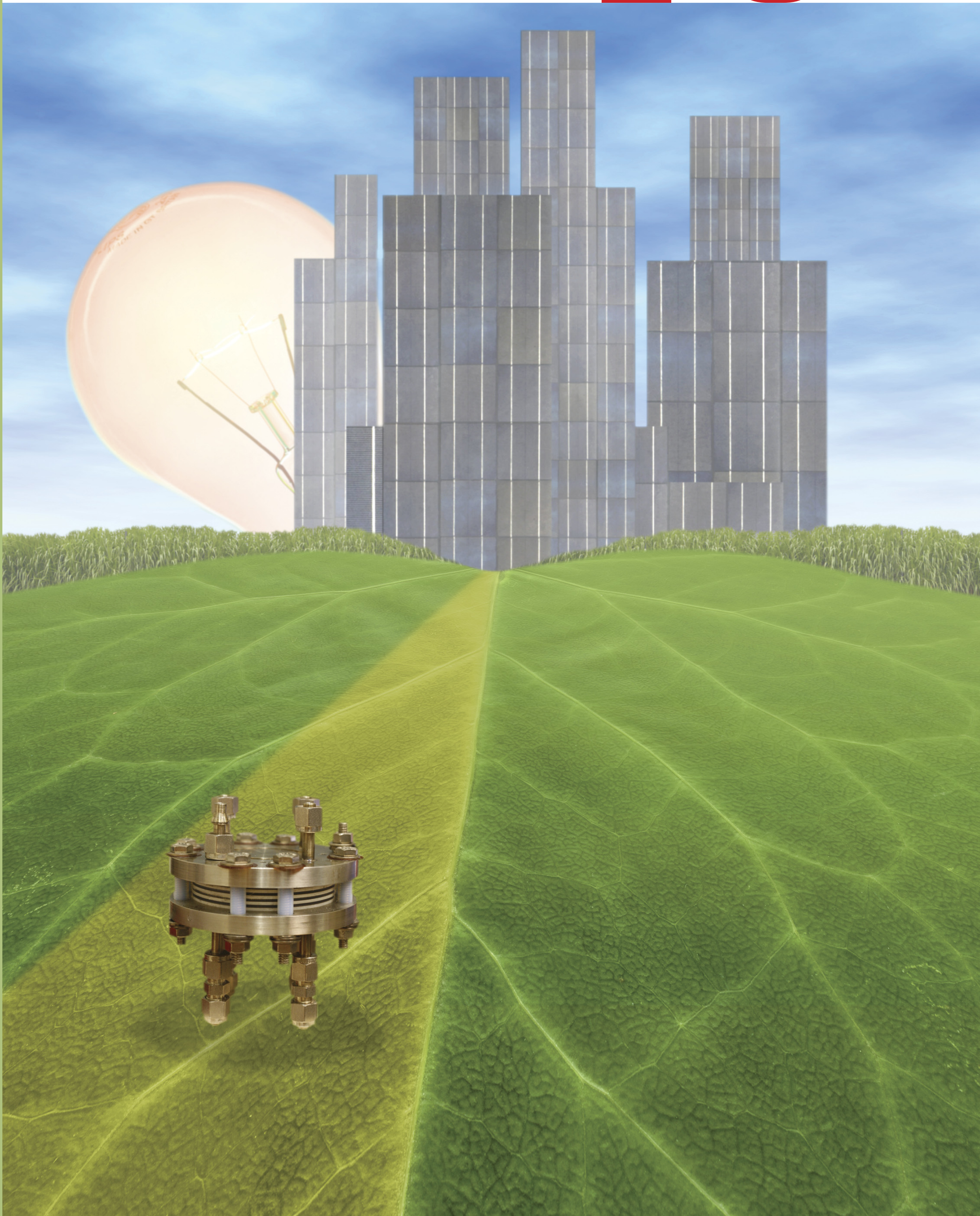
CALIFORNIA
INSTITUTE OF
TECHNOLOGY

E&S
ENGINEERING AND SCIENCE

Volume LXXI,
Number 2,
2008

IN THIS ISSUE

Alternative Energy
for a Sustainable
Future



From the Editor:

As the summer wears on and the price of gasoline goes up even faster than your electric bills, no doubt you worry from time to time about our nation's, and the world's, energy future. (If you don't, go re-read "Powering the Planet" by Nathan S. Lewis in the 2007, Number 2, issue of *E&S*.) Our current global energy consumption is some 13 tera (trillion) thermal watts, a number that's projected to at least double by 2050. If we're going to meet that demand in a sustainable, carbon-neutral way, where is the energy going to come from?

In this special issue on alternative energy, you'll see some of the avenues Caltech faculty are pursuing. The first feature article describes a way of making butanol, a better motor fuel than ethanol, without using food crops. The next two articles deal with transforming sunlight—far and away the most plentiful source of energy available to us—into hydrogen, a chemical fuel that can be stored and used after dark. The final one discusses fuel cells, which liberate that energy by turning the hydrogen back into water. These articles were drawn from last fall and winter's NRG 0.1 lecture series, which looked at energy options from carbon sequestration to nuclear fusion. (Streaming videos of the entire series can be found at http://nrg.caltech.edu/.)

Caltech is working to make a difference in other ways as well. Up front in Random Walk, you'll find out how the campus is becoming a greener place, and read about a new laboratory to be devoted to studying climate change.

It's a long haul from a tabletop demonstration (or a rooftop of solar cells) to changing the world, but the journey of 1,000 miles begins with a single step.

—Douglas L. Smith

A view of the 210 freeway (and the Lake Avenue Metro Rail station) at 11:30 p.m. If we are going to become a solar-powered society, we're going to have to figure out how to run our civilization at night.

California Institute
of Technology

E&S
ENGINEERING AND SCIENCE

Volume LXXI, Number 2, 2008

On the cover: Will we follow the yellow-green road to sustainability? The traveler in the foreground is a fuel cell. The hilltops in the background are sown with miscanthus, a fast-growing, nonfood biofuel crop. The Emerald City is made of solar cells, and a lightbulb in the role of the sun shines over all.

Engineering & Science (ISSN 0013-7812) is published quarterly at the California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125. Annual subscription $20.00 domestic, $30.00 foreign air mail; single copies $5.00. Send subscriptions to Caltech 1-71, Pasadena, CA 91125. Third-class postage paid at Pasadena, CA. All rights reserved. Reproduction of material contained herein forbidden without authorization. © 2008, California Institute of Technology. Published by Caltech and the Alumni Association. Telephone: 626-395-3630.

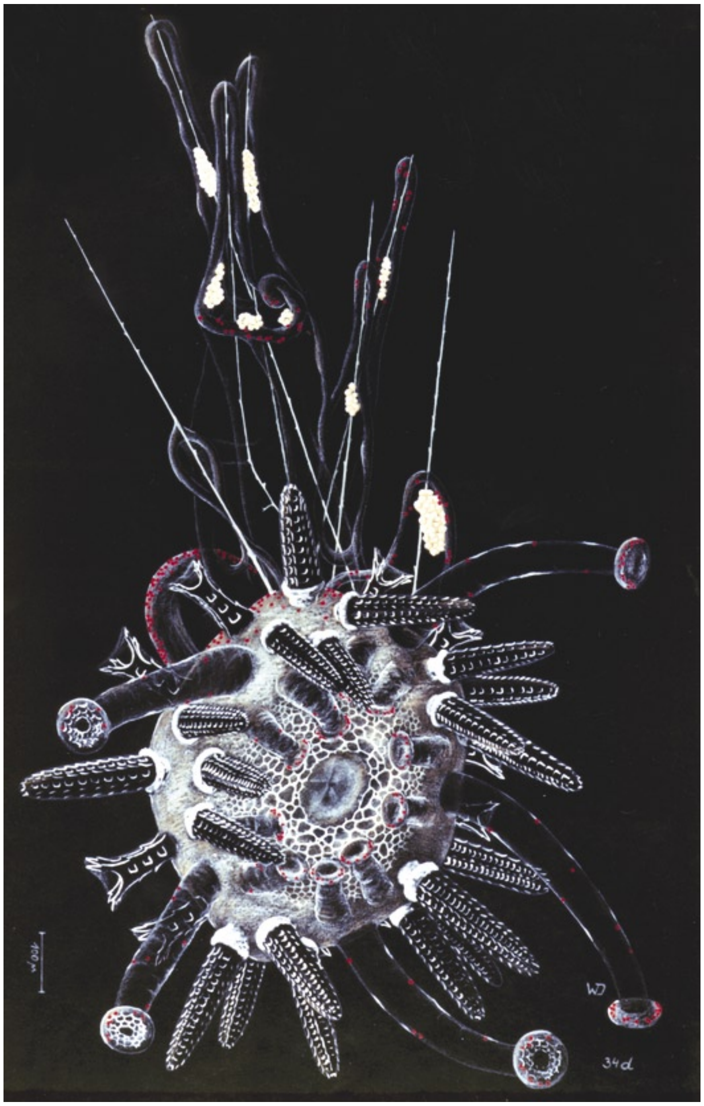
PICTURE CREDITS: Cover, inside front cover, 16, 19-23, 25-26, 28-31, 33, 36-39 — Doug Cummings; 2 — G. Czihak; 4, 8, 9, 23 — Bob Paz; 5 — Elisabeth Nadin; 6 — Harper Beresford, Liming Wang; 7 — Yue Shen; 11 — NASA/JPL-Caltech/U. of Arizona; 12 — DeVane Webster; 13, 14 — S. Long lab, U. of Illinois; 15 — David Jones; 17 — Chris Snow; 19 — Christopher Voigt; 24 — Brendan Kayes; 25 — Michael Filler; 29 — Elizabeth Santori; 31 — Doug Smith; 32 — Honda; 33, 35 — Haile lab

Robert M. Kieckhefer
President of the Alumni Association
Robert L. O'Rourke
Vice President for Public Relations

STAFF: *Editor* — Douglas Smith
Writer — Marcus Woo
Contributing Writers — Sarah Green, Elisabeth Nadin, Kathy Svitil, Ann Wendland
Copy Editors — Allison Benter, Barbara DiPalma, Michael Farquhar, Elena Rudnev
Business Manager — Debbie Bradbury
Circulation Manager — Susan Lee
Photographer — Robert Paz
Graphic Artist, Layout — Douglas Cummings

Visit us online at **http://EandS.caltech.edu**

BUILDING A SEA URCHIN, ONE CELL AT A TIME



This nightmarish creature that one might attribute to Hieronymus Bosch is actually a metamorphosing sea-urchin larva about two millimeters in size. The embryonic skeleton of thin rods in the larva's arms remain, while adult skeletal elements—spines, plates, and tube foot disks—have already appeared.

"Cats beget cats and frogs beget frogs, so how you develop depends on what genome you've inherited," says Eric Davidson, the Chandler Professor of Cell Biology at Caltech. Now, for the first time ever, Davidson's lab has mapped in its entirety the complex network of genes responsible for creating a specific cell—a skeletal cell, in this case, not in a cat or a frog but in a sea urchin.

Genes, of course, are the assembly instructions for creating an organism, and in 2006, the Baylor College of Medicine Human Genome Sequencing Center, along with Caltech's Davidson and Senior Research Associate in Biology Andy Cameron, plus researchers from more than 70 other institutions, published the entire 814-million-letter instruction book for the California purple sea urchin (*Strongylocentrotus purpuratus*). This genome, as it's called, is about one-fourth the size of the human genome and contains some 23,300 genes.

That was the easy part. The challenge now is to tease out the relationships between these genes—how they turn one another on and off at specific times in the embryo's development to create the panoply of adult cell types.

Davidson's team focused on a cell line that takes in minerals from seawater to build skeletal rods. The gene regulatory network that drives this process can be thought of as a blueprint, but unlike a regular blueprint, which describes how static pieces of a structure fit together, the gene regulatory network is a dynamically changing plan, with the relationships between genes at one stage providing the basis for the next stage. The work, coauthored by postdoc Qiang Tu and Paola Oliveri, now of University College London, appeared in the April 22 issue of the *Proceedings of the National Academy of Sciences*.

Says Davidson, "We've reached the point where everything you see in a microscope for this cell lineage can be interpreted in terms of what we know about this control program. The network concerns only one day in the life cycle of an animal that lives for 50 or a hundred years, and only one cell lineage of the embryo, but it is a step forward to be able to relate the biology to the regulatory DNA sequence in this way."

In a second paper in the same issue, Davidson and postdoc Feng Gao report that this regulatory network evolved from another skeletal-cell-forming network present in adult urchins. Sea urchins are the only echinoderms—which also include starfish, brittle stars, sea cucumbers, sand dollars, and other creatures—to have an embryonic skeleton made from this cell lineage as well as an adult one. By analyzing the gene regulatory network, Gao and Davidson were able to show that the embryonic skeleton arose because a substantial portion of the adult skeleton's regulatory apparatus had been hijacked. This happened when the control systems for several genes at the top of the adult hierarchy got mutated in such a way as to come under the embryonic cell lineage's control, at which point the entire downstream adult network became active in the embryonic lineage. The fossil record shows that this change happened some 250 million years ago. "Gene regulatory network redeployment is one way of introducing novelties into an animal's body plan during evolution," says Gao.

Davidson's lab is pressing on to decipher the other gene regulatory networks, hoping to eventually crack the code for the whole embryo. "The evolution of animals is due to changes in the structure of these gene regulatory networks, so this work provides us with an opportunity to study evolution in a new and decisive way," he says. ☐—*KS/DS*

LEAN, GREEN CALTECH

By the time your carpool arrives at Caltech, you've read two papers in the *AIChE Journal*, downed a cup of coffee, and discussed the subtleties of the Lakers game. When the car pulls into its prime, designated space, you head for the office by way of the Red Door Café. Because you brought your Caltech mug, your rich, organic coffee costs only 81 cents. You blow the savings on a muffin, though, slipping the unbleached napkin it came with into a solar trash compactor on your way out. Your hands are still full as you step into your office, but the renewable-energy-fueled lights sense your presence and switch on, brightening the daylight that streams in through thermally efficient windows.

Sound like a rosy portrait of a more sustainable future? Actually, this kind of morning is already possible, even common, at Caltech. With help from private benefactors and partnerships, the Institute is working hard to slash pollution and waste, minimize future costs, and help environmental technologies gain a foothold.

Caltech has firm ground to build on. Its recycling program, nearly 50 years old, diverted 1,248 tons of waste from landfills in 2006; it was named the city of Pasadena's Recycler of the Year in 2007. Caltech produces almost 80 percent of its own electricity—a natural-gas-fired turbine puts out 10 megawatts, and the turbine's waste heat makes steam that spins another two megawatts out of a second turbine and also heats labs and offices. A 2003 upgrade of this cogeneration system doubled its power output while lowering the emission of smog-forming nitrogen oxides and carbon monoxide by 17.4 percent.

Even so, college campuses—especially research-oriented ones—use a lot of electricity, water, and other resources. Caltech, as a research leader in clean energy and climate change, has a particular obligation to walk the walk, and members of an ad hoc sustainability committee established in 2007 by Vice President for Business and Finance Dean Currie are examining every aspect of campus life. As committee member Carol Carmichael—a faculty associate in engineering and applied science, and wife of President Jean-Lou Chameau—commented in the *California Tech,* "We want to ensure that the resources entrusted to us are used for teaching and discovery, and not for maintaining expensive, potentially unsustainable practices or forms of infrastructure."

Think committees don't do much? Members of this one have changed Caltech's purchasing, cleaning, and landscaping practices; established Summer Undergraduate Research Fellowships (SURFs) to study Caltech's environmental impacts; created incentives to carpool, bike, walk, and take public transit to Caltech; and helped catalyze "green" building and the ongoing installation of Pasadena's largest solar-power facility.

It's hard to miss the changes. Biodegradable paper- and corn-based cups, cutlery, and to-go containers have replaced petroleum-based standbys at campus eateries, which now mete out unbleached napkins in single-napkin dispensers. Solar-powered trash compactors have appeared on the Olive Walk and on the Chandler patio. Not much larger than trash cans, each holds 150 gallons—even if the trash truck makes 80 percent fewer visits, they still won't be filled to overflowing. Motion-detecting lighting, compact-fluorescent bulbs, dual-flush toilets, waterless urinals, and Energy Star appliances save electricity and water across campus, thanks to Associate Vice President for Facilities Jim Cowell, the committee chair, and Senior Director of Institute Housing Tim Chang, also a member. Further, the housing office has enrolled all off-campus units for which it pays the bills in the Pasadena Water and Power (PWP) residential "All Green" program, 100 percent of whose electricity comes from wind farms. Director of Buildings and Grounds Delmy Emer-

George Hines (BS '08) checks out the "Big Belly" solar-powered trash compactor outside the Red Door Café.

son, also on the committee, has instituted green cleaning practices on campus, supplying the custodial staff with economical, concentrated, nontoxic cleansers. Emerson's groundskeeping staff is on the same page, reducing water use by landscaping with drought-tolerant plants and refining drip-irrigation systems. As *E&S* was going to press, John Onderdonk began work as the Institute's first sustainability program manager to lead and coordinate these efforts.

This summer, four SURF students will research Caltech conservation, supported in part by benefactors such as Kiyo Tomiyasu (BS '40) and his wife, Eiko. Mentored by sustainability committee member and mechanical engineering professor Melany Hunt, Stassy Petkova will quantify Caltech's greenhouse-gas emissions from 1990 to the present, Daniel Alvarez and Silas Hilliard will study Caltech's energy use and evaluate conservation opportunities, and Tyler Hannasch will focus on ways to reduce electricity consumption in the undergraduate Houses.

What's *not* happening is vital, too. Hundreds of cars stay out of L.A. traffic and campus parking spaces because of programs directed by sustainability committee member Kristina Valenzuela, Caltech's transportation coordinator. The latest statistics show that Caltech has 141 registered carpools, two vanpools, 276 holders of discounted public-transit passes, 193 registered walkers, and 400 participants in bike-to-work programs. Participants enjoy incentives including monthly raffles, rainy-day parking permits, and guaranteed rides home in case of illness or emergency.

But the two biggest changes on campus are the least noticeable. The first—stringent environmentally friendly building standards—might just look like good design. The second—a massive new solar facility—will be above eye level on Caltech roofs.

All new construction and renovations will adhere to the U.S. Green Building Council's Leadership in Energy and Environmental Design (LEED) guidelines. The three buildings under way—the Annenberg Center for Information Science and Technology, Schlinger Laboratory for Chemistry and Chemical Engineering, and Cahill Center for Astronomy and Astrophysics—will earn gold-level LEED certification. Each building will use 30 percent less water than comparable buildings. The Cahill and Annenberg Centers will use 24–28 percent less energy, while the Schlinger Lab will conserve 17–21 percent. But don't expect to see pallid scientists in gray laboratories—daylight will illuminate 75 percent of rooms in the Cahill and Annenberg Centers and 90 percent of the Schlinger Lab. The buildings won't have those dizzying new-paint, new-carpet, and new-plywood smells either: each project uses low-emission materials, keeping volatile organic compounds such as formaldehyde out of circulation. According to a state government task force, the average California green-construction premium of $4 per square foot yields a $67 return over 20 years, maximizing the long-term impact of the gifts provided by Warren (BS '44, MS '46, PhD '49) and Katie Schlinger, the Annenberg Foundation, Charles and Anikó Dér Cahill, Fred (BS '62) and Joyce Hameetman, Stephen Bechtel Jr., and others.

Caltech is also investing in solar energy, leasing the rooftops of three parking garages and four buildings to solar-power companies in order to generate 1.2 megawatts of electricity. The solar plants will offset 7 percent of Caltech's peak power use, and it's the dirtiest and most expensive power—part of the 20-odd percent currently purchased from PWP, half of which comes from burning coal. (It doesn't hurt that PWP raised its rates 20 percent in the first half of 2008.) The first solar plant, under construction atop Holliston Parking Garage, will be the largest in Pasadena. When all seven solar rooftops are up and running, according to Cowell, "we'll have one of the largest university solar facilities in the country."

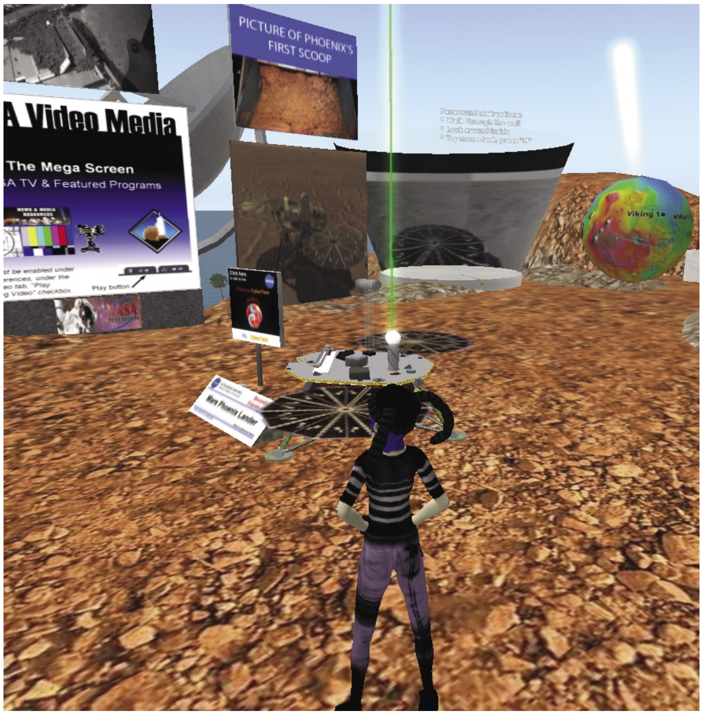
Private companies will design, install, finance, and maintain the new power plants, selling all of the power back to Caltech at rates that start at just over 10 cents per kilowatt-hour and that will rise less than 4 percent per year for 15 years. Cowell expects PWP rates, which now top 14 cents per kilowatt-hour, to continue to rise by 5 to 10 percent per year. Cowell's also pleased about the relatively short contracts. "For 15 years, they give us lower, more stable rates and greenhouse-gas reductions," says Cowell, "and then, if we want them to, they take it all away. My feeling is that we're going to invent better panels in 15 years and want to put up our own technology. Or maybe we'll want to do something else. The world is going to be a different place, and I don't have a crystal ball."

It hardly takes a crystal ball to see a future in which people call for campuses to use less power and water and generate less pollution and trash. The simple, low-cost steps Caltech is taking now will set the stage for greater innovation. As Bill Irwin, senior director of facilities management, puts it: "We take a lot of pride in what we have accomplished to date, but we are even more excited about what the future holds." □—*AW*

JPL GETS A SECOND LIFE

I'm perched on the edge of Mars's Victoria crater, squinting to make out the sediment stratification in the walls across the way. Actually, it's my avatar—my virtual persona—dodging a Martian dust devil as I amble through the alternate reality created by Caltech's Jet Propulsion Laboratory (JPL) in the online world called Second Life. Since JPL's mission is to explore worlds outside the one we know, it's only fitting that it should be breaking ground here. Second Life is an Internet portal to . . . anywhere. In this virtual world, users pick a character to walk or fly through spaces designed by other users. JPL's piece of real estate is called Explorer Island. Like the ceiling of the Great Hall at Hogwarts, Explorer Island's sky mirrors JPL's real-time weather; the deer that wander JPL's grounds in real life graze in front of the simulated visitor center. Except on Explorer Island, they can fly.

At the entrance to Explorer Island, you're greeted with a pop-up memo listing upcoming NASA events. These workshops, exhibitions, and launches from the real world are open to audience participation on the island. In the "virtual world auditorium," you can even participate in NASA meetings through your avatar. Of course, says Charles White, senior member of JPL's technical staff and creator of Explorer Island, "social norms of real life apply." You can contribute your input to the meetings, but scientists reserve the right to mute or even eject anyone who misbehaves.



At JPL's site in Second Life, you can walk around displays from Victoria crater or the Phoenix landing site, or sit in on a real NASA organizational meeting. Just watch out for those dust devils!

Every Tuesday at 1:00 p.m. in the adjacent NASA neighborhood, called CoLab—the Collaborative Space Exploration Laboratory—NASA researchers mingle with the public. These meetings were originally designed to gather scientists from different parts of the world into the same virtual meeting room, but now any visitor is invited to sit in. The discussions can range from designing spacecraft to creating software for the virtual world or anything in between, as long as the members avoid topics that fall under the ITAR—International Traffic in Arms Regulations—umbrella.

But the coolest thing for most people is exploring places that JPL missions have visited. The magic of JPL's presence in what White calls a "persistent synthetic environment" is the use of real data. (White, aka "Jet Burns" on Second Life, welcomes each new visitor with a pop-up card full of information. For example, those dust devils ". . . can be three times larger than a full tornado on Earth. In Second Life, you and two other friends can ride them around Mars Mountain.")

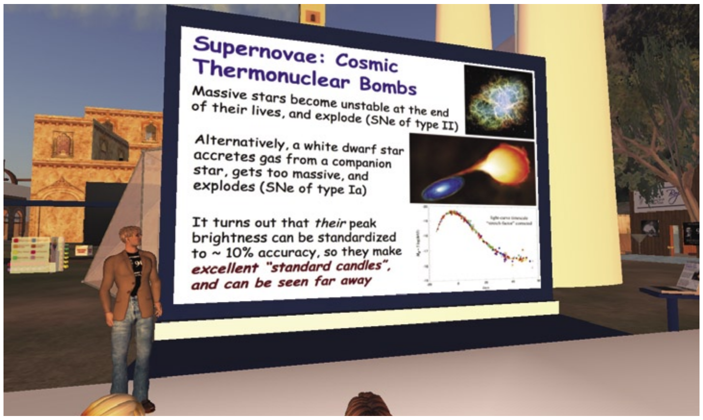
White likes to tell of an avatar who said he cried for 10 minutes when he realized he was standing at the edge of Victoria crater. This is the story that brought me to the crater, which is no artist's interpretation, but the real deal—or as real as you can get without actually going to Mars. It's built from photos taken by the rover Opportunity, which crawled into it last September to explore the layered sedimentary rocks that are thought to have been deposited long ago, when water flowed. You can also trudge over rugged red terrain to various exhibits, but watch out for those dust devils and the giant airbag that sweep by every so often. If you're quick, you can catch a ride on the airbag, whose route will change once you hop aboard.

As you descend from the Mars mock-up, you climb a ramp carpeted in the latest views of Titan's methane lakes. From there you can ascend the scaffolding of Explorer Island's launching pad, highlighted with glowing red spotlights. The Mars Phoenix lander was carried aloft by a Delta II rocket on August 4, 2007, in the first simulcast launch on Second Life, says White. Around 40 avatars attended, filling the program's capacity. The Dawn spacecraft, which will visit the asteroid Vesta and the former-asteroid-now-dwarf-planet Ceres, followed on September 27. The pad now has room for 100 avatars, and it filled to capacity on January 31, when Explorer I lifted off on the 50th anniversary of the real-life event. An audio tape of the 1958 launch accompanied the rocket's ascent, giving visitors the realest taste they're likely to get of America's entry into the Space Age.

Visitors can still follow bright yellow signs to the Phoenix landing, which was celebrated on May 25 in Second Life as it was in real life. In the large display area, you can investigate a mockup of the lander to your heart's content, check out real images of Phoenix on the surface of Mars and its first scoop of Martian soil, and even pick up a free Phoenix T-shirt for your avatar.

For the time being, Explorer Island is still in the research phase. White anticipates that interactions like the ones facilitated in this virtual world—where anyone can talk to a NASA scientist and scientists can meet "outside the lab"—are as inevitable as e-mail. "Virtual worlds will just get better and better and more powerful. We need to explore this," he says. "The world is virtual, but the communication and the experiences are real. People talk about it as if they were there."

Caltech Professor of Astronomy George Djorgovski agrees. He was recently featured at Second Life's SciArt Media Learning Center, where he regaled an audience of around 50 avatars during "A Special Online Event: The Richard Feynman 90th Birthday Party / Astronomy and Physics Virtual Conference," otherwise known as "Dick's Digital Nonagentennial Commemoratory Colloquium." After his lecture, Djorgovski received an e-mail from one of the attendees, who wrote, "You've had a big influence on my son. We listened to your talk together, and the day after, he insisted that I buy him a physics book (he's seven). Since then he's been asking me quiz questions on black body radiation, entropy, force, and quarks!" Says Djorgovski, "I'd say it was worth it, if I got a seven-year-old interested in physics!" □—*EN*



Supernovae: Cosmic Thermonuclear Bombs

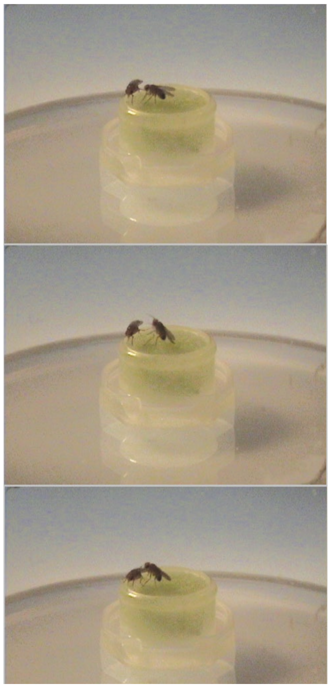
Massive stars become unstable at the end of their lives, and explode (SNe of type II)

Alternatively, a white dwarf star accretes gas from a companion star, gets too massive, and explodes (SNe of type Ia)

It turns out that *their* peak brightness can be standardized to ~ 10% accuracy, so they make *excellent "standard candles", and can be seen far away*

Left: "Curious George" Djorgovski gives a cosmology lecture at a Second Life bash honoring the late Richard Feynman.

FRATERNIZING FLIES HAVE FEWER FIGHTS



Above: A pair of sumo-wrestling fruit flies. The lunge, in which one fly rears up on its hind legs and charges the other, is the insect's most common fighting move.

If you have cable TV, chances are during bouts of channel surfing you've experienced snippets of something known as the Ultimate Fighting Championship. Literally a no-holds barred contest, two opponents enter the ring—the Octagon, to the initiated—and anything goes until one achieves "submission" over the other. What began as an ethically murky real-life Thunderdome has spawned legions of fans, best-selling books, reality shows, and devoted bloggers.

It would seem the draw of the Octagon has even reached as far as the lab where Caltech scientists led by David Anderson, the Sperry Professor of Biology and a Howard Hughes Medical Institute investigator, use a miniature version (the Octette?) to study aggression in fruit flies. Their recent paper in the *Proceedings of the National Academy of Sciences* suggests that two distinct inputs—genetic and environmental—converge at a particular gene to shape the decision to fight. The work was done by grad student Liming Wang, the first author of the paper, with Anderson in collaboration with postdoc Heiko Dankert and Professor of Electrical Engineering Pietro Perona.

In the study, male fruit flies were housed either in isolation or in groups of 10. After three days, pairs of flies from each group were placed in a plexiglass arena. The flies raised in isolation fought roughly half of the time, while the socialized flies essentially never fought. The isolated flies, Anderson says, would begin frantically running around and chasing each other when paired up. In stark contrast, the group-housed flies "just sat placidly eating, like cows grazing in a meadow . . . as if they couldn't care less about their neighbors."

The scientists repeated the experiment, this time after moving half of the initially isolated flies to a group setting for another three days while keeping the other half in isolation. The still-solitary flies were even more likely to fight, engaging their rivals 80 percent of the time, while their once-aggressive counterparts now rarely fought. This showed that a fly's level of aggression was both reversible and situational. In other words, the likelihood that a fly would fight depended on its most recent social experience, regardless of its prior circumstances.

Anderson's group then analyzed the genetic profiles of both sets of flies and identified genes that behaved differently in the isolated and the socialized flies. Comparing this list to one of genes that had been shown by Herman Dierick and Ralph Greenspan of the Neurosciences Institute in San Diego to be associated with aggressiveness, Anderson's group found one gene on both lists—the unimaginatively named *Cyp6a20*.

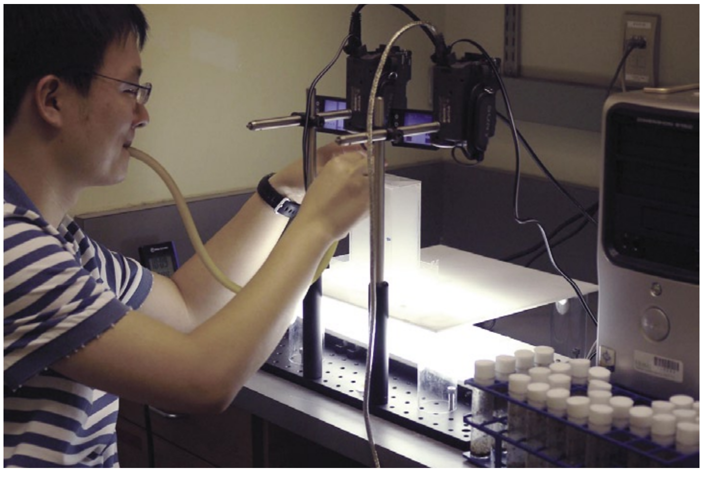
This overlap was surprising, given the different methods used by the two labs to generate aggressive flies. The San Diego group bred flies for aggressiveness over dozens of two-week generations, resulting in a stable, hyperaggressive fly lineage. Anderson's lab focused on social experience, a stimulus measured in days. "We have a common genetic target that acts on different time scales," Anderson says.

A balance of inherited and environmental inputs makes sense from an evolutionary standpoint. Genes promoting aggression would have obvious benefits in territorial defense and reproductive success; but a mechanism for tempering this innate aggressiveness, for providing situation-specific control of the decision to engage a rival, would also convey an advantage. Sometimes you want to be a lover, not a fighter—the guy who brawls at the slightest drink-sloshing gets bounced from the bar before he can collect very many phone numbers.

Cyp6a20's precise function in regulating aggressiveness remains a mystery, but Anderson has an intriguing hypothesis. While measuring levels of *Cyp6a20* in flies, the researchers found it preferentially in the antennae, the fly's organ of smell, suggesting it might act in pheromone sensing. *Cyp6a20* belongs to a large family of genes that also includes one responsible for converting testosterone to estrogen in vertebrates. The balance between these two hormones has been shown to influence fighting behavior in birds, fish, and mice, and it's possible that an analogous system is at work in flies.

If pheromones do help control fly aggressiveness, then Anderson believes "the important question is 'What changes in the brain of the flies that so alters their behavior?'" Socialized flies could be curbing their responses to an aggression-promoting signal, or they could be responding to an aggression-suppressing cue. These two pathways might produce very different patterns of gene activity in

Wang uses a fly aspirator—a piece of tubing with a plastic tip—to transfer the flies from their vials into the arena, the eerily glowing container. Simply point the tip at a fly, inhale gently (a plug prevents you from swallowing the fly), move the tip to where the fly should be, and puff!



individual nerve cells.

So in the end, what do the exploits of a few fruit-fly gladiators mean to the rest of us? The fact that genetics and environment intersect at the seat of a complex behavior like aggressiveness, and that this can occur on the scale of a single gene, gives us a new understanding of just how exquisitely regulated our responses can be. As is so often the case when science delves into the "how" of something, we see that the initial question was overly simple. It's not nature versus nurture, but how much nature versus how much nurture or, perhaps, when nature versus when nurture. Unmasking the constantly shifting balance of power between the two is far more riveting than anything the Octagon can offer on pay-per-view. □—*SG*

The light fixture in Robinson's vestibule is an armillary sphere—an ancient astronomical tool—decorated with the signs of the zodiac. Note the compact fluorescent bulb.

FROM THE BIRTH OF GALAXIES TO THE FATE OF THE PLANET

"The bandwagon of saving the planet from environmental pollution and from suffocation is well occupied now. Indeed, everyone is on it. Being on it is rather like being against sin, and, as in the case of sin, the universal practice is to point the finger at other people. . . ." Al Gore, 2007? Nope. It's Caltech president Harold Brown in a March 1970 article in these very pages that also pointed out the potential of greenhouse gases to cause substantial climate change. Brown closed thus: "Unless Caltech can contribute something unique, we do not want to add another element to the near infinity of activities that have been generated by the universal enthusiasm about the protection of the environment. What we are thinking about is . . . an Environmental Laboratory. A reasonable size to aim for would be 25 to 30 professionals, plus part-time activity by interested Caltech faculty and students."

Caltech's environmental scientists must be pinching themselves—this 40-year dream is slated to come true in August 2010. Trustee Ronald Linde (MS '62, PhD '64) and his wife, Maxine, have established an $18 million endowment to create the Ronald and Maxine Linde Center for Global Environmental Science, which will focus on natural and human-caused variations in Earth's climate and be housed in the former Robinson Laboratory of Astrophysics. When its current residents move to the new Cahill Center for Astronomy and Astrophysics in 2009, Robinson's heavy, wooden doors will close for some 18 months as the building transforms into the Linde + Robinson Laboratory for Global Environmental Science.

Already renowned for deciphering the mystery of smog in the '50s, Caltech established one of the nation's first environmental-health engineering programs in 1960. The first professor was Jack McKee, who had joined the faculty as a sanitary engineer in 1949. He was followed by civil engineers Norman Brooks (PhD '54) and Fredric Raichlen, biologist-turned-environmental-scientist Wheeler North (BS '44, MS '50), and chemical engineer Sheldon Friedlander, a pioneer in aerosol studies.

In 1969, the Institute added an option in environmental engineering science that granted master's and doctoral degrees. Next came the Environmental Quality Laboratory, organized in 1971, which was not a lab per se, but a "think tank" that produced several major policy studies on California's environmental problems. Its facilities were split between a house (since demolished) and a few offices in Dabney Hall of the Humanities. Twenty years later, Bank of America made possible the Environmental Analysis Center, an open-access, user-operated instrumental facility that that will relocate to the Linde + Robinson Laboratory.

So, how many engineers does it take to solve an environmental problem? Trick question. Even small problems slip into several disciplines, and big problems like climate change necessitate the kind of collaboration that Caltech is famous for. The Environmental Science and Engineering Program now includes biologists, chemists, earth scientists, engineers, and physicists.

These people are scattered through seven buildings—imagine what they'll be able to achieve when they're finally working in one. For example, John Seinfeld, who studies the physics of air pollution and explores atmospheric modeling, works halfway across campus from Tapio Schneider, who also researches global circulation of the atmosphere. Chemical physicist Mitchio Okumura studies stratospheric chemistry up Wilson Avenue from planetary scientist Yuk Yung, recognized for his work in stratospheric ozone depletion.

MacArthur Fellow Paul Wennberg, the Avery Professor of Atmospheric Chemistry and Environmental Science and Engineering, will direct the Linde Center. "Caltech is really good at providing the essential ingredients—great

More zodiacal signs can be seen in the library's light fixtures and on Heinsbergen's stenciled ceiling.

facilities, great students, and great professional staff. That's what attracts the best and brightest scientists, people who can pose the big questions and solve big problems."

Wennberg hopes to round out the team with at least four more professorships: a glaciologist, who would study climate-change-related ice melt and its effects on sea level; a physical oceanographer, who would investigate temperature change in the abyssal ocean (thermal expansion of the Pacific could make Palm Springs a future Newport Beach); a biogeochemical carbon specialist to analyze how biology controls carbon; and a researcher to look into how clouds and moisture change when the climate changes. Data from JPL, a world leader in space-based observation of Earth, will complement the program's field- and laboratory-based research.

Bob Walp (BS '51, MS '53), a lead donor to the new Associates Graduate Fellowship in Global Environmental Science, agrees Caltech has a vital role to play. "There's such chaos and ignorance in this area. That's terrible when such incredible stakes are involved. Caltech's wonderful interdisciplinary environment gives it an advantage. I don't think it needs immense task groups and large amounts of money to make progress. It really just takes a few imaginative people. Caltech has been active in environmental matters at least since I first got here right after World War II, when the smog really hit Los Angeles. Arie Haagen-Smit, the organic chemist, made a big splash discovering the constituents of smog and developing technology to reduce it. That's just one person—and the air's cleaner."

The Linde + Robinson Laboratory will set precedents in the sustainable renovation of research facilities in historic buildings. The elegant entrance, cozy library, and grand staircase will regain their splendor, showcasing elaborate metal- and woodwork, Spanish-influenced bookcases, and a beamed, stenciled ceiling attributed to noted muralist Anthony Heinsbergen, whose other commissions include the Los Angeles City Hall and the Hollywood Roosevelt and Beverly-Wilshire Hotels. Fresh air and sunlight will find their way to the depths of the sub-sub-basement, thanks to the repurposing of a solar-telescope shaft that punches through all five floors of the building, and basement dwellers will enjoy "garden-level" outside views as well. The project will emphasize recycled, nontoxic materials and win a gold—if not platinum—certification from the U.S. Green Building Council's Leadership in Energy and Environmental Design (LEED) Green Building Rating System, and energy-efficient technology will curb the climate center's own potential climate impact.

The Linde Center will draw talented young scholars, and Caltech will need to support them. To this end, Foster and Coco Stanback have endowed a postdoctoral fellowship, a graduate fellowship, and a "discovery fund." The Caltech Associates have established the Associates Graduate Fellowship in Global Environmental Science to pay one first-year graduate student's tuition and stipend annually.

Graduates of the new program will seed the field with scientist-engineers used to multi-dimensional thinking. As Provost Ed Stolper notes, "Few programs have taken this step of bridging environmental science and conventional environmental engineering—yet it is an approach we believe will be critical to training future leaders." ☐—*AW*

And ringed Saturns grace the lamp chains in the hallways.

BRACE YOURSELF!

It's a good thing that Lucy Jones didn't want to scare us, as she kept assuring the capacity crowd for the press conference in Caltech's Beckman Auditorium on June 4—if she did, the audience would probably have been reduced to blubbering imbecility. Jones, a Caltech visiting associate in geophysics and the chief scientist of the United States Geological Survey's Multi-Hazards Project, was describing the scenario created for what will be the largest earthquake drill ever held in the United States.

"ShakeOut," as it's called, will cut loose at 10:00 a.m. sharp on Thursday, November 13, and features a magnitude-7.8 quake on the San Andreas fault that begins under the shores of the Salton Sea at Bombay Beach, and in 90 terrifying seconds ruptures 180 miles of fault to well west of Lancaster. The ground will move sideways 44 feet in places, and the sedimentary layers of the L.A. basin will quiver like angry Jell-O for 55 seconds—an eternity compared to the magnitude-6.7 Northridge quake's seven seconds. It will take up to three minutes for all of the shaking to die out in some places.

The freeways that cross the fault will be reduced to rubble, and our other lifelines—railways, power lines, and aqueducts—will fare no better. "We'll have 13 million victims," Jones said, "and we'll need help from the Bay Area and Arizona at a time when I-10 and I-15 have been cut."

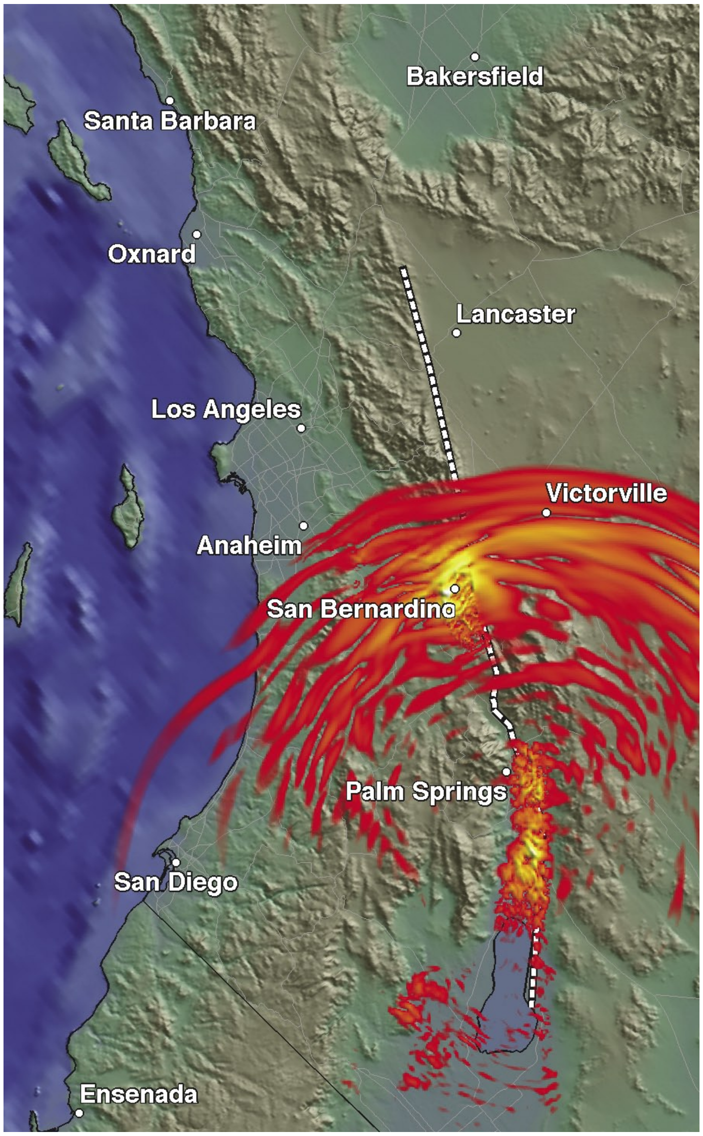
"This is nearly as big as the event that just hit China," said the USGS's Ken Hudnut, a Caltech visiting associate in geophysics, who, like many others involved in ShakeOut, wears a red silicone wristband for the Chinese earthquake victims. Hudnut and Brad Aagaard (MS ’95, PhD ’00) created a highly detailed specification of the earthquake source. Hudnut then oversaw the quake’s computer modeling, in which the San Andreas fault was divided up into some 18,000 “sub-faults,” each about 500 meters square, along which the slip was forced to propagate, mimicking the rupture of the real thing. (Hudnut also plans to model some of the scenario’s larger aftershocks, one of which is a 7.2 on the Sierra Madre fault, aimed right at Pasadena.) Robert Graves (MS ’88, PhD ’91) of URS Corporation turned this data set into a detailed simulation on the University of Southern California’s high-performance computer cluster, calculating the shaking experienced across the Southland at points spaced on a two-kilometer grid. The ShakeOut simulation project was coordinated by the Southern California Earthquake Center (SCEC), and several other SCEC institutions participated.

The ShakeOut scenario, all 308 pages, was constructed by over 300 experts from the USGS, Caltech, SCEC, UCLA, and elsewhere who used Graves’s results to create a plausible picture of likely damage to buildings, roads, pipelines, and the like, which in turn were used to project casualties and economic losses. For example, Swaminathan Krishnan (PhD ’03), assistant professor of civil engineering and geophysics, and postdoc Matthew Muto modeled the respose of multiple 20-story steel-frame buildings at each grid point, paying special attention to the dozen or so locations that have cluseters of tall buildings.

“It’s not the worst case, but it’s a real good estimate of what we can expect,” said Federal Emergency management Agency geophysicist Michael Mahoney. Since our building codes are stricter than China’s, only five 11- to 20-story steel-frame buildings collapse completely, and just one percent (45,000) of the region’s lesser structures are total losses, with one in 25 wood-framed houses and apartment buildings suffering significant damage. With no Santa Ana winds to fan the 1,600 blazes that are started by car crashes, downed power lines, and the like, a mere 133,000 single-family houses are destroyed. “Find an open space of refuge—a park, or a school, perhaps—in your neighborhood,” said Michael Freeman, chief of the Los Angeles County Fire Department. “Where would you go if several city blocks are burning?”

The point to all this, of course, is for local, state, and federal agencies to plan their responses. “How do you deal with an event that will literally break the system?” said SCEC director Thomas Jordan (BS ’69, MS ’70, PhD ’73). Thousands of cops, firefighters, and paramedics will be deployed in the statewide “Golden Guardian” exercise, and logistics will be a big focus. “You’ll have to think about how you’ll feed your first responders three days later,” as Jones pointed out—no easy task, even though the ports and the airfields are largely intact, when all the roads are impassable. Getting electricity, water, and other basic services restored will take days to weeks, and some of the hardest-hit areas will be doing without for months. And then there’ll be the 1,800 dead and 50,000 injured to deal with. . . .

But this isn’t just for the pros—millions of ordinary Californians, in their schools, businesses, places of worship, or just at home, will take part in the drill, not only by “Dropping, Covering, and Holding On, as the slogan goes, but by creating or updating their own disaster plans. (See http://www.shakeout.org/.) There’s no time like the present to get prepared—as Jones says, “A large earthquake is definitely in our future.” ☐—*DS*



Simulation by Robert Graves. Rendering by Geoff Ely, UCSD/San Diego Supercomputer Center.

Ground motions in the ShakeOut scenario 60 seconds after the rupture begins. Yellow regions are experiencing sideways motions of one meter per second or more.

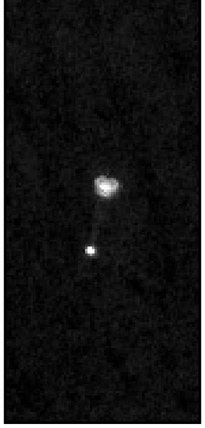
PHOENIX HAS LANDED

On May 25, the Phoenix spacecraft landed safely in the northern polar region of Mars. The lander is now exploring the possibility that liquid water once existed on the red planet.

In 2002, the Mars Odyssey orbiter revealed evidence of water ice hidden beneath the surface of northern Mars. Phoenix's mission, then, is to dig below that surface and analyze soil and ice samples to study the planet's water history. Although Phoenix isn't designed to look for signs of life, it will analyze evidence about whether the icy soil has ever been a hospitable environment for life. Liquid water, which might have existed as late as 100,000 years ago, could have given rise to microbial life; and some bacterial spores, which could remain in a dormant state for millions of years, might be lurking in the soil.

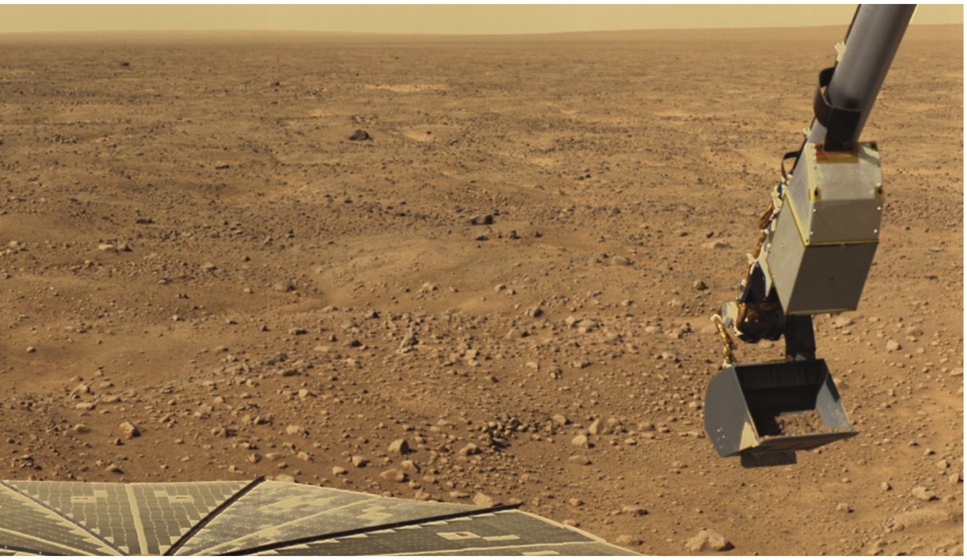
Three weeks into the mission, scientists said they'd hit pay dirt—or rather, ice. Digging into a trench 5 centimeters deep and 30 centimeters wide, Phoenix uncovered chunks of white stuff on June 15. At the time, researchers thought it could be either ice or some sort of salt. But when the white chunks disappeared four days later, the scientists knew they had to be ice. Only ice, which sublimates from solid to gaseous form, could have vanished so abruptly. In an adjacent trench, Phoenix's robotic scoop hit a hard layer at the same depth as those ice chunks, suggesting the presence of more water ice.

Led by the University of Arizona in partnership with JPL and Lockheed Martin, who built the craft, Phoenix rose from the technological ashes of previous missions. The craft uses instruments adapted from the Mars Polar Lander, which crashed in 1999, and the Mars Surveyor lander, whose mission was cancelled just a year before its scheduled launch in 2001. Phoenix was the first spacecraft since the Viking missions in the 1970s to successfully employ rockets to land, as opposed to using the airbag system designed for Mars Pathfinder and used by Spirit and Opportunity. ☐—*MW*



Phoenix's parachute slows its descent. This image, taken by the Mars Reconnaissance Orbiter's High Resolution Imaging Science Experiment (HiRISE) camera, was the first of a spacecraft landing on Mars.

The HiRISE camera took this snapshot of the landing site after touchdown. The lander, with its solar panels open, appears as a bluish dot at the top. The black smudge on the right is the heat shield and its impact mark, and the lower part of the image shows the parachute, attached to the bottom of the capsule shell.



The spacecraft's solar panels and robotic arm are seen in this image of Mars's western horizon, which Phoenix took shortly after landing.

Below: Called Dodo-Goldilocks, this trench shows chunks of white stuff, which scientists say is ice. Although ice on the Martian surface is not a new discovery (the polar ice caps have water ice, for instance), to see pieces up close—a major part of Phoenix's mission—is cause for excitement.

PICTURE CREDITS: 2 — G. Czihak; 4, 8, 9, 23 — Bob Paz; 5 — Elisabeth Nadin; 6 — Harper Beresford, Liming Wang; 7 — Yue Shen; 11 — NASA/JPL-Caltech/U. of Arizona

The Race for New Biofuels

by Frances H. Arnold

New technology, developed just over the last few years, has now allowed us to design microorganisms—almost from the ground up—that will provide new sources of fuel. Transportation fuel counts for about 28 percent of the U.S. total energy use, 22 percent of world's energy use, and 27 percent of global carbon emissions. Most of that fuel comes from petroleum. We get about 40 quads of petroleum (enough energy to burn a 100-watt lightbulb for more than 13 million years) from domestic and imported sources, of which 60 percent goes to transportation.

Instead of chewing up fossil fuels for transportation, we need a more sustainable strategy for two main reasons, the first of which is the security of supply. About 60 percent of our oil is imported, much of it from countries that don't like us very much and lie in unstable parts of the world. The total economic and societal costs of these imports—including, for example, the costs of defending interests in the Middle East—are not reflected in the already very high cost of oil today, which has reached more than $130 a barrel. Clearly, the less we import, the better.

The other reason for developing biofuels is climate change. We're interested in fuels derived from plant materials because overall, they're carbon neutral. Green plants take solar energy, water, and carbon dioxide, and convert them into biomass, which is what we call the plant material we can use for fuel. Then, some magnificent microorganisms turn the biomass into liquid fuel. When you burn the fuel, growing plants eventually reabsorb the emitted carbon dioxide, giving you a carbon-neutral cycle. Growing plants is a simple system for capturing carbon, and as long as you don't use up a lot of fossil fuels during any part of the process—for example, by using gasoline to truck biomass to the ethanol facility or using a great deal of fertilizer—you come out even. The key to assessing this technology is to look at whether you get more energy out than you're putting in with fossil fuels.

That's the essence of the debate over biofuels—most notably corn ethanol—that you might be reading about. I won't go into that debate, other than to tell you that corn ethanol probably creates as many problems as it solves, and is likely to be only a short-term solution to jump-start a biofuels industry. To turn corn into fuel, you take the 72 percent of the corn kernel that's starch and break it down into a simple sugar, called glucose, with the aid of an enzyme. Then, using a process that we've all been fond of for thousands of years—that is, brewing beer with the help of microorganisms—we ferment the glucose. However, growing and processing the corn requires substantial amounts of resources like energy, water, and fertilizer. The yield is low, because you only get a small amount of biomass that you can convert to ethanol—about five tons per acre of corn. And, because you're turning food crops into fuel, corn ethanol production helps to drive up prices of food, like the cost of tortillas in Mexico. That trade-off is unacceptable. Ethanol may be good in certain drinks, but it isn't necessarily the best fuel we can conceive of. We make ethanol simply because we know how.

Ethanol may be good in certain drinks, but it isn't necessarily the best fuel we can conceive of. We make ethanol simply because we know how.

The alternative to using corn or other food-based crops for fuel is to use cellulosic feedstock. In the short term, we're talking about things like rice straw; corn stover, which consists of the leaves, stalks, and other waste matter from corn; bagasse, which is what's left over after you extract the juice from sugar cane; and corn fiber, the byproduct of milling corn into syrup. In the long term, we need to move toward dedicated energy crops, such as switchgrass or miscanthus, which not only produce as much as 30 tons of biomass per acre, but also need minimal water and nutrients and grow very rapidly. A study by the Department of Energy and the Department of Agriculture estimates that the United States could produce 1.3 billion tons of cellulosic biomass per year, without having a grossly negative impact on food supply. A back-of-the-envelope calculation shows that 1.3 billion tons is the energy equivalent of some three billion barrels of oil—a considerable fraction of the total U.S. annual consumption of about seven billion barrels. Biofuels aren't going to solve the energy problem alone, but their contribution can be significant.

So the good news is that there's a lot of energy stored in biomass and the United States is in a very good position to be making renewable fuels. The bad news is that photosynthesis isn't very efficient. In the midlatitudes, where we live, only 1.2 percent of the sun's energy, averaged over the course of a year to allow for daily and seasonal fluctuations and weather patterns, is converted to chemical energy in the form of biomass. Additionally, growing biofuels requires a lot of land—we'd have to use much of the currently marginal and unused farmland to grow energy crops. There are also major engineering problems, the biggest being that biomass in its natural form is not something you can put into your automobile. You have to convert biomass to liquid fuel.

So why is this so darn hard? Why isn't there a biomass-to-fuel factory on every block? The reason is that plants have evolved to defend their structural integrity. They eventually give up and degrade, but they're pretty robust. Some 25 percent of the plant is this stuff called lignin, which is chemically similar to asphalt, and very few things can break down asphalt. They say you can make anything from lignin except money. It's basically trash—you can't break it down, and you can't convert it into anything useful, at least not in an economical fashion. So it just gets burned to provide energy for the rest of the process.

Miscanthus, a tropical grass, grows up to 11 feet tall.

Fortunately for us, about 70 percent of a plant is cellulose and hemicellulose, polymers that can be broken down into sugars microbes can use. (Wood and plant fibers like cotton are mostly cellulose.) The cellulose's sugars, however, are physically inaccessible. The glucose units in the polymer chains form tightly packed layers in a crystalline structure. The cellulose chains, in turn, form tight bundles called microfibrils in which regions of glucose units in this crystalline array alternate with regions of glucose chains in an amorphous configuration. Any large enzyme that could break down the cellulose into its glucose units if the cellulose were in solution would have trouble getting in there in the first place, unless some substantial and expensive pretreatment were done to make the chains physically accessible. There's no easy chemical solution to this problem. Right now people are using grinding and treatment with acids to break up the microfibrils, but you'd need an awful lot of acid to make an impact on our oil consumption. Also, too much acid can ruin the sugars. We need to use more biology and less chemistry to develop environmentally friendly methods for making this cellulosic glucose accessible to the microbes that make the fuel.

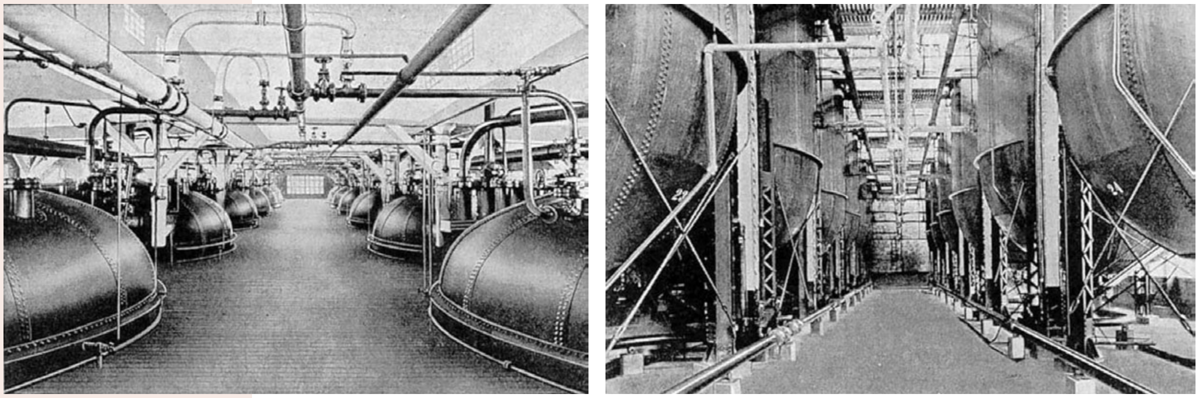
Brazil, a major ethanol producer, ferments glucose straight from sugar cane—a process that's both easy and, especially with current high oil prices, profitable. Brazil basically runs its auto fleet on domestically produced ethanol, and has become a supplier of ethanol to the rest of the world. In the United States, ethanol is primarily made from corn. Corn kernels are mostly starch, so processing them requires an enzyme to break the starch down into sugars that can be fermented. This extra step makes it more expensive. When we begin producing dedicated biofuel crops such as switchgrass, which don't even have a high starch content, we'll have to go through even more mechanical and chemical steps to break down the cellulose, and this will drive up the capital cost of the biofuel facility. The good news is that the feedstock, which is a major factor in fuel costs, will be less expensive than sugar or corn.

If you take a step back, you see that ethanol isn't even the most attractive of fuels. The energy content of ethanol is a lot lower than gasoline, delivering only .7 times the mileage. Moreover, the existing fuel distribution infrastructure cannot be used to store and deliver ethanol. Ethanol has a high vapor pressure, and because of its high affinity for water, it readily takes up water and corrodes the tanks and pipelines that carry oil. Also, ethanol can only be blended with gasoline up to about 10 percent before car engines need to be modified.

As a result of these problems, and the fact that ethanol can't be used to fuel trucks or jets, many people are interested in alternatives to ethanol. In fact, alternatives are becoming possible because of the genetic-engineering revolution. Within the last 30 years or so, biologists, chemical engineers, and just about everybody else have become able to tinker with DNA. Even high-school students do molecular-biology experiments with kits that can be ordered from any chemical supply house. We can engineer bacteria to produce all kinds of molecules, so we can sit back and ask ourselves, if we don't want ethanol, what do we want? What could be supplied in a biologically friendly and environmentally friendly fashion? Hydrocarbons that look like petroleum, of course, would be very nice, but nobody has demonstrated such a technology that's close to being practical yet. One good possibility, however, is ethanol's bigger cousin, butanol.

Corn, switchgrass, and miscanthus grow side by side in experimental plots in Urbana, Illinois. These fields are two years old.

Andrew Leakey

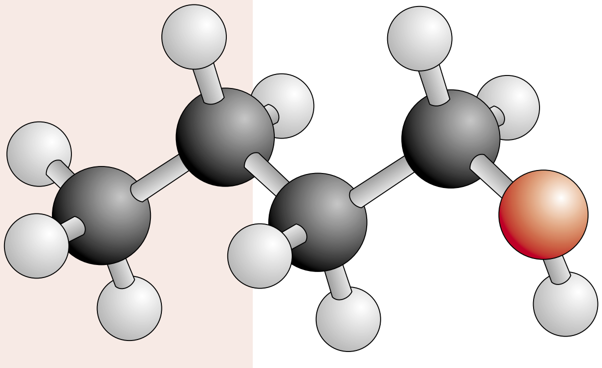


Founded at the end of World War I, the Commercial Solvents Corporation was a leader in making butanol with Weizmann's fermentation methods. The left photo shows the tops of the 50,000-gallon tanks at a butanol plant. The tank bottoms are shown on the right.

BETTER BIOFUELS WITH BUTANOL?

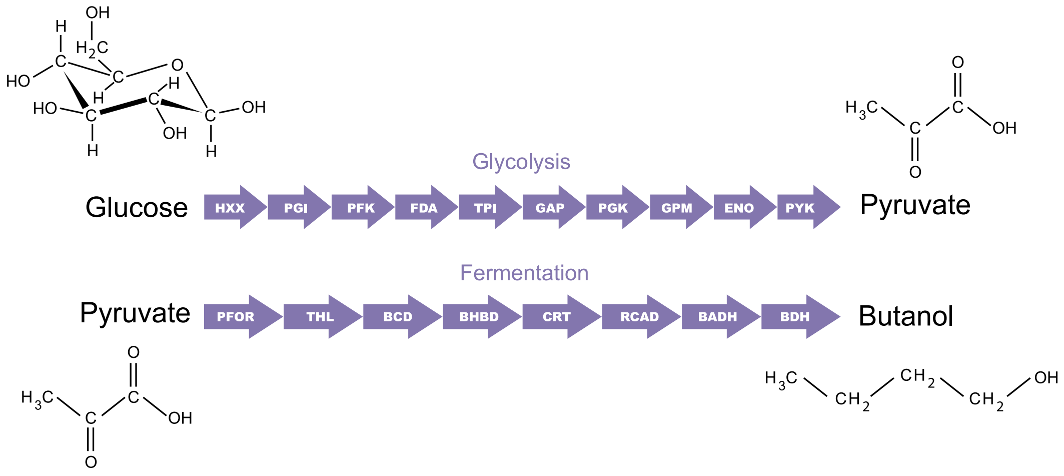
Ethanol has only two carbons while butanol has four, which makes it more energy-rich. Butanol's low water content (it has less affinity for water than ethanol) and high energy content are right up there with gasoline. Butanol can be distributed and stored in existing pipelines and tanks. It burns cleanly, without any kind of modification to gasoline engines, and it can be blended with gasoline at any ratio. Furthermore, you can make other fuels—gasoline, diesel, or jet fuel—from butanol using well-known chemical processes. Butanol was, in fact, one of the most important commercial fermentation processes in the mid-20th century. Because the last butanol plants were closed down just before the genetic-engineering revolution, the organisms that were used to make butanol commercially have not been genetically modified to improve their productivity.

Like everything else, making butanol started off as a defense application. Chaim Weizmann, a chemist who later became the first president of Israel, was awarded a patent in 1916 for his method of producing acetone from the bacterium *Clostridium acetobutylicum*. The acetone was used to make an artillery-shell propellant called cordite, also known as smokeless powder, for World War I. The bacteria also produced butanol and ethanol as by-products. By 1927, people had recognized that butanol was a good motor fuel and solvent, and had started breeding strains of microbes to increase the butanol content of the product mix. By the next decade, there were large plants containing big wooden vats of fermenting clostridia that produced butanol from molasses, which was a waste product of sugar processing, or from potatoes. But in the 1950s, petroleum became a cheaper source of fuel and of chemical feedstocks, which was the other main use of butanol. Butanol plants in the West closed in the 1960s, and the last remaining ones in the Soviet Union and South Africa closed in the 1980s. However, the organisms that were used to make butanol are now sitting in the freezer of a South African researcher who moved to New Zealand more than 20 years ago.

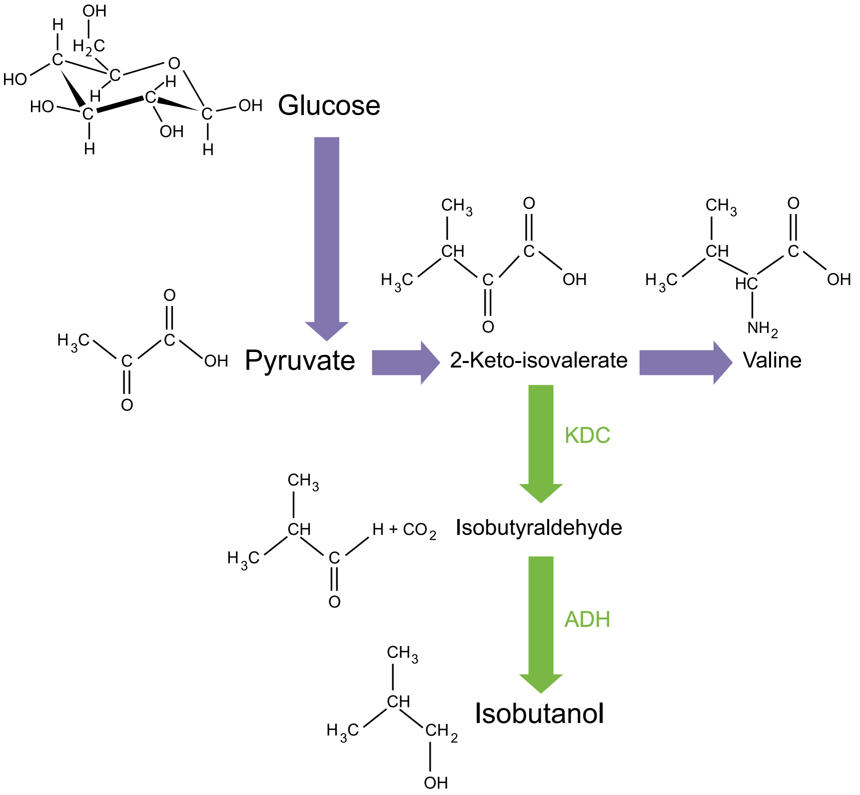


A ball-and-stick rendering of butanol. The black spheres are carbon atoms; white, hydrogen; and red, oxygen.

We could just pull those microbes out of the fridge, put them back in those huge 50,000-gallon tanks, and start making butanol again on an industrial scale. The problem is that these microbes put too many of their resources into survival and reproduction, which is what evolution has bred them to do. The old manufacturing method was very good at converting your investment into a lot of organisms and just a little bit of money. The butanol is produced as a metabolic by-product, in relatively low yield, as part of a mixture with acetone and ethanol. Butanol is also toxic to the organisms that make it, so making it in bulk is not at all attractive to them. The organisms that make ethanol, on the other hand, can produce a broth that's over 10 percent ethanol; sake is about 12 to 18 percent ethanol. We've been breeding those guys for thousands of years, and they can tolerate a lot of ethanol. We haven't been working as hard on butanol, because you can't drink the stuff. We could try to improve on these organisms, but the process would be slow and difficult.



Inside the bacterium that ferments butanol, a series of enzymes (arrows) converts glucose into pyruvate; another chain of steps then turns pyruvate into butanol.



E. coli **has a series of catalytic steps that turns pyruvate into an amino acid called valine. Jim Liao at UCLA hijacked that pathway, and by introducing two new enzymes, keto-acid decarboxylase (KDC) and alcohol dehydrogenase (ADH), he engineered** ***E. coli*** **that produced isobutanol instead of valine.**

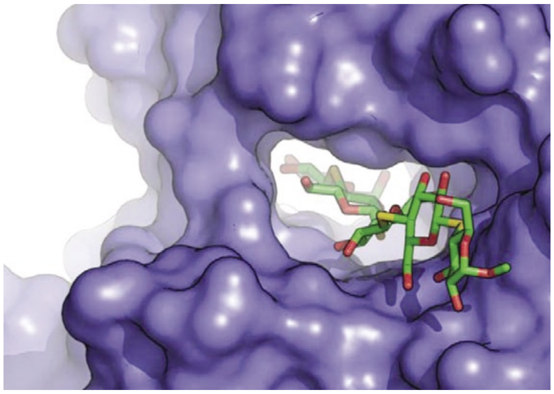
A butanol-producing clostridium, to a first approximation, is a little bag of catalysts that takes up glucose and converts it into a molecule called pyruvate, which is the cell's major source of energy. Pyruvate is an intermediate in a biochemical pathway inside the organism that's common to both ethanol and butanol production. Producing ethanol from pyruvate just takes a couple of steps, but making butanol is a long, tortured process involving intermediates that are quite costly to the cell in terms of the energy and catalysts required. Some of these intermediates also lead to ethanol, further lowering the yield.

People like me—we call ourselves synthetic biologists now, that's our new marketing term—view microbes as the chemical factories of the future. Our plan is to start more from scratch and create an organism that is specifically designed to make butanol. My colleague, Jim Liao at UCLA, had a great idea. He pointed out that the cells already have a pathway—a series of catalytic steps—that turns pyruvate into an amino acid called valine. He envisioned a branch off of that pathway that makes a form of butanol called isobutanol in just two additional steps. Not only is this pathway not very toxic to the cell, it's also one that the cell is predisposed to use, because cells can make valine at high levels.

And with the revolution in genetic engineering, we can actually build this organism. Jim chose first to modify the *E. coli* bacterium because we already know a lot about it, and have identified all its genes and the vast majority of its pathways. It's a ready-made chassis, if you will. But that doesn't necessarily mean *E. coli* is going to be a useful butanol maker. However, it's a great proof of concept.

Remember that the catalysts for each of these steps, the enzymes, are all encoded in the bacterium's DNA. When I talk about reprogramming these cells, I'm talking about modifying their DNA so that they make the enzymes that I want them to make. To do that, we have to figure out the DNA code for those enzymes (and any associated controllers) and then synthesize that DNA. Not too many years ago, I had to actually synthesize little pieces of DNA by hand. It would take me hours, and I could only make short pieces, and those pieces were full of errors. Today I can just punch in a sequence and e-mail it to my favorite supplier. For less than a dollar a base pair, they will synthesize the gene and send it back to me in a few days or a few weeks. Basically, we can make any DNA we want and insert it into the bacteria.

Jim Liao's group did exactly that. He hijacked the valine pathway at an intermediate molecule called 2-keto-isovalerate. Remember, I said it takes



An enzyme called cellobiohydrolase II (blue) pulls a cellulose polymer chain (green) through a hole in the enzyme. The enzyme is one of many that breaks down cellulose.

only two steps from there to make isobutanol. The first step is turning 2-keto-isovalerate into isobutyraldehyde, which the 2-keto-acid decarboxylase, or KDC, enzyme does. Then you convert isobutyraldehyde to isobutanol with an enzyme called alcohol dehydrogenase, or ADH. So Jim took a KDC gene from a bacterium called *Lactococcus lactis* and the ADH gene from *Saccharomyces cerevisiae*, better known as baker's yeast or brewer's yeast, and put them in *E. coli*. And lo and behold, the bacteria started making isobutanol. But they could also make many other things from pyruvate, so he optimized the yield by getting rid of those competing pathways by knocking out the DNA that encodes them, which diverted more of the flow to isobutanol. (He had to do that very carefully, because some of that DNA encodes things that are important for the growth of the organism.) He was able to make up to 20 grams of isobutanol per liter of the microbial broth—86 percent of the theoretical yield, which was better than the best reported butanol production from any natural organism, even at the height of industrial butanol production.

CUTTING THROUGH THE CELLULOSE

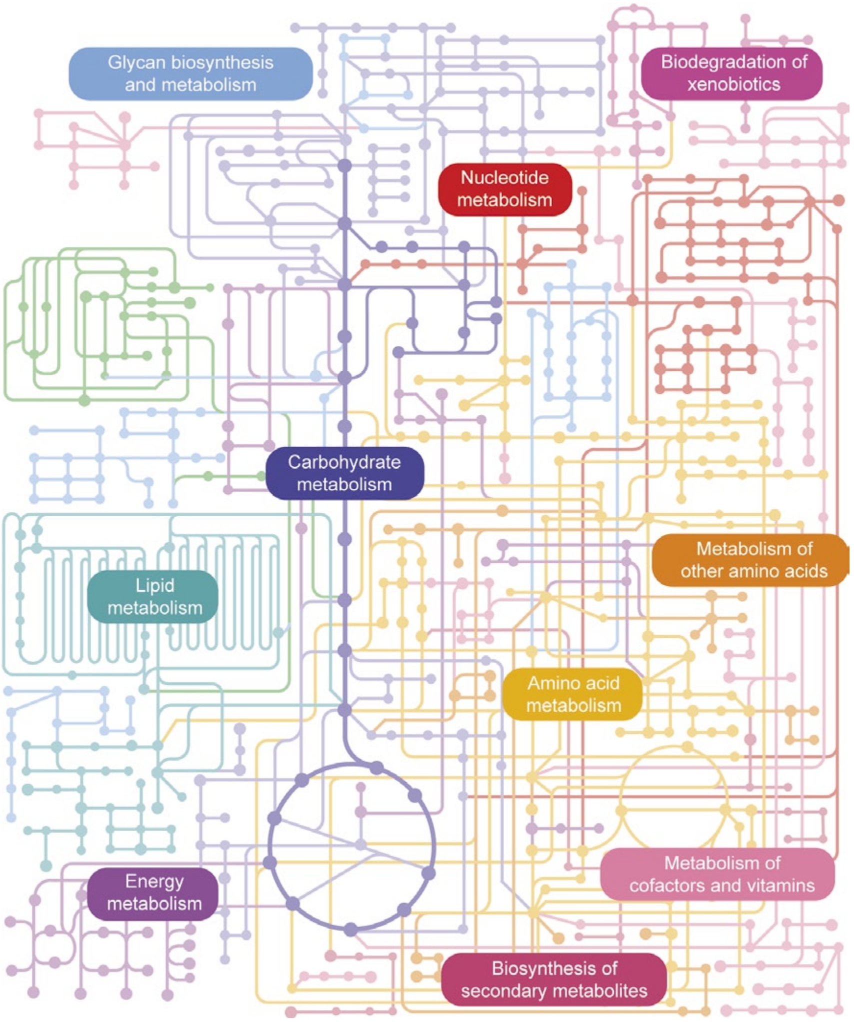
So far, everything I've told you is about turning glucose into butanol. But could we get (iso)butanol from cellulose? To have the simplest and cheapest possible process, we'd like to consolidate all the steps into a single organism that degrades the biomass into glucose, and then converts the glucose into butanol, all in a single pot.

Cellulose degradation, however, is the most complicated and difficult step of producing butanol—or any other biofuel. If cellulose broke down easily, plants would turn into sugary ooze when licked, and they don't do that. The problem is that cellulose-degrading enzymes have a hard time attacking those bundled cellulose polymers. So after the cellulose is pretreated to make it more amorphous and accessible, there's a concerted attack involving a whole bunch of enzymes doing different things simultaneously to break the cellulose down into glucose. These enzymes are collectively called cellulases.

A subset of cellulases called endoglucanases cuts the middle of the cellulose polymer chains in the amorphous regions. This frees up the ends of the crystalline areas for another group of enzymes, called cellobiohydrolases, to attack. A cellobiohydrolase is a fascinating molecular machine that pulls a chain through a hole in the middle of the enzyme to bite off two sugar units at once, making a chemical unit called cellobiose. The two ends of the crystalline chain are different, and each is degraded by a different cellobiohydrolase. You're now left with a bunch of cellobioses, and an enzyme called beta-glucosidase comes and cuts them into individual sugar molecules, which the microbes can then convert into biofuel.

Breaking down cellulose takes a lot of enzymes and time, and is expensive, so researchers across the world are trying to discover novel cellulases—or engineer new ones—that will do a better job. Right now, industry uses a cellulase system that was discovered during World War II when someone's tent got chewed up in the jungles of Borneo by a fungus called *Trichoderma reesei*. We haven't moved to a substantially better system since then. The engineering and production have been improved, but the enzymes themselves have hardly been modified.

Some bacteria package all their cellulase enzymes into little molecular factories called cellulosomes on their cell surfaces. One could envision constructing such cellulose-chewing factories on the surface of your butanol-producing organism—which would be a lot of fun to do. The cellulases would break down cellulose and deliver it straight to the organism for fuel production. So Caltech and UCLA have started a synthetic-biology challenge to create such a microbe. We are working



Kyoto Encyclopedia of Genes and Genomes

This map of a cell's metabolic pathways could be taken for a circuit diagram or a particularly elaborate subway map. Boosting the cell's isobutanol yield required shutting off some pathways and rerouting others.

together to combine powerful, new cellulases from Caltech with the isobutanol pathway discovered at UCLA.

None of this is as easy as I've made it seem, however. Even a supposedly simple organism like *E. coli* is a complex beast. When I said we understand how *E. coli* is programmed, I lied. All those simple one-way pathways through which we convert glucose to isobutanol with this series of catalysts are very nice, but all these catalysts are sitting inside a cell that's got a whole bunch of other molecules working at the same time as it reproduces, grows, and responds to its environment. All of the pathways involved in breaking down cellulose or producing isobutanol regulate and interact with each other and with other pathways the cell needs to survive. It's an incredibly complex system that we really don't understand well, and if we're able to make isobutanol from cellulose, we're darn lucky. Furthermore, Jim made 20 grams of isobutanol per liter of the microbial broth, but we're going to need to make even more than that if this system is going to be practical.

Who Needs Melville?

Some people think we can turn biology into an engineering discipline, making analogies between engineering living systems and engineering other forms of matter, from buildings to circuit boards. In this view, bacteria are little robots, programmed by their DNA to respond to their environment. The set of interactions among the genes and proteins in a regulatory network is like an integrated circuit in a silicon chip that embodies a function in its hardware. We should be able to have a little parts book where we can pull devices—a little piece of a circuit or a catalyst, or a little controller—from a parts list and construct the butanol-production pathway. We would write the DNA program by finding the desired code—the parts from our parts list—on a website, assembling them into one long sequence, and then sending it to a DNA-synthesis facility. We'd get our custom-made DNA in the mail the next day, and we'd put it into the bacteria, and they'd start doing what we've programmed them to do. This is the dream of the synthetic-biology community.

On the other hand, that dream belies the complexity of biology, and the fact that these systems are highly dynamic and interacting. There's a lot of redundancy in how DNA codes for a particular function, and there are many ways to tweak it and subtly alter its function. Unfortunately, we don't know what DNA sequence will encode a particular outcome. We don't know how to write down the DNA sequence that would make a "super" cellulase do exactly what we want. If we can't even make a single cellulase, how are we going to make synthetic biology so predictable that we can build a new organism that will efficiently make large quantities of new biofuels?

Every year, a set of tongue-in-cheek awards called the Ig Nobel Prizes is given for dubious scientific achievements. Real Nobel laureates and other scientific luminaries attend the award ceremonies, which are held at Harvard and feature a science opera and "nano-lectures," in which people are challenged to describe a technical topic in 24 seconds and to write a corresponding abstract that anybody can understand in seven words or less. For the human genome project, in which the complete DNA sequence that goes into making a human being was determined, MIT's Eric Lander wrote, "Genome. Bought the book. Hard to read." In other words, even if you know the sequence, you don't know what it does—there are too many possible outcomes, and the details matter.

It's the same in synthetic biology—if you can't even read a genome, how are you going to write it? If I'm ever asked to give a nano-abstract about engineering these organisms, I'm ready: "Genome. Great story! Hard to write." So what do you do when you've got writer's block? You get a good editor, of course. Creating the genome for an artificial organism that will perform some specified function is a bit like writing *Moby Dick* by using Google. You have an outline of what you want to say, so you do a Google search on the key ideas—say, "white whale." You copy and paste what you find, and you've got *Moby Dick*—but a really awful version of it. For synthetic biology, the right editor is evolution, which takes all sorts of sequences that are not terribly meaningful, and converts them into beautiful literature by iterative trial and error, selecting the ones that perform better and better.

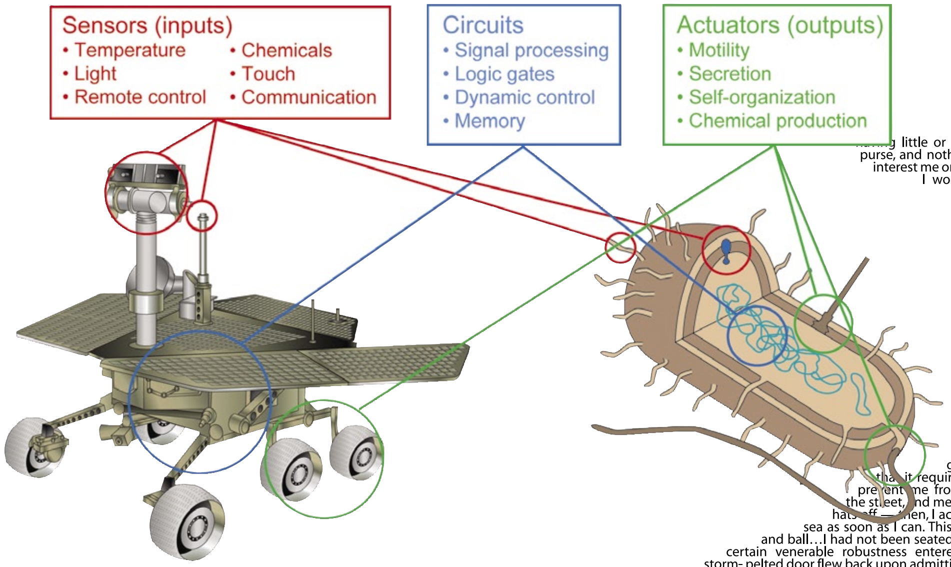
You should have walked out of here shaking your heads when I told you I was going to convert cellulose to butanol, and that I was going to write a DNA sequence that was going to do it. But the fact that we have a great editor means it's not a crazy idea. Evolution is a massively parallel system—a billion of these little organisms are growing and reproducing all at once in every milliliter of our growth medium. All we have to do is make lots of mutations to them, and then, as God-like creatures that decide who lives and dies, we can select the strains that solve our problem—i.e., produce isobutanol from cellulose—and let them reproduce. We set up a high-throughput screening system that measures how much isobutanol they produce, and we throw away the strains that don't produce much. We save the ones that make the most butanol, continually refining and optimizing them until the problem is solved. This is called directed evolution, and it's just like breeding new strains of, say, roses or sheepdogs, only we can go through several generations in a few weeks.

We have just started this project—the equivalent of finding some of the key paragraphs of our *Moby Dick*. The paragraphs—in our case, genes—don't flow together yet, and some have not even been drafted, but we've got plenty of ideas and, thank goodness, a good editor. □

Frances H. Arnold is the Dickinson Professor of Chemical Engineering and Biochemistry. She earned her BS (1979) in mechanical and aerospace engineering at Princeton University, and her PhD (1985) in chemical engineering at the University of California, Berkeley, where she continued as a postdoc for a year before joining Caltech as a visiting associate in 1986. She has earned many awards and honors, including induction into the National Academy of Engineering in 2000 and the Institute of Medicine of the National Academies in 2004. In May, she was elected into the National Academy of Sciences.

This article was edited by Marcus Woo.

Bacteria and robots share many design elements. The dream for the synthetic-biology community is to one day be able to write a DNA "program," synthesize the DNA, and then put it into a bacterium that will do what the programmer intends it to do.



Call me Ishmael. Some years ago — never mind how long precisely — having little or no money in my purse, and nothing particular to interest me on shore, I thought I would sail about a little and see the watery part of the world. It is a way I have of driving off the spleen, and regulating the circulation. Whenever I find myself growing grim about the mouth; whenever it is a damp, drizzly November in my soul; whenever I find myself involuntarily pausing before coffin warehouses, and bringing up the rear of every funeral I meet; and especially whenever my hypos get such an upper hand of me, that it requires a strong moral principle to prevent me from deliberately stepping into the street, and methodically knocking people's hats off — then, I account it high time to get to sea as soon as I can. This is my substitute for pistol and ball…I had not been seated very long ere a man of a certain venerable robustness entered; immediately as the storm- pelted door flew back upon admitting him, a quick regardful eyeing of him by all the congregation, sufficiently attested that this fine old man was the chaplain. Yes, it was the famous Father Mapple, so called by the whalemen, among whom he was a very great favorite. He had been a sailor and a harpooneer in his youth, but for many years past had dedicated his life to the ministry…Savage though he was, and hideously marred about the face — at least to my taste — his countenance yet had a something in it which was by no means disagreeable. You cannot hide the soul. Through all his unearthly tattooings, I thought I saw the traces of a simple honest heart; and in his large, deep eyes, fiery black and bold, there seemed tokens of a spirit that would dare a thousand devils…Suddenly the waters around them slowly swelled in broad circles; then quickly upheaved, as if sideways sliding from a submerged berg of ice, swiftly rising to the surface. A low rumbling sound was heard; a subterraneous hum; and then all held their breaths; as bedraggled with trailing ropes, and harpoons, and lances, a vast form shot lengthwise, but obliquely from the sea. Shrouded in a thin drooping veil of mist, it hovered for a moment in the rainbowed air; and then fell swamping back into the deep. Crushed thirty feet upwards, the waters flashed for an instant like heaps of fountains, then brokenly sank in a shower of flakes, leaving the circling surface creamed like new milk round the marble trunk of the whale…Ho, ho! from all your furthest bounds, pour ye now in, ye bold billows of my whole foregone life, and top this one piled comber of my death! Towards thee I roll, thou all-destroying but unconquering whale; to the last I grapple with thee; from hell's heart I stab at thee; for hate's sake I spit my last breath at thee. Sink all coffins and all hearses to one common pool! and since neither can be mine, let me then tow to pieces, while still chasing thee, though tied to thee, thou damned whale! Thus, I give up the spear!"… Buoyed up by that coffin, for almost one whole day and night, I floated on a soft and dirge-like main. The unharming sharks, they glided by as if with padlocks on their mouths; the savage sea-hawks sailed with sheathed beaks. On the second day, a sail drew near, nearer, and picked me up at last. It

PICTURE CREDITS: 19 — Doug Cummings; 12 — DeVane Webster; 13, 14 — S. Long lab, U. of Illinois; 15 — David Jones; 17 — Chris Snow; 19 — Christopher Voigt

Solar Fuel I: Rods and Stones

By Douglas L. Smith

"He who cannot store will have no power after four" is a favorite mantra of Nate Lewis (BS '77, MS '77), Argyros Professor and professor of chemistry, in a nod to the late Johnnie Cochran Jr. But the stakes here are even higher than the outcome of O. J. Simpson's trial for double murder—Lewis is talking about saving our civilization by running it on solar energy. Solar cells make electricity, and if you have a secret method for storing enough juice to keep the lights burning across America—or even the Los Angeles basin—while the sun is down, he advises you to "go out and buy electricity at night for a nickel a kilowatt-hour, sell it to all your neighbors for 25 cents a kilowatt-hour by day, and then fund your own solar-energy research institute with the profits."

The most promising avenue is to store solar energy in chemical form, as a fuel that can be used on demand. Plants do this via photosynthesis, turning sunlight, water, and carbon dioxide into sugar molecules containing lots of high-energy chemical bonds. Lewis and many other researchers worldwide are trying to take a leaf from photosynthesis, as it were, by finding a method for turning sunlight into fuel—without all the complex cellular machinery. "Photosynthesis is beautiful, and it has many lessons to teach us," Lewis says. "Birds with feathers are not good models for 747s, but we knew birds could fly, so we were inspired to build airplanes."

The easiest fuel to make is hydrogen gas, H_2. Simply stick a couple of electrodes in a vat of water and run the current through them—the positive electrode makes O_2, and the negative one makes H_2. "Burning" the H_2 in a fuel cell later gives you water back again, plus the stored electricity. Small, pilot-scale electrolyzer plants, as water-splitting facilities are called, already exist, but they use a lot of really expensive components, and they're not exactly the sort of thing you could put on the roof of your house, or even in your back yard. Lewis's goal is to repackage tons of complicated equipment into tiny assemblages of cheap materials that could be installed almost anywhere. "We're going to make fuel from the sun with no wires," he says. To do this, the light-harvesting and water-splitting machines have to be one and the same, not an assortment of components spread out over a solar farm.

The Hole Story

A conventional solar cell uses a cheese-and-cracker arrangement of two slabs of silicon, *n*-type and *p*-type, and the place where the cheddar meets the Triscuit is called the *p-n* junction. *N*-type silicon is "doped" with traces of phosphorus or arsenic, atoms of each of which have five electrons in their outer shell instead of silicon's four. Four of the dopant's electrons pair up with electrons in adjoining silicon atoms to make the chemical bonds that hold the slab together, leaving the fifth one at liberty, if given a little shove, to wander through the crystal. Similarly, in *p*-type silicon, the dopant—boron or gallium—has only three electrons in its outer shell. The dopant atom makes three and a half bonds, if you will, to its silicon neighbors, and the absent electron, or "hole," is essentially a free-floating positive charge. An electron from an adjoining atom will readily jump over to fill it, moving the hole to the atom the electron abandoned.

When light hits the solar cell, the photons will penetrate some distance into the silicon before being absorbed, and the longer the wavelength (or the redder the light), the deeper they go. It takes 300 microns, or three-tenths of a millimeter, of silicon to soak up all the wavelengths that make up visible light, and herein lies the problem. When a silicon atom in either layer absorbs a photon, an electron gets excited, creating an electron-hole pair. If the silicon atom is in the *n*-layer, the electron can happily skate away to become part of the current, but then what happens to the hole? In order to maintain the charge balance and keep the current flowing, the hole has to make its way to the safe haven of the *p*-type layer, on the opposite side of the *p-n* junction, running a gantlet of onrushing electrons in the process. (Because they are out of their element, if you will, these much-set-upon holes are called "minority carriers.") Any defect in the crystal's lattice structure makes a natural trap where electrons and holes can recombine, dissipating their energy as wasted heat. Free electrons generated in the *p*-type layer face a similar struggle. The upshot is you need ultrapure—and therefore very expensive—silicon to make solar cells.

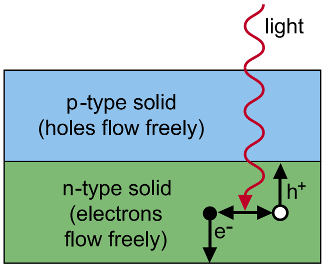
Grow Your Own Aspen Forest

But what if, instead of using a flat plate of silicon, you made nanorods—teeny, tiny cylinders oriented so that the light shines down their central axes? The minority carriers would just have to reach the cylinder's skin to make it to safety, and the odds of an electron falling into a hole drop drastically. "This is exactly what nature does," remarks Lewis. "This is what leaves do. The cells absorb light over the long axis and transport the heavier particles—the water vapor and the nutrients—over the short axis. That's what the retinal rod cells in your eyes do. This principle is found throughout nature, and yet it's never been implemented in solar-cell design."

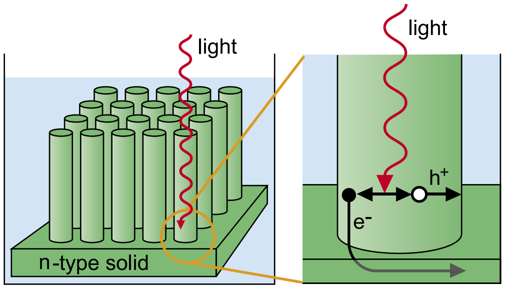
Even better, you don't need a layer of the opposite type of silicon—simply toss the rod in a beaker of salt water, which conducts electricity quite readily, and the liquid-solid interface acts as the finish line for the minority carriers' sprint to safety. Once they cross into the liquid, they are ready to split water molecules into H_2 and O_2. All you have to do is coat the silicon surface with catalysts that will facilitate the reactions.

Harry Atwater, Hughes Professor and professor of applied physics and materials science, and Lewis tested the notion by growing what Lewis calls "an aspen forest" of nanorods, each some three microns long and about a quarter of a micron thick, on a conductive backing. The complex growth process used standard technology for making silicon chips, but for reasons that will become clear momentarily, Josh Spurgeon (MS '06), a Lewis grad student working on this joint project, made the first nanoforest of cadmium selenium telluride instead. This material generates electricity by absorbing blue light, which takes about one micron's worth of semiconductor. But such a photocell doesn't work under red light, which takes three microns to absorb, because the minority carriers can only make it about a micron before being sopped up by a lattice defect. Spurgeon shone light in all the colors of the rainbow on a submerged nanorod array and on a CdSeTe slab made by the same method and compared the results. The slab and the rods both performed about the same under blue light, but the nanorods kept on soaking up photons all the way through the visible spectrum. "But we didn't want to wait around for the rods to grow," says Lewis. His grad student James Maiolo treated a silicon slab with hydrogen fluoride, etching so many holes in it that they overlapped to leave spires. "We wanted to make the equivalent of rods to see if they would work, or if the theory was missing something." It wasn't.

Light will travel a certain distance into a crystal before being completely absorbed. When a photon is absorbed by a solar cell, a pair of opposite charges in the form of an electron (e^-) and a hole (h^+) are produced. If either one has to travel too far through unfriendly territory, as the hole does in this traditional slab design (below left), it is likely to recombine with its opposite and no current will flow. In the nanorod design (below center and, blown up, below right), the light can penetrate to any depth and the holes can still escape out the sides and into a conductive liquid.



Slab design



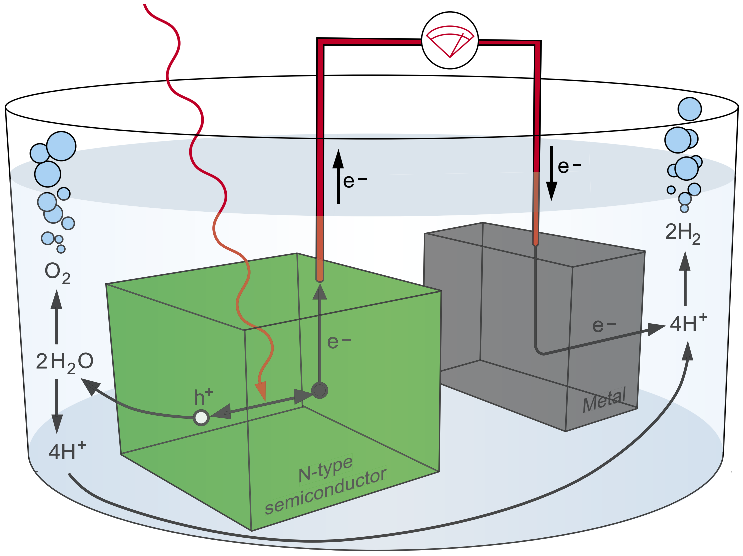
Rod design

Not So Fast . . .

If making hydrogen from sunlight were that simple, however, you wouldn't be reading this article. There are still three big problems to solve. The first is really only a problem when you try, as Lewis and Atwater are, to make fuel from the sun without using wires: H_2 and O_2 production need to be kept separate. This makes collecting the hydrogen easier, and prevents the gases from recombining to make water as they form. All fuel-producing solar cells to date isolate the oxygen-producing electrode from the hydrogen-producing electrode with either distance or a membrane. The simplest design uses a single semiconductor to absorb the light. In this case, it's an *n*-type semiconductor that acts as the oxygen-producing electrode. The holes leap into the drink and suck electrons out of the water molecules in a process called oxidation, creating O_2 gas and protons—the electron-deprived nuclei of hydrogen atoms. The electrons go through a wire to the hydrogen-producing electrode, usually platinum metal or the like, where they rejoin the newly produced protons that have diffused through the water (or across the membrane) to make H_2—a process called reduction.

The second problem with splitting water is fundamental chemistry: oxidation is brutal. Strong oxidants tear chemical bonds apart—fire is an oxidative process, and think of what would happen to your favorite shirt if you spilled concentrated bleach on it. Since the goal is to get rid of the wire—and, incidentally, the very expensive precious-metal electrode to which it's attached—the hydrogen-producing electrode needs to be a *p*-type semiconductor fused seamlessly with the *n*-type to inject electrons into the water. Unfortunately, known *p*-type semiconductors don't last long when exposed to strong oxidants. This includes elemental silicon itself, says Lewis. "Silicon is not stable under oxidizing conditions in water. It makes sand—SiO_2."

The third problem we will come to shortly.



In this water-splitting solar cell, the light absorber is the oxygen-making electrode, an *n*-type semiconductor. The surrounding water acts as the *p*-type layer, accepting the holes, which convert water molecules into O_2 and H^+.

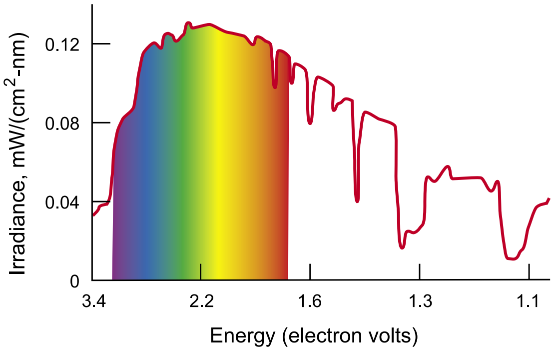
Fool's Gold and Rust

Proving that the nanorod idea worked allowed Lewis's and Atwater's groups to consider using nontraditional materials to collect light. "For instance," says Lewis, "iron oxide has been rejected in solar cells because it's very defective as found in nature. You need three microns of rust to absorb sunlight, and the carriers can only move 20 nanometers, so the other 2.99 microns are just wasted. But if we make rods 20 nanometers wide and three microns long, we can still move the carriers sideways. The same thing occurs with fool's gold, which is iron pyrite, FeS_2. So we are now trying to make solar cells out of fool's gold and rust, and you can decide whether we're completely crazy or only partially crazy."

The good news is that there's a whole class of defect-riddled minerals that can absorb light to make electricity while withstanding the oxidative assault. Some of them, such as titanium dioxide, or TiO_2, the coloring agent in white paint, are also in abundant supply and available at rock-bottom prices—two absolutely fundamental considerations if the technology is to be adopted on a global scale. "They are very stable materials. These literally *are* rocks; they're oxidatively inert, they're photochemically inert," says Lewis. "The bad news is that they would work better if we were inhabiting the moon instead of the earth, because they have a band gap where they start to absorb light that is about three electron volts or higher." The band gap is the energy difference between the state that an electron is in when it is firmly attached to its atom—the so-called "valence band"—and the state it gets kicked into once it absorbs a photon and gains enough energy to hop from atom to atom—the "conduction band."

Unfortunately, three electron volts is borderline ultraviolet. Earth's ozone layer screens out most sunlight at higher than that energy, so the efficiency of those materials is limited to a few percent at best. The light that actually makes it down to us starts at about 2.75 electron volts on the purple end, hits peak intensity at about 2.35 electron volts in the blue-green region, and then slowly trails away down through the infrared. The optimal band gap for catching everything with a single material is about 1.4 electron volts, which is actually in the near-infrared. It only takes 1.23 volts to split water, but there's a catch—and that's the third problem.

The band gap not only has to be big enough, it has to be in the right spot, energetically speaking. For example, iron oxide's band gap is 2.2 electron volts, but the electrons thus liberated aren't very energetic. From an electrochemical point of view, making H_2 from water and making O_2 from water are two entirely separate reactions; worse, they operate at different energy levels. If you use an iron-oxide photon absorber, "you can still make oxygen, but you can't make hydrogen any more,"



This plot shows the intensity of the sunlight reaching the earth's surface versus the amount of energy per photon in electron volts.

Lewis says. "Absolute energies count. The electrons that are promoted to the conduction band aren't reducing enough to reduce water to make hydrogen. It's like climbing a wall—going three feet up doesn't put you a foot over the top if you start out four feet down."

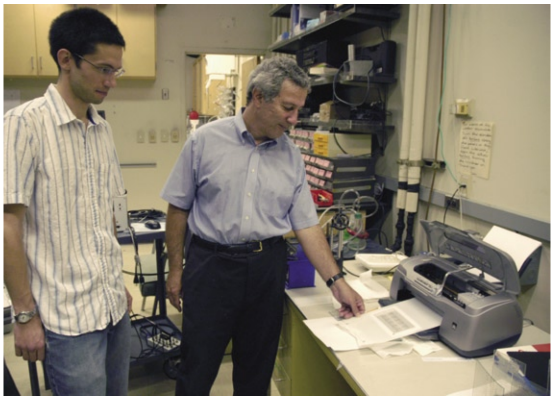
All the Oxides That Are Fit to Print

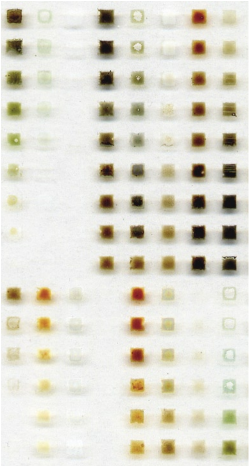
Just because no known oxidatively stable material has a big enough band gap at the right energy level doesn't mean that such a substance doesn't exist. The quest for something that would fill the bill was taken up in 2006 by Rhodes Scholar Todd Gingrich (BS '08) and grad student Jordan Katz (PhD '08), as detailed in *Caltech News* 2008, No. 1. The idea was to test tiny samples of thousands of candidates as fast as possible by modifying a $140 inkjet printer to spit swatches of metal salts dissolved in water onto thin glass plates. The print head mixes the salts in exacting proportions, just as it would faithfully render a sunset from cyan, magenta, yellow, and black inks, but the output looks more like a color-calibration page than a vacation photo—up to 250 tiny test squares on a single sheet. A 500°C oven bakes the dissolved metals into metal oxides. "We choose our metal oxides in an Edisonian educated-guess fashion," Lewis says. "We see which ones give us the right energy levels to reduce water to hydrogen, and then we investigate which ones stay around after one day of operation. We're building up a database to try to give theorists a guide to help us find the next generation of materials."

Lewis's lab is sticking to metal oxides because, well, they're already as oxidized as they can get. "The chemist's intuition is that whatever oxidizes water to oxygen will be sufficiently oxidizing that if we don't have an inherently stable, nearly ionic chemical bond such as a metal oxide, we're going to eat our semiconductor alive." This tactic has uncovered a couple of promising materials already, but Lewis is not betting the solar farm on one printer—he's also working on a Plan B.

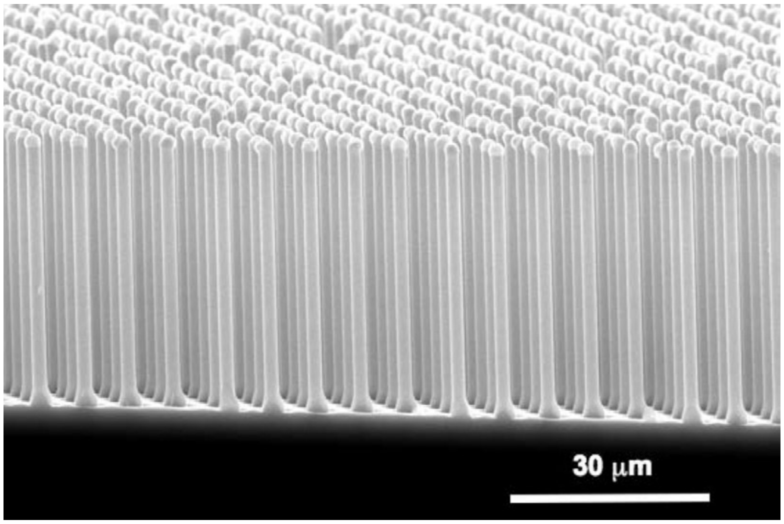
Things would be greatly simplified if one material didn't have to do everything. Nature uses such a divide-and-conquer strategy—a plant's photosynthetic system uses two light-absorbing components that together provide the oomph to drive the reaction. The photosynthetic machinery within such a cell straddles a membrane that isolates and protects the hydrogen-producing apparatus from the harsh oxidants on the other side. In a membrane-based, two-part inorganic system, the hydrogen-producing side could be powered by metal sulfides. Metal sulfides have chemical compositions similar to the active catalytic sites in the enzymes used by a family of photosynthetic microbes called green sulfur bacteria to eke out a living in low-light, oxygen-free environments. These hardy bugs have even been found in hydrothermal vents called black smokers on the deep ocean floor, where they subsist on the dim glow of the hot vent itself. The oxygen-producing side could use good old iron oxide, and if the two types of nanorods could somehow make electrical contact through the membrane, the system wouldn't need wires.

"This gives us the ability to retain the chemical stability of two separate materials," says Lewis, "while not also asking one single material to deliver the full energy needed to split water. The design





Top: Katz (left) and Lewis watch a glass plate come out of the printer. Right: A portion of a typical plate.



A cornfield of silicon nanorods grown from seeds of gold. The scale bar is 30 microns, or millionths of a meter.

is actually the inverse of a fuel cell, where hydrogen and oxygen come in, protons go across the membrane, and out comes electricity. Instead, in our cell, in comes the energy source, protons go across the membrane, and out comes chemical fuel. We're driving it in reverse."

Bringing in the Sheaves

This all sounds horribly complicated, but the Lewis lab has hit on a very clever way to make the integrated system. The process can be done on any scale, which is vital for any technology intended to supplant fossil fuels, and if the work with fool's gold—an iron sulfide—and rust is successful, the raw materials would be dirt cheap, which is even more important. For the moment, the people putting the pieces together are using silicon nanorods, because the industrial techniques for making them are well established.

> "Some day some fellow will invent a way of concentrating and storing up sunshine . . . When we learn how to store electricity, we will cease being apes ourselves; until then we are tailless orangutans." — Thomas Edison

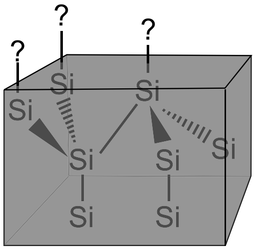
The process starts with an ultrapure silicon wafer, but it can be reused over and over again, as grad student Spurgeon has shown—successive generations of rods grown on the same wafer look just as good as the first batch. The rod-growing technique was developed by grad student Brendan Kayes (MS '04), who is coadvised by Atwater and Lewis, along with Atwater postdoc Mike Filler and coworkers. It begins with a pattern of tiny gold dots that can be laid down on the wafer by any of various means, and which become the growth template. Their diameter is the size of the nascent nanorods, and the spacing between them is the spacing between the rods in the array. The rods are grown through a process called chemical vapor deposition, in which the gold, now in little molten globules, reacts with gaseous silicon chloride ($SiCl_4$) in a hydrogen atmosphere at a temperature of 1,000°C. When the solution becomes supersaturated with silicon atoms, the excess precipitates out at the bottom of each droplet, becoming one with the silicon wafer below. "The gold rides on top, as the silicon starts to deposit, and you continue that growth process," Lewis explains. "It literally grows like cornstalks in a field." Turn off the gas flow, and you can stop the growth at any height you like. Even better, says Lewis, "We can do this with copper. We can do this with nickel. We don't need gold as the catalyst."

However, there's a really good reason people have been making solar cells out of slabs instead of rods. If you picture the layer of atoms that forms the surface of a slab, a silicon atom sitting there can have three of its four bonds—which point to the four corners of a tetrahedron centered on the silicon atom—easily connected to other silicon atoms in the surface layer. The fourth bond sticks out into space. These "dangling bonds" are prime locations for charge carriers to recombine. A slab has limited surface area, while a nanorod is basically all surface area—you couldn't ask for a better way to maximize the number of dangling bonds. "So if we don't have a way of tying up those dangling bonds, then we don't have much hope of actually making good devices out of them," says Lewis.

The nanorods end the manufacturing process with their dangling bonds capped with hydrogen atoms. Unfortunately, Si—H bonds are oxidatively unstable in air. "We do a lot of fundamental chemistry in our group, so we developed a method using phosphorus pentachloride or PCl_5, and zit medicine, benzoyl peroxide, to convert the silicon-hydrogen bonds to Si—Cl bonds," says Lewis. Another set of steps replaces every chlorine atom with a methyl group, CH_3. "The silicon-carbon bonds are sufficiently strong that they fool those surface silicon atoms into thinking that they're just like the bulk material. There are no dangling bonds left at the surface—less than one electrical defect in every 100,000 surface atoms." This work was done by then-postdocs Hossam Haick and Patrick Hurley, along with collaborators Peidong Yang of UC Berkeley and his grad student Allon Hochbaum.

Solar Panels You Can Unroll

For the next step, postdoc Kate Plass has developed a remarkably simple process for embedding the nanorods in a membrane. She uses a type of silicone rubber called polydimethyl siloxane, or PDMS—a common waterproof sealant that, says Lewis, is "more affectionately known to people on



Every silicon atom has four bonds, not all of which are shown here. The "dangling" bonds stick out of the surface of the crystal, and *something* has to cap them off.

A piece of nanorod-embedded plastic.

the street as fish-tank goop." Plass carefully pours a thin layer of PDMS over the nanorods until she almost, but not quite, covers their tips, leaving them exposed to make contact with the water later. She gives the surface a close shave, literally, with a razor blade, and then she peels the goop off in one smooth, sharp motion, like doing a hot-wax treatment to get rid of unwanted body hair. (Howling and jumping around like Mel Gibson in *What Women Want* or Steve Carell in *The 40-Year-Old Virgin* is optional.) Just as the hairs go with the wax, the nanorods go with the goop, shearing off neatly at their bases and leaving the silicon wafer ready to take another round of metal dots. The liberated nanorods retain their original parallel orientation and regular spacing, only now "they are in a piece of plastic that we can roll up," Lewis says.

Plass has so far made nanorod-embedded membrane squares more than a centimeter on a side. Scaling the process up should not pose any great difficulties, but it will take something more than just building very large tweezers.

Before being embedded, the *p*-type silicon nanorods in a demonstration system would be coated with cobalt, which acts as a catalyst for H_2 production. Postdoc Steve Maldonado is working on that angle. The *p*-type membrane would be laminated back-to-back with a second membrane containing *n*-type, oxygen-producing nanorods of iron oxide coated with a cobalt-oxide catalyst; sandwiched between the two would be an electrically conductive layer.

The idea is that eventually this technology might be developed to the point where the solar-membrane laminate could be sandwiched between two more layers of plastic that would allow water to bathe the nanorods. The entire assembly would then be manufactured in large rolls that would be sold at home-improvement stores, the way rolls of insulation are sold today. (The main difference, of course, would be that you'd unroll this stuff on top of your roof, instead of in the attic underneath.) With an eye toward this, the Lewis lab is starting a collaboration with Mory Gharib (PhD '83), the Liepmann Professor of Aeronautics and professor of bioengineering, to measure the membranes' mechanical properties to discover how far one can be bent without fracturing the rods.

There is one last hitch, however. Remember those naked protons that got stripped off the water molecules and that have to cross the membrane and reunite with their electrons to make H_2? Fish-tank goop is impermeable, so a more porous membrane will have to be found. "Either that," says Lewis, "or we're going to have to poke lots of little tiny holes in it."

"We haven't yet built a full system," says Lewis. "But we have a clear path toward being able, in two sheets of plastic, to at least demonstrate a prototype system that could take water to hydrogen and oxygen with sunlight. As Melvin Calvin said at my first Department of Energy meeting in 1982, 'It is time to build an actual artificial photosynthetic system, to learn what works and what doesn't work, and thereby set the stage for making it better.'" Now, only 25 years later, it may finally be on the brink of happening. A Caltech-MIT initiative called "Powering the Planet," about which you will read more in the next article, has set itself the goal of creating a solar-fuel generator that uses Earth-abundant elements, needs no connecting wires, can be scaled up with existing manufacturing technologies, and is 10 times more efficient than photosynthesis.

Calvin wasn't the first to have this idea. Lewis is also fond of quoting Thomas Edison, who in 1910 told Elbert Hubbard, in Volume 1 of the latter's series of books called *Little Journeys to the Homes of the Great*, "Some day some fellow will invent a way of concentrating and storing up sunshine to use instead of this old, absurd Prometheus scheme of fire. I'll do the trick myself if some one else doesn't get at it." (Apparently, it never quite made the top of his to-do list.) Edison went on to say, "Sunshine is spread out thin and so is electricity . . . the trick [is], you see, to concentrate the juice and liberate it as you needed it. . . . This scheme of combustion to get power makes me sick to think of—it is so wasteful. . . . When we learn how to store electricity, we will cease being apes ourselves; until then we are tailless orangutans. You see, we should utilize natural forces and thus get all of our power."

Adds Lewis, "In the end, by far the biggest energy source available to humans is the sun. Now, we can't afford to use it, but in the future we can't afford *not* to use it. Nature figured this out, but from a 'product' point of view, photosynthesis is a failed solution; the fastest-growing plants, on a yearly basis, store less than 1 percent of the total sunlight that hits an average acre over a year. We can do better, we have to do better, and we will do better. The question is not if, but when and how. Someday, you'll paint your house with solar paint [that's another article for another day—*DS*], and instead of putting up solar pool heaters, we will roll out solar fuel generators." □

Nathan S. Lewis (BS '77, MS '77), Caltech's Argyros Professor and professor of chemistry, got in on the ground floor of the solar-fuel game as an undergrad working with Harry Gray (see following article). Lewis got his PhD at MIT in 1981, and earned tenure at Stanford before returning to Caltech in 1988. He's been working on the photochemistry of semiconductor-liquid interfaces (including an effort to develop solar paint) ever since, with time out for such side projects as developing an electronic nose and helping to debunk cold fusion.

PICTURE CREDITS: 20-23, 25 — Doug Cummings; 23 — Bob Paz; 24 — Brendan Kayes; 25 — Michael Filler

Solar Fuel II: The Quest for Catalysts

by Harry B. Gray

Sunlight, leaves, and water can make clean energy. They can also make pretty pictures, as in this cyanotype, also called a "sun print."

We know how to make electricity from sunlight. You can buy a silicon solar array with a 30-year guarantee, put it on your roof, and make your electric meter run backwards. And if you turn off the lights at night, and do other nice things instead, you'll get a check at the end of the month instead of a bill. And you'll be happy. So why don't we just convert the entire planet now, using technology that we have? There are two big problems. The first is it's not cheap. The cost of photovoltaic solar power is at best maybe 25 cents per kilowatt hour, which is several times the cost of traditional sources—fossil fuels, nuclear, and so on. Of course, oil is going up fast, and so if oil hits three or four hundred dollars per barrel, solar at its current price will be a bargain. But before then, if we could get the cost of solar conversion down to about 10 cents a kilowatt hour, people would start to buy in in large numbers, and we could convert the planet to run on solar electricity.

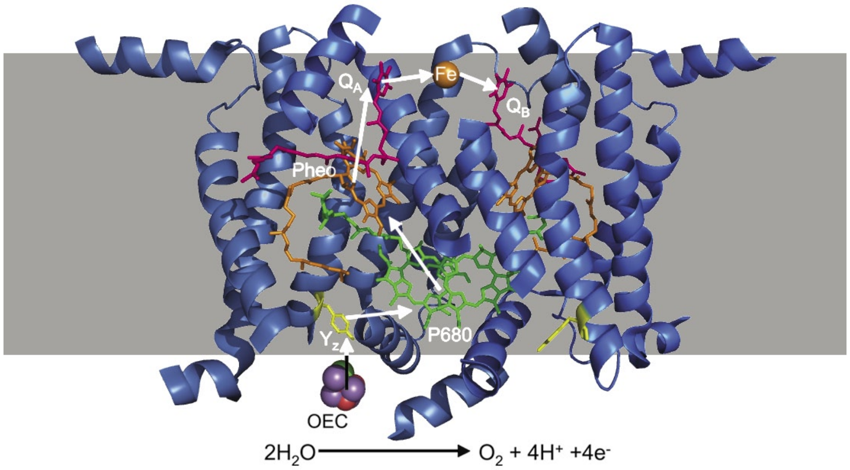
But there's a bigger problem. Even if we had all the cheap photovoltaics we could ever need, we can't store electricity in large quantities—you either use it or lose it. So I'm going to talk about using solar cells to make chemical fuel. If we could make fuel when the sun is shining, we could use it after dark, and the storage problem would be solved. Specifically, I'll talk about splitting water molecules. If you start with two molecules of water, H_2O, and add energy—ZAP!—you can make two molecules of hydrogen, H_2, which you can compress and store, and one molecule of oxygen, O_2, which you release to the atmosphere. We did this as little kids when we put two electrodes in a beaker of water and hooked them up to a battery. We got hydrogen gas bubbling up from the cathode and oxygen gas bubbling up from the anode. We want to do the same thing as grownups, but using the sun as our energy source instead of a battery, and we need to scale it up a little. In a solar-powered world, we'd run the H_2 through fuel cells, which generate electricity by recombining hydro-

> There isn't enough platinum on the planet to meet our energy needs, even if we used every single atom. And we need to save some for jewelry and best-selling albums. . . .
>
> Which leads to the big unanswered question: What are the H_2- and O_2-making catalysts going to be if they're not going to be platinum?

gen and oxygen to make water. We'd use solar energy to split water, store the energy in the H—H bonds we made, and get electrical energy out when we ran the reaction in reverse. The fuel cells would run 24/7, making electricity all the time, and the water splitter would make enough extra hydrogen during the day to power the fuel cells at night.

The Swedes and the Norwegians will be happy about this, because they can make their fuel in the summer, when the sun never goes down, and they can run their houses and everything else in the winter, when the sun never comes up. Here in California, we'd have solar-fuel plants along the Pacific Ocean, next to water-purification plants. We'd need an enormously abundant water supply to make hydrogen on the scale we'd need to run L.A., and so in a dream scenario, we'd have a big solar-fuel plant splitting seawater into O_2 and H_2. (We wouldn't even need to desalinate the water first! We need a certain amount of salt in the water—we call it an electrolyte—to make the reaction work.) We'd run the hydrogen through a big electric-power facility next door, and then we'd send the clean, fresh water that comes out of the fuel cells into the municipal water system. So we'd solve the energy crisis and the water crisis at the same time. There are technical details to work out, and I don't know if anybody has done any serious engineering studies on it, but that's my dream.

We know we can make fuel from sunlight, because nature does it. That's where we get all the fossil fuels we have now. The sun has been shining on plants for a long, long time, and their photosynthetic system is highly optimized. The system transforms carbon dioxide into carbohydrates—sugars and starches, which plants use to store energy, and cellulose, from which plants makes their cell walls. Over millions of years, these carbohydrates have become coal, oil, and natural gas.



In green plants, the manganese-containing oxygen-evolving complex (OEC) in Photosystem II (blue ribbons) plucks electrons from water molecules. The electrons hop to a tyrosine (Y_Z, yellow), a chlorophyll (P680, green), a pheophytin (Pheo, orange) and two quinones (Q_A and Q_B, magenta), not to mention an iron atom (Fe), and eventually cross the chloroplast's membrane (gray) to a second light-absorbing system, Photosystem I, which reunites them with their protons.

Structure after K. N. Ferreira, et al., *Science*, Volume 303, pp. 1831–38, March 19, 2004. Rendering by Gretchen Keller.

Nature's Way: Fragile Organic Molecules

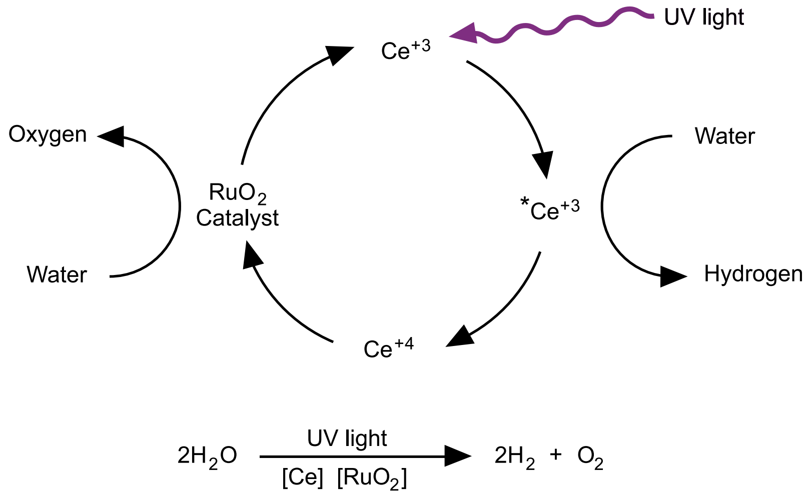
The photosynthetic machinery lives in organelles called chloroplasts, whose membranes contain green chlorophyll molecules. Photosynthesis starts with a chlorophyll molecule absorbing a photon of sunlight. This excites an electron, which hops off the chlorophyll molecule and gets siphoned away by a chain of electron carriers. The charge separation is vital—otherwise, the negatively charged electron would quickly lose the extra energy it picked up from the sunlight by falling back into the "hole," or positive charge, left on the chlorophyll.

Green plants have no use for electricity—they want to make carbohydrates. So the hole on the chlorophyll molecule gets filled by an electron from a handy water molecule, which then releases a proton. (A proton, of course, is all that's left of a hydrogen atom once you've stolen its electron.) The chlorophyll is now ready to absorb another photon, and the light-harvesting process repeats. Meanwhile, the newly liberated proton gets pumped across the chloroplast's membrane, where other enzymes reunite it with the electron that was siphoned away from the chlorophyll molecule, and use the reconstituted hydrogen atom to reduce carbon dioxide to carbohydrates. "Reduction," in the chemical sense, means to add one electron or more to an atom or molecule. When a hydrogen atom is the reducing agent, a proton often comes along for the ride.

Meanwhile, the water molecules' oxygen atoms have to go somewhere, so a manganese catalyst on the inside of the chloroplast's membrane puts the leftover oxygen atoms together in pairs to generate the O_2 that we breathe. The chloroplast winds up with four electrons and four protons on one side of its membrane, and one molecule of O_2 on the other. All of the charges balance, no atom is left behind, and everybody's happy.

We don't need to make carbohydrates, we just want to make H_2. Even so, figuring out a way to mimic photosynthesis is going to be one of the biggest challenges for chemists in this century. Over 20 years ago Eli Greenbaum, working at the Oak

The granddaddy of inorganic solar-fuel makers was developed in the 1950s. Ultraviolet light kicks a cerium ion (Ce^{+3}) into an excited state ($^*Ce^{+3}$), which promptly sheds the extra energy and an electron by jolting a hydrogen atom off a water molecule to become Ce^{+4}. The catalyst scrounges replacement electrons from other water molecules, liberating oxygen.



$$2H_2O \xrightarrow[\text{[Ce] [RuO}_2\text{]}]{\text{UV light}} 2H_2 + O_2$$

Ridge National Laboratory in Oak Ridge, Tennessee, took the chloroplasts out of green leaves and dipped them into a platinum solution until they were thinly coated with the metal. Then he dried them off and put them in a flask of water. When he shone sunlight on the flask, he got H_2 off the platinum surface, and the marvelous manganese catalyst made O_2. The catch is that once he took the chloroplasts out of the green leaves, they could no longer repair themselves. Protein molecules are fragile things, and any oxidant strong enough to turn water into O_2 will make short work of them. The process makes very energetic states of O_2, which, with the other powerful oxidants involved, including the manganese catalyst itself, oxidize the component proteins into useless organic glop within 30 minutes. But a leaf is a wonderful synthetic factory that just rebuilds the apparatus back again. So after Eli exposed his chloroplasts to sunlight for a few hours, all he had left was an ugly sludge in the bottom of the flask—something that I have seen many times.

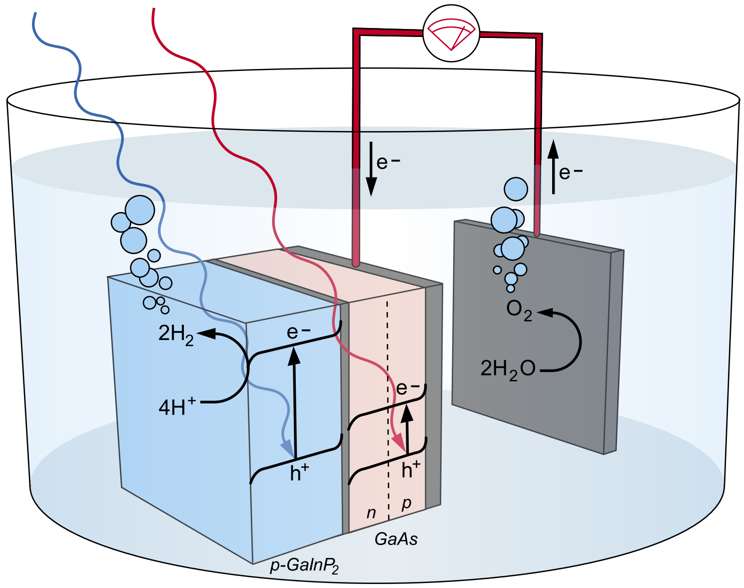
THE HARD WAY: INDESTRUCTIBLE INORGANICS

So why not make an inorganic mimic of photosynthesis that contains no proteins and never poops out? This field took off in the 1950s, when several independent researchers developed a cerium-based water-splitting system. In it, light hits a cerium ion, Ce^{+3}, converting it into Ce^{+4} and kicking out an electron that reduces water to H_2. Then a ruthenium dioxide catalyst strips an electron from a water molecule to make O_2 and give you back Ce^{+3} so the cycle can begin again. This system will run forever, because it is made of hard, inorganic components. The only problem is it requires deep ultraviolet light, and no deep ultraviolet light gets through the ozone layer. This system doesn't split any water at the surface of the earth, but it's great in space. So when we have to vamoose to another planet, because of all the problems here, we will take a lot of cerium with us and a little bit of ruthenium dioxide, and we'll be just fine.

Nate Lewis, who is now Caltech's Argyros Professor and professor of chemistry, was an undergraduate in my group in 1977, and he knew he could do better. He and grad student Kent Mann [PhD '77] developed a binuclear rhodium system—if you put two rhodium atoms together, they interact to absorb lots of visible light. In fact, they will absorb red light, the lowest-energy visible light that reaches Earth's surface. Kent and Nate shone light on their rhodium-rhodium system, and sure enough, hydrogen streamed out in a beautiful way. This was an important milestone in the solar-fuel field, because it was the first time anyone had ever made H_2 from sunlight, with an inorganic catalyst, in a homogenous system that actually stored energy. However, we could never get the quantum yield of hydrogen—the number of H_2 molecules we made per photon absorbed—to be better than one percent. Unfortunately, you have to have a quantum yield in the 50–70 percent range in order to have any chance of a reasonable efficiency for the process as a whole. After years of studying the mechanism, we figured out that there was a very inefficient step in it that limited our H_2 production, so the rhodium pair went the way of all systems.

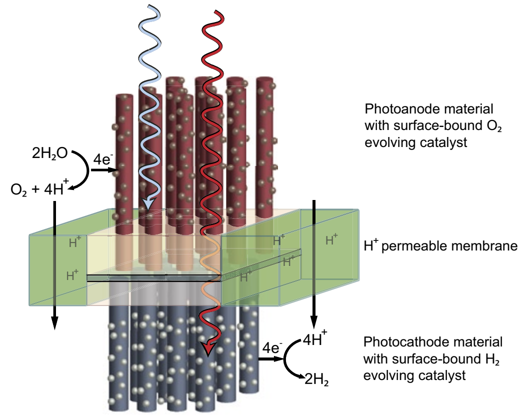
But there is hope. In 1998, John Turner at the National Renewable Energy Laboratory (NREL), in Golden, Colorado, built a device that is far, far more efficient than natural photosynthesis or almost anything else. (Incidentally, John got into the photoelectrochemical water-splitting racket while he was a postdoc with Fred Anson (BS '54), Caltech's Gilloon Professor of Chemistry, Emeritus, from 1977 to 1979.) John's world-record water-splitter has two layers of semiconductors—gallium arsenide and gallium indium phosphide. Gallium arsenide absorbs reddish light, and gallium indium phosphide absorbs bluish light, so this tandem array absorbs most of the sunlight that comes in. H_2 molecules form on the gallium indium phosphide surface, sucking electrons out of a platinum electrode and creating holes that in turn pull electrons from water molecules, thereby oxidizing water to O_2. (To oxidize something in an electrochemical sense means to remove electrons from it—or add holes to it, which is the same thing.) The system works beautifully. Its overall efficiency is better than 10 percent—and, because of wavelength and thermodynamic considerations and so forth, 18 percent is about as high as you can get. So the good news is that John's wonderful water splitter is efficient; the bad news is that John's wonderful water splitter costs $10,000 per square centimeter to make.

So now all we have to do is build something similar out of cheap, Earth-abundant materials. Not platinum. There isn't enough platinum on the planet to meet our energy needs, even if we used every single atom. And we need to save some for jewelry and best-selling albums. Gallium is probably OK, but not arsenic, which is toxic. We need something environmentally friendly that will do as well as NREL's wonderful cell. To find it, we have formed an unholy alliance with our East Coast branch, MIT. We call this alliance Powering the Planet, a very modest sort of title, and the MIT head is Dan Nocera [PhD '84], a former grad student of mine. He works with Kit Cummins and Jonas Peters, who used to be a professor here at Caltech but recently defected to MIT because they clearly need the help, as you will see momentarily.



The NREL water-splitting cell uses two semiconductors (blue and pink) to absorb two wavelengths of visible light that, combined, give electrons enough energy to reduce hydrogen. (For a fuller explanation of what this means, and what the letters *n* and *p* signify, see "Solar Fuel I," which begins on page 20.) The intermediate, lower-energy electrons recombine with holes in the conductive layer between the semiconductors.

POWERING THE PLANET

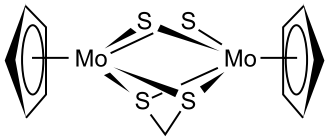


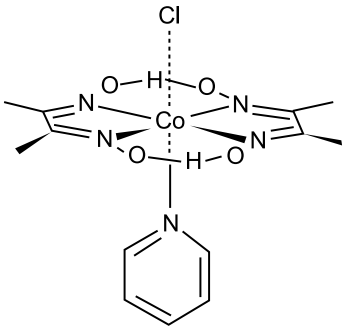
The National Science Foundation–supported Caltech-MIT "Powering the Planet" design will use two sets of light-absorbing nanorods to get the necessary energy boost.

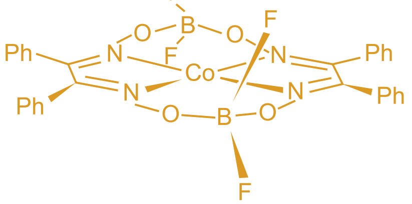
We are collaborating to build a nanorod-catalyst device to split water. A membrane in the device acts like the chloroplast's membrane, keeping the O_2-making and H_2-making sides of the system away from each other. This is important for several reasons, including the fact that we don't want the two gases recombining explosively. Embedded in the membrane are silicon nanorods to harvest the sunlight, and several grad students and postdocs in Nate Lewis's group are working on that part. The nanorods stick out of both sides of the membrane, and will be coated with a different catalyst on each side of it. High-energy blue light gets absorbed on the anode side of the membrane, making holes that interact with a catalyst—perhaps a metal oxide, like zinc oxide or titanium dioxide—to make O_2. Lower-energy red light gets absorbed on the cathode side of the membrane, where another catalyst reunites the electrons (those that have worked their way down from the anode end of the nanorod, plus the nearby ones the red light has knocked loose) with the naked protons that have diffused through the membrane to make H_2.

Nate's group and my group are working on the H_2 catalyst, which we have a pretty good idea how to make. The stickler is the oxygen side. This is the problem that comes up over and over and over again in solar-fuel formation, the fact that nobody has ever developed a good molecular catalyst for the oxidation of water to O_2. Since we have no clue, really, how to make the catalyst for the O_2 anode, we naturally assigned that part to MIT.

Which leads to the big unanswered question: What are the H_2- and O_2-making catalysts going to be if they're not going to be platinum? Platinum is our old friend. It does everything. It catalyzes the oxidation of water to O_2, and the reduction of protons to H_2. But we've got to replace platinum, because there's not enough of it in the world, and we can't do what nature does. Nature uses big proteins. The ones that split off hydrogen from water are called hydrogenases, and their catalytic sites are pairs of iron atoms—a simple, Earth-abundant material. Marcetta Darensbourg at Texas A&M and Tom Rauchfuss at the University of Illinois at Urbana-Champaign have built the main parts







Three candidate hydrogen-making catalysts. Above: A two-molybdenum molecule made at the Pacific Northwest National Laboratory. Above, right: A cobalt complex from France. Right: Caltech's contender, which also contains cobalt.

of these active sites that have the correct geometry without being surrounded by proteins, and they don't work very well. This is the story of inorganic mimics of proteins—the proteins tune the active sites' properties in very subtle and brilliant ways, which we have not figured out how to do.

So we don't go with this mimic-of-the-biological-stuff approach, at least for hydrogen. Dan Nocera and Nate Lewis organized a Gordon Research Conference on solar fuels in 2007 that assessed all the inorganic, nonplatinum hydrogen catalysts around. Three winners came out. One is a dimolybdenum system that Dan DuBois at the Pacific Northwest National Laboratory has worked on, and one is a cobalt system that Vincent Artero and Marc Fontecave at the Université Joseph Fourier in Grenoble, France, developed. The third was originally developed at Iowa State in the 1980s by Jim Espenson [BS '58], was recently improved by Xile Hu when he was a postdoc here at Caltech, and is now being worked on in my lab by grad student Jillian Dempsey. The DuBois molecule and the Caltech one are both very good. They operate at very close to the optimum voltage to make H_2. This is a critical feature, because if the system's voltage is more than the optimum, the extra energy is wasted. And if the voltage is insufficient, the reaction doesn't go at all. But Dan's molecule contains sulfur, which can be nasty, and ours is easier to make, so we think the Caltech one looks like a real winner.

Jillian is well along to working out its mechanism, using the laser flash-quench techniques pioneered by Faculty Associate in Chemistry Jay Winkler [PhD '84], who oddly enough also used to be a grad student of mine. The question is whether it takes two cobalt hydrides crashing together to split off H_2, or whether an incoming proton can pluck the hydrogen atom off a single cobalt hydride—in other words, does each cobalt atom act alone, or do you need to have them work in pairs? The distinction is very important, because if we want to improve the catalytic rates so that they are really fast, *really* fast, approaching the biological rates, we have to design our molecules to fit the mechanism. At this point, it looks like it's two cobalts diffusing toward each other, in which case we want to design a system that tethers them together and will reduce the diffusion time tremendously. The hydrogenase enzyme spits out some 6,000 H_2 molecules per second; our best cobalt catalyst is not as active, but our tethered systems may be the answer.

Last summer Carolyn Valdez, a Summer Undergraduate Research Fellowship (SURF) student in our group who had just finished her freshman year at Caltech, made such a tethered binuclear cobalt system with Jillian. It looks very promising. It's not quite right yet—we still need to tune the voltage a little—but so far, it looks extremely good. I think we're well on the way to having a very active, Earth-abundant catalyst for making H_2.

JUST ONE SMALL PROBLEM . . .

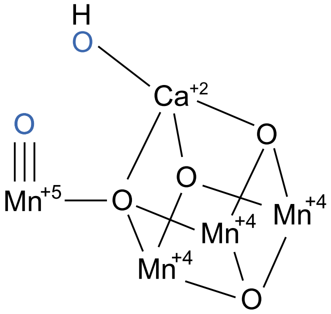
The problem, as I said, is water oxidation. The MIT side. And, to be fair to them, this is by far the toughest problem. We haven't improved on molecular catalysts for water oxidation in a quarter of a century. The best thing we've got is a blue Ru-bpy (pronounced "roo-bippy," as in "you bet your bippy") dimer introduced by Tom Meyer at the University of North Carolina, Chapel Hill, in 1982. Ru-bpy is a molecule my lab has been studying for a very long time. There's even a drink at the Ath named for it. Ru-bpy is short for ruthenium-bipyridine—an Ru^{+2} ion sitting at the center of an array of organic molecules called bipyridines that are really good at absorbing light. Postdoc Kristine Kilså in my lab made Ru-bpy systems that, combined with the proper catalysts, could produce H_2 with yields approaching 80 percent. But on the O_2 side, Ru-bpy systems are terrible. (Oxygen production from water by Ru-bpy systems is one of those reactions that runs much, much better in the journals than it does in the lab.) Whereas the O_2-producing manganese catalyst in green leaves turns over in thousandths of a second, generating tremendous amounts of oxygen so that we can live on this planet, Meyer's famous blue dimer turns over only a few times each day. I think "rolls over" is a better way to describe it. And it only produces 10 to 25 O_2 molecules before it craps out altogether. It's likely that the problem is our old friend, oxidative degradation. It's much easier to oxidize the bipyridines than to oxidize water, so it is hard to avoid bipyridine oxidation to carbon dioxide.

After many years of hard work, the structure of nature's manganese catalyst was finally solved by two teams working independently. Jim Barber of Imperial College London and Wolfram Saenger at the Free University of Berlin managed to grow crystals of the assembly of proteins containing the manganese catalyst and do X-ray diffraction studies on them, so we know, roughly, what it looks like. So people now have ideas about how the mechanism might work, but I'm sure they're wrong, because we have never learned *anything really definitive* about mechanisms by solving these big structures. Mechanistic studies take many years and involve an enormous amount of effort. We still don't know how the nitrogenase catalyst works—nitrogenase is what bacteria use to convert N_2 into ammonia and eventually amino acids—and Doug Rees, the Dickinson Professor of Chemistry, solved that structure here at Caltech 15 years ago.

But we knew one thing, long before the structure had been solved. The catalyst has four manganese ions, so we will probably need four metal atoms—one for each electron in the double bond of the O_2 molecule. Otherwise, it's too much punishment for one metal atom to take; it's much easier to make four holes on four atoms than to strip four electrons off a single atom. Multielectron reactions are very hard to do, and they need very elaborate structures to keep everything in the right place. That's why the only good water-oxidation catalyst we have is the one in green leaves that nature evolved.

My group is taking a different approach. We believe that if we take an enzyme that will reduce O_2 by four electrons, we should be able to tweak it, through protein engineering, into a catalyst that will oxidize water. Its catalytic center is already set up for a four-electron, four-proton reaction, and all the atoms are already in the right positions—the intermediate states in the oxygen-reduction reaction must be very similar to what we would need to go backwards and generate O_2 instead of consuming it.

Grad student Kyle Lancaster in my group has decided to work on a beautiful, blue protein called copper efflux oxidase, because three of its four copper atoms form a catalytic center that reduces O_2 to water. Kyle can grow this protein in *E. coli*, and we may even call on Frances Arnold, the Dickinson Professor of Chemical Engineering and Biochemistry, to help us through a directed-evolution strategy; another of our collaborators, Corey Wilson at Yale, likely will contribute to this effort. (Corey is currently a Gordon Moore Scholar here at Caltech.) The trick will be to change the voltage at which the system operates from one that supports the reduction of O_2 to a much higher one that will support the oxidation of water.



Photosystem II's manganese-based oxygen-evolving complex has three manganese (Mn) atoms, four oxygen (O) atoms, and a calcium (Ca) atom at the corners of a cube, plus a fourth manganese atom in a higher oxidation state that acts as the wedge in the water splitter to make an O_2 molecule out of the two oxygen atoms shown in blue. How that cube and the protein drapery around it make this happen is anybody's guess.

The sands of time are running out on fossil fuels, but with silicon nanorods, the future may be the times of sand. From left: Kyle Lancaster, Carolyn Valdez, Harry Gray, Jillian Dempsey, and Jay Winkler contemplate this conundrum.

Some time in this century, we're going to stop taking from nature and start paying back. We're going to be able to take the components of our atmosphere—carbon dioxide, nitrogen, and oxygen—combine them with seawater and, with sunlight as our energy source, make not only fuels, electricity, and pure water, but pretty much everything else you can think of: plastics, pharmaceuticals, and food. I really believe that this is where we're headed, and that this will be the Century of Chemistry. So you can see there's a lot riding on the ability to create O_2 from water, and I hope we can make it work. ☐

Harry Barkus Gray got his PhD in 1960 at Northwestern University under professors Fred Basolo and Ralph Pearson, who cowrote the "bible" of inorganic chemistry. Gray came to Caltech as a full professor in 1966, and is the Beckman Professor of Chemistry and the founding director of the Beckman Institute. He has published 17 books and more than 730 research papers. He has received innumerable awards for his work in inorganic photochemistry and bioinorganic chemistry, including the National Medal of Science in 1986 from President Reagan, the Priestley Medal from the American Chemical Society in 1991, and the Wolf Prize in 2004.

This article was edited by Douglas L. Smith.

PICTURE CREDITS: 26, 28-31 — Doug Cummings; 29 — Elizabeth Santori; 31 — Doug Smith

From Solar Fuel Back to Electricity

By Marcus Woo

Burning clean hydrogen, Honda's new FCX Clarity is now available for a three-month lease running at about $600 a month. But before you rush out to get one, note that the car is only available to those living near hydrogen-fuel stations in the Southern Californian cities of Torrance, Santa Monica, and Irvine.

This summer, a new fuel-cell car will be hitting the streets of Los Angeles. Instead of belching out carbon dioxide and toxic fumes, this car—running on hydrogen gas—releases nothing but water. Honda's FCX Clarity is now being leased to a limited number of people who live in those parts of Los Angeles equipped with hydrogen-fuel stations. California has approximately two dozen hydrogen-fuel stations, about half of which are in Los Angeles. Boasting an equivalent gas mileage of 68 miles per gallon and a 270-mile range, the car is part of the nation's push toward fuel-cell technology to reduce foreign-oil dependence and to combat climate change. In his 2003 State of the Union speech, President George W. Bush introduced the Department of Energy's Hydrogen Fuel Initiative. With a 2007 budget of $274 million, the program aims to develop the production, storage, and delivery of hydrogen, as well as fuel-cell technology for vehicles and stationary uses.

While the buzz surrounding fuel cells has centered on fancy new cars, transportation is not the only thing fuel cells are good for. Fuel cells are not an energy source, but rather an efficient and, most importantly, clean way to convert chemical energy—in the form of hydrogen, methanol, or methane, for instance—into electricity. "It's a direct competitor to any other kind of power plant," says Sossina Haile, professor of materials science and chemical engineering. Haile's lab is among the leaders in fuel-cell technology. Recently, the lab has made several major advances, developing materials for record-breaking and potentially revolutionary fuel cells that, one day, may help power the world.

When a fuel cell runs on carbon-based fuels, it converts the energy stored in chemical bonds into electricity in a much cleaner and more efficient way than combustion does, reducing the amount of carbon dioxide emitted per unit energy. Thus fuel cells could serve as an important intermediate in the transition toward an alternative-energy economy.

But the ultimate goal, of course, is to use only clean fuels. Haile envisions putting a fuel-cell plant next to a solar power facility that would produce hydrogen fuel. In addition to producing electricity, solar power splits water into oxygen and hydrogen. The hydrogen, then, would be put into the fuel cells, which recombine it with oxygen to recover the stored energy. So at night, when photons are lacking, the fuel cells would provide clean power. "It's like having the sun in your back pocket," Haile says. "You use it when you need it."

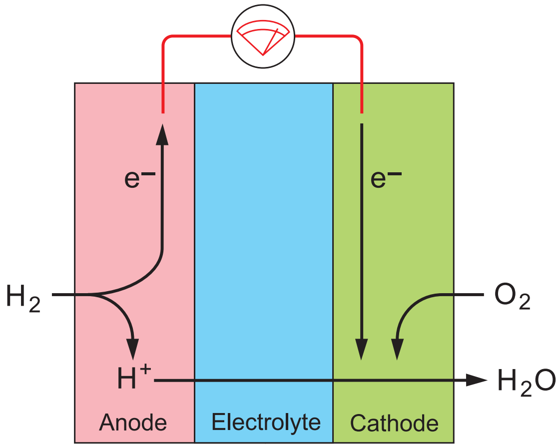
WHICH FUEL CELL WOULD GOLDILOCKS CHOOSE?

"Fuel cells combine the best of batteries and the best of combustion engines," Haile says. Like a battery, fuel cells operate via a clean, well-controlled reaction. But like a combustion engine, fuel cells are easily refueled—you don't have to wait hours for one to recharge. Even better, a tiny fuel cell is just as efficient as a giant one. A coal-fired power plant, on the other hand, has to reach a certain size before it attains a decent efficiency. Since a small and therefore cheap fuel cell is just as good as a big and therefore expensive one, you don't have to invest a lot of money to get an efficient power plant. "You can buy whatever your capital allows you to," Haile says. "In that regard, it's very useful for the developing world, which is in desperate need of electricity, but does not have the capital to invest in large power plants."

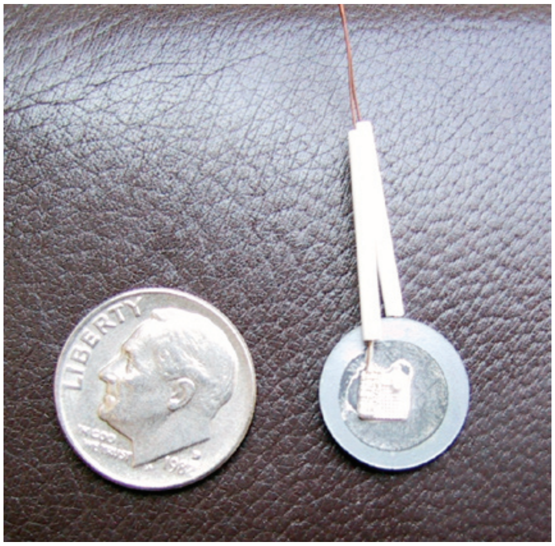
A fuel cell is based on a reaction in which a fuel, such as hydrogen, and oxygen produce water and energy. Left alone, hydrogen and oxygen "want" to join together as water and acquire a lower overall energy state—always nature's preference. A fuel cell controls this reaction and channels the energy into electric current. There are zero emissions—neither greenhouse-causing carbon dioxide (when the fuel is hydrogen) nor toxic by-products like nitrous oxide or sulfuric oxide.

The cell separates the hydrogen from the oxygen with an electrolyte, a material that allows only ions to pass through. The hydrogen still wants to react with oxygen, but the only way it can do so is to lose its electrons and become ionized. The electrolyte acts as a gatekeeper of sorts, preventing molecular hydrogen from going straight to the oxygen and reacting. Instead, the electrolyte only allows the hydrogen ions—protons—to pass. Meanwhile, the electrons flow out through a circuit, creating the desired electrical current, and continue to the other side of the cell where the oxygen is. Called the cathode, this is where the protons, electrons, and oxygen react to form water vapor.

When using fuels other than pure hydrogen, the reactions are more complicated, but the principle of combining hydrogen with oxygen to create water and energy is the same. In a methanol-based fuel cell, for example, methanol reacts with water at the anode, producing carbon dioxide, hydrogen ions, and electrons.



How a simple hydrogen fuel cell works. In the anode, hydrogen gas is split into protons and electrons. The protons cross the electrolyte membrane while the electrons generate electrical current. At the cathode, the electrons rejoin the protons, and along with oxygen, react to form water.



At just over a centimeter in diameter, this prototype fuel cell is made with a nickel and cerium-oxide anode, cerium-oxide electrolyte, and a barium-strontium-cesium-colbalt-iron-oxide cathode. The cathode is made from a new solid-oxide material that enables the fuel cell to give record power outputs for operation at intermediate temperatures.

The key part of the fuel cell is the electrolyte, which determines the fuel cell's operating temperature. Temperature, in turn, determines how fast the reaction happens. The higher the temperature, the more the molecules and ions scurry about, and the faster the reaction and the more efficient the fuel cell. The operating temperature can be lowered, however, by using catalysts to speed up the reactions.

A car needs a fuel cell that works at a relatively low temperature. It would take too long to warm up your engine to 1,000°C every time you go to the store to pick up a loaf of bread. The latest fuel-cell cars, such as the FCX Clarity, use a cell made with polymer electrolyte membranes—also called proton exchange membranes, or PEMs—which operate at temperatures of 70°C to 90°C. The membrane works by allowing water molecules to ferry protons from the hydrogen side, called the anode, to the oxygen side, the cathode. Embedded in the membrane are pockets of water, and when a water molecule acquires a proton, it becomes an ion called hydronium, which crosses the membrane into the cathode and delivers the proton. What's difficult is to maintain a balance of water between the anode and cathode, ensuring that the water molecules return to the anode side after the protons are delivered. Another downside is that the membrane is permeable to methanol, requiring major feats of engineering to get this fuel to work with PEM fuel cells. If the methanol goes directly to the oxygen, electrons aren't stripped and no electric current is made. Instead, the methanol just burns—sometimes quite vigorously. And finally, because a PEM cell has to run at low temperatures—otherwise the water would evaporate—it's less efficient, even with catalysts.

Current technology demands that the catalyst be made from precious metals like platinum. If all the vehicles in the United States ran on PEM fuel cells as they're currently configured, 25 million kilograms of platinum would be needed. This is a problem, as the estimated supply of all the world's platinum is only 32 million kilograms. "We might free ourselves from having to import petroleum," Haile says, "but then we would simply become a platinum-importing nation."

The highest-temperature fuel cells, on the other hand, don't need catalysts at all. But, they cost a lot more to make because materials that can withstand high temperatures during operation require high temperatures—and therefore lots of energy—to process. If some fuel cells are too cold and others too hot, would something in the middle be just right? Fortunately, there are fuel cells that operate at in-between temperatures, including phosphoric-acid and alkali fuel cells. Phosphoric-acid fuel cells were promoted in the 1990s, Haile says, but they were never able to produce enough power. The electrolyte was corrosive, and the platinum catalyst would become caked in phosphoric acid. Alkali fuel cells are very efficient, but they react quickly with carbon dioxide and make solid potassium carbonate, which kills the cell. This not only ruled out carbon-containing fuels, such as methane or methanol, but keeping a fuel cell protected from carbon dioxide in the atmosphere is expensive. Alkali fuel cells have found their niche, though. They power NASA's spacecraft, since there's no carbon dioxide in space.

At first, they used a compound called cesium hydrogen sulfate, which is physically similar to salt. But when they tried their new fuel cells, they got something no one would want on any dinner table.

A few years ago, Haile's group came up with a completely new kind of fuel cell—one that even Goldilocks might like. Using electrolytes made from materials called solid acids, the researchers have built fuel cells that operate at a "warm" 250°C. This is not hot enough to be expensive, but still warm enough to be efficient without needing a lot of catalysts. At first, they used a compound called cesium hydrogen sulfate, which is physically similar to table salt. But when they tried their new fuel cells, they got something no one would want on any dinner table.

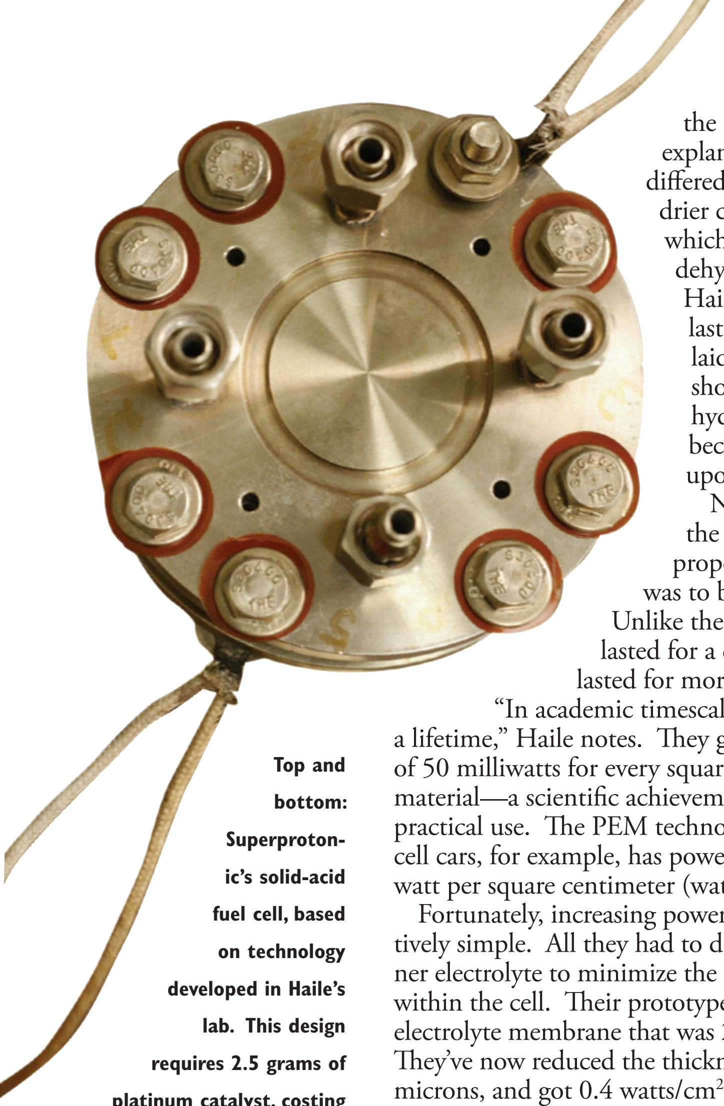
A Radical Idea, Rotten Eggs, and a Start-Up

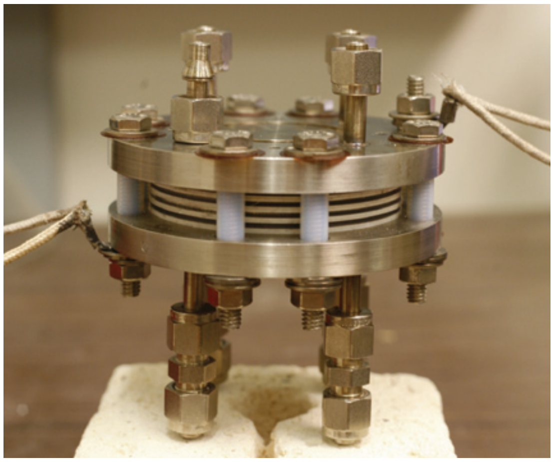
After reaching a certain temperature, solid acids become conductive, enabling protons to travel through the material. In cesium hydrogen sulfate ($CsHSO_4$), the bisulfate group (HSO_4^{-2}), made from a sulfate and a hydrogen ion, forms a tetrahedron, or four-sided pyramid. At ambient temperatures, the pyramids are aligned, like soldiers at attention. But when you crank up the heat, they start to fidget, and eventually become completely disordered. They twitch fast—reorienting themselves every 10^{-11} seconds or so—and when they do, they can pass a hydrogen ion to an adjacent bisulfate group. Protons are handed off from one group to another as they make their way through the electrolyte. They don't need an intermediary like hydronium (H_3O^+) to give them a lift. "Perhaps it's because I'm originally from Ethiopia that I like to say that our protons run across the electrolyte on their own two legs—they're marathon runners," Haile says. "They don't need to have a big limo, the water molecule, to carry them around."

Two former graduate students, Calum Chisholm (MS '01, PhD '03) and Dane Boysen (MS '01, PhD '04) played key roles in developing the cesium-hydrogen-sulfate fuel cell. The cells reached reasonable power densities, Haile says, but then after about a day—or sometimes just a few hours—they would die. This was a puzzle until the researchers smelled something rotten. "It took a long time to figure out that the sulfur in the sulfate was turning into H_2S, which is hydrogen sulfide, a fantastic poison. Fortunately, your nose is very sensitive to it, and that was how—once we pulled the test station out of the fume hood—we realized we were making it." (Hydrogen sulfide is also responsible for the smell of rotten eggs.) "It's bad, bad news for the fuel-cell catalyst. So we had to go back to the drawing board."

Haile and Boysen knew, from a separate study, that cesium hydrogen phosphate, another solid acid with similar structure, became conductive at a similar temperature. But some other researchers argued that the conductivity was due to dehydration: heating the material squeezed out water molecules in the form of hydronium and hydroxide (OH^-) ions, they said, making the material conductive. The debate raged in the literature for 20 years over whether cesium hydrogen phosphate undergoes a "superprotonic" transition the way cesium hydrogen sulfate does.

Haile's group reasoned that if conductivity were not due to dehydration—and instead was an inherent property of the material—keeping the humidity high while heating the material would still cause a transition to high conductivity. And indeed, when they heated their samples in a high-water-vapor atmosphere, they saw the transition. Varied groups came up with varied results because they didn't keep well-controlled conditions, Haile says. Experimental results in humid Moscow, which favored





Top and bottom: Superprotonic's solid-acid fuel cell, based on technology developed in Haile's lab. This design requires 2.5 grams of platinum catalyst, costing about $126, to run a 60-watt lightbulb.

the "superprotonic" explanation, for instance, differed from those in the drier climate of Pasadena, which initially favored the dehydration explanation. Haile says that over the last few years they've laid the debate to rest, showing that cesium hydrogen phosphate becomes superprotonic upon reaching 230°C.

Now that they knew the material behaved properly, the next step was to build a fuel cell. Unlike the sulfate cell that lasted for a day, the new one lasted for more than 100 hours. "In academic timescales, this is basically a lifetime," Haile notes. They got a power density of 50 milliwatts for every square centimeter of material—a scientific achievement, but too low for practical use. The PEM technology used for fuel-cell cars, for example, has power densities of one watt per square centimeter (watt/cm^2).

Fortunately, increasing power densities is relatively simple. All they had to do was make a thinner electrolyte to minimize the electrical resistance within the cell. Their prototype in 2004 had an electrolyte membrane that was 250 microns thick. They've now reduced the thickness to only 25 microns, and got 0.4 watts/cm^2, within a factor of two of the best fuel cells—which operate at much higher temperatures or use a lot of precious-metal catalysts.

Former postdoc Tetsuya Uda, who is now a professor at Kyoto University, then tested the device with different fuels. One of the problems with PEM cells is that they're permeable to methanol. But because solid acids are, well, solid, methanol can't penetrate the electrolyte. After the researchers added a so-called reformer catalyst, which extracts hydrogen from potential fuels without needing any precious metals, their solid-acid fuel cell performed with methanol about as well as it did with pure hydrogen, and much better than PEM fuel cells did with methanol. The fuel cell also worked with ethanol—popular these days as a biofuel—and a related potent potable, vodka.

The 2001 sulfate-based prototypes could power a 60-watt lightbulb for $2,000, Haile says. It's now down to $125, which still isn't exactly a bargain. The high cost is primarily due to the platinum catalyst, but Haile says they can further reduce the amount of platinum they need. One way to do this is to use platinum nanoparticles. Because of their tiny sizes, the surface area where the reaction occurs goes way up, and a smaller amount of platinum is just as effective.

Solid-acid fuel cells are immune to another problem that plagues their liquid and wet-polymer-electrolyte brethren. The platinum particles don't get coarse. The liquid causes the smaller particles to dissolve and the bigger ones to grow, reducing their total surface area and thus the effectiveness of the catalyst.

Haile hopes to eliminate the need for platinum completely. By pushing the operating temperature up to 250°C and beyond, one could, in principle, build a fuel cell that runs efficiently enough that a catalyst isn't needed at all.

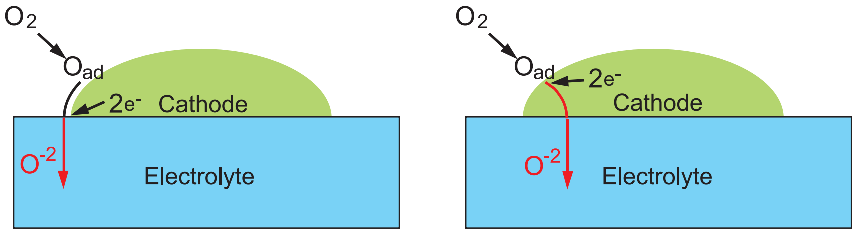
Other than a couple of groups in Japan and Russia who have dabbled in solid-acid fuel cells, Haile's lab is the only one doing significant work, she says, since this technology is such a major departure from the norm. "We're a little too far ahead for anyone else to try to get into the game." But the novelty of the technology also means they have a lot of learning to do. While dozens of labs around the world have been studying other fuel-cell technologies for decades, no one knows much about solid acids. "We're starting out from complete scratch, with no knowledge base whatsoever," Haile remarks. "That means there's huge potential, but very little to build upon."

In 2003 Chisholm, Boysen, and Uda founded a company called Superprotonic Inc. (SPI) to develop solid-acid fuel cells. They're looking at how to scale up the cells made in the laboratory to fuel-cell stacks that can power real devices. Early this year, the company delivered pre-commercial prototypes to customers for testing. The company is making fuel cells for a variety of applications, including auxiliary power units for long-haul diesel trucks and power units that generate heat and electricity for homes.

Meanwhile, if anyone else is looking to start a company, Haile's lab has yet another fuel cell that's ready for commercial development.

Send in the Oxygen

Solid-oxide fuel cells (SOFCs) operate at the highest temperatures, up to 1,000°C. Along with low-temperature fuel cells such as the PEMs, SOFCs have enjoyed high levels of investment and development in the last few years, Haile says. Because high temperatures render catalysts unnecessary and spark fast reactions, they're the most efficient, although high temperatures also hike up



In a solid-oxide fuel cell, oxygen is captured by adsorption on the cathode surface. The adsorbed oxygen (O_{ad}), however, can only join with the electrons in places where the resulting oxygen ions have somewhere to go. (Eventually, of course, they want to pass through the electrolyte and react with the hydrogen). In previous fuel-cell designs (left), oxygen ions could travel through the electrolyte but not through the cathode, so adsorbed oxygen had to diffuse along the surface toward the intersection of the cathode, electrolyte, and air. But the new cathode material (right) does allow oxygen ions to pass through, so the adsorbed oxygen can combine with the electrons anywhere on the cathode surface, increasing the fuel cell's power output.

the manufacturing cost. Well over a decade ago, the Department of Energy determined that the SOFCs at the time, which ran at 800 to 1,000 degrees, were too expensive, and said that the operating temperatures had to be brought down to 500 to 800 degrees.

Lower temperatures slow the ions trying to cross the electrolyte membrane, but even when thinner membranes were developed to solve this problem, the power output of the fuel cell was too low. What was needed was a new cathode material.

On the cathode side, oxygen has to react with electrons to become oxygen ions. The problem is that the reaction can only happen where the oxygen ions have a place to go: the corner where the cathode joins the electrolyte (see figure above). The fuel cell has a small number of these sites, so the reaction proceeds slowly. Researchers in Haile's lab thought they could speed things up if they found a new cathode material that allowed oxygen ions to pass through, which would make the cathode's entire surface available. In 2003, they eventually found that barium strontium cobalt iron oxide (written as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$), which Haile's graduate students call alphabet soup, did just that.

The exact details as to why this material works so well aren't fully understood, but the reason has to do with inherent defects in the crystal structure. "What's quite phenomenal about this material is that normally you would expect three oxygen atoms in each crystal unit," Haile explains. "As far as we can measure, one out of six oxygen atoms are missing, and yet it stays together. I find this exceptionally fascinating." These missing oxygen atoms, called oxygen vacancies, allow other oxygen ions to travel through, boosting the fuel cell's reaction rates.

The new fuel cell produced one watt/cm^2 at only 600°C, a record at this intermediate temperature. This technology, Haile adds, is ready to leave the lab and become a commercial enterprise. Unlike the solid-acid fuel cells, whose uniqueness required a start-up company to develop it, solid-oxide fuel-cell technology is established enough that many other companies could easily pick it up. This hasn't happened yet, but Haile's hopeful that someone will license it and work with them to develop commercial fuel cells. As with many other alternative-energy technologies, the key with fuel cells is making them cost effective. "They're viable today," Haile says. "It's just, at what price?"

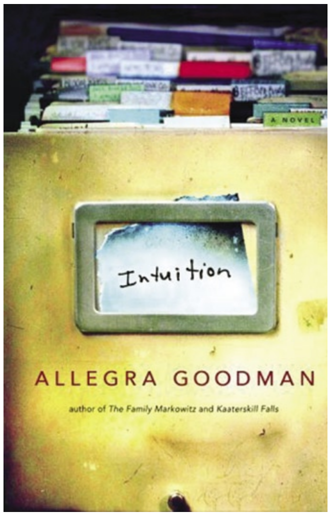
Both solid-acid and solid-oxide fuel cells are technologies for stationary power. Fuel-cell cars may get more press, but the reality is that portable fuel cells pose the most engineering hurdles, Haile says. Not only are stationary fuel cells closer to commercial viability, they are more important for solving the energy and climate crises. While cars contribute a large fraction of the world's carbon emissions, they're not the biggest problem. Stationary fuel-cell technology has the best chance of changing the future of the planet. "That's where you have the biggest environmental impact in terms of global warming," she says.

The researchers develop their fuel cells without any particular fuel in mind. "I like to say we're fuel agnostic," Haile says. Since the question of fuels quickly enters into the messy realm of policy, and no one knows which fuel will turn out to be the best choice, her lab focuses on the engineering. In any case, fuel cells are not an energy source, as we saw earlier. Instead, they're a way to harness chemical energy, and if that energy isn't produced cleanly, you're not solving the problem—just shifting it to another place. No technology is a solution by itself because each type only tackles one aspect of the energy and climate problem, she says. "Fuel cells are not an energy solution—they're just part of it."

Haile says fuel cells will eventually reach wide, commercial use—the question is just when. But when asked to speculate, she laughs and demurs. "I've been asked that for the past decade, so I better not answer." ☐

Professor of Materials Science and Chemical Engineering Sossina Haile earned her BS (1986) and PhD (1992) from MIT, and her MS (1988) from the University of California, Berkeley. Prior to joining Caltech in 1996, she was an assistant professor at the University of Washington, Seattle. From 1991 to 1993, Humboldt and Fulbright Fellowships took her to the Max Planck Institute for Solid State Research in Stuttgart, Germany. She has received numerous awards, including the NSF National Young Investigator Award, the J. B. Wagner Award of the High Temperature Materials Division of the Electrochemical Society, the Coble Award from the American Ceramics Society, and the Robert Lansing Harding Award of the Minerals, Metals, and Materials Society.

PICTURE CREDITS: 32 — Honda; 33, 36-39 — Doug Cummings; 33, 35 — Haile lab



Intuition
Dial Press, 2006
385 pages
$13.00

Novelists, playwrights, and poets are increasingly attracted by scientific themes—C. P. Snow's lament about the "Two Cultures" notwithstanding—but attempts at authentic literary portrayals of scientific practice are still rare. Perhaps this is not so surprising; after all, how easy is it to construct a gripping tale out of cleaning glassware and tending to lab rats? In light of the central and pervasive role of science in contemporary society, though, it would be nice to see more authors taking on that challenge. (See the website LabLit.com, which is "dedicated to real laboratory culture and to the portrayal and perceptions of that culture—science, scientists and labs—in fiction, the media and across popular culture.")

Allegra Goodman's novel *Intuition* is a significant recent contribution to this genre. It tells the story of a research group led by two senior scientists, Sandy Glass and Marion Mendelssohn, at the fictional Philpott Institute in Cambridge, Massachusetts, and consisting of a number of postdocs (among whom Cliff and Robin play the most important dramatic roles) and technicians. Goodman spent a good deal of time talking with and observing researchers at the Whitehead Institute, and it shows: the book does a good job of depicting the quotidian routine of a research lab, the small triumphs and frustrations its members regularly encounter, and the relationships and interactions between them.

Furthermore, Goodman does her best to portray all her characters as "real people" (as opposed to the myth of impersonal scientific researchers) with multiple motivations. I found this aspect much less successful, but that is largely a matter of personal literary taste. I do not care to be *told*, rather than *shown*, what the characters are like, and how we are supposed to think about them. From the very beginning I repeatedly encountered passages—for example, that Marion is "fearsome, implacable, dark eyes glowering" while Sandy is "always cheerful, brimming with the irrepressible joy of his own intelligence"—that made my heart sink. But those who do not object to this style will probably find the book an enjoyable and entertaining read.

The plot is also entertaining, as well as timely and interesting. It concerns a case of possible fraud: Cliff has discovered a viral treatment which appears to make tumors disappear in mice; urged on by aggressive Sandy, the group goes public at an early stage, attracting intense worldwide interest; but Robin, who is assigned to drop her own work and follow up on Cliff's, cannot reproduce his findings. She begins to suspect dishonesty, eventually taking her concerns outside the lab, and a major brouhaha erupts.

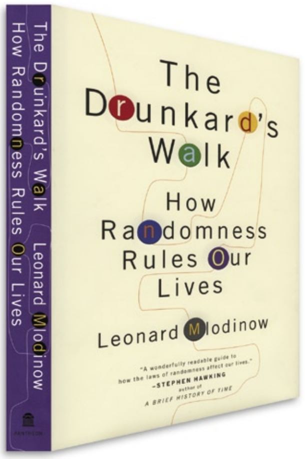
Goodman appropriately tries to highlight the ambiguities inherent in such conflicts, but her effort is problematic, for two main reasons. First, almost no scientific details are provided (for which the author, not a scientist, can certainly be partially excused); it is never clear just what is under dispute. The obvious question is whether or not Cliff deliberately cheated; but since Goodman writes from an omniscient point of view, and puts us inside his head throughout, it is hard to see that this *is* an open question (shades of Agatha Christie's *The Murder of Roger Ackroyd*?). Unless one deliberately suspends close consideration, this narrative line does not hold together at all well.

A much more serious problem with the plot arises from the evolution of the public controversy, which proceeds roughly as follows: after getting no sympathy from coworkers and colleagues, Robin goes to a disgruntled ex-member of the Glass/Mendelssohn group, who passes her suspicions along to two self-anointed fraudbusters at the "Office for Research Integrity in Science" of the NIH, who launch a full-blown investigation that attracts the attention of a powerful, abrasive Congressman, who summons the group to a hearing. . . .

Does this begin to sound familiar? It should: these developments (and many others) closely track those of the Imanishi-Kari/O'Toole conflict from the 1980s, well documented by former

Caltech historian of science Dan Kevles in his 1998 book *The Baltimore Case*. Borrowing from real life is, of course, common practice, but the book contains the usual disclaimer: "Any resemblance to actual persons, living or dead, events, or locales, is entirely coincidental." Expecting us to believe *that* is asking far too much of coincidence; nor is there any mention of any precedent or sources in the acknowledgments. It is ironic, and more than a little disappointing, that in exploring the subject of intellectual misconduct, the author might be charged with having committed a pretty good dose of it on her own part. □—*JL*

Jay A. Labinger is a Faculty Associate in Chemistry and an occasional book reviewer for E&S.



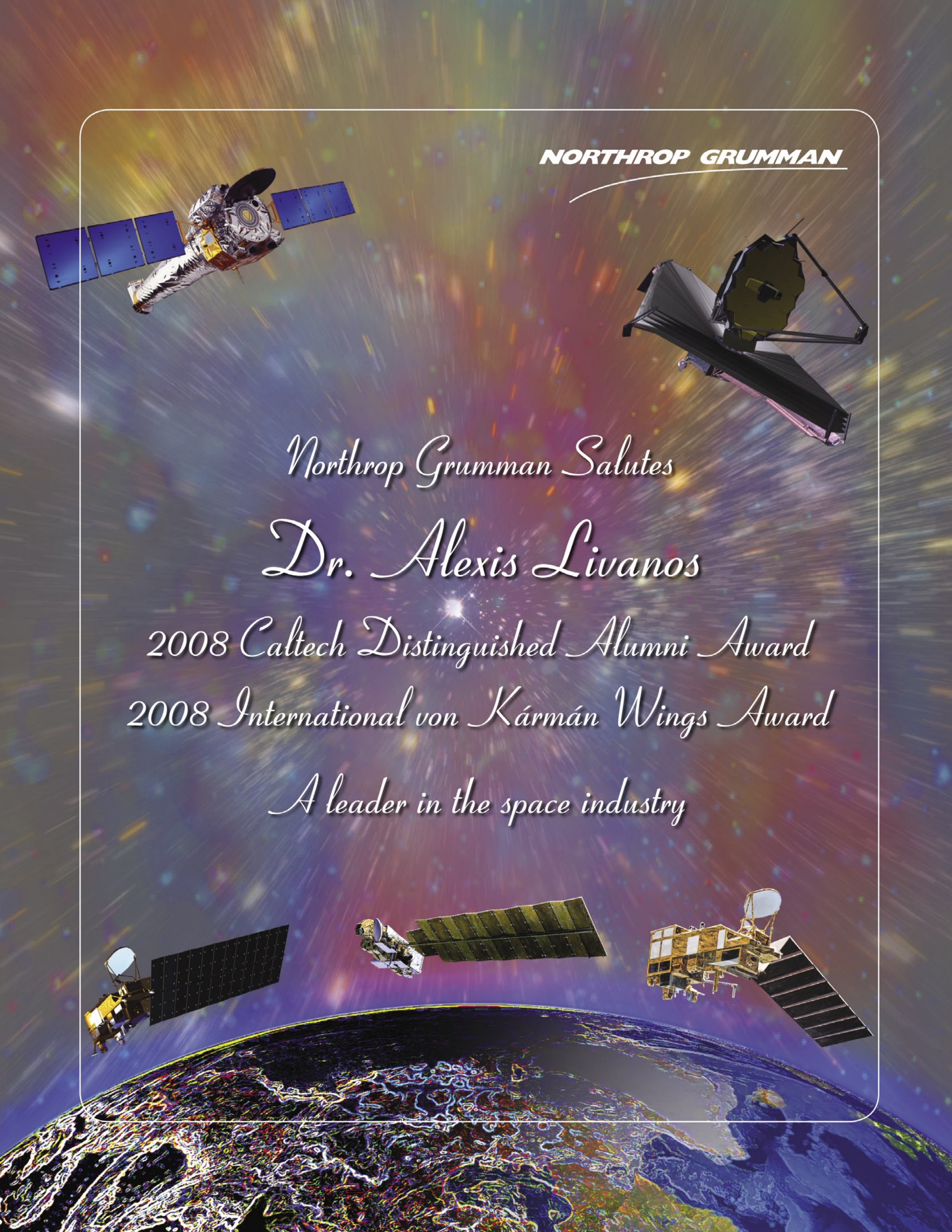
The Drunkard's Walk: How Randomness Rules Our Lives
Pantheon Books, 2008
252 pages
$24.95

According to the cliché, the only certainty in life is uncertainty. But while tragic accidents, lucky breaks, and close calls often determine the difference between success and failure—or even life and death—our fates aren't just the result of rolling the dice. At least so says Leonard Mlodinow, a lecturer in statistics and computation and neural systems and author of *The Drunkard's Walk: How Randomness Rules Our Lives.* His new book argues that by understanding the profound role of randomness in our daily lives, we can not only make better decisions and acquire a deeper perspective of the world, but also recognize that in many cases, the power to control our destinies is still within our grasp.

The title is taken from a mathematical description of random motion—such as the random path of an air molecule traveling across a room—and, as Mlodinow notes, serves as a metaphor for our meandering lives. *The Drunkard's Walk* is a highly readable tour of probability and statistics, taking us on a narrative path that isn't random, but deliberate and illuminating. Mlodinow shows how we frequently misjudge randomness—underestimating the significance of randomness in business and sports, and seeing patterns where there are none. The history of how mathematicians developed the tools to understand probability and statistics over the last several hundred years forms the narrative backbone, serving as a springboard for introducing basic mathematical concepts. The book, however, is at its best when discussing statistics with contemporary examples, such as the O. J. Simpson trial, psychology experiments, and baseball.

Laced with humor and chock-full of anecdotes and examples, *The Drunkard's Walk* makes statistics clear and entertaining, and challenges us to think more critically. Mlodinow writes, for example, about inherent errors in political polling and standardized tests. And while engrossed in stories of lottery-winners and girls named Florida, the reader learns about Pascal's triangle and Bayesian statistics while hardly realizing it.

In the more speculative and final chapter, Mlodinow argues that chance plays as big a role—if not the biggest—in determining our individual successes as talent, citing the lucky breaks that sparked the careers of Bruce Willis and Bill Gates. For the rest of us floundering around the middle of the bell curve, the recognition that the successful aren't necessarily the best lends some hope. Just as throwing the dice more often improves the chances of winning at the craps table, persistence in life increases the probability of success, Mlodinow says. The moral is another well-worn message: despite the inherent ups and downs of life, we should never give up. □—*MW*



NORTHROP GRUMMAN

Northrop Grumman Salutes

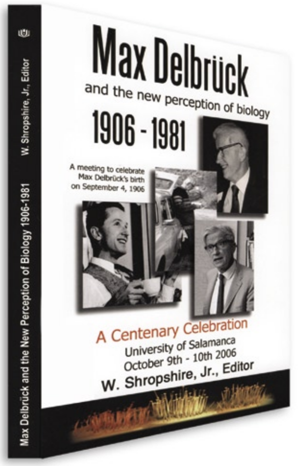
Dr. Alexis Livanos

2008 Caltech Distinguished Alumni Award

2008 International von Kármán Wings Award

A leader in the space industry

Books (cont'd)



Max Delbrück
and the New Perception of Biology
AuthorHouse, 2007
279 pages
$15.49

Max Delbrück (1906–1981) was a founding figure of molecular biology, sharing the 1969 Nobel Prize in Physiology or Medicine for his work on gene replication. A physicist by training who began his career in the lab of Lise Meitner, he became interested in genes in the 1930s and had already made important contributions before becoming a Caltech professor in 1947; he remained on the faculty here for the rest of his life. This book collects the reminiscences given at a celebration at the University of Salamanca in honor of his centenary year—one of three such; for an account of the Caltech one, see *E&S*, 2007, No. 1. The editor, Walter Shropshire Jr., was a research fellow in biology at Caltech from 1957 to 1959. □—*DS*

Letters

I very much enjoyed your article about the late David Elliot. I was an undergraduate at Tech in the 1963–67 time period, and had the great good fortune to be able to take history courses from both Elliot and Huttenback, and English courses from Peter Fay (and I learned to write for news from your predecessor).

The courses about the British Imperial experience in India were absolute gems, taught by people who had been part of the Raj and understood it from both the point of view of historians and participants.

My favorite experience was a class meeting at the Huttenback's home—he was at that point the Master of Student Houses as well as a history professor—and one of the students asked the Huttenbacks and Elliot what it was actually like to live for a number of years in India at that time. Mrs. Huttenback's eyes narrowed ever so slightly, and then she smiled and gently asked, "Do you know that there are seven different kinds of amoebic dysentery?"

BTW, I was an unlikely Caltech student. My father had been professor of California history at City College of San Francisco, and my mother was an English teacher. . . .

Thanks again for your article. Keep up the good work!

Robert D. Parker (BS '67)

Caltech and JPL have left an indelible imprint on the historical record. Among the outstanding faculty are many who have reached beyond their original fields in academe, and pursued new horizons with vision and courage. My father, Fritz Zwicky, was a pioneer in the field of astronomy and astrophysics, pronouncing the amazing theory of Dark Matter in the 1930s. It is not widely known that his efforts also extended to jet propulsion. While serving as research director at Aerojet Engineering Corporation (1943–1949), he helped develop the JATO motors referred to in your article ["From Rockets to Spacecraft: Making JPL a Place for Planetary Science," by Eric M. Conway, *E&S* 2007, No. 4]. He also holds important patents in jet propulsion, including for ramjets and hydrojets.

The enclosed photograph shows him receiving the Presidential Medal of Freedom, given to him at the Aerojet offices in Azusa on September 21, 1949, for his wartime efforts. Dan A. Kimball, Undersecretary of the Navy for Air, is pinning the medal on his lapel while Brigadier General T. C. Chapman of the U.S. Air Force assists. The citation reads, in part, "As Technical Representative, United States Strategic Air Forces in Europe, he contributed immeasurably to Air Technical Intelligence. His initiative, remarkable linguistic abilities, broad knowledge of physics and chemistry as pertains to the art of rocketry—together with an outstanding ability to exploit a foreign technology in rockets, guided missiles and associated equipment for further utilization by the United States, made his services most valuable to our war effort."

Barbarina Zwicky

E&S *welcomes letters. Send correspondence to Editor,* E&S *magazine, Caltech Public Relations, Mail Code 1-71, Pasadena, CA 91125, or e-mail dsmith@caltech.edu. We reserve the right to edit any letters selected for publication for length, content, and clarity.*

GIUSEPPE ATTARDI
1923 – 2008

Giuseppe Attardi, whose work linked degenerative diseases and aging to genetic mutations, died at his home in Altadena on Saturday, April 5. He was 84 years old.

Attardi, Caltech's Steele Professor of Molecular Biology, was among the first scientists to delve into the processes through which DNA's information is transferred. He identified all the genes in the DNA in human mitochondria—the organelles in plant and animal cells that help convert food into energy. He then developed techniques for investigating genetic diseases, including Alzheimer's, and for studying aging in general, which he discovered is associated with changes in mitochondrial DNA (mtDNA).

Born in 1923 in Vicari, Italy, a Sicilian town of fewer than 3,000 people, Attardi earned an MD from the University of Padua in 1947. He remained there for almost 10 years as an assistant professor in the Institute for Histology and General Embryology.

Attardi visited Caltech on a Fulbright Fellowship in 1959–1960. He returned for good in 1963 as an assistant professor of molecular biology and was promoted to associate professor that same year. It was at Caltech that Attardi turned his interests to mitochondria, establishing that mtDNA is an active, working genome, independent of the genomes of the cells in which the mitochondria reside. This spurred research into the organelle's genetic machinery.

Associate Professor of Biology David Chan calls Attardi a leading figure in identifying the products and functions of the mitochondrial genome. Attardi and a student developed a technique in which they replaced the mtDNA of a human cell line with the mtDNA from diseased cells. This allowed them to distinguish the roles of mtDNA and the genome of the nucleus —where the rest of a cell's DNA resides—in causing the disease. With this technique, they could also examine the relationship between changes in mtDNA and changes in cell function caused by the disease. "Many labs have used his approach to understand how mutations in mtDNA diseases affect mitochondrial function," Chan says.

"Giuseppe was one of the founders of what is now a central and still-expanding area of molecular cell biology," adds Attardi's colleague and friend Gottfried Schatz, emeritus professor of biochemistry at the University of Basel's Biozentrum, in Switzerland. "His unique insights bore magnificent fruits with the landmark description of the transcription map of mammalian mtDNA, as well as the precise characterization of the mechanism of mitochondrial diseases and the dynamics of human mitochondrial genomes."

In recent years, Attardi's lab has focused on how mtDNA replicates, on detecting mutations that result from aging, and on discovering what effects those mutations have. The team found that older people carry a significantly greater number of genetic defects in a specific region of their mtDNA, suggesting that cell aging begins in the mitochondria.

"He has been a central figure in mitochondrial research for several decades. One of the things I will always remember about him is his constant excitement for all types of biological questions," Chan says. "I think his intense curiosity is one reason he accomplished so much as a scientist."

Schatz adds, "To him, science was everything, and he never tired of discussing the latest experiments. Yet he also embodied a vanishing breed of scientists whom I would define as 'gentlemen intellectuals.' He had a superb grasp of European history and world culture, had mastered French and German at a very high level of proficiency, and even in his most spirited discussions refrained from personal invective or overt aggression. To me, he was an example of how science can keep us young in spirit, and ennoble us."

Attardi's awards include two Guggenheim Fellowships; election to the National Academy of Sciences; the Antonio Feltrinelli International Prize for Medicine from the Accademia Nazionale dei Lincei; the Passano Foundation Award in 2000; and the Gairdner Foundation International Prize.

Attardi is survived by his wife and colleague, Anne Chomyn (PhD '79), senior research fellow, emeritus; a son, Luigi Attardi, of Rome; a daughter, Laura Attardi, of Palo Alto, who is a professor of cancer biology at Stanford University; and a grandson, Marcello Attardi, of Palo Alto. ☐—*EN*

J. KENT CLARK
1917 – 2008

On Friday, May 2, Professor of Literature, Emeritus, J. Kent Clark—Caltech's own Tom Lehrer—had his final show at the Athenaeum. The celebration of Clark's life (he had died of heart failure on March 3) played to a packed house and included live performances of six of Clark's songs, including "The Richter Scale," which has had nationwide airplay on the Dr. Demento Show. (For the lyrics, see E&S *2007, No. 1, page 43.) Between numbers, colleagues and family members told—largely in his own words, as culled from his oral history and other sources—his story and the story of the Caltech Stock Company, formed in a time when life was slower and faculty members had the leisure to rehearse musical revues.*

Justus Kent Clark was born on September 29, 1917, on the Utah-Idaho border. Emcee Michael Boughton (BS '55) introduced him thus: "I had two polygamist great-grandfathers. One of them [Clark's namesake, Israel Justus Clark] and one grandfather spoke Shoshone better than the Shoshones. Among the first sounds I remember are the howl of coyotes and the blast of my father's 16-gauge Remington as he shot sagehens to feed the threshers. Well, Rod [Rodman Paul, a history professor and expert on the American West] and I used to discuss frontier topics once in awhile, and one day he said, 'Kent, why don't you write Western History?' I said, 'Rod, I don't *have* to write Western History; I *am* Western History.'"

Clark's father was a wheat farmer who lost the property in the post-World-War-I agricultural depression, forcing the family to move first to Brigham City and then Ogden, Utah. Recalled son Jeff, "Dad spent many summers living with his mother's family on the Kent farm. Here he was exposed to the legendary Kent fondness for traditional music, music that would tell stories." Clark's own aptitude surfaced early—in the fourth grade, he, with big sister Mary on the piano, "won second prize and the then-munificent sum of two dollars and fifty cents (about $40.00 these days)" in a talent show.

Clark studied English at Brigham Young University. In the spring of his junior year, he decided to forego his usual summer job at a grain elevator for something more fun. He wrote, "Utah Parks, which ran Bryce [Canyon National Park], hired kids there—college kids—to be bellhops and waitresses and so on, and the kids put on shows every night. They were really hired for their musical talent." So he worked up "a repertoire of songs, including some hillbilly numbers" with a couple of friends, hitchhiked 250 miles to Cedar City, and talked his way into a job for the three of them—sans audition. He met his first wife, Ora "Christie" Christensen, at BYU; they married in 1939, just in time to go to Stanford, where he had been accepted into the English doctoral program.

Upon passing his orals in 1943, he got drafted and sent to radar school in Tampa, Florida, "home of cockroaches and mosquitoes, but nicer than, say, Iwo Jima or Normandy." As a second lieutenant, he served as supply officer for a radar outfit in the Philippines and honed his bridge game. "The electrical engineers of the Battalion could all count to thirteen, and [we] played bridge every night."


"Clark and Davis, shows written while you wait." Elliott Davis, at the piano, and Kent Clark—also frequently known as "Man Super"—work up some material in this 1960s photograph.

Clark returned to Stanford upon his discharge, but grading papers for composition classes left no time for his own research. Caltech offered him an instructorship in 1947. "They doubled my salary and halved the size of my classes, and they had the Huntington Library a mile away, where I could do my doctoral dissertation on Jonathan Swift's politics. I thought I would return to Stanford after the dissertation was done, but . . . I made a wonderful discovery. Caltech undergraduates were actually bright across the board—with higher verbal aptitudes than the students at Stanford."

The couple had three children, daughter Kay and sons Jeff and Don, born at four-year intervals. Said Don, "Dad's motto was, 'No two in college at the same time.'"

Don described Kent's reentry into showbiz. "Dad recalls, 'In 1953, when my daughter was at Allendale Elementary, we put on a PTA show. A talented clown named Elliott Davis, who plays the piano brilliantly and has a fine musical imagination, and I got together and wrote the first of three shows for Allendale.' Elliott was a self-described 'kept lawyer,' working for a large insurance underwriter, who had worked his way through college playing piano and banjo. My dad would often present him with words and a skeletal tune, which Elliott would enhance and wrap chords around.

"One of my favorites from the PTA shows is 'Give Us Men,' sung by women about the benefits of getting men to turn up at PTA meetings. I've always admired this refrain: 'Teas don't please us, please don't tease us, we won't go there./We won't meet unless you seat a man or so there.'"

Word got around, and in 1954 Clark was asked to organize *The Road to Stockholm* in honor of chemistry professor Linus Pauling's (PhD '25) first Nobel Prize. He dragged Davis in, of course, and the next year *This is Science*, performed for a meeting in Pasadena of the American Association for the Advancement of Science, drew 1,500 people. "As my dad says, 'It was the first full-length show we did. From there it was like getting into sin.'"

And thus was born the Caltech Stock Company, composed of faculty, staff, students, and spouses—"the brightest cast in show business," Clark used to call them. Over the next 20 years, the company would perform 10 full-length musicals, and innumerable special shows, with Clark and Davis doing book and music.

Clark wrote, "I had stumbled into an egghead's paradise and an inexhaustible source of musical comedy. . . . Besides its own vocabulary, where 'troll' means what is now 'nerd,' Caltech has the wacky, bright, polysyllabic vocabulary of science.

"Now, the Caltech Stock Company was a special subset of the Caltech family devoted to musical comedy, to honoring our great friends, and to explaining the family to itself. . . . You don't become a real member of the Caltech faculty and family simply by signing a contract and showing up. . . . You know you've arrived when you quit saying 'those flakes' and start saying 'our flakes.'"

Clark's lyrics were uniquely erudite, said Don—for example, in "Los Angeles," (*What Makes Beadle Run*, 1961) "The air they breathe is loaded with ozone and tar/The bees all wheeze, and the birds all have chronic catarrh."

Christie Clark died in 1970, and in 1972 Kent married Joanne Straub Goldman, a union that ended in divorce in 1987. In 1992, he married Carol Brunner Pearson, his research assistant at the Huntington Library since 1958.

Emcee Boughton recounted Clark's self-described "one and only contribution to the happiness of the Huntington," abetted by noted Shakespeare scholar Hardin Craig. "When I came to the Huntington, all the men, staff and scholars, wore jackets and ties; and Mr. Gifford (once butler to Henry Huntington) looked positively starched as he sat at the entrance desk. Well, one day when I didn't have classes at Caltech, which also demanded coats and ties, I came to the Huntington in a sports shirt. You should have heard the buzz. I thought they might throw me out bodily, and staff member Mary Isabel Fry asked, in a stage whisper, if I was wearing my pajama tops. I stuck it out, but it seemed clear that I'd better not try it again. Then the miracle happened. Next day Hardin Craig showed up in a sports shirt—and that was that. Papa Craig ranked just below, or slightly above, the Holy Trinity, and no one dreamed of criticizing him. The dam had broken and from that day to this, men have been wearing sports shirts at the Library."

Some of the cast of ***Beautiful Beckman*** **(1975), the Stock Company's last full-length musical. In rear, on table, from left: Shirley Marneus, soon to be the founder and director of Caltech's theater arts program, and Dan Erickson. Middle row, standing: Gary Lorden (BS '62), associate professor of mathematics; Dave Wood (BS '41, MS '46, PhD '49), professor of materials science; Bill Corcoran (BS '41, MS '42, PhD '48), professor of chemical engineering and vice president for institute relations; Dick Dean (BS '45), professor of mathematics; Bob Oliver, professor of economics; Ward Whaling, professor of physics; Ed Hutchings, editor of *E&S*; Jim Knowles, professor of applied mechanics. Front row, kneeling: Cynthia Corngold; Clark; Connie Wood; and Jackie Knowles.**

Alan Jutzi, the Huntington's curator of rare books, told how, with Swift as his springboard and the library's holdings to dive into, Clark became an expert on English history of the late 17th and early 18th centuries. His favorite subjects were Swift's political enemies, the Whartons—Thomas, the earl, and Goodwin, whom Clark called "the flaky brother," writing, "If Goodwin Wharton had not existed, he could not have been invented." This led to two scholarly biographies: *Goodwin Wharton* (1984), and *Whig's Progress: Tom Wharton between Revolutions* (2004), and a historical novel, *The King's Agent* (1958), which Clark said "made him rich for three weeks."

Jutzi also spoke of the Huntington's lunchtime bridge games, where he claimed Kent and Carol *really* met. A score of 6,280 points on July 15, 1974, caught the attention of nationally syndicated bridge guru Alfred Sheinwold, who "visited for one hour in 1977 and went away with several games that made his column. The bridge Tzar of all this was Kent . . . followed with no less exuberance by Carol."

Professor of English, Emeritus, Jenijoy LaBelle, Caltech's first female professor, who asked to be introduced as both family member and flake, described what Clark called "his greatest contribution to undergraduate education." She said, "Were it not for Kent, I might not be standing before you today as a member of the faculty. This isn't the place to speak about my tenure case in the '70s, but my heart will always be full of gratitude to Kent for his support. . . . He championed me by writing letters, memoranda, and his famous screed. I know that his biography on Goodwin Wharton, published by Oxford, would have come out three or four years earlier had he not devoted so much of his energy and his considerable talent for irony to my struggle."

Boughton had the last word. "Behind it all, however, was Kent the teacher. We learned that even professors could enjoy life, and we were encouraged to do so also. Somehow the core of talent we were could be enriched, and it didn't even hurt very much.

"He taught me to read—Homer, Shakespeare, Swift, Joyce, Maugham, Salinger. Even the *Chicago Tribune*. . . .

"With those as implements, he split open a narrow reverence for hard science to let in a world of words to be savored and thought about."

Clark is survived by his wife, Carol, three children by his first wife, three stepdaughters, four grandsons, and one stepgrandson. ☐—*DS*

WE AREN'T
BIG TALKERS,
BUT OUR NUMBERS
SURE ARE.

FOR THE SECOND YEAR IN A ROW, TIAA-CREF RANKS IN THE TOP 10 OF THE LIPPER/BARRON'S FUND FAMILY SURVEY, RANKING #9 OF 67 FUND FAMILIES FOR 2007.*[1]

A high ranking in the survey means we've had strong performance for our participants and their retirements, no small feat considering the recent volatility of the market. We've maintained our position near the top not by chasing trends, but by delivering steady performance to create consistent growth over time.

Call 800 TIAA-CREF or visit tiaa-cref.org/investments to learn more.

*Based on asset-weighted total returns.

TIAA CREF

FINANCIAL SERVICES FOR THE GREATER GOOD®

[1] The Lipper/Barron's Fund Family survey uses an asset-weighted ranking system. Each fund's return was measured against all those in its Lipper category, and the resulting percentile ranking was then weighted by asset size relative to the fund family's other assets in its general category. The family's overall ranking was then determined by weighting the five fund categories in proportion to their overall importance within Lipper's fund universe. Due to the fund merger in April 2007, the TIAA-CREF mutual funds are no longer eligible for inclusion in the 5-year ranking. Ten-year rankings are not yet available. TIAA-CREF ranked 7th out of 67 in the 2006 Lipper/Barron's one-year survey and 38th out of 62 in the 2006 five-year survey. Past performance cannot guarantee future results. **All TIAA-CREF investment vehicles are subject to market and other risk factors.** TIAA-CREF Individual & Institutional Services, LLC, and Teachers Personal Investors Services, Inc., Members FINRA, distribute securities products. C41426 © 2008 Teachers Insurance and Annuity Association-College Retirement Equities Fund (TIAA-CREF), New York, NY 10017.

Consider the investment objectives, risks, charges and expenses carefully before investing. Call 877 518-9161 or visit tiaa-cref.org for a current prospectus that contains this and other information. Read it carefully before investing.

Engineering & Science

California Institute of Technology
Pasadena, California 91125