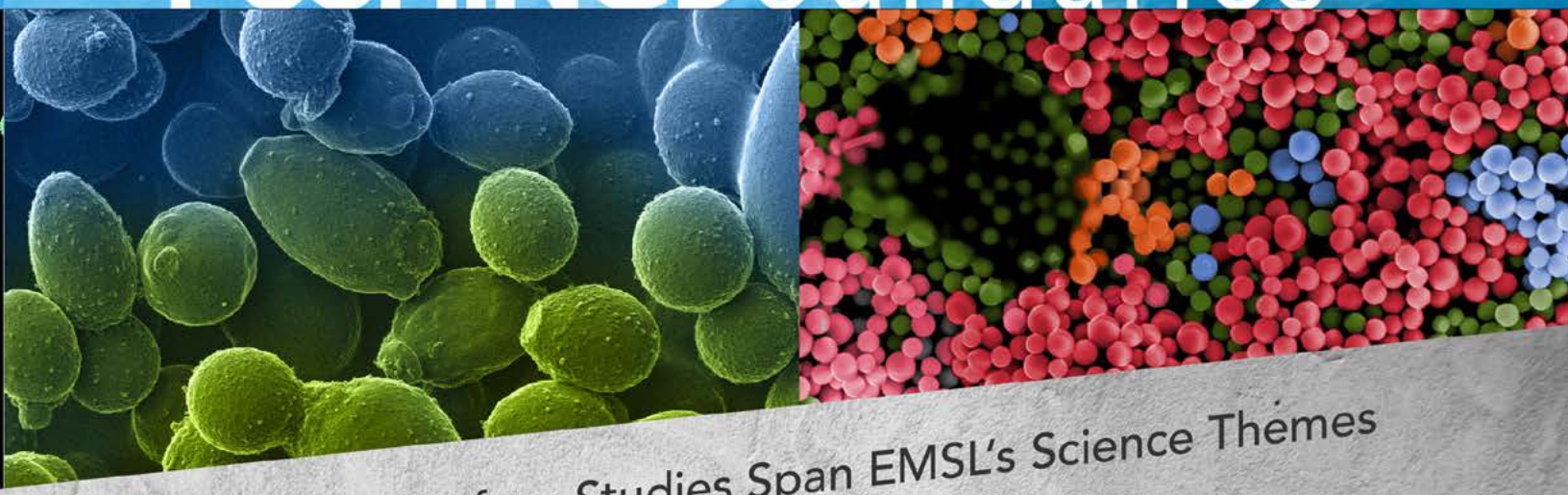
theMolecularBond

EMSL

SCIENTIFIC INNOVATION THROUGH INTEGRATION

February 2016

PUSHINGBoundaries



Interfacial Surface Studies Span EMSL's Science Themes

Also inside this issue:

Deadline for JGI-EMSL Letters of Intent Nears

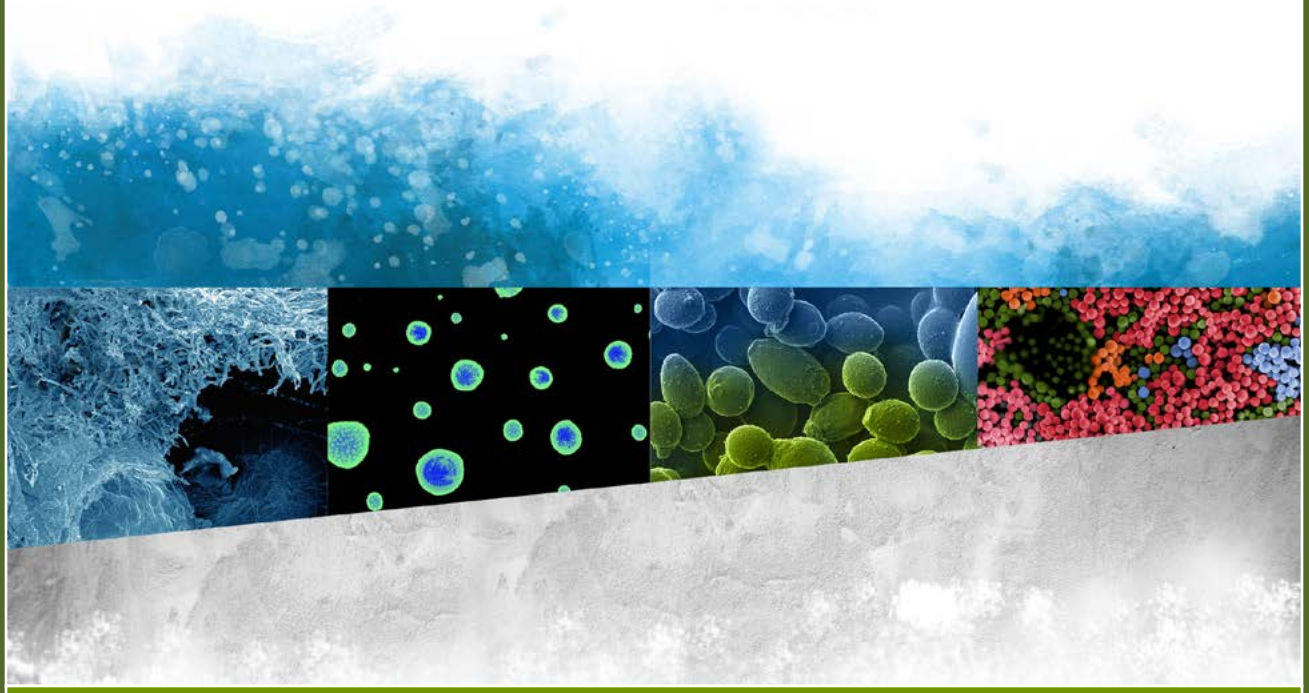
Latest Version of NWChem Released

EMSL Scientist has Paper of the Year

Optimizing Microbes to Produce Biofuels and Chemicals

Developing Better Ways to Detect Environmental Contaminants

Solid-liquid interface studies have a long history at EMSL. The insights gained from this research spans across all four of EMSL's Science Themes in areas including terrestrial ecosystems, energy materials, aerosols and biological systems. With improved understanding of interfacial events, scientists working at EMSL have developed more predictive models and made significant advances in addressing real-world challenges. EMSL's focus on solid-liquid interface research has pushed the development of new instruments and techniques to better study these complex surfaces for even greater scientific results.



About *The Molecular Bond*

The Molecular Bond is EMSL's bimonthly newsletter for users, potential users and other interested individuals. EMSL Communications oversees the production of *The Molecular Bond*.

EMSL, the Environmental Molecular Sciences Laboratory, is a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research in the Office of Science. Located at Pacific Northwest National Laboratory in Richland, Wash., EMSL offers an open, collaborative environment for scientific discovery to researchers around the world.

Its integrated computational and experimental resources enable researchers to realize important scientific insights and create new technologies. More information about EMSL is available at: www.emsl.pnnl.gov

To request additional copies or to subscribe, contact: EMSL Communications at email: emslcom@pnnl.gov

EMSL

Pacific Northwest NATIONAL LABORATORY

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A close up of a scientist loading a sample into the sample holder for the environmental transmission electron microscope, or ETEM, housed in EMSL's Quiet Wing. The ETEM allows researchers to perform microscopic and spectroscopic *in-situ* measurements relevant to catalytic and geochemical studies important to energy and environmental applications. (EMSL file photo)

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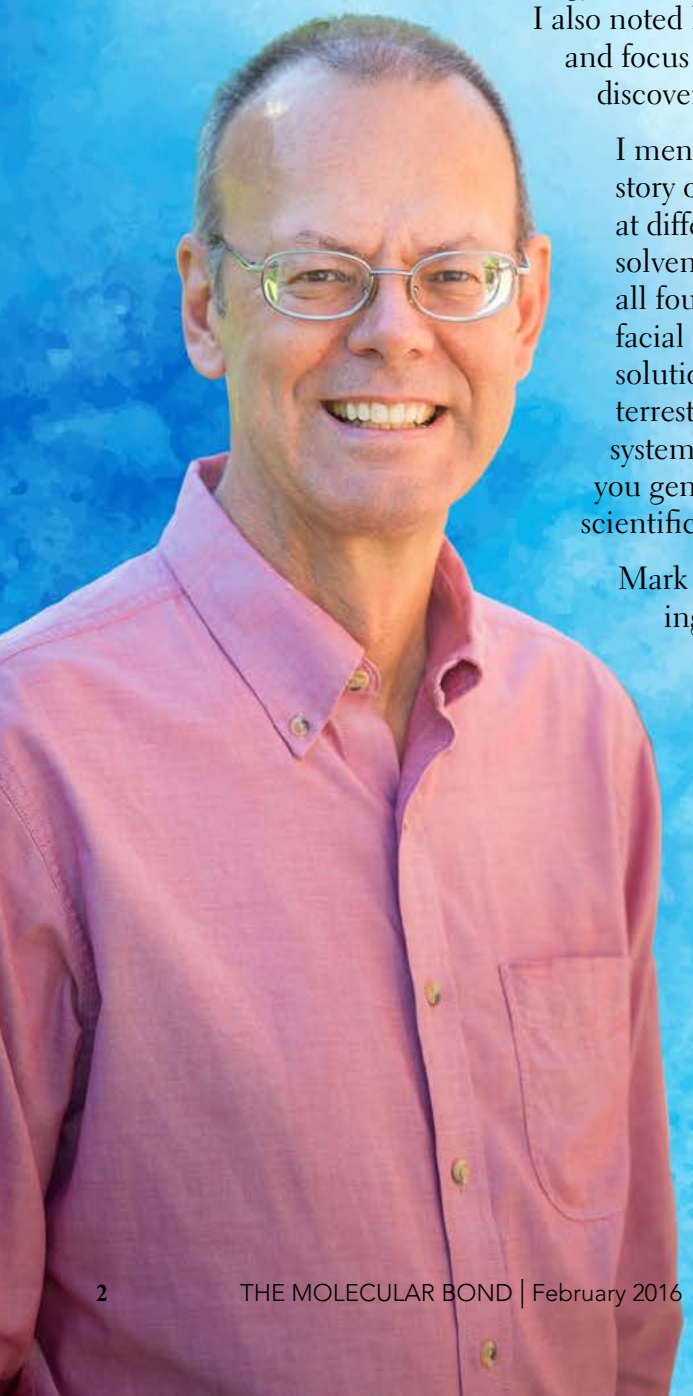
FROM THE DIRECTOR

Harvey Bolton



In my December "From the Director" message I listed EMSL's Science Themes – Atmospheric Aerosol Systems, Biosystem Dynamics and Design, Energy Materials and Processes, and Terrestrial and Subsurface Ecosystems. I also noted how these four themes help guide our research investments and focus our user projects to accelerate scientific innovation and discovery.

I mention this because of the unique approach taken in the cover story of this issue of *The Molecular Bond*. This issue's feature looks at different studies at EMSL that explore solid/liquid interfaces and solvent mediated processes. What's unique is this research crosses all four of EMSL's Science Themes. By better understanding interfacial events, we can improve predictive models and develop better solutions to real-world challenges, particularly those dealing with terrestrial and subsurface, biological, aerosol, and energy materials systems – EMSL's Science Themes. I hope the cover story helps you generate ideas to expand your research possibilities using EMSL scientific expertise and capabilities.

Mark your calendar and plan to attend the 2016 EMSL user meeting Sept. 12-13 in Richland, Wash. The theme for this year's meeting is a holistic view of the terrestrial carbon, nutrient and hydrologic coupled cycles including exchange and transformations between the atmosphere, plant, microbe and soil components at molecular to ecosystem scales and is being jointly organized by Science Theme Lead Nancy Hess and Plant Sciences Director Christer Jansson. The meeting will feature internationally recognized plenary speakers, including keynote presenter Mary Firestone, University of California, Berkeley. Watch for more information.

I hope you engage with us to advance your science through collaboration.

—Harvey

Laboratory Fellow and EMSL Science Theme Lead Don Baer delivers a "how to" seminar on EMSL's Science Theme Research call for proposals on Feb. 12. Entitled "Working with EMSL: FY 2017 call for proposals," the presentation included tips on how to write a successful proposal as well as EMSL's review process and criteria. The seminar was EMSL's first Periscope broadcast using the live video streaming Twitter app. (EMSL file photo)

NEWS & KUDOS

Deadline Approaching for JGI-EMSL Letters of Intent

FICUS
Facilities Integrating Collaborations for User Science

The deadline for submitting Letters of Intent to the Facilities Integrating Collaborations for User Science, or FICUS, call between the Department of Energy Joint Genome Institute, or DOE JGI, and EMSL is April 4 at 11 p.m. PDT.

This call is part of the collaboration between user facilities stewarded by the DOE Office of Biological and Environmental Research. The FICUS program was established to encourage and enable researchers to more easily integrate the expertise and capabilities of multiple user facilities into their research.

The JGI-EMSL call represents a unique opportunity for researchers to combine the power of genomics at DOE JGI and molecular characterization at EMSL in one proposed research project. Successful applications will focus on high risk/high payoff projects in the focused topic areas that can be completed on an accelerated timeline as compared to the standard CSP or science theme projects. In addition, they must utilize a broad range of the capabilities of each facility and generate datasets beyond what each of these facilities could generate by itself.

Proposal package guidance is available at the Call for Letters of Intent for FY 2017 JGI-EMSL Collaborative webpage at http://1.usa.gov/1njqmNN.

Questions regarding EMSL's user program or specifics about the call may be directed to the User Support Office at emsl@pnnl.gov, 509-371-6003.

Biofuel Tech Straight From the Farm

A team of researchers from five institutions report in the journal *Science* on Feb. 18 that anaerobic gut fungi perform as well as the best fungi engineered by industry in their ability to convert plant material into sugars that are easily transformed into fuel and other products.

"Nature has engineered these fungi to have what seems to be the world's largest repertoire of enzymes that break down biomass," said Michelle O'Malley, lead author, professor of chemical engineering at the University of California, Santa Barbara, and EMSL user.

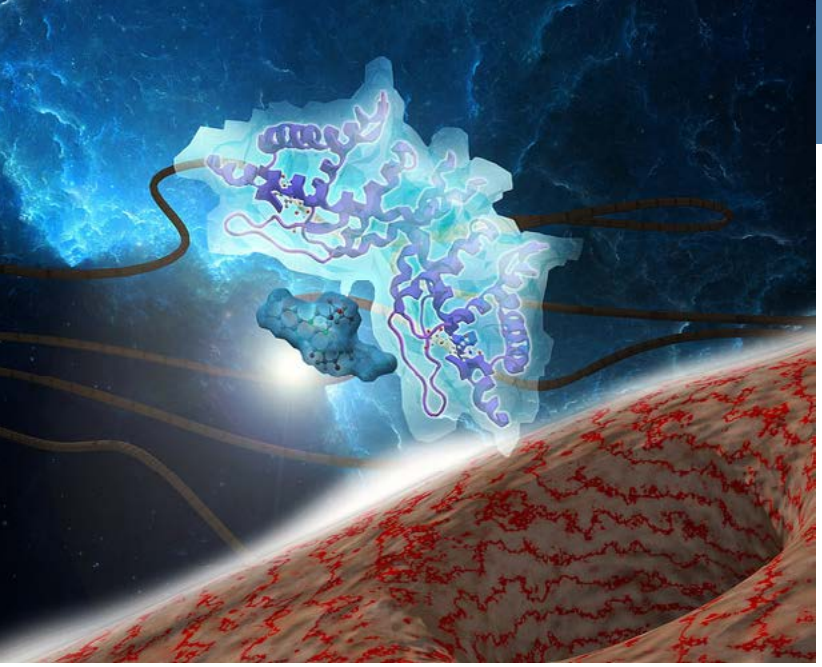
The study used the expertise and capabilities at two Department of Energy Office of Science User Facilities: EMSL at Pacific Northwest National Laboratory, or PNNL, and the DOE Joint Genome Institute. The study is the first to result from a partnership between the two facilities called Facilities Integrating Collaborations for User Science, or FICUS. The partnership allows scientists around the world to draw on capabilities at both Office of Science user facilities to get a more complete understanding of fundamental scientific questions.

The team also included scientists from EMSL/PNNL, DOE JGI, the Broad Institute of MIT and Harvard, and Harper Adams University.

Reference: Solomon KV, CH Haitjema, JK Henske, SP Gilmore, D Borges-Rivera, A Lipzen, HM Brewer, SO Purvine, AT Wright, MK Theodorou, IV Grigoriev, A Regev, DA Thompson, and MA O'Malley. 2016. "Early-branching gut fungi possess a large, comprehensive array of biomass degrading enzymes." *Science*, February 18, 2016. DOI: 10.1126/science.aad1431.

Read the PNNL news release: http://1.usa.gov/1oPPfRB.

Harvested from the manure of goats, horses and sheep, anaerobic gut fungi pictured here help herbivores digest stubborn plant material. (Image courtesy of University of California, of Santa Barbara)



An illustration of a vitamin mimic (small blue structure) binding to a protein (larger coiled structure) to gain entry into the cell.

Microbes Take Their Vitamins

Scientists at Pacific Northwest National Laboratory, or PNNL, and Argonne National Laboratory have developed a "vitamin mimic" – a molecule that looks and acts just like a natural vitamin to bacteria – they can track and measure in living cells. Their research offers new insights into the inner workings of living microbes that are useful for the study of Earth's carbon and nutrient cycle and development of new fuels.

The research team used the vitamin mimics to collect information about how vitamins enter the cell and interact within the cell. The scientists utilized EMSL capabilities for the study, and the work was funded by the Department of Energy Office of Science. The findings were published in *ACS Chemical Biology*.

Reference: Anderson LN, PK Koech, AE Plymale, EV Landorf, A Konopka, FR Collart, MS Lipton, MF Romine, and AT Wright. 2015. "Live cell discovery of microbial vitamin transport and enzyme-cofactor interactions." *ACS Chemical Biology*, Dec. 15, 2015. DOI: 10.1021/acschembio.5b00918.

Read the PNNL news release: http://1.usa.gov/1RW4Mvi.

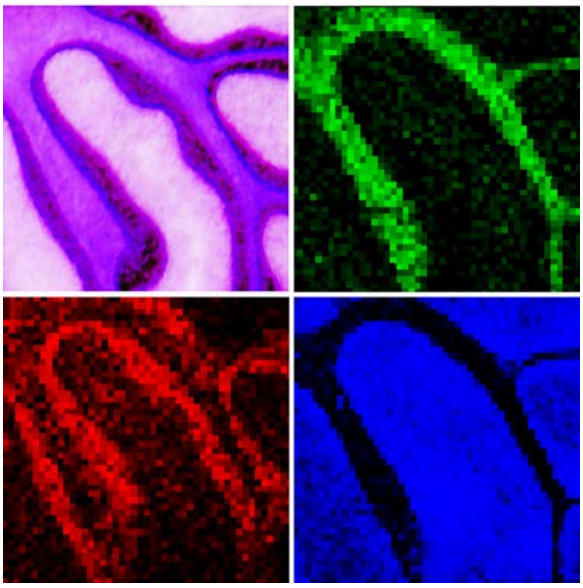
Special Issue of *Microscopy Today* Features EMSL

Laboratory Fellow and EMSL Science Theme Lead Don Baer is the guest editor of the March 2016 special issue of *Microscopy Today* focused on advances and applications of surface analysis methods. The special edition also features three articles co-written by EMSL scientists and users based on their research using EMSL capabilities.

The special issue will include five articles, and Baer is a co-author on two of the EMSL-contributed research articles. The first, "Use of XPS to Quantify Thickness of Coatings on Nanoparticles" was co-written with David Castner and Yung-Cheng Wang, both with the University of Washington. Baer also co-authored "Multimodal and *In-Situ* Chemical Imaging of Critical Surfaces and Interfaces in Li Batteries" with EMSL scientists Arun Devaraj, Mark Engelhard, Chongmin Wang and Zihua Zhu.

Christopher Anderton, EMSL, and Lara Gamble, University of Washington, jointly wrote the third EMSL-contributed article "Secondary Ion Mass Spectrometry Imaging of Tissues, Cells and Microbial Systems."

Microscopy Today is a trade magazine owned by the Microscopy Society of America.



Cover art for the March 2016 special issue of *Microscopy Today* showing biological samples.

Wang Article Named Paper of the Year

Journal of Materials Research, or *JMR*, editorial board selected EMSL Staff Scientist Chongmin Wang's article "*In situ* transmission electron microscopy and spectroscopy studies of rechargeable batteries under dynamic operating conditions: A retrospective and perspective view" as 2015 *JMR* Paper of the Year.

"The award recognizes excellence in advancing materials knowledge through written scholarship, and your paper demonstrates that superbly," wrote Ellen Kracht, publications manager for the Materials Research Society, or MRS, which publishes *JMR* in partnership with Cambridge University Press.

As part of the award, *JMR* will make Wang's paper freely accessible in perpetuity on its publication site on Cambridge Journals Online. The award will be formally announced at the 2016 MRS Spring Meeting in Phoenix.

Reference: Wang CM.2015."*In situ* transmission electron microscopy and spectroscopy studies of rechargeable batteries under dynamic operating conditions: A retrospective and perspective view." *Journal of Materials Research* 30(3):326-339. DOI:10.1557/jmr.2014.281.

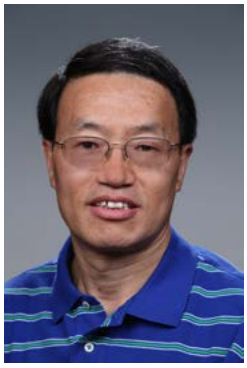
Wang Receives MRS Award

The Materials Research Society, or MRS, has selected EMSL Scientist Chongmin Wang and two peers, Niels de Jonge with Leibniz Institute for New Materials and Frances Ross with IBM T.J. Watson Research Center, co-recipients of the 2016 Innovation in Materials Characterization Award.

The award honors outstanding advances in materials characterization that notably increase knowledge of the structure, composition, *in-situ* behavior under outside stimulus, electronic behavior, or other characterization feature, of materials.

According to the announcement letter from MRS President Kristi Anseth, the MRS board of directors selected Wang, de Jonge and Ross from a large group of extraordinary nominees "for seminal contributions to the imaging of specimens in liquids using transmission electron microscopy, revolutionizing the direct observation of materials processes, batteries during operation and biological structures."

The award includes an engraved trophy and cash prize of $5,000, which will be split among the three winners. They will receive the award during 2016 MRS Spring Meeting, and they will deliver a presentation for this award at the meeting.



Chongmin Wang

EMSL Releases NWChem 6.6

EMSL recently released version 6.6 of NWChem, its premier open-source computational chemistry software. NWChem allows researchers to tackle challenging problems in various areas of chemistry including biochemistry, geochemistry, catalysis, energy storage/conversion materials and atmospheric chemistry.

NWChem is an electronic structure code and offers a unique environment for molecular modeling that integrates various methodologies across length and time scales and provides scalable implementations of quantum chemical methods capable of taking advantage of existing and emerging supercomputer architectures.

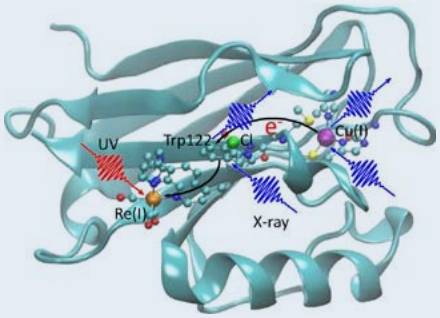


Image shows the electron transfer pathway in re-modified azurin. Simulations were performed with NWChem. The artwork was featured in the article "Monitoring Long-Range Electron Transfer Pathways in Proteins by Stimulated Attosecond Broadband X-ray Raman Spectroscopy" in *The Journal of Physical Chemistry Letters*, 2014, 5, 3656–3661

"The 6.6 version of NWChem provides the users novel capabilities that can be employed in cutting-edge studies of chemical processes in complex environments," said Karol Kowalski, technical lead and senior research scientist at EMSL. "Significant progress has been achieved thanks to the collaboration between the core development team, external contributors and computer scientists – this is an excellent example of the co-design effort."

NWChem is being continuously updated and developed to include new theoretical methodologies and new parallel algorithms. Since many-core hybrid computers, such as Cascade at EMSL, will dominate the landscape of high-performance computing, the development of novel algorithms that can take advantage of their tremendous computational power is currently one of the most pressing issues in computational chemistry. The NWChem team has achieved considerable success in deploying these algorithms and making them available to a broad computational chemistry community. Several new algorithms for hybrid computers had been enabled in the 6.6 release of NWChem.

NWChem 6.6 comprises a long list of new capabilities, including:

- New *ab-initio* molecular dynamics module for molecular and finite systems
- Several new implementations of the solvation models including COSMO
- New parallel-in-time integrators for molecular dynamics
- Improved parallelization of the Density Functional Theory implementations
- Intel MIC implementations of the multi-reference coupled-cluster methods.

The new NWChem release also offers a streamlined installation environment, which significantly simplifies porting and compiling NWChem on various platforms.

Developed at EMSL, NWChem is one of the U.S. Department of Energy's premier computational chemistry tools. Highly scalable and portable, NWChem runs on a wide range of platforms from supercomputers, such as EMSL's Cascade and DOE's leadership class computing facilities, to desktop computers. NWChem is widely used at universities, other national laboratories and computer centers around the world. Since becoming open source at the end of 2010, the software has been downloaded more than 70,000 times.

The software, released under the Educational Community License 2.0, can be downloaded from the NWChem website at http://bit.ly/1OuWHK3. NWChem 6.6 user documentation is also available.

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

Interfacial Surface Studies Span EMSL's Science Themes

Boundaries can set limits or offer opportunities. At EMSL, studies of critical reactions at interfaces between solids and liquids provide insights into systems spanning all four of EMSL's Science Themes – Atmospheric Aerosol Systems, Biosystem Dynamics and Design, Energy Materials and Processes, and Terrestrial and Subsurface Ecosystems. With better understanding of interfacial events, scientists can improve predictive models and contribute solutions to real-world systems. These cross-cutting questions and impacts spur development of new instruments and techniques to better probe these complex surfaces. Pushing past these boundaries expands EMSL's frontiers, too.

Solid-liquid interface studies have a long history at EMSL, noted Don Baer, science theme lead for Energy Materials and Processes. A workshop report from the early days, when the facility being planned was called the Molecular Science Research Center, highlighted interfacial studies as "a critical area" with important roles in waste processing, detection and storage as well as contaminant transport in soils and groundwater.

Over time, research efforts expanded to include dynamic processes in energy materials, aerosols and biological systems. At the same time, EMSL developed new capabilities to enable understanding and control of chemical reactions at these interfaces. Among later goals that were set – and met – the user facility's scientists developed methods for *in-situ* studies, devised instruments that combined spectroscopy with microscopy to drill down to nanoscale levels, and enhanced experimental and theoretical techniques to understand and design increasingly complex materials.

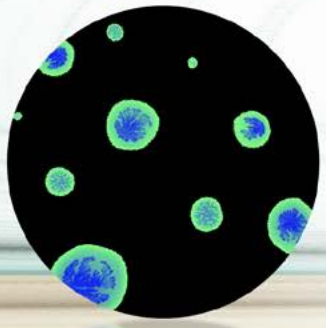
"There are now a suite of capabilities getting us to the point where we can say we are really beginning to have tools to understand these complex interfaces and conditions," said Baer. "It's important to a wide range of technologies and natural processes, so there are many different research pipelines for interfacial research at EMSL."

Just Add Water

The foundation of solid-liquid interfacial research at EMSL really started with geosciences – with reactions that start when water hits the surface of minerals – according to Baer.

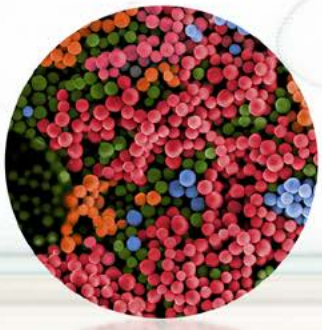
Such fundamental studies continue to drive EMSL research projects, among them are those related to "mineral trapping" for carbon sequestration. When gaseous CO_2 gets pumped deep into suitable subsurface environs, high pressure and temperature conditions incite a phase change to "wet" supercritical CO_2, or $scCO_2$, a viscous substance that can react and form carbonate minerals. But it takes a thin film of water to kick-start the process.

EMSL's Science Themes

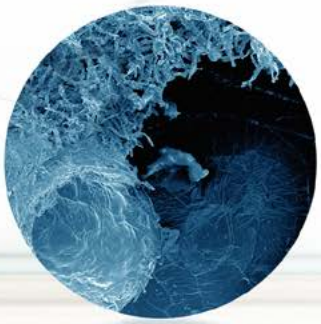


Atmospheric Aerosol Systems

Biosystem Dynamics and Design



Energy Materials and Processes



Terrestrial and Subsurface Ecosystems

"There's a lot of new science here," said John Loring, a geochemist at Pacific Northwest National Laboratory. He leads a Department of Energy Basic Energy Sciences project on mineral reactivity and transformations in adsorbed water films as it applies to $scCO_2$. More specifically, Loring and his colleagues study forsterite, a basalt mineral component, to find optimal thresholds for the thickness of water films that coat the mineral and accelerate reactions that lead to solidified carbon. Among other things, they want to know why reactions slow down when water films are less than a nanometer thick.

Historically, infrared, or IR, spectroscopy has been the workhorse for studying these reactions. Recently, Loring developed a new sophisticated IR capability: high-pressure IR spectroscopic titrations. This uses mirrors to toggle between two optics in the cell: a transmission IR that precisely accounts for water sorbed onto the mineral surface, and a more surface-specific, attenuated total reflectance IR, which collects spectra as the mineral reacts. In addition, tiny aliquots of water can be titrated into the cell, at pressure.

Loring knows how much water was added to the cell, and he measures how much water remains dissolved in the $scCO_2$ using the transmission method optics. The difference between the amount of water added to the cell and the amount that remains in the supercritical phase, is the amount of water sorbed onto the mineral in the cell, explained Loring. "In that way, we can tell something about reactivity of the mineral at a given amount of sorbed water," he said. "It's been a nice breakthrough."

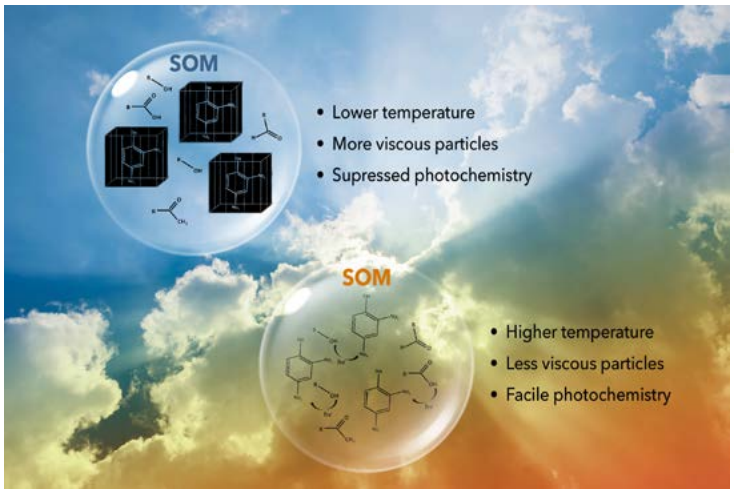
The impact of water and $scCO_2$ on the surface of clays is another aspect that factors into carbon sequestration. Fundamental, molecular scale processes related to clay-water-$scCO_2$ interactions are investigated by longtime EMSL users and collaborators James Kirkpatrick, a professor of geological sciences and chemistry and dean of the College of Natural Science at Michigan State University, and Geoffrey Bowers, an associate professor of chemistry at Alfred University in New York.

"Clays are everywhere in the near-surface environment of Earth's crust," noted Kirkpatrick. "They have a layered, sheet-like structure with very large surface areas where interactions with cations and water can affect mineral surfaces."

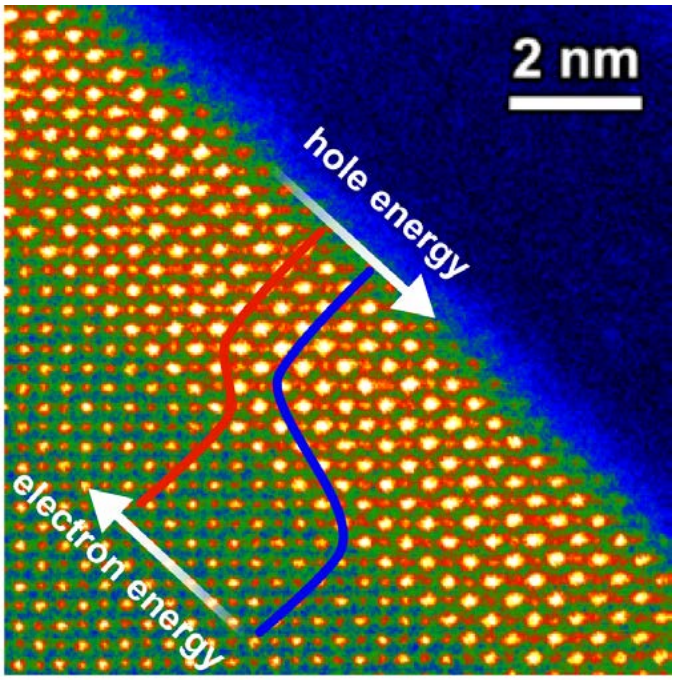
With access to EMSL's helium-ion microscope and the high-pressure magic angle spinning nuclear magnetic resonance, or NMR, tools, Bowers and Kirkpatrick have been able to explore molecular scale events *in situ* to make better predictions about macroscopic systems.

Specifically, they've delved beyond water-clay interactions at pristine interfaces to examine more authentic, "dirty" interfaces where minerals and organic matter, or OM, interact. Their NMR studies help identify how ions and fluids are bound and how they move at these complex interfaces. The helium-ion microscope lets them visualize how clay and OM interact on a microscopic scale, guiding interpretation of NMR results.

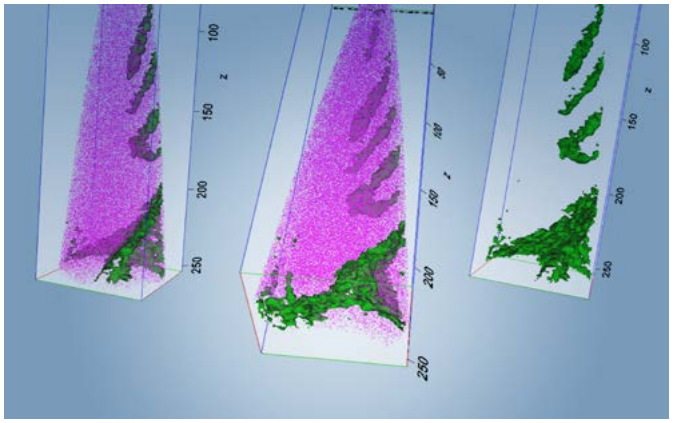
In previous work they found that adding calcium to a clay-water-OM system resulted in microscopic structures strongly affected by pH. However, NMR probing on the molecular scale



Researchers use organic aerosols as solvents for studying chemical reactions of 2,4-Dinitrophenol, or DNP. They found at low temperature and humidity DNP molecules become "caged" and cannot move.



A superlattice constructed with a "working" interface that separates electrons from holes. Such a structure could destroy organic compounds like a carboxylic acids. By building a lattice with only holes on the surface, those holes can now "work" unfettered by the electrons positioned elsewhere in the lattice. They'll make the acid fall apart by destabilizing the bond between the carboxyl group and the rest of the molecule.



Researchers mapped 3-D distribution of lithium at the sub-nanometer spatial resolution and correlated it with the distribution of transition metal cations and oxygen using a unique modern microscopy method called atom probe tomography, a high-resolution 3-D imaging capability, at EMSL.

showed that OM had little influence on the binding and dynamics of a vast majority of calcium ions. "That's important information because data from pristine systems are often what gets into models," said Bowers. "If we saw substantial differences in ion behavior with OM present, then models wouldn't be predicting right answers."

Now, the two are looking at the effect of $scCO_2$ on hydration and movement of molecules through clay and clay-OM systems. Although work is still in early phases, Bowers said: "Preliminary results suggest some nuclear waste material could become a solution for CO_2 storage."

Special Solvents

Another way to look at interfacial reactions is to modify solvents that mediate them.

In collaboration with EMSL, researcher Seema Singh, director of Biomass Pretreatment at the Joint BioEnergy Institute, or JBEI, is developing "designer" solvents to break down the protective lignin outer layer of cellulose.

The very things that make lignin useful to plants, a rigid structure that is hydrophobic to water and resistant to microbes, are the same factors that make it so intractable for breaking down into biofuels, Singh explained.

She's testing various ionic liquids – salts that are liquid at room temperature because they have cations too big to allow crystallization – under a range of pH conditions, to disassemble lignin into aromatic components that could be funneled into industrially useful products. Ultimately, this DOE/JBEI-funded research will lead to methods for converting lignin itself into "high-value chemicals."

Singh's efforts to precisely profile these reactions rely on a suite of EMSL instruments: mass spectrometry, NMR and electron paramagnetic resonance spectroscopy, and computer modeling capabilities.

Another innovative approach in atmospheric research is to use aerosols themselves as solvents.

In a recent paper, a team of scientists from the University of California at Irvine, the University of British Columbia and EMSL described using organic aerosols as solvents for studying chemical reactions of 2,4-Dinitrophenol, or DNP.

Under normal conditions, the aromatic pollutant, DNP dissolves into aerosols and can quickly diffuse throughout the particle, accessing both the surface and interior of the particle. However as temperature or relative humidity drops, aerosols become more viscous, and DNP become immobile. In this study, the team showed increasing viscosity made molecules so sluggish photodestruction reactions driven by solar radiation also slowed down.

This finding has implications for air-pollution models in areas of extreme cooling or dry climates. The National Oceanic and Atmospheric Administration and the National Science Foundation funded these studies.

Solid-Liquid Electrolyte Relations

Interfacial reactions are a major challenge in making long-lived lithium batteries, or finding other materials that might become better batteries.

With lithium, or any type of rechargeable battery, problems are three-fold: first, ions need to be able to travel easily through the electrolyte between the cathode and anode; second, that travel slows as electrolyte-electrode interactions degrade electrode surfaces over time; and third, the electrolyte and electrode age and form different chemicals that impact overall reactivity.

"Everything is dynamic so it's very difficult to get good resolution and see what's happening at these interfaces under operating conditions," said Chongmin Wang, EMSL scientist.

Despite that difficulty, Wang and his collaborators, with funding from Joint Center for Energy Storage Research, developed an *in-situ* approach within a transmission electron microscope at EMSL. This atomic-level imaging enabled researchers to follow subtle changes to the battery after rounds of charging and discharging.

More recently, with EMSL's atom probe tomography, Wang and his colleagues mapped the distribution of lithium ions and transition metal elements in cathodes, gleaning insight into ways ions are progressively lost during charge-discharge cycles.

In the future Wang wants to design battery components from "modern materials" that are more stable and exclude factors that interfere with battery longevity, or use crystals with tailored surface structures.

"No breakthroughs ... yet we are making progress," said Wang.

Beyond Batteries

While some surfaces or interfaces cause undesired effects during reactions, Scott Chambers, a Wiley Research Fellow in EMSL, carefully constructs superlattices to put them to work.

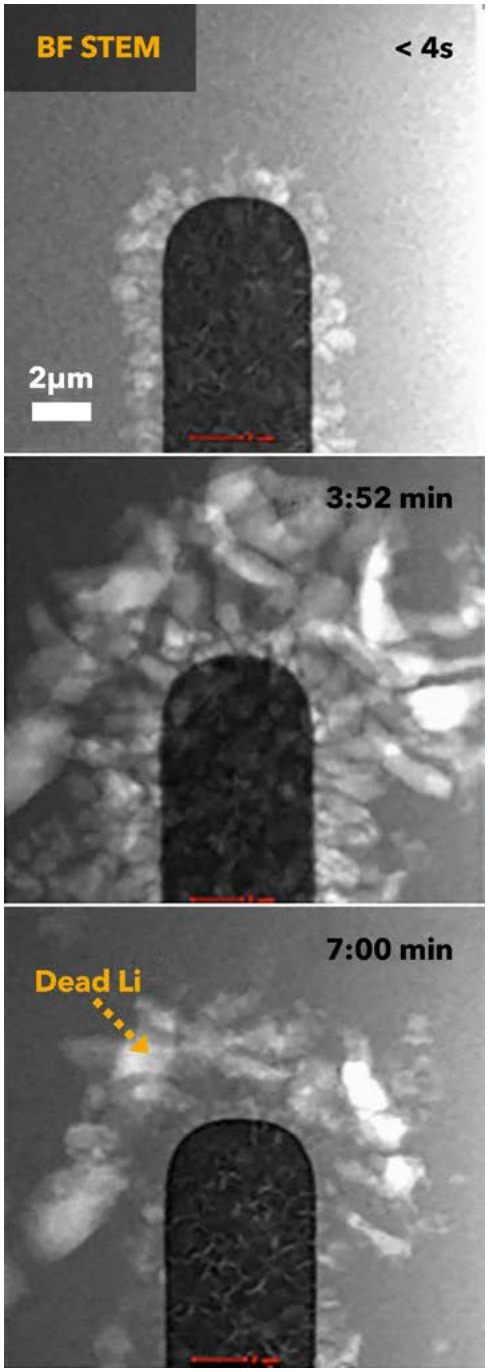
The idea is to synthesize a lattice of repeating materials (A-B-A-B- …) with atomic layer control, so the resulting electronic structure separates electrons and "holes." In this way, wherever an electron-hole pair is created by light absorption, the electron goes to material A and the hole goes to material B. The surface material dictates which charged particle is on the surface. This kind of separation prevents electron-hole pair recombination, a process that keeps electrons and holes from doing useful chemical work.

"Our approach is on the fundamental side, trying to understand at an atomistic level how best to control this chemistry," said Chambers.

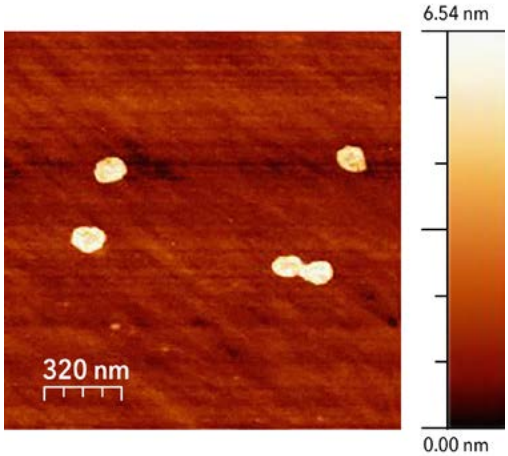
This approach has a great deal of promise for water splitting to make hydrogen and oxygen. Although simple in concept, water splitting is a complex process that requires considerable energy.

"Water electrolysis requires both an electron and a hole, each of sufficient energy to drive the two half-cell reactions. It is difficult to find one material with the right band structure to carry both particles at sufficient energy to do the job," Chambers said.

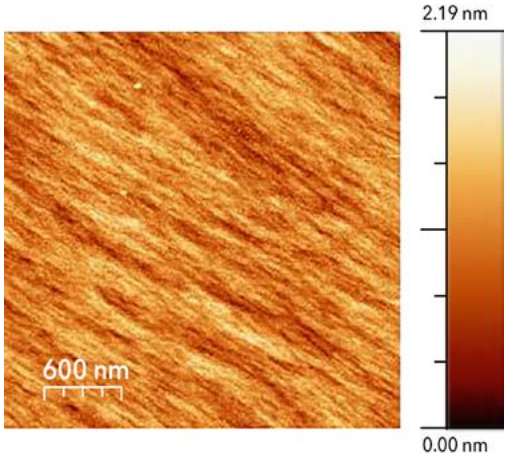
With advanced epitaxial oxide film deposition methods developed at EMSL over the past two decades, Chambers plans to synthesize different materials optimized to do each half-cell reaction. Then, the two could be combined into one cell, put under water and irradiated with sunlight, and used to generate O2 and H2 using nothing but the sun's enormous energy output, Chambers explained.



These images allow precise measurements and descriptions of what happens inside the battery: lithium is deposited on the platinum anode at the beginning (top), during (middle) and end (bottom) of the second cycle. Residual "dead lithium" can be seen on and around the anode.



This forsterite surface is imaged in dry supercritical CO_2, or $scCO_2$, prior to exposure to $scCO_2$ containing water.



Precipitates are formed on the surface of forsterite after two hours of exposure to water saturated $scCO_2$.

"If we can do this, it would go a long way toward solving some of our energy problems," said Chambers. "We'd have the perfect fuel: very combustible and with no carbon footprint."

Surface Arrangements

Which end is up? The importance of orientation and conformation of molecules on surfaces plays out in every interfacial reaction. The trick is finding ways to visualize those structures and how they change during reactions – particularly as complexity scales up.

EMSL Scientist Hongfei Wang developed a high-resolution vibrational sum frequency generation spectroscopy technique that boosts spectral resolution by 10-20 times. By increasing the ability to see small structural differences, the instrument enhances research in many areas. For instance, catalysis relies on understanding how surface molecules are affected by solvents and absorbents. This method can also be particularly useful for studying biological interactions of cells or bacteria because surface membranes are usually "buried" in an environment that prevents applying other imaging techniques.

Still, Hongfei found room for improvement. He is now developing a high-resolution version of "second-order Mei scattering." This builds on the Mei scatter technique that – similar to radar, but using the shorter wavelength of light – analyzes the way light from one photon scatters after it interacts with a particle. The new version, based on Hongfei's doctoral degree studies, provides direct *in-situ* measurement of the surface of the particles because it scatters two photons and sums those reflected frequencies into one, thus providing a selective probe of the particle surface. With this higher resolution, Hongfei hopes to enhance research capabilities in energy, environmental, material and biological sciences by obtaining unprecedented molecular specificity.

Building on Strengths

In addition to innovations in instruments, EMSL's computational capabilities will play an increasingly important role in advancing research across the board, said Baer.

A recent workshop report noted NWChem was one of the user-facility's foundational strengths. This open source, high-performance computational chemistry package was created by a consortium of developers and is maintained at EMSL. Over the years, NWChem has become a key component in the integration of experiment and theory at EMSL.

Now, efforts are underway to expand NWChem to include increasingly complex environments, such as multi-scale simulations of cellular metabolites in biological systems. Then, engineering to integrate such data with more sophisticated instruments in development, will position EMSL at the leading edge of research. ■

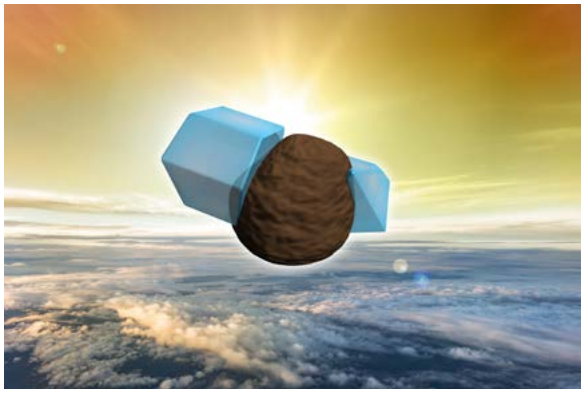
Elizabeth Devitt is a science journalist and freelance writer.

EMSL, the Environmental Molecular Sciences Laboratory, is a national scientific user facility sponsored by the Department of Energy's Office of Science. Located at Pacific Northwest National Laboratory in Richland, Wash., EMSL offers an open, collaborative environment for scientific discovery to researchers around the world. Its integrated computational and experimental resources enable researchers to realize important scientific insights and create new technologies.

SCIENCE HIGHLIGHTS

Environmental Conditions Affect Air Pollutant Degradation

Low temperature and humidity slow down photochemical reactions



Sunlight plays a major role in degrading toxic pollutants in atmospheric particles, but it has not been clear how environmental conditions affect photodegradation rates. A recent study demonstrated for the first time that low temperatures and low humidity increase viscosity of atmospheric particles and slow down photodegradation of toxic pollutants trapped in particles.

The findings suggest air pollutants trapped within particles in polar regions or at high altitudes will have longer lifetimes than those in warm, humid regions. By shedding new light on reactions happening inside and on surfaces of atmospheric particles, such as those produced in large cities on smoggy days, the study could lead to the development of more accurate air pollution models.

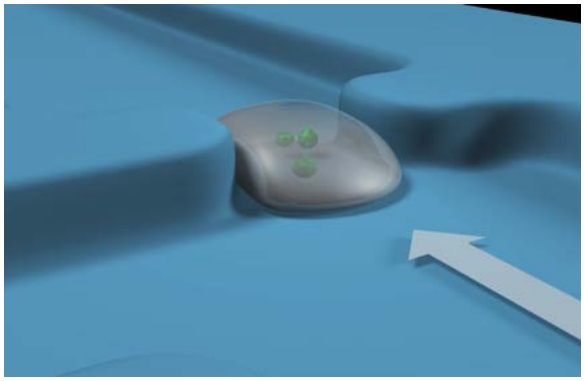
Funding: This work was supported by the U.S. Department of Energy's Office of Science (Office of Biological and Environmental Research) including support of EMSL, a DOE Office of Science User Facility; Department of Commerce; National, Science Foundation; and Natural Sciences and Engineering Research Council of Canada.

Publication: Hinks ML, MV Brady, H Lignell, M Song, JW Grayson, AK Bertram, P Lin, A Laskin, J Laskin, and SA Nizkorodov. 2016. "Effect of viscosity on photodegradation rates in complex secondary organic aerosol materials." *Physical Chemistry Chemical Physics*. DOI: 10.1039/C5CP05226B.

Participating Organizations: University of California at Irvine, The University of British Columbia, EMSL and PNNL.

Optimizing Microbial Bioproduction of Fuels

Identifying factors that contribute to cell-to-cell variability in lipid production



Microbial strains engineered to produce a large amount of lipids hold tremendous promise for the production of biofuels and chemicals. A recent study shed light on underlying causes of microbial cell-to-cell variability in lipid production.

The findings reveal conditions within cells and in the surrounding environment interact to contribute to variability in lipid production. The new insights could lead to strategies that optimize the use of engineered microbial strains for the production of important biofuels and chemicals.

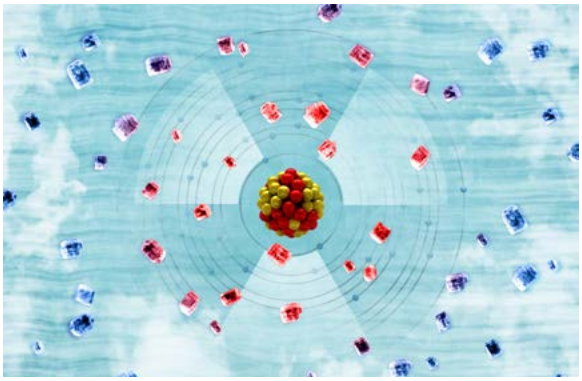
Funding: This work was supported by the U.S. Department of Energy's Office of Science (Office of Biological and Environmental Research) including support of EMSL, a DOE Office of Science User Facility; the National Institute of General Medical Sciences of the National Institutes of Health; and a Linus Pauling Fellowship from the Pacific Northwest National Laboratory.

Publication: Vasdekis AE, AM Silverman, and G Stephanopoulos. 2015. "Origins of cell-to-cell bioprocessing diversity and implications of the extracellular environment revealed at the single-cell level." *Nature Scientific Reports* 5,17689. DOI: 10.1038/srep17689.

Participating Organizations: University of Idaho, EMSL and the Massachusetts Institute of Technology.

Detecting Technetium in Groundwater

Novel approach uses salt-based sensor



Technetium-99, or 99Tc, is a long-lived radionuclide byproduct of the nuclear fuel cycle, making it a major radiological concern at nuclear waste repository sites that requires on-site monitoring. When exposed to moderately oxidizing conditions, 99Tc is readily converted to pertechnetate, or TcO_4^- – a highly soluble anion that can migrate into groundwater and the environment. Existing methods for on-site monitoring of TcO_4^- in groundwater require a complicated series of analytical steps due to low Tc selectivity and sensitivity. A novel approach has been demonstrated that uses highly selective and sensitive platinum salt to detect and quantify TcO_4^- in groundwater.

The new ion recognition approach has potential for the development of a field-deployable and highly accurate sensor for monitoring TcO_4^- in groundwater, river water and watersheds. This work could have a broad impact on remediation efforts, paving the way for the development of similar salts for detection of other important environmental contaminants.

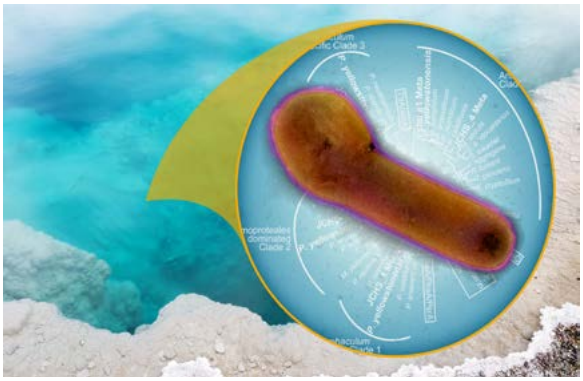
Funding: This research was supported by Laboratory-Directed Research and Development Program at Pacific Northwest National Laboratory, or PNNL; National Science Foundation; Office of Biological and Environmental Research; and Office of Environmental Management Sciences Program.

Publication: Chatterjee S, AE Norton, MK Edwards, JM Peterson, SD Taylor, SA Bryan, A Andersen, N Govind, TE Albrecht-Schmitt, WB Connick, and TG Levitskaia. 2015. "Highly Selective Colorimetric and Luminescence Response of a Square-Planar Platinum(II) Terpyridyl Complex to Aqueous TcO_4^-." *Inorganic Chemistry*. DOI:10.1021/acs.inorgchem.5b01664.

Participating Organizations: PNNL, EMSL, University of Cincinnati and Florida State University.

Yellowstone Microbes

Some microbes adapt to Yellowstone's hot springs



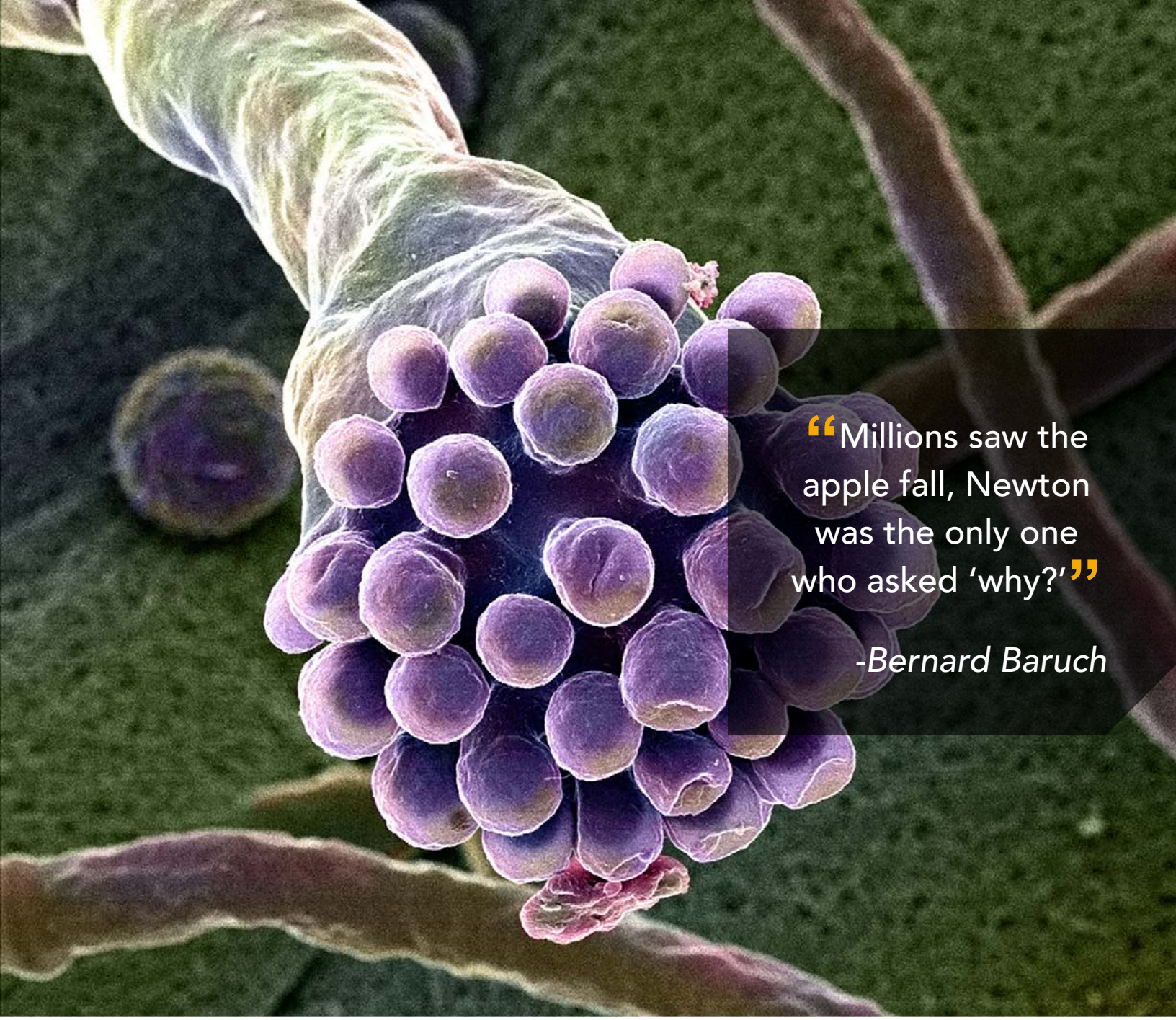
A wide variety of microbes thrive at high temperatures such as those found in hot springs of Yellowstone National Park. Archaeal populations from the order *Thermoproteales* are especially abundant in these environments. But none of these organisms from the park have been isolated or sequenced, despite their importance in mediating biogeochemical cycles of sulfur, arsenic and carbon. To address this gap in knowledge, researchers recently isolated and sequenced *Pyrobaculum yellowstonensis* strain WP30 from Joseph's Coat Hot Spring in Yellowstone and characterized this strain's unique physiological attributes and metabolic capabilities.

Researchers related biological features of *P. yellowstonensis* to geochemical processes occurring in its natural environment using microbiological, geochemical and genomic techniques. The results provide an important foundation for developing an understanding of the distribution and function of these microbial populations in high-temperature environments.

Funding: This research was supported by the Genomic Science Program, Office of Biological and Environmental Research and Pacific Northwest National Laboratory Foundational Scientific Focus Area.

Publication: Jay ZJ, JP Beam, ZJ Jay, A Dohnalkova, R Lohmayer, B Bodle, B Planer-Friedrich, M Romine, and WP Inskeep. 2015. "*Pyrobaculum yellowstonensis* Strain WP30 Respires on Elemental Sulfur and/or Arsenate in Circumneutral Sulfidic Geothermal Sediments of Yellowstone National Park." *Applied and Environmental Microbiology*. 81:5907-5916. DOI:10.1128/aem.01095-15.

Participating Organizations: Montana State University, Bayreuth University and EMSL.

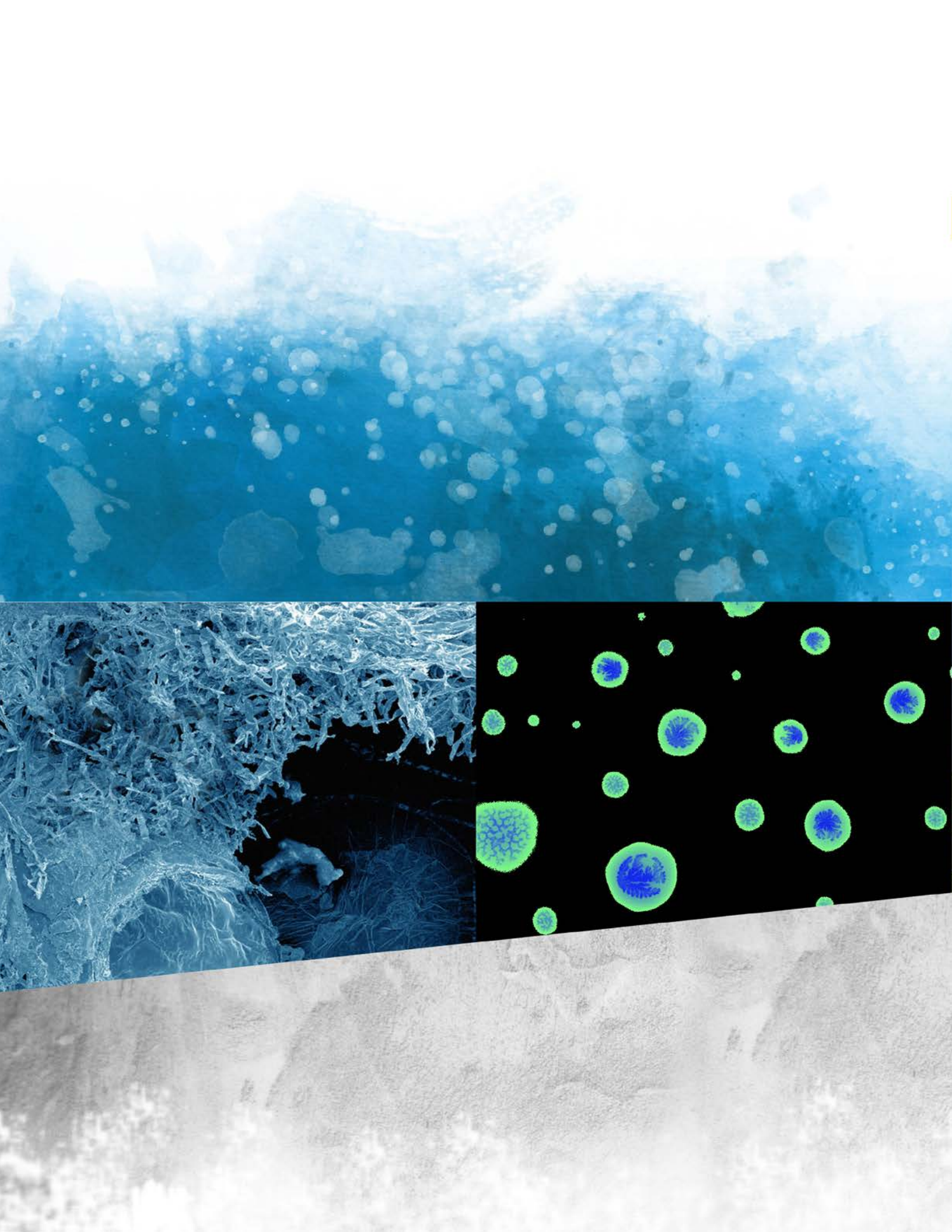


"Millions saw the apple fall, Newton was the only one who asked 'why?'"

-Bernard Baruch

About this Art

The beauty of this mutant strain of the fungus *Trichoderma reesei* belies the organism's potential for dismantling biomass. The study and characterization of the fungus – particularly its proficient production of biomass-degrading enzymes – are critical for the development of more efficient and economical methods for turning biomass into fuels and other products. Scientists from the University of Nebraska and the University of Maryland have been identifying and characterizing *T. reesei's* enzyme secretion control pathways. The work was conducted through a collaborative user project at EMSL. The project resulted from an EMSL-DOE Joint Genome Institute call for proposals and was funded by DOE's Office of Biological and Environmental Research. Image was captured with a helium ion microscope at EMSL.

Team Members

Bruce Arey, PNNL; Scott Baker, EMSL; Steve Harris, University of Nebraska; and Mark Marten, University of Maryland. (Image colorized.)