theMolecularBond

EMSL

SCIENTIFIC INNOVATION THROUGH INTEGRATION

August 2015

Making the Most from Carbon in Plants

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2014 M.T. Thomas Award Recipient Announced

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As part of his sudies of brown rot fungi, Jonathan Schilling is researching organisms such as *Fomitopsis cajanderi* shown on a spruce tree stump. The fungus is emerging parallel to the annual rings, creating the pattern. (Image provided by Jonathan Schilling, University of Minnesota)

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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U.S. DEPARTMENT OF ENERGY

EMSL Scientist Danny Perea looks into EMSL's atom probe tomography instrument, which he and an international team of scientists used to locate aluminum clusters responsible for the shutdown of catalytic activity in zeolites, a material used by industry to produce fuel and other chemicals. Find out more about this research on page 4. (PNNL file photo)

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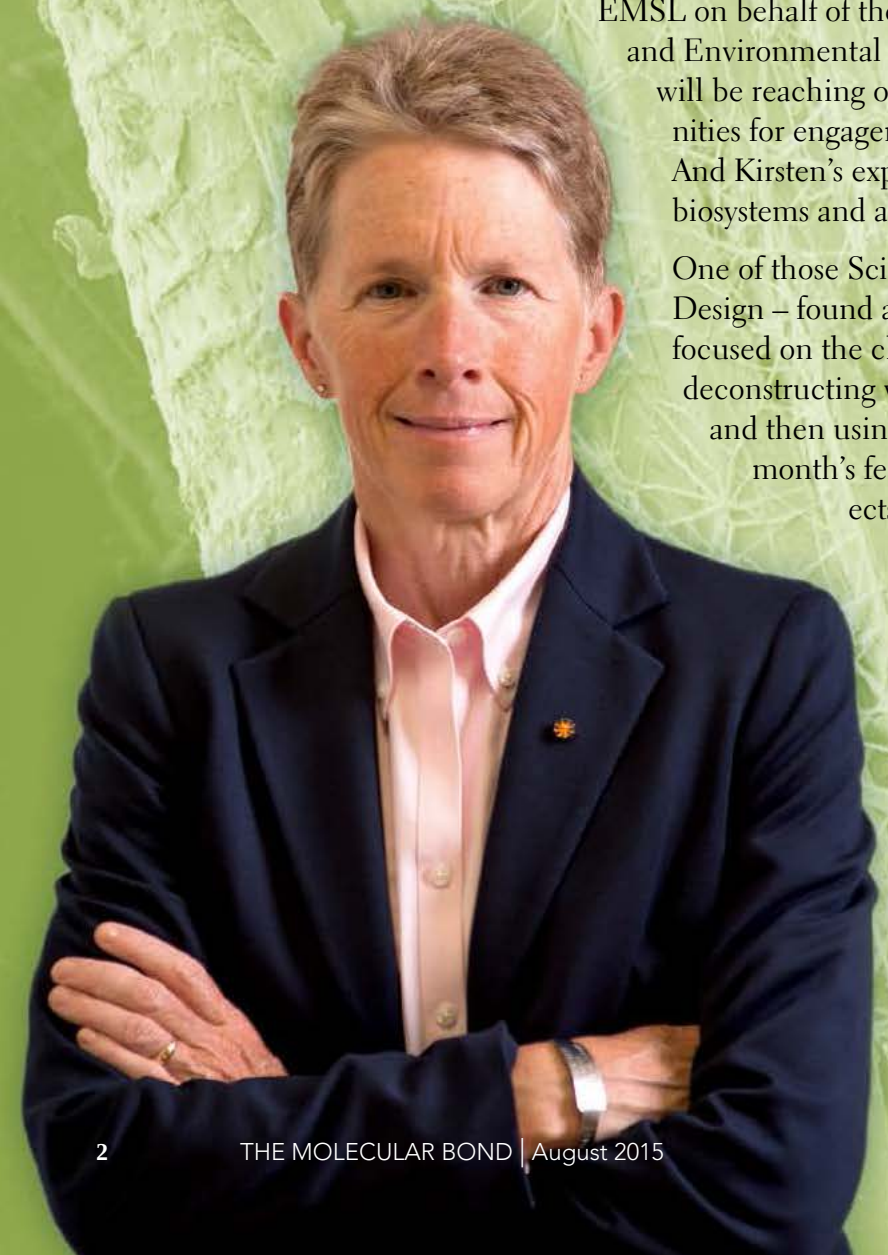
FROM THE DIRECTOR

Allison Campbell



I'd like to introduce two new scientific leaders to the EMSL family: David Stahl, who joins us in a dual appointment from the University of Washington to become our Chief Scientist, and Kirsten Hofmockel, as a senior research scientist who will take lead in enhancing integration across our Science Themes. Both are well known in the community served by EMSL on behalf of the Department of Energy's Office of Biological and Environmental Research. As Chief Scientist, I expect David will be reaching out to many of you to generate greater opportunities for engagement with EMSL scientists and capabilities. And Kirsten's expertise sits in the sweet spot of our terrestrial, biosystems and atmospheric research.

One of those Science Themes – Biosystem Dynamics and Design – found an interesting cluster of projects this year focused on the challenge scientists have encountered in deconstructing woody biomass efficiently and cost effectively and then using it to create biofuels and biochemicals. This month's feature article explores these researchers' projects and how they're leveraging EMSL expertise and capabilities to answer tough questions about these tough challenges.

It's also heartening to see how these EMSL projects scale the globe, from the Joint BioEnergy Institute in California to a fungal diversity center in The Netherlands. I encourage you to read this month's cover story and let us know how we can help advance your research in much the same way.

—*Allison*

The "Electron Microscopy for Biological, Environmental, and Energy Research (EMBEER) Symposium," organized by the Chemical Imaging Initiative and EMSL at the Pacific Northwest National Laboratory, was held on July 29-30 at EMSL. More than 100 attendees listened to the symposium's 25 invited speakers. The poster session, shown here, featured 27 submissions. Find out more about another EMSL-sponsored 's science meeting on page 5. (EMSL file photo)

NEWS & KUDOS

Gu Garners MSA Albert Crewe Award

Meng Gu

Microscopy Society of America has named Meng Gu, a former Pacific Northwest National Laboratory postdoctoral research associate, as the 2015 recipient of the Albert Crewe Award for his outstanding work at EMSL that led to the discovery of nickel segregation in battery materials.

MSA started the Albert Crewe Award to recognize the distinguished contributions to the field of microscopy and microanalysis in the physical sciences by a postdoctoral fellow within six years since doctoral graduation. Gu received his award at the August Microscopy & Microanalysis 2015 Annual Meeting.

Gu is currently an analytical research scientist at Dow Corning in Midland, Mich. As a PNNL postdoc, he worked under the direction of EMSL Senior Research Scientist Chongmin Wang, who nominated him for the award. Gu's research at EMSL explored 3-D chemical imaging and clarifying scientific problems in energy storage and conversion systems. The Department of Energy's Office of Energy Efficiency and Renewable Energy funded Gu's battery materials research with support from the Chemical Imaging Initiative at PNNL.

Gu received his PhD at the University of California, Davis, and earned his bachelor's degree at Shanghai Jiao Tong University, Shanghai City, China.

Kelly Joins Editorial Panel for *Scientific Reports*

Ryan Kelly

Scientific Reports has invited EMSL Senior Research Scientist Ryan Kelly to serve as an editorial board member. *Scientific Reports* is a journal from Nature Publishing Group, the publishers of *Nature*.

Kelly is the capability lead for EMSL's Instrument Development Lab and microfabrication facility. He will serve as an editorial board member for the journal's chemistry field led by editorial advisory panel member Professor Yi Cui from Stanford University.

Scientific Reports recruits editorial board members for an initial two-year term. The members' principal responsibilities include:

- Assess if submitted manuscripts should be sent for peer review.
- Manage the peer review of manuscripts and make final editorial decisions.
- Act as an advocate for the journal.

Nature Publishing Group launched *Scientific Reports* in 2011 as a multidisciplinary, online-only, open access publication covering all areas of the natural sciences. It currently has an impact factor of 5.6 and is the 5th ranked journal in the category of Multidisciplinary Sciences according to Thompson Reuters Journal Citation Reports.

Dutta Garners 2014 M.T. Thomas Award

Arnab Dutta

Arnab Dutta has been named recipient of EMSL's 2014 M.T. Thomas Award for Outstanding Postdoctoral Achievement. Dutta came to Pacific Northwest National Laboratory as a post-doctoral research associate in 2012 to research bio-inspired molecular catalysts.

EMSL will honor Dutta at a ceremony Sept. 30. He will make a presentation on his research at that time and a reception will follow.

The selection committee reviewed the nominations for seven outstanding postdoctoral candidates. According to the recommendation report, the committee was particularly impressed by Dutta's "scientific progress as a postdoc, the quality of his work, and his productivity as measured by the number and potential impact of his publications."

Dutta's notable accomplishments during his time at PNNL and EMSL include:

- Discovering the first water-soluble, homogeneous, synthetic H_2 oxidation catalyst complex $[Ni(P^{Cy}_2N^{Gly}_2)_2]^{4+}$.
- Achieving enzyme-like reversibility for the water-soluble, homogeneous synthetic molecular catalyst by changing outer coordination sphere functionalities (glycine to arginine), and further tuning by temperature.
- Successfully immobilizing the catalyst $[Ni(P^{Cy}_2N^{Gly}_2)_2]^{4+}$ on an electrode surface for fuel cell applications in an experiment that also enabled, for the first time, direct comparison of enzymes and molecular catalysts.

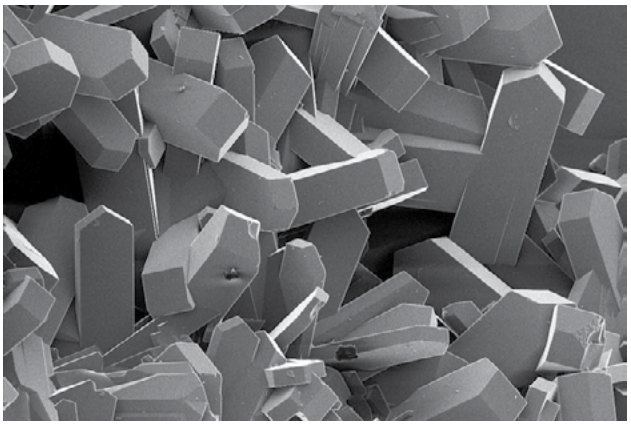
He has published seven scholarly papers, with one in process, based on his research using EMSL resources. He is the first author on four of these papers, including one in *PNAS*. The other papers were published in *Angewandte Chemie International Edition*, *Account of Chemical Research*, *Chemical Communications* and *JACS*. The average impact factor of his seven papers is 11.6. Dutta has also given two invited conference presentations.

Dutta is currently an assistant professor at Indian Institute of Technology Gandhinagar, India. Before coming to PNNL, Dutta was a research assistant at Arizona State University starting in 2007. He earned a doctorate in chemistry from Arizona State University, a master's in chemistry from Indian Institute of Technology Bombay, India, and a bachelor's with honors in chemistry from Presidency College, University of Calcutta, India.

EMSL presented the first M.T. Thomas Award in 1996 in honor of Dr. M. Tom Thomas, who joined the EMSL project team in 1987 and served in various leadership capacities. The award acknowledges outstanding accomplishments by postdoctoral fellows who conduct their research at EMSL.

Aluminum Clusters Shut Down Molecular Factory

Industry uses zeolites to convert oil to gasoline, but the exact chemical transformations occurring within zeolites is not well understood. An international team, including scientists at EMSL, created the first 3-D atomic map of a zeolite with



These coffin-shaped growths make up one variety of porous materials called zeolites.

EMSL's atom probe tomography. The images confirmed what scientists suspected: When aluminum atoms in zeolites bunch up, zeolites lose their catalytic properties. The team's findings reported in *Nature Communications* could help to improve industrially important zeolites used to produce fuel, biofuel and other chemicals.

Read the Pacific Northwest National Laboratory news release at http://1.usa.gov/1ecHajT.

Reference: Perea D, I Arslan, J Liu, Z Ristanović, L Kovarik, B Arey, J Lercher, S Bare and B Weckhuysen. 2015. "Determining the Location and Nearest Neighbors of Aluminum in Zeolites with Atom Probe Tomography." *Nature Communications*. DOI: 10.1038/ncomms8589.

Rice Holds Promise for Greenhouse Gas Reductions, Bioenergy

Rice is a major food source for a majority of the world's population, but it's also a significant source of manmade atmospheric methane, a potent greenhouse gas. An international team of researchers, including Christer Jansson, director of plant sciences at Pacific Northwest National Laboratory and EMSL, developed a new strain of rice. The new rice, known as SUSIBA2, emits virtually no methane during growth, and

it contains more starch for a richer food source and biomass for energy production, according to a study in *Nature*. Researchers created SUSIBA2 rice by adding a gene from barley into common rice. SUSIBA2 rice is the first high-starch, low-methane rice that could offer a significant and sustainable solution controlling this source of methane.

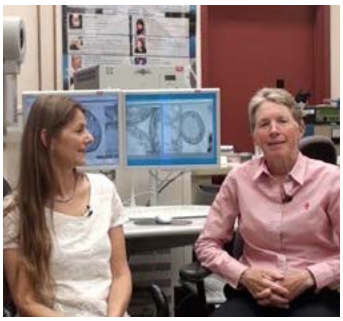
Read the PNNL news release at http://1.usa.gov/1EnXGVw.

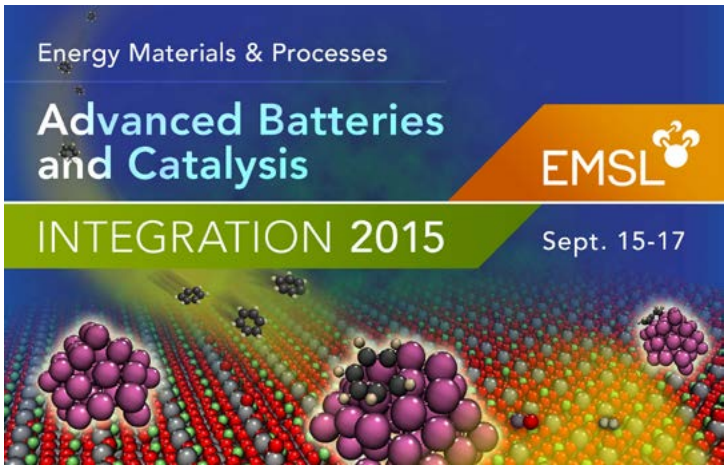
Reference: J. Su, C. Hu, X. Yan, Y. Jin, Z. Chen, Q. Guan, Y. Wang, D. Zhong, C. Jansson, F. Wang, A. Schnurer, C. Sun. Expression of barley SUSIBA2 transcription factor yields high-starch low-methane rice, *Nature* July 22 (online), 2015, DOI: 10.1038/nature14673.

In addition to a near elimination of greenhouse gases associated with its growth, SUSIBA2 rice produces substantially more grains for a richer food source. The new strain is shown here (right) compared to the study's control. Image courtesy of Swedish University of Agricultural Sciences

EMSL on YouTube – iDirector

EMSL Director Allison Campbell talks with EMSL Senior Research Scientist Alice Dohnalkova about her science background and her research investigations of microbes and their environments using electron microscopy. Campbell also interviews EMSL Senior Research Scientist Kim Hixson about her research in plant science. The videos are part of Campbell's monthly iDirector interview series available on EMSL's YouTube channel at http://bit.ly/1vy5t02.





Reminder for EMSL User Meeting

Registration closes Sept. 9 for "EMSL Integration 2015: Energy Materials and Processes for Advanced Batteries and Catalysis." EMSL's annual science meeting will be held Sept. 15-17 at EMSL.

This year's annual meeting focuses on advanced batteries and catalysis research at the molecular level. Researchers from around the world and from academia, industry and government research labs are encouraged to attend. The meeting is open to EMSL users and non-users.

The agenda includes:

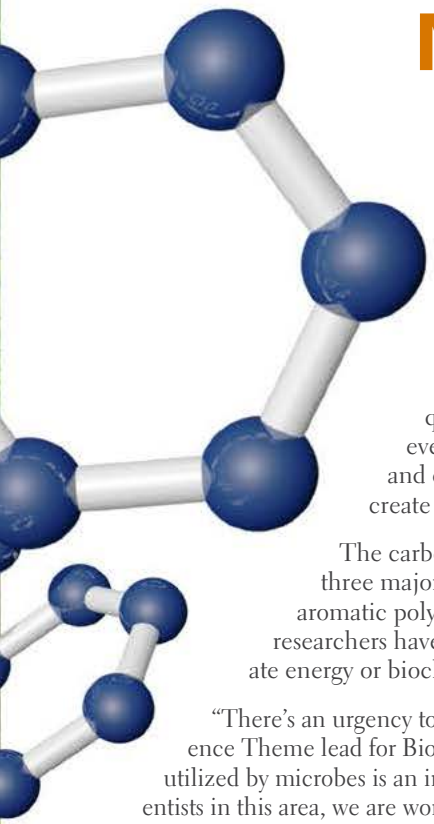
Sept. 15-16 – Battery Boot Camp. The group will work on a previously identified challenge associated with advanced batteries and advanced battery materials, discuss how EMSL capabilities are currently used to address the challenge, and then spend a day in small groups with EMSL scientists working on the challenge.

Sept. 17 – Full day of plenary speakers with morning sessions focused on batteries and afternoon sessions focused on catalysis, followed by a poster session, including a student poster competition and a vendor-sponsored dinner.

On Sept. 18, the Pacific Coast Catalysis Society is holding its annual meeting at EMSL. Attendees of the EMSL user meeting are encouraged to attend the society's symposium.

More information and registration is available on the meeting website: http://1.usa.gov/1BMTtPr.

Jonathan Schilling has studied the brown rot fungus *Laetiporus sulphureus*, also known as chicken of the woods, shown here growing on an oak. (Image provided by Jonathan Schilling, University of Minnesota)



Making the Most from Carbon in Plants

Meeting the challenge of creating sustainable bioproducts from lignin

Carbon is money. Nowhere is this more evident than in our dependence on hydrocarbons in the form of fossil fuels. Scientists and engineers have been grappling with the question of what alternate carbon sources are available when our demand for fossil fuels eventually outstrips our supply. This challenge has provided motivation to use expertise and equipment available at EMSL, the Environmental Molecular Sciences Laboratory, to create technologies that use sustainable carbon sources from biomass.

The carbon in the most abundant forms of biomass, wood and non-woody plants, is made up of three major components: cellulose and hemicellulose, which are sugar polymers; and lignin, an aromatic polymer. Although the sugars in cellulose and hemicellulose can be fermented to biofuels, researchers haven't found an effective way to use lignin, which is about a third of the biomass, to generate energy or biochemicals.

"There's an urgency to increasing the economic viability of biofuels and bioproducts," said Scott Baker, the Science Theme lead for Biosystem Dynamics and Design at EMSL. "Understanding how lignin is deconstructed and utilized by microbes is an important science challenge. Through the EMSL User Program projects working with scientists in this area, we are working to accelerate and amplify the impact of lignin deconstruction research."

Dissolving Wood with Liquid Salt

Difficulties degrading lignin have hampered exploitation of the full potential of lingnocellulosic biomass currently used in biotechnology for the production of biofuels and renewable chemicals. The challenge of overcoming these difficulties undergirds much of the lignin deconstruction research at EMSL. For the most part, early technologies to deconstruct wood (such as those in pulp and paper mills) have disregarded lignin for its potential as a source of renewable chemicals and typically burn it for heat and power production. This mentality of lignin as waste stream has been carried over into newer biotechnological processes for producing biofuels.

"The main goal has basically been to get rid of lignin so that cellulose can be easily digested using enzymes," said Seema Singh, director of Biomass Retreatment at the Department of Energy-funded Joint BioEnergy Institute, or JBEI. Singh disagrees with this idea; however, "If you want to be self-reliant for energy security and not dependent on foreign oil you cannot just make fuel, you have to replace the whole barrel of oil."

> If you want to be self-reliant for energy security and not dependent on foreign oil you cannot just make fuel, you have to replace the whole barrel of oil.

According to Singh, using biomass to replace all of the uses of a barrel of oil requires the production of industrially relevant chemicals with aromatics. This is where lignin is important. "Lignin is the only source of renewable aromatics," she added.

Creating biomass-based equivalents to what can be found in a barrel of oil is the focus of the project Singh is working on with EMSL, in partnership with JBEI and the Sandia National Laboratories. She and her team have two major interdependent goals. The first is to find ionic liquids effective for dissolving wood-bound lignin into its component aromatic molecules. The second goal is to determine how these aromatic molecules can be combined to create high-value chemicals.

To achieve the first goal, Singh plans to use EMSL's mass spectrometry, nuclear magnetic resonance and electron paramagnetic resonance spectrometer capabilities to determine the composition and structure of lignin's component molecules. This will involve dissolving lignin and lignin-like chemicals in ionic liquids.

Ionic liquids are salts that are liquid at room temperature. Like table salt, they are made up of a positively charged ion and a negatively charged ion (cation and anion respectively). In contrast to salts that are solid at room temperature, in ionic liquids the cation is large in comparison to the anion, preventing crystallization. (*Continued on page* 8)

Jonathan Schilling's research focuses on the degradation action of brown rot fungi, like this *Fomitopsis pinicola*, a red-banded polypore brown rot fungus growing on a spruce log. (Image provided by Jonathan Schilling, University of Minnesota)

One third of your biomass is lignin, and right now there is no compelling use for that, like there is for sugars

Using ionic liquids as solvents allows scientists to pick and choose the ions they use to make the salt. "We call them designer solvents," said Singh. "So I can have an ionic liquid that only solubilizes lignin, or cellulose, or both." Often with little added heat or pressure to speed up the reaction.

Singh's second project goal will use computing resources from both EMSL and JBEI to model and understand the reaction mechanisms required to build industry-relevant chemicals. She is especially interested in creating platform chemicals, which are chemicals that can be used as building blocks for high-value products.

Mapping Fungal Pathways

Blake Simmons, chief science and technology officer and vice president of the Deconstruction Division at JBEI, is one of EMSL's collaborators and an EMSL Willey Fellow. The object of Simmons' research, which is funded by JBEI and Sandia National Laboratories, is to create a metabolic map of the pathways used by microorganisms to degrade lignin.

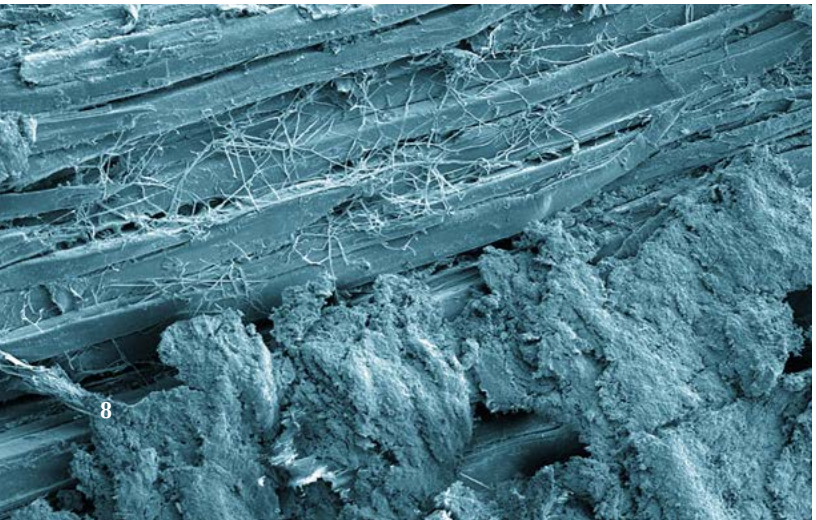
"We have a [mapping] device that is really good at understanding central metabolism and sugar metabolism in organisms, but there's still very little known at that same level of detail, nuance and robustness around lignin conversion," said Simmons.

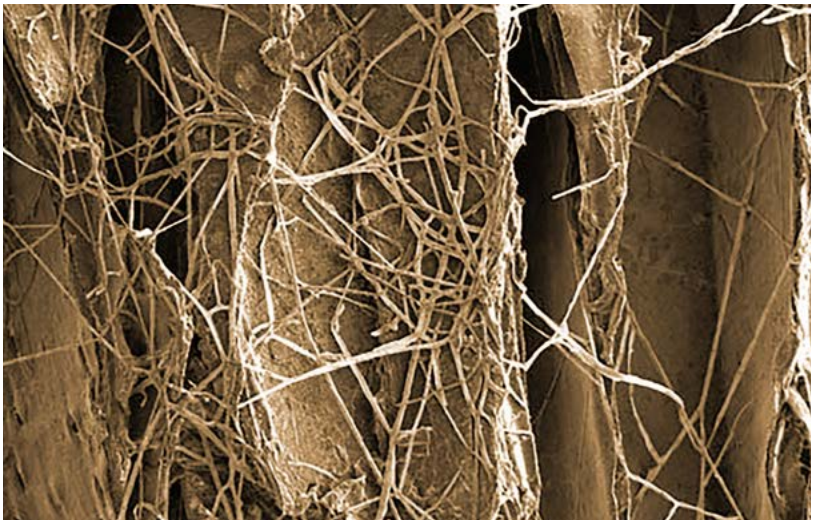
To achieve a deeper understanding of lignin metabolism, four organisms will be grown on aromatic molecules similar to lignin degradation products. Simmons plans to then elucidate the active pathways in the organisms using EMSL's new 21 Tesla mass spectrometer for metabolites, an Orbitrap mass spectrometer for proteomics and the SOLiD sequencing platform for transcriptomics.

These four organisms are only the first of many that will ultimately make up a much larger database available to the scientific community. According to Simmons, "We want to build that understanding of the metabolic networks in organisms that can use lignin as a carbon source, and then develop a predictive biology tool about understanding its metabolism."

Simmons' goals echo and complement those of Singh. "One third of your biomass is lignin, and right now there is no compelling use for that, like there is for sugars," said Simmons. But because lignin makes up such a large fraction of total woody biomass he's convinced there are better uses than waste. "I don't think many industries would throw away or burn a third of [their] input feedstock just because [they] don't know what to do with it," Simmons added.

Ronald de Vries' research seeks to understand how white rot fungi degrade woody biomass. Microscopic images show hyphae, the filamentous structure of a fungus, present on the wood surface, images at 100 µm and 10 µm. (Image provided by Ronald de Vries, CBS-KNAW Fungal Biodiversity Center)





A System-Level Understanding of Fungus

Ronald de Vries, group leader of fungal physiology at the CBS-KNAW Fungal Biodiversity Center in The Netherlands, asked himself one particular question as he was writing his EMSL user proposal – "What would be something we would do with EMSL that we would never be able to do without EMSL?"

This question was important to de Vries because working with EMSL provides him with unprecedented access to expertise and equipment. "The combination of tools they have at EMSL is not likely to be found anywhere else, certainly not in Europe," he said.

De Vries' user proposal will put EMSL through its paces with an exhaustive analysis of different strains of white rot fungi, also known as basidiomycetes. De Vries, and his collaborators from the University of Helsinki, Kristiina Hildén and Miia Mäkelä, intend to use a swath of EMSL capabilities to gain a system-level understanding of the colonization and degradation of woody biomass by white rot fungi both at the strain level and in its two different sexual phases. The research plan includes transcriptomics, proteomics, metabolomics and microscopy. "We had something like 500 samples in total for all the different analyses," said de Vries. Generating the samples took seven months of full-time work from one of his Ph.D. students.

He and his collaborators are hoping to incorporate the multi-omics data into a model. They also want microscopy visualization of both the asexual parent form (the monokaryon) as well as the sexual form, which is seen in nature as a mushroom (the dikaryon). Little is known about the lignin-degrading properties of each sexual form, or how each colonizes wood. "We want to visualize how the fungus enters the wood, and does it grow over the surface or does it penetrate?" said de Vries.

Reaching Around the Corner

Visualization of fungal activity is also a key component of the research of Jonathan Schilling, associate professor at the University of Minnesota. A proposal he submitted in response to an EMSL special call is focused on looking into the degradation action of brown rot fungi.

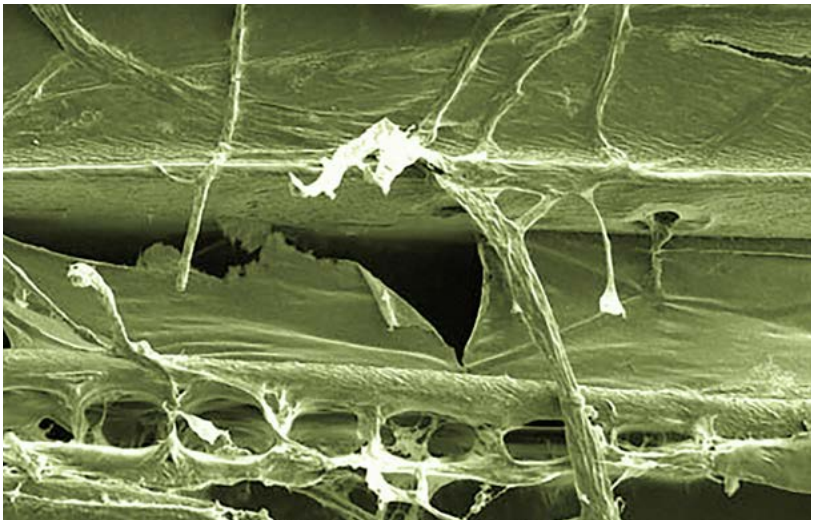
The fungus itself is unique because it uses a kind of pretreatment on the wood. "The initial step [in degradation] is believed to not involve enzymes, but instead a bunch of oxidative chemistry that reduces strength in the wood," said Schilling.

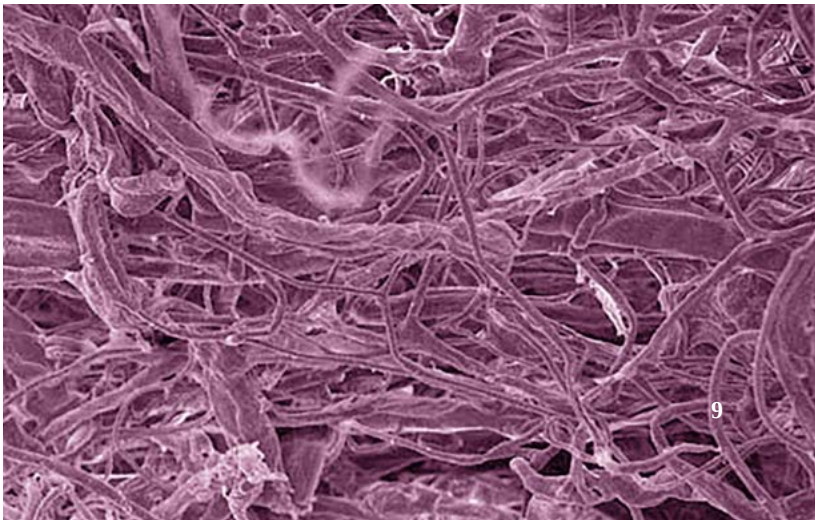
> They're trying to stick their hand around the corner and grab the sugars out from the wood

According to Schilling, brown rot fungi circumvent the lignin barrier, "They're trying to stick their hand around the corner and grab the sugars out from the wood," he said. This strategy has led to them being overlooked in terms of biotechnology, and most of the early research on these organisms focused on how they caused structural damage to wood buildings. "I think most people would assume that a system that degrades lignin – which is very unique – is the thing to focus on," said Schilling, but from his perspective, brown rot fungi, with its combined pretreatment and enzymatic action, allows for a system-level understanding of the degradation process.

In recent years, research and government institutions have begun to recognize potential applications for these fungi that have historically been regarded as a nuisance. These changes have been reflected in Schilling's funding sources; the Department of Energy provided funding for the work he's doing with EMSL, including an early career award for studying these unique mechanisms. (*Continued on page 10*)

To study of the degradation of woody biomass by white rot fungi, Ronald de Vries uses microscopy to view the numerous hyphae, the filamentous structure of a fungus. These hyphae are penetrating into the wood sample, images at 30 µm and 10 µm. (Image provided by Ronald de Vries, CBS-KNAW Fungal Biodiversity Center)





Blake Simmons is developing a metabolic map of the pathways microorganisms use to degrade lignin. These lignin extractions from ionic liquids are used in his research. (Image provided by Blake Simmons, Joint BioEnergy Institute).

Schilling's prior research examined the activity of brown rot fungus at the micrometer scale, but that level of resolution didn't provide the detail necessary to see the unique set of reactions taking place at the junction between the fungus and the wood.

Now Schilling and his collaborators can image fungal reactions down to the sub-micrometer with EMSL's helium ion microscope in the Quiet Wing. They also will be able to see where certain functions are expressed in the fungal tissue by binding fluorescent molecules to the genes and visualizing their spatial distribution using a structured illumination microscope.

"The work at EMSL is really valuable for us because the tools are spatial and high-resolution, and there are excellent scientists there to help us harness [the tools'] potential. We are mapping things that are happening in space and getting a feel for not just one enzyme or one gene but for multiple moving parts," said Schilling, "In this era of big data, these spatially resolved approaches are key."

The findings from the woody biomass deconstruction projects taking place at EMSL, when combined together, will culminate in a more comprehensive understanding of lignin degradation and the assembly of lignin-based chemicals. This added knowledge brings a renewable and sustainable energy future a little closer.

For Baker, achieving this future will ultimately depend on the cost of carbon. Which means not throwing away, or burning, that most valuable of resources.

"Carbon is key," said Baker, "we don't want to leave any carbon on the table." ■

Amy Boaro is a post-doctoral researcher at Pacific Northwest National Laboratory.

SCIENCE HIGHLIGHTS

Soil Science

How to improve soil carbon models

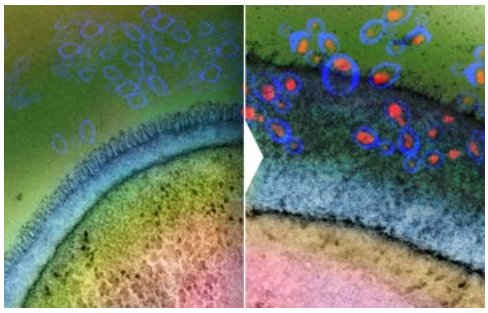
Soil contains the largest amount of terrestrial carbon on the planet, so a small change in soil carbon can have a large impact on atmospheric carbon dioxide levels and climate change. Yet changes in soil carbon remain one of the largest unknowns in the global carbon budget. Furthermore, identifying major driving forces controlling soil carbon dynamics remains a key research challenge. This study compared estimates of soil carbon storage and loss from 10 terrestrial biosphere models and two observation-based data sets to identify sources of variability among models and develop recommendations for future modeling and experimental efforts.

Researchers provided key recommendations for filling major gaps in knowledge, which will reduce uncertainties in terrestrial biosphere models. This study paves the way for accurate estimates of global soil carbon dynamics. Accurate assessment of the soil carbon reservoir is essential for understanding the impact of environmental changes on soil carbon stocks, predicting soil carbon dynamics and effect on climate change.

Funding: This research was supported NASA's Research Opportunities in Space and Earth Sciences, and Department of Energy's Office of Biological and Environmental Research through the Earth System Modeling Program and Subsurface Biogeochemical Research Program as part of the SBR Scientific Focus Area.

Publication: Tian H, C Lu, J Yang, K Banger, DN Huntzinger, CR Schwalm, AM Michalak, R Cook, P Ciais, D Hayes, M Huang, A Ito, AK Jain, H Lei, J Mao, S Pan, WM Post, S Peng, B Poulter, W Ren, D Ricciuto, K Schaefer, X Shi, B Tao, W Wang, Y Wei, Q Yang, B Zhang and N Zeng. 2015. "Global Patterns and Controls of Soil Organic Carbon Dynamics as Simulated by Multiple Terrestrial Biosphere Models: Current Status and Future Directions." *Global Biogeochemical Cycles*. doi:10.1002/2014GB005021.

Participating Organizations: Auburn University, EMSL, Laboratoire des Sciences du Climat et de l'Environnement, Montana State University, NASA, National Institute for Environmental Studies, National Snow and Ice Data Center, Northern Arizona University, Oak Ridge National Laboratory, PNNL, Stanford University, Tsinghua University, University of Illinois at Urbana-Champaign and University of Maryland.



Yeast Biofuels

Optimizing biofuel production in yeast

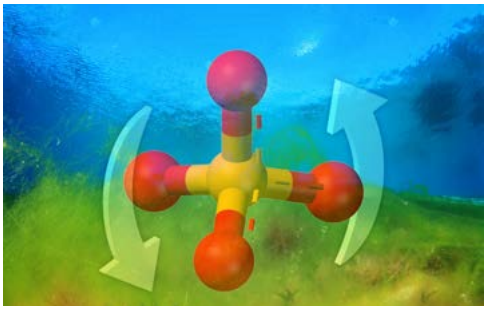
With increasing emphasis on sustainable energy sources, lipid-derived biofuels have been proposed as a promising substitute for fossil fuels. In particular, the yeast species *Yarrowia lipolytica* has strong potential as a biofuel-producing organism because it accumulates large amounts of lipids, but little is known about the key biological processes involved. To address this gap in knowledge, a recent study identified and characterized major pathways involved in lipid accumulation from glucose in *Y. lipolytica*.

This study sets the stage for efforts to engineer yeast to optimize lipid accumulation and maximize the yield of carbon-based products. Because lipids from *Y. lipolytica* have chemical properties similar to those of diesel fuel, they can be readily used as biodiesel using current vehicles and existing infrastructure at gas stations. For this reason, harnessing lipids from *Y. lipolytica* could represent a practical approach for transitioning more quickly to a biofuel-based energy system.

Funding: This research was supported by the Department of Energy's Office of Biological and Environmental Research.

Publication: Pomraning KR, S Wei, SA Karagiosis, Y-M Kim, A C Dohnalkova, BW Arey, EL Bredeweg, G Orr, TO Metz and SE Baker, 2015. "Comprehensive Metabolomic, Lipidomic and Microscopic Profiling of *Yarrowia lipolytica* During Lipid Accumulation Identifies Targets for Increased Lipogenesis." *PLOS ONE*. •DOI: 10.1371/journal.pone.0123188

Participating Organizations: EMSL and PNNL.



Coastal Contamination

Phosphorus recycling in estuary dead zones

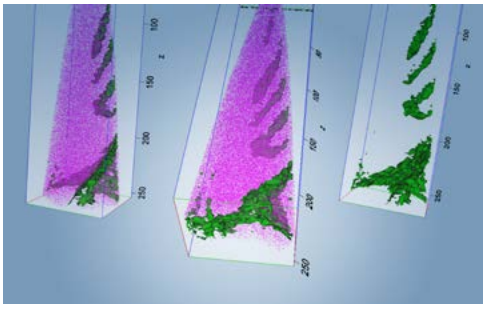
The Chesapeake Bay is the largest and most productive estuary in the United States, containing more than 1,500 square miles of wetlands that provide critical habitat for fish, shellfish and wildlife. This unique ecosystem is in jeopardy due to excessive levels of nutrients such as phosphorus from both man-made activities and natural processes. These nutrients fuel summertime blooms of harmful algae at the surface as well as low-oxygen conditions in deep waters where many bottom-dwelling organisms cannot survive. A recent study identified an unexpected phosphorus-recycling process as the predominant source of phosphorus in the mid-Bay sediment in the Chesapeake Bay.

Restoration of the Chesapeake Bay has been very costly and challenging because there are multiple man-made and natural nutrient sources from sediments, land and air, and because nutrient cycling pathways are complex. By providing a detailed understanding of one way phosphorus is introduced and recycled in the bay, the findings provide new insights into how this nuisance nutrient could support harmful algae growth and sustain low-oxygen conditions. Ultimately, this research could be useful for developing strategies that effectively restore water quality in this vital fishery ecosystem.

Funding: This research was supported by the U.S. Department of Agriculture and Delaware Experimental Program to Stimulate Competitive Research.

Publication: Joshi SR, RK Kukkadapu, DJ Burdige, ME Bowden, DL Sparks and DP Jaisi. 2015. "Organic Matter Remineralization Predominates Phosphorus Cycling in the Mid-Bay Sediments in the Chesapeake Bay." *Environmental Science & Technology*. doi:10.1021/es5059617.

Participating Organizations: University of Delaware, Old Dominion University and EMSL.



Better Batteries

Imaging the nanoscale world inside a battery

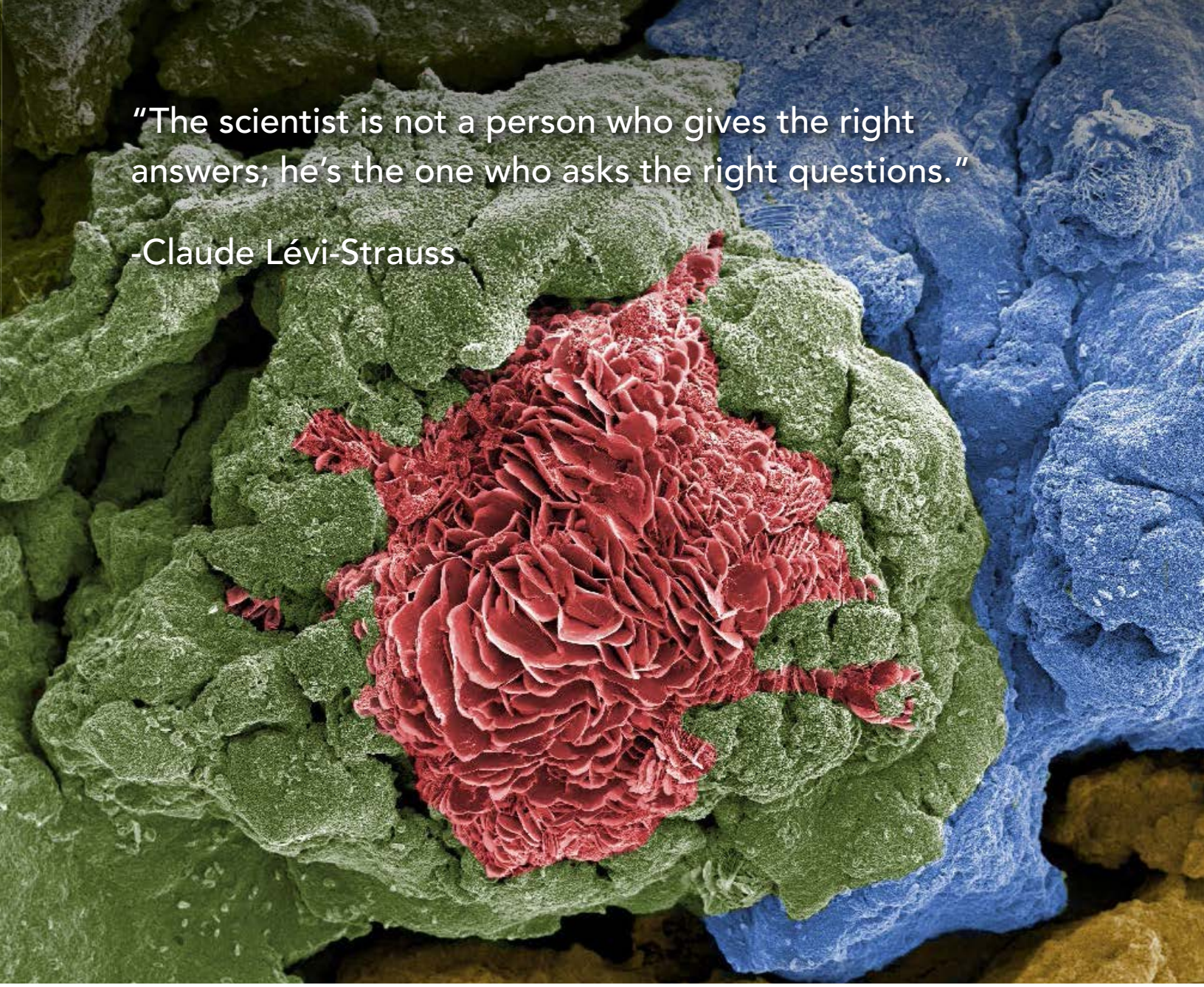
Rechargeable Li-ion batteries are common in portable electronics and in today's plug-in hybrid electric vehicles. Current generation cathode materials lose their structural integrity after repeated charge-discharge cycling, resulting in voltage fading and capacity loss. Understanding the actual mechanisms of degradation is needed to design longer lasting and higher performance batteries, but degradation has been extremely difficult to study in detail due to the challenge of imaging and quantifying the distribution of light elements in Li-ion battery electrodes. To examine this degradation process in unprecedented detail, researchers are using a variety of advanced methods to monitor changes in the distribution of elements in fresh cathodes and cathodes at different stages of cycling. The new measurements have revealed an obscure and unexpected capacity-loss mechanism that occurs in some formulations of a new electrode being designed to enhance performance of advanced Li-ion batteries.

Understanding how cycling affects the nanoscale distribution of elements that make up Li-ion battery cathodes is a critical step toward developing next-generation cathode materials to achieve the highest battery performance. The element lithium, essential to Li-ion batteries, is very difficult to analyze. Current results show the Li distribution after different degrees of cycling, thereby providing information critical to the design of electrodes. The results suggest an important role for atom probe tomography in accelerating battery development. By offering new insights into cycling-dependent capacity loss, this research could help guide efforts to design Li-ion battery materials with prolonged lifetimes suitable for use in long-range electric vehicles and other demanding energy storage applications.

Funding: This research was supported by Laboratory-Directed Research and Development funds from the Chemical Imaging Initiative at PNNL.

Publication: Devaraj A, M Gu, R Colby, PF Yan, CM Wang, JM Zheng, J Xiao, A Genc, JG Zhang, I Belharouak, D Wang, K Amine, and S Thevuthasan. 2015. "Visualizing Nanoscale 3-D Compositional Fluctuation of Lithium in Advanced Lithium-ion Battery Cathodes." *Nature Communications*. doi:10.1038/ncomms9014

Participating Organizations: EMSL, PNNL, FEI Company, Qatar Foundation, and Argonne National Laboratory.



About this Art

Mineral dusts that fly into the atmosphere during dust storms in Asian deserts can travel across oceans in clouds and reach the Western U.S. These particles influence the rain and snow pack in the region by acting as ice nuclei in the atmosphere. With industrial development, emissions of sulphates and nitrate gases to the atmosphere have increased. These gases can form acids that react with dust particles in the atmosphere, changing their ability to cause rain and snow fall, and affecting global climate. A group of scientists at EMSL, in collaboration with scientists at Pacific Northwest National Laboratory's Atmospheric Measurements Laboratory, are studying these acid reactions with mineral dust aerosols using high resolution characterization and studying their impact in ice nucleation. The work was funded by PNNL's Chemical Imaging Initiative. The image was captured with the scanning electron microscope at EMSL.

Team members

Project team members include: Arun Devaraj, Manjula Nandasiri and Shuttha Shutthanandan, all with EMSL; Gourihar Kulkarni and Alex Guenther, both with PNNL; and Nitesh Madaan, a Ph.D. intern at PNNL now with Evans Analytical Group. The image was created by Devaraj. (Image colorized.)