Large Synoptic Survey Telescope have targeted the fully depleted CCD technology that was developed at LBNL but now requires improved performance in order to meet the science goals.

The areas that we are emphasizing in this work are increasing the quantum efficiency (QE) at both blue and red wavelengths, reducing the detector readout noise, increasing the readout speed, and exploring methods to achieve single-photon detection. The QE work requires technology development at the LBNL MicroSystems Laboratory (MSL) while the other efforts involve design efforts and close collaboration with our industrial partner Teledyne DALSA. We have worked closely with engineers at DALSA to explore advanced technology concepts including the use of finer line-width lithography for smaller feature sizes, and thinner gate insulators allowing for smaller channel-length transistors for the output amplifiers of the CCDs.

*Accomplishments*

We have demonstrated improvements in QE at blue wavelengths by reducing the thickness of the ohmic contact that is needed to terminate the electric field at the back side of the CCD. This effort required significant fabrication technology development in the MSL. We also experimentally investigated the use of $ZrO_2$ as an anti-reflection (AR) layer in collaboration with a group in the LBNL Environmental Energy Technologies Division that had experience with this material for energy-efficiency applications. The combination of a 10 nm thick, backside ohmic contact layer with a $ZrO_2/SiO_2$ AR coating resulted in an improvement in the QE at a wavelength of 350 nm of nearly a factor of 3. Red QE improvement has been demonstrated with thicker substrates.



We designed a new wafer layout that was submitted to DALSA, and the fabrication of a 24 wafer lot was successful based on early testing results. A photograph of one of the wafers is shown. A new fabrication process flow was developed in order to implement the advanced technology steps described above. These new steps are designed to improve the noise performance, and several of the CCDs have aggressively designed output stages that utilize the technology enhancements explored in this fabrication run. Also included in the wafer design are CCDs that use non-destructive readout amplifiers to achieve sub-electron noise via multiple sampling of the signal charge, and CCDs with 16 output channels to increase the readout speed. We have produced the first set of back-illuminated devices and detailed testing has begun. We expect that the possible improvements demonstrated during the testing effort will be considered for future implementation in CCDs that will be of use to the scientific community.

New Monolithic CMOS Sensors on a Fully Isolated Substrate
Principal Investigator(s): Maurice Garcia-Sciveres

Project Description:

15 Years ago all digital cameras used CCD image sensors. Today they all use CMOS image sensors. This led to widespread interest in the potential for scientific applications. But development of an “ideal” monolithic device, where the sensing function places no restrictions on the electronic circuits and the fill factor is 100%, has so far proven elusive. This LDRD is to design and fabricate a proof of principle, radiation tolerant demonstrator for particle physics and x-ray detection that may finally realize this ambition. This project received end-of-year finding in FY12 and full-year funding in FY13 and FY14. FY14 is the final year, with the goal of fabricating a demonstrator chip exploiting the full capabilities of the 130nm feature size CMOS process being used for this work.

FY13 Accomplishments:

A first prototype chip was designed in FY12 and fabricated in FY13. This chip contains an active pixel matrix with 64 rows by 20 columns. Working devices were received in February 2013 and then tested to validate the design methods used and simulation results. These tests were successful, leading to submission and presentation of results at the International Image Sensor Workshop (IISW) in June 2013. Following this, devices were irradiated at the Los Alamos LANSCE proton beam in early September to a maximum dose of 30Mrad. Testing of the irradiated devices is being carried out in FY14. Before irradiation the charge collection diode junctions could be reverse-biased up to 11V , at which point general breakdown was reached. At 10V bias the achieved input referred rms noise was about 200 electrons for pixels with a size of 22um x 225um, and about 25 electrons for 12um x 12um pixels. These values are consistent with simulation results. Threshold dispersion without tuning for the full array was measured to be 530 electrons rms, with reduced to 25 electrons after using the in-pixel threshold adjustment included for this purpose. An unexpected effect was uncovered indicating charge multiplication at bias voltages well below breakdown, suggesting some localized discharge. Also, while the results were consistent with simulation, the noise was at the high end of expected range. These effects combined mean that the noise in the larger pixels is too high to resolve the expected signal from charged particles. These findings defined two main goals for FY14 (in addition to measurement of radiation effects): understanding the detailed geometry and placement of the process implants in order to control the breakdown voltage, and prototyping the minimum possible pixel size to control the capacitance.

**Transforming Infrared Astronomy with Nanostructure IR Filters**

Principal Investigator(s): (Saul Perlmutter and Xiang Zhang)

*Project Description*

New telescope techniques that can explore objects in deep space with high resolution and sensitivity in near-IR region are highly demanded for the study of properties of dark energy and dark matter over time. However, near-IR observations from the Earth's surface are extremely challenging because of the bright background emitted from the atmosphere. Fortunately, these emission lines are intrinsically very narrow ($\approx 5\times10^{-6}\,\mu$m), covering only a small fraction of the total spectrum, and the continuum between the lines is typically as dark as zodiacal light, *viz*. the background level directly observed from space. Therefore, selectively filtering the OH emission light will enable high sensitive deep space near-IR measurements from the ground.

We will develop **an innovative metamaterial optical filter system (astrofilter)** for highly sensitive near-IR observation by selectively removing the OH emission lines from the Earth's atmosphere. Different from natural materials, the physical properties of a metamaterial is not primarily dependent on its chemical constituents, but rather upon the structures of the building blocks which are much smaller than light wavelengths. By tailoring effective optical properties of the nanoscale layered structures, the metamaterial filter system has the potentials to provide sharp spectral filtering line-width and high transmission of residual signals, which will be otherwise impossible for traditional techniques based on natural materials. The metamaterial near-IR filter system will also be fully compatible with existing telescopes and other instruments because of the large acceptance angle, moderate diameter, and thin filter thickness.

*Accomplishments*

Our most significant accomplishment has been to develop a target-oriented optimization algorithm for designing the multilayer IR filter with high optical performance. Our algorithm combines *the needle optimization* and *the tunneling method* to search for the global minimum of spectrum difference between our design and the target. We also adopt the distributed scheme to successfully design the metamaterial with a hundred alternatively stacked FK51A (schott glass) and Silica layers. Total transmitted OH narrow-line flux can be suppressed down to 5.28%, while the filter transmission for the galaxy continuum remains at a high level of 70.66%.

We have also successfully employed further optimization to make each reflection band in the spectrum narrow, deep, and near square profiled [Fig. 1(a)]. Our approach provides optimized reflection bands with a width approximately 0.12 nm. The astrofilter will be working at a large acceptance angle, *e.g.* 1000 arcsec.

We have also explored the state-of-art fabrication process of growing multilayer thin films with well-controlled thicknesses and surface roughness by electron beam physical vapor deposition system (Fig. 1(b)). The roughness of each layer has been controlled less than 1% of its thickness.

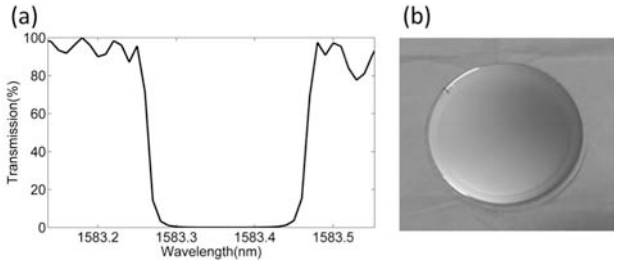



Figure 1: (a) An optimized metamaterial astrofilter reflection band with narrow, deep, and near square profile. (b) Multilayer nanostructure coated on a 2 inch glass wafer with well-controlled thicknesses and surface roughness.

We are in the process of employing a new reversal method that can further improve the filter design with less number of layers and thinner total thickness.

# High Voltage Up and Down Converters for Low Power Low Density Detector Instrumentation

Principal Investigator: Henrik von der Lippe

## Project Description

This project pursues the development and prototyping of integrated DC-DC converters for use in fully-integrated detector readout ICs. Two distinct design tracks are targeted to different detector applications. One is the development of medium power density DC-DC down converters for use in next generation, fully integrated HEP read-out ICs (i.e. ATLAS upgrade at CERN). The integration of a DC-DC down-converter in this application could significantly lower the overall detector mass by reducing the wire mass, thereby achieving the required low detector cross-section required for future experiments. Second, the development of high voltage (i.e. 40V) DC-DC up-converters could allow for monolithic avalanche photo diode (APD) detectors for medical imaging and other applications (i.e. SSPMs).

The design of fully integrated, high power density down-converters in standard CMOS processes is a relatively new area of research, made possible by the smaller feature sizes and increased capacitance density available with modern processes. We have been specifically following the applicable research of the Berkeley Wireless Research Center (BWRC), with the intent to extend conversion ratios beyond 2:1 for our application area. Many technology-specific parameters must be optimized to successfully implement high efficiency, high power density converters. The development of high voltage up-converters is less demanding with regard to the required power density (low), but has more complex design requirements for maintaining all devices at specified safe operating voltages with reasonable efficiency.

## Accomplishments

CMOS DC-DC converter design offers a nearly unlimited combination of topologies, conversion ratios, transistor voltages, process feature sizes, etc. To reduce this huge design space, we have developed a methodology that allows us to analytically select good design candidate topologies and conversion ratios, and only then move to schematic implementation, optimization, and evaluation of the select designs. From these results, we have narrowed the design space considerable for the implementation of a second-generation prototype. This prototype would fold in the results of the first prototype (received and tested) to achieve a complete implementation achieving power density in the range of 10-100 $mW/mm^2$, at a ratio 4:1 or better.

The first prototype IC, a 4:1 down-converter fabricated in 65 nm CMOS has been evaluated and has demonstrated nearly identical performance compared to the design simulation. The correlation between the simulated and measured power and voltage efficiency indicates that our methodology is sound, and can be used to develop higher performance designs with a high level of confidence in the result. More study is needed with regard to the robustness of the technologies utilized with respect to their reliability and lifetime in this application.

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Sheraz Gul, Jason K. Cooper, Jinghua Guo, Vittal K. Yachandra, Junko Yano, and Jin Z. Zhang "Effect of Al3+ Co-doping on the Dopant Local Structure, Optical Properties, and Exciton Dynamics in Cu+-doped ZnSe Nanocrystals" ACS Nano 7, 8680–8692 (2013) Url:DOI:10.1021/nn402932q

Debajeet K. Bora, Yelin Hu, Sebastian Thiess, Selma Erat, Xuefei Feng, Sumanta Mukherjee, Giuseppino Fortunato, Nicolas Gaillard, Rita Toth, Krisztina Gajda-Schrantz, Wolfgang Drube, Michael Grätzel, Jinghua Guo, Junfa Zhu , Edwin C. Constable, D.D. Sarma, Hongxin Wang, Artur Braun "Between Photocatalysis and Photosynthesis: Synchrotron spectroscopy methods on molecules and materials for solar hydrogen generation" J. Electr. Spectr. Relat. Phonom. (accepted 2012)

ALS-MacDowell LB11020 New opportunities in Hard X-ray Tomography - High Temperature and Elemental Imaging

**Presentations**

Invited Talk by Dr. Robert O. Ritchie "Three-Dimensional Tomographic Characterization of Advanced Ceramic Textile Composites under In Situ Loading at Ultrahigh Temperatures" at 2013 TMS Annual Meeting & Exhibition on 03/04/2013 at the symposium on Three-Dimensional Materials Science VII

Invited talk, R.O.Ritchie – the David Turnbull Lecture titled "Real-Time Imaging of the Structure and Mechanical Properties of Engineering and Biological Materials at Multiple Length-Scales" at MRS Spring 2013 on 12/03/2013 at Boston, MA

B.Cordonnier, Rheophysics and Energy of Magmas: a perspective for volcanic fluid dynamics Earth Observatory of Singapore, (2013)

B.Cordonnier , Under stress we gain in momentum but ultimately we fail: Flow limits of magmas and implications to volcanology. University of Bristol, UK, (21013)

Benoit Cordonnier1, Thibault Duretz2, Phillippe Yamato3, Boris Kaus4, Michael Manga5, Non-Newton Man: An exploration of magmatic shear thinning sources.IAVCEI-International Association of Volcanology and Chemistry of Earth Interior, Kagoshima- Japan July 2013

A. Haboub1, Hrishikesh A. Bale2, James R. Nasiatka1, Brian N. Cox3, David B. Marshall3, Robert O. Ritchie1,2, Alastair A. MacDowell1, R. Ritchie2, Wim Degruyter4, Benoit Cordonnier4, Michael Manga4, Ben Andrews4, Three-dimensional tomographic characterization of advanced ceramic textile composites and magma texture under in situ loading at ultrahigh temperatures. ALS User Meeting October 2012.

Hrishikesh Bale, A. Haboub, Alastair MacDowell, J. Nasiatka, Brian Cox, David Marshall, Robert Ritchie, Three-dimensional tomographic characterization of advanced ceramic textile composites under in situ loading at ultrahigh temperatures, Invited Talk, Symposium: Three-Dimensional Materials Science VII, 2013 TMS Annual Meeting, MARCH 3-7, 2013, , San Antonio, Texas1.

Nagi N. Mansour, Francesco Panerai, Alexandre Martin, Dilworth Y. Parkinson, Alastair A. MacDowell, Abdelmoula Haboub, Timothy A. Sandstrom,Tony Fast, Gerard L. Vignoles, and Jean Lachaud, New Approach To Light-Weight Ablators Analysis: From Micro-Tomography Measurements to Statistical Analysis and Modeling AIAA 44th AIAA Thermophysics Conference, San Diego. June 2013

Abdelmoula Haboub, Alastair A. MacDowell, Stefano Marchesini, Diworth Y. Parkinson: Coded Aperture Imaging for Fluorescent X-rays-Biomedical Applications, Proc. Fully Three-Dimensional Image Reconstruction in Radiology and Nuclear Medicine, Lake Tahoe, June 2013.

**Journals/Reports**

Bale, H., A. Haboub, A.A. MacDowell, J.R. Nasiatka, D.Y. Parkinson, B.N. Cox, D.B. Marshall, and R.O. Ritchie, "Real-time quantitative imaging of failure events in materials under load at temperatures above 1,600 degrees C," Nature Materials 12, 40-46 (2013).

B. N. Cox, H. A. Bale, M. Blacklock, T. Fast, M. Novak, V. Rajan, R. Rinaldi, R. O. Ritchie, M. Rossol, J. Shaw, Q. D. Yang, F. Zok, and D. B. Marshall, “Stochastic Virtual Test Systems for Ceramic Composites”, Proceedings, Composites Week @

Leuven and TexComp-11 Conference, Leuven, Belgium, Aug. 2013. (doi: 10.1111/xxx)

M. N. Rossol, J. Shaw, H. Bale, R. O. Ritchie, D. B. Marshall and F. W. Zok, "Characterizing Weave Geometry in Textile Ceramic Composites using Digital Image Correlation", Journal of The American Ceramic Society, vol. 96 (8), 2013, pp. 2362-2365. (doi: 10.1111/jace.12468)

B. N. Cox,H. A. Bale,M. Begley,M. Blacklock,B. C. Do,T. Fast,M. Naderi,M. Novak,V. Rajan,R. G. Rinaldi,R. O. Ritchie,M. Rossol,J. H. Shaw,O. Sudre, Q. D. Yang,F. Zok and D. B. Marshall, "Stochastic Virtual Tests for High-Temperature Ceramic Matrix Composites", Annual Review of Materials Research, Volume 44, 2014 (in press)

ALS-Shapiro LB13038 Ultra-high Resolution Microscopy of Nano-materials by Scanning X-ray Diffraction Microscopy

D.A. Shapiro, Y. Yu, T. Tyliszczak, J. Cabana, R. Celestre, W. Chao, K. Kaznatcheev, A.L.D. Kilcoyne, F. Maia, S. Marchesini, Y. S. Meng, T. Warwick, L.L. Yang, and H. A. Padmore, "X-ray Microscopy with Near Wavelength Limited Spatial Resolution", under peer review for Nature

D.A. Shapiro, M. Farmand, T. Tyliszczak, R. Celestre, A.L.D. Kilcoyne, F. Maia, S. Marchesini, T. Warwick, L.L. Yang, and H. A. Padmore, "A new instrument for nano-tomography at the Advanced Light Source", in preparation

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ALS-Voronov LB13004 Next Generation Grating for Spectroscopy and Pulse Compression

D.L. Voronov, T. Warwick, and H.A. Padmore, "Multilayer-coated Blazed Gratings with Variable Line Spacing and a Variable Blaze Angle" (to be published).

D.L. Voronov, L.I. Goray, R. Cambie, E.M. Gullikson, T. Warwick, V.V. Yashchuk, and H.A. Padmore, "High-Order Multilayer Coated Blazed Gratings for High Resolution Soft X-Ray Spectroscopy" (to be published).

D.L. Voronov, S. Diez, P. Lum, S.A. Hidalgo, T. Warwick, N. Artemiev, and H.A. Padmore, "Fabrication of X-Ray Gratings by Direct Write Mask-Less Lithography", Proc. of SPIE 8848, (2013) 88480Q.

D.L. Voronov, T. Warwick, H.A. Padmore, "X-Ray Diffraction Gratings: Probing New Approaches", Invited talk at Helmholtz-Zentrum Berlin (BESSY) 10/01/2013

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C.Sanchez-Hanke; F. Siewert; D. Smith; D. Voronov, “Grating Optics”, Chapter of the report DOE Workshop in X-Ray Optics for BES Light Source Facilities, March 27-29, 2013, Washington, D.C. https://docs.google.com/a/lbl.gov/file/d/0B74dHuNh4CtiOUFfQU1XcF9SYWs/edit

R. Conley, R. Soufli, Hisataka Takenaka, A. Aquila, S. Hau-Riege, D. Windt, Ch. Morawe, A. Macrander, D. Voronov, E, Dooryhee, Yong Cai, “Thin Films”, Chapter of the report of DOE Workshop in X-Ray Optics for BES Light Source Facilities, March 27-29, 2013, Washington, D.C., https://docs.google.com/a/lbl.gov/file/d/0B74dHuNh4CtiRDBhNDRvOFNNU1k/edit

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D. Shapiro, S. Roy, R Celestre, W Chao, D. Doering, M. Howells, S. Kevan, D. Kilcoyne, J. Kirz, S. Marchesini, K. A. Seu, A. Schirotzek, J. Spence, T. Tyliszczak, T. Warwick, D. Voronov, H. A. Padmore, “Development Of Coherent Scattering And Diffractive Imaging And The COSMIC Facility At The Advanced Light Source”, Journal of Physics: Conference Series 425 (2013) 192011.

ALS-Wang LB12022 Grazing Incident Soft X-ray Scattering for Organic Photovoltaics

Collins, B.Akira., Z. Li, J.R. Tumbleston, E. Gann, C.R. McNeill, and H.W. Ade, “Absolute Measurement of Domain Composition and Nanoscale Size Distribution Explains Performance in PTB7:PC71BM Solar Cells,” Advanced Energy Marterials 3, 65-74 (2013).

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Guo, C., Y-H. Lin, M.D. Witman, K.A. Smith, C. Wang, A. Hexemer, J.W. Strzalka, E.D. Gomez, and R. Verduzco, “Conjugated Block Copolymer Photovoltaics with near 3% Efficiency through Microphase Separation,” Nano Letters 13(6), 2957-2963 (2013).

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CH-Abergel LB12001 Global Transcriptome, Deletome and Proteome Profiling of Yeast Exposed to Radioactive Metal Ions: a Tool to Distinguish Radiation-Induced Damage From Chemical-Toxicity

M. Sturzbecher-Hoehne, C. Goujon, G. J.-P. Deblonde, A. B. Mason, and R. J. Abergel, "Sensitizing curium luminescence through an antenna protein to investigate biological actinide transport mechanisms" J. Am. Chem. Soc., 2013, 135, 2676-2683 DOI: 10.1021/ja310957f

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CH-Belkacem et al LB11004 Scientific Tools in Multi-Dimensional X-ray Spectroscopy and Coherent Diffractive Imaging

F. Weise, D.M. Neumark, S.R. Leone, and O. Gessner, "Differential near-edge coherent diffractive imaging using a femtosecond high-harmonic XUV light source", Opt. Express 20, 26167 (2012), http://www.opticsexpress.org/abstract.cfm?URI=oe-20-24-26167

CH-Chandler LB13005 Asymetric Responses of Systems Far From Equilibrium

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CH-Gilles LB12006 Photo-switchable Metal Organic Frameworks for CO2 Sequestration

N. Nijem, H. Bluhm, M. L. Ng, M. Kunz, S. R. Leone, M. K. Gilles, "Preferential nitric oxide adsorption over water in photoreduced unsaturated metal center HKUST-1" Journal of American Chemical Society, submitted Nov 25, 2013.

CH-Head-Gordon (Martin) LB13036 New Algorithms for Performing and Analyzing Large Scale Electronic Structure Calculations

R.J. Azar, P.R. Horn, E.J. Sundstrom, and M. Head-Gordon, "Useful lower limits to polarization contributions to intermolecular interactions using a minimal basis of localized orthogonal orbitals: Theory and analysis of the water dimer", J. Chem. Phys. 138, 084102 (2013). (http://dx.doi.org/10.1063/1.4792434)

J. Thirman and M. Head-Gordon, "Electron correlation can give anti-binding contributions to intermolecular interactions", J. Phys. Chem. Lett. (submitted).

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E.-H. Yap and T. Head-Gordon, "Calculating the Bimolecular Rate of Protein–Protein Association with Interacting Crowders". 2013, J. Chem. Theory Comput. 9(5), 2481-2489.

CH-Shuh LB12020 Developing f-electron Soft X-ray Spectroscopy Simulation, Theory, and Experiment for Clean Energy Materials

R. Copping, B. Jeon, D. Pemmeraju, S. Wang, S. J. Teat, M. Janousch, T. Tyliszczak, A. Canning, N. Grønbech-Jensen, D. G. Prendergast, and D. K. Shuh, "Towards equatorial planarity about uranyl: Synthesis and structure of tridentate nitrogen-donor {UO2}2+ complexes," Inorg. Chem., submitted (2013).

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CH-Wilson LB12030 Oxidative Transformations of Organic Aerosol

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CS-Haranczyk LB12009 An Optimization-based Strategy for Computational Design of Nanoporous Carbon-Zero Materials

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CS-Li (Xiaoye) LB11018 Next Generation Computing for X-Ray Science

S. Chourou, A. Sarje, X. Li, E. Chan and A. Hexemer. "HipGISAXS: A Massively Parallel Code for GISAXS Simulation", March Meeting of the American Physical Society, Baltimore, Maryland, March 18-22, 2013.

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CS-Oliker LB13007 High-Performance Parallel Graph-Analysis for Key Genomics Computations

V. Strnadova, A. Buluc, J. Chapman, J. Gilbert, J. Gonzalez, S Jegelka, D. Rokhsar, L. Oliker, "Efficient and Accurate Clustering for Large-Scale Genetic Mapping", 2014 SIAM International Conference on Data Mining (SDM'14), submitted.

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J.J. Donatelli, and J. A. Sethian. "Algorithmic framework for X-raynanocrystallographic reconstruction in the presence of the indexingambiguity." Proceedings of the National Academy of Sciences 111.2 (2014): 593-598, http://www.pnas.org/content/111/2/593.full.pdf+html?sid=b01e80f6-a5a0-4ef6-ba86-da6266e91326

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CS-Ushizima LB12021 Quantitative Image Analysis for Computational Modeling

**Presentations**

D.M. Ushizima, “Computer vision algorithms for image-based experiments", The Berkeley Institute for Data Science (BIDS) Data Science Faire, Dec 2013.

D.M. Ushizima, A. H. Gomes, C. M. Carneiro, A.G.C. Bianchi, “Automated Pap Smear Cell Analysis: Optimizing the Cervix Cytological Examination", International Conference on Machine Learning and Applications, Miami, FL, Dec 2013.

D.M. Ushizima, “Multimodal and Multiresolution Analysis and Visualization of Experimental Data”, INFORMS: Data Mining in Medical Decision Making and Bioinformatics Applications, Minneapolis, MN, Oct 2013.

D.M. Ushizima, J. Correa, D. Skinner, E.W. Bethel, “Analysis and visualization of image-based experiments", Biomedical research: current challenges in computing conference (C3), IBM sponsored, Sep 2013.

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D.M. Ushizima, “Data analysis and visualization for the Brain Initiative”, LBNL Brain Workshop, talk - host: Lawrence Berkeley National Laboratory, 2013.

D.M. Ushizima, “Aquisicao de imagens digitais em experimentos cientificos: desafios, resultados e perspectivas”, invited talk – host: Universidade Federal de Ouro Preto, MG, Brazil, Jul 2013.

D.M. Ushizima, “Analysis and Visualization of high throughput experiments”, Workshop on Driving Discovery: Visualization, Data Management, and Workflow

Techniques, Advanced Photon Source Center for Nanoscale Materials Electron Microscopy Center, invited talk - host: Argonne National Laboratory, May 2013.

D.M. Ushizima, "Image analysis of experimental data", Workshop of the Program on Statistical and Computational Methodology for Massive Datasets, talk - host: Statistical and Applied Mathematical Sciences Institute (SAMSI), Research Triangle, MD, May 2013.

D.M. Ushizima, A.G.C. Bianchi, W. Guo, "Characterization of MRI brain scans associated to Alzheimer's disease through texture analysis", International Symposium on Biomedical Imaging: from Nano to Macro, Apr 2013.

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B. Moritz, A. Kemper, M. Sentef, T. Devereaux, J. Freericks, "Electron-Mediated Relaxation Following Ultrafast Pumping of Strongly Correlated Materials: Model Evidence of a Correlation-Tuned Crossover between Thermal and Nonthermal States," Physical Review Letters, August 2013 http://dx.doi.org/10.1103/PhysRevLett.111.077401

A. Kemper, M. Sentef, B. Moritz, C. Kao, Z. Shen, J. Freericks, T. Devereaux, "Mapping of unoccupied states and relevant bosonic modes via the time-dependent momentum distribution", Physical Review B, July 2013 http://dx.doi.org/10.1103/PhysRevB.87.235139

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L. Lin, S. Shao and W. E, "Efficient iterative method for solving the Dirac-Kohn-Sham density functional theory", J. Comput. Phys. 245, 205, 2013

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A. Damle, L. Lin and L. Ying, "Pole expansion for solving a type of parametrized linear systems in electronic structure calculations", submitted, 2013

L. Lin, Y. Saad and C. Yang, "Approximating spectral densities of large matrices", submitted, 2013

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NE-Canon LB11043 Defining an Ecosystem to Support Data -Intensive Science

**Presentations**

L. Ramakrishnan, S. Canon, "Experiences in Building a Data Packaging Pipeline for Tomography Beamline", Big Data Analytics: Challenges and Opportunities (BDAC-13) Workshop. Held in conjunction with ACM/IEEE SC13, November 2013.

L. Ramakrishnan, P. K. Mantha, Y. Yao, S. Canon, "Evaluation of NoSQL and Array Databases for Scientific Applications", Data Cloud Workshop. Held in conjunction with ACM/IEEE SC13, November 2013

E. Dede, M. Govindaraju, D. Gunter, S. Canon, and L. Ramakrishnan, "Semi-structured Data Analysis Using MongoDB and MapReduce: A Performance Evaluation," ScienceCloud Workshop. Held in conjunction with ACM HPDC13, June 2013

Z. Fadika, M. Govindaraju, S. Canon, and L. Ramakrishnan, "Evaluting hadoop for data-intensive scientific operations," IEEE Cloud Computing, 2012.

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ESD-Bouskill LB12004 Developing a Mechanistic High-Latitude Soil Carbon and

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Bouskill NJ, 'Trait-based modeling in microbiology: Greying the Black box', ICoN 3, nitrification network meeting. Tokyo, Japan. September, 2013.

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Bouskill NJ, Riley WJ, Tang J., "Benchmarking high-latitude ecosystem models using observational meta-analysis", In preparation for Ecology Letters

ESD-Brodie LB13017 Integrative mapping of soil heterogeneity at the microbial scale

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ESD-Chambers LB13044 Tropical Forest Ecosystems under a Changing Climate

R.G. Knox, J.Q. Chambers, N. Higuchi, "Sensitivity of Amazon forest trees to rising atmospheric CO2 concentration", Global Change Biology, In prep.

ESD-Davis LB11007 Effect of Secondary Mineral Coatings on Biogeochemical Processes

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J. Davis, H. Guo, B. Lai, P. Ercius, K. Kemner, P. Fox, D. Singer, A. Minor, and G. Waychunas, "Characterization of secondary mineral grain coatings and their role as diffusion-controlled sinks and sources for metal contaminants", American Chemical Society National Meeting, April 2013.

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ESD-Jansson,C LB11011 CYANOALKANES: Engineering Cyanobacteria for Phototrophic Production of Jet Fuel

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ESD-Romps LB11044 Interactions among Cloud Processes, Convection, and Climate Change

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ESD-Tokunaga LB11034 Testing a New Soil Carbon Sequestration Strategy by Accelerating Calcite Precipitation in Soils

Y.-S. Han and T.K. Tokunaga, "Soil carbon sequestration through anhydrite- and gypsum-treatment: Laboratory tests". Manuscript submitted to Journal of Environmental Management, June 2013.

EETD-Caldas LB13043 Generative Design Methods for Integration of Energy and Sustainability in Early-Stage Architectural Design

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M. Gobet, T. Nosach, S. Greenbaum, M. Shirpour and M. Doeff, "Nuclear Magnetic Resonance Studies of Sodium Titanate Cathode Materials for Na-ion Batteries" 224th Meeting of the Electrochemical Society, San Francisco CA Oct. 27-Nov 1 Abstract #24947. http://www.electrochem.org/meetings/biannual/224/

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EETD-Sohn LB13013 Integrated Assessment Capability for Sustainable Water-Energy Co-Management

LL Dale, N Kirali, D Millstein, M Carnall, S Vicuna, N Borchers, E Bustos, J O'Hagan, D Purkey, C Heaps, J Sieber, WD Collins, MD Sohn, "An integrated assessment of water-energy and climate change in Sacramento, California: How strong is the nexus?" Applied Energy, Submitted December 2013

EETD-Wang, Y LB13014 LIGTT Integrated LDRD Proposal Part 1. The Design and Evaluation of an Inexpensive, Fuel-Efficient and Super Low-Emissions Biomass Cookstove

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Y, Wang., D, Wilson., K, Lask., A, Gadgil., "Laboratory Characterization of Ultrafine Particle Number Size Distributions and Other Pollutants from Traditional and Improved Biomass Cookstoves", American Association of Aerosol Research (AAAR) 32nd Annual Conference, Portland, Oregon, 2013.

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EETD-Zormpa LB13016 A Novel Nanoscale Chemical Analysis System for Low-Cost Solar Materials

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V. Zorba and R.E. Russo "Nanoscale Plasma Spectrochemistry" Pittcon 2013 conference, Philadelphia, PA (March 2013)

V. Zorba "Ultrafast Laser Induced Breakdown Spectroscopy for 3-Dimensional Chemical Imaging" SciX 2013 conference, Milwaukee, WI (October 2013).

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GN-Mavrommatis LB12017 Computational Data management and Analysis Methods for the Study of a Rapidly Expanding Genome and Metagenome Sequence Data Space

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GN-Pennacchio LB13021 Function-Based Approaches for Distant-Acting Enhancer Discovery

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B. McMorran "Experiments with Free Electron Vortex States" Physics Colloquia, Wesleyan University (Middletown), and Trinity College (Hartford), CT; Feb 14&15, 2013

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B. McMorran "Electron Vortex Beams" Advances in Structural and Chemical Imaging Workshop (ASCI 2013), Victoria, BC; May 29, 2013

T. Harvey "Small-Pitch Electron Diffraction Holograms Patterned on Inorganic Resist with Electron Beam Lithography" 57th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication (EIPBN "3-Beams"), Nashville, TN; May 30, 2013

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PBD-Hillson LB12027 Principles of Context-Controlled Standardized Biological Parts for Predictable and Rapid Assembly of New Biological Function

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PBD-Holton LB13029 SINBAD: Simultaneous INverse Beam Anomalous Diffraction

**Presentations**

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PBD-Loque LB12014 Engineering of a Positive Feedback Loop to Improve Wax Deposition and Plant Water Use Efficiency

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PH-Bebek LB13033 Higher Performance CCDs for Next Generation Dark Energy Experiments

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PH-Garcia-Sciveres LB12040 New Monolithic CMOS Sensors on a Fully Isolated Substrate

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