bines climate sensitivity and carbon cycle feedbacks (2), is most important for a more reliable estimate of which climate targets are still achievable.

As the emissions scenarios considered here illustrate, even well-intentioned and effective international efforts to limit climate change must face the hard physical reality of certain temperature targets that can no longer be achieved if too much carbon has already been emitted to the atmosphere. Both delay and insufficient mitigation efforts close the door on limiting global mean warming permanently. This constitutes more than a climate change commitment: It is the fast and irreversible shrinking, and eventual disappearance, of the mitigation options with every year of increasing greenhouse gas emissions.

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PLANETARY SCIENCE

A Wet and Volatile Mercury

Observations by the MESSENGER spacecraft are revealing details of Mercury's dynamic atmosphere.

Paul G. Lucey

One of the more startling discoveries in planetary science was that the poles of Mercury feature deposits that are extremely bright at radar wavelengths (1), interpreted to be due to the presence of thick water ice. Because Mercury's rotation axis is almost normal to the plane of its orbit, the temperature of polar craters largely or completely shaded from the Sun should be very low. On the Moon, for example, where the rotation axis tilt is similarly small, the polar temperatures in permanently shadowed regions have been measured by infrared radiometry to be as low as 25 K (2). These topographic depressions might be expected to contain cold-trapped volatile material that might be introduced by comets, water-bearing asteroids, or other sources. On pages 292, 300, and 296 of this issue, Lawrence et al. (3), Paige et al. (4), and Neumann et al. (5) report on the latest results from the MESSENGER (MErcury Surface, Space ENvironment, GEochemistry, and Ranging) mission confirming the expectations that the atmosphere of Mercury is indeed a wet volatile one, as well as providing the odd surprise.
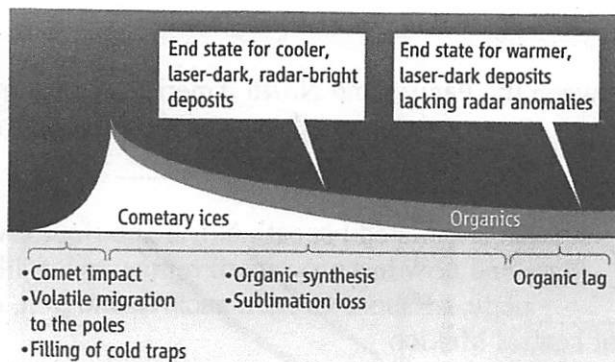
Compounds other than water ice have been suggested to account for the radar observations, with sulfur being of particular interest given the extremely high temperatures of equatorial Mercury and the abundant evidence for volcanic activity on the small planet (6). However, Lawrence et al. report depressed neutron fluxes at Mercury's north pole and show that only high concentrations of hydrogen confined to the known radar-

bright locations are consistent with the neutron flux measured at both high and intermediate energies. Thermal modeling supports their conclusion. Paige et al. apply a thermal model of the polar Moon to polar Mercury to estimate the surface and shallow subsurface temperatures, supported by detailed topography measured by the MESSENGER laser altimeter and validated with lunar remote radiometric measurements. They find that the radar-bright areas are almost exclusively confined to places where shallow subsurface temperatures hover near 100 K or less, and owing to the exponential dependence of vol-

Atmosphere dynamics. Mercury's polar cold traps appear to have been filled by one or more comet impacts that introduced massive quantities of water and other volatile vapors in the tenuous atmosphere that promptly migrated to the polar cold traps. Ices began to immediately sublimate, and to acquire organic lag deposits, probably from radiation-induced chemical synthesis. The colder parts of the poles now exhibiting radar anomalies retained water ice below the lag deposit, while in warmer portions the ice entirely sublimed away, leaving the low-reflectance organic residue. Not depicted are the rare very-high-reflectance spots that are confined to the coldest portions of the pole. These may indicate a slow continuous production of water from small wet meteorites, solar wind proton interactions with oxygen in Mercury's surface, or inhibition by the very low temperatures of the organic synthesis occurring elsewhere.

 atility on temperature, water is the only compound with the right volatility and cosmochemical abundance to account for the radar anomalies. On the other hand, maximum temperatures experienced by most of these radar-bright regions are too high to sustain surface ice, so that if ice is responsible for the radar features, it must be buried by a few centimeters of insulating material, such as dry Mercury soil.

These results fulfilled promises made by the MESSENGER scientists that Mercury's enigmatic polar volatile would be identified. But polar measurements contained a major surprise. The laser altimeter carried on the spacecraft, which provided the topographic measurements enabling the detailed thermal modeling, also measured the reflectance of Mercury's surface in the unilluminated polar regions. This instrument compares the strength of the outgoing laser pulse to the return power, normalized to the range to the surface. Pioneered on Mars and the Moon, this method measures the normal albedo of the surface without the influence of local topography or the need for solar illumination, which is weak or absent at the poles. Before MESSENGER's arrival at Mercury, it was anticipated that bright surface deposits of ice or sul-

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1. MATCHING

____ Composition of the upper crust   1. peridotite

____ Presumed composition of the lower   2. 100-200Km
crust.

____ depth of the first mantle transition zone   3. 200-300Km

____ mineralogical change in this zone   4. 400Km

____ depth of the second mantle transition zone   5. 700Km

____ mineralogical change in this zone   6. 700-3000 Km

____ depth range of the lower mantle/mesosphere   7. 3000-4500 Km

____ depth range of the asthenosphere for most   8. spinel to perovskite
    authors.

____ source of the geomagnetic field   9. olivine to spinel

                                                        10. silicic igneous and meta rx

                                                        11. basic "   "   "   "

2. The boundary between the Pacific and North American plates in the Gulf of California consists of _____ (plate boundary type) that trend/strike ___ - _____ alternating with _____ (aa) that trend ___ - _____.

3. The once giant plate that subducted beneath North and South America is called the _____ Plate and now has only small remnants left like the _____plate, offshore Oregon and Washington, or the _____ plate offshore of central Mexico.

4. What rock property do you need to know to convert 2-way reflection times into depth?
_____

5.   Match the <u>BEST</u> V_p value/range of values to the "lithology".

_____ .   most clastic sedimentary rocks   1. 1000'/s (320 m/s)
_____   rocks need to be blasted   2. 2,500'/s
_____   most silicic igneous & meta rocks 3. 5,000'/s (1.5 m/s)
_____   top of mantle   4. 2 to 5 Km/s

fur might be associated with the radar anomalies. Neumann *et al.* did find this association, but also found the opposite—that the surfaces of the radar anomalies are not bright, but are typically quite dark relative to average Mercury reflectance with rare exceptions.

Paige *et al.* synthesized these observations to suggest that the dark deposits are due to organics more refractory than water ice, either directly deposited with the ice as part of the same process, or formed in situ by a low-temperature organic synthesis. Production of organics by irradiated cometary ices is well established in the laboratory and has been invoked to explain planetary and astrophysical observations of comets and the interstellar medium (see the figure). Paige *et al.* suggest that as a result of exposure to solar wind and ultraviolet radiation, complex organic radiolytic products are formed from ices and accumulate as a protective lag

deposit that ultimately shields ice from further sublimation. They further note that dark deposits are observed to be more extensive than radar-bright material, and also occur in locations with somewhat higher model temperatures. This is evidence that ice deposits were more widespread in the past, and that the dark deposits in areas with higher temperature and lacking radar anomalies are relic deposits of this earlier era. A few restricted portions of the polar surface are substantially brighter than typical for Mercury, and Paige *et al.* show that these surfaces are cold enough to preserve surface frost against sublimation loss.

Prior to the MESSENGER results, polar ice at Mercury (and the Moon) was generally accepted, but the new data reveal a dynamic history of these deposits. The presence of the organic lag deposits strongly indicates that comets are the source of the polar volatiles, because other proposed sources are barren

with respect to the critical elements needed for organic synthesis. The results also show that the charging of the cold traps can temporarily overcome thermal instability and can be used to derive a high lower limit on the amount of water vapor that can be at least transiently retained in a transient atmosphere of Mercury in a comet impact to account for the distribution of the dark deposits.

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CHEMISTRY

Re-Engineering Nature's Catalysts

Alison R. H. Narayan and David H. Sherman

An engineered enzyme catalyzes a reaction that is fundamentally different from that catalyzed by the natural enzyme.

Natural systems have inspired many scientific and technological advances (*1*). Materials design seeks to duplicate the fiber optical features of glass sponges (*2*); inorganic chemical complexes are modeled after enzyme active sites; and synthetic chemistry strategies parallel the biosynthetic pathways that produce complex natural product molecules (*3*). Scientists have also directly manipulated nature's tools through enzyme and metabolic pathway engineering. On page 307 of this issue, Coelho *et al.* (*4*) report that a bacterial cytochrome P450—a protein that naturally catalyzes C–H bond oxidation—can be engineered to efficiently produce highly strained cyclopropanated products. This work demonstrates the biomimicry paradigm in reverse, where altering the function of one of nature's most versatile biocatalysts is directed to a transformation originally conceived and implemented by synthetic chemists.

Throughout evolutionary time, enzymes have continuously morphed to perform specific functions on defined substrates in living cells. Advances in molecular biology have enabled new strategies to maximize the synthetic utility of particular enzymes and

to expand their substrate scope and catalytic activity. Directed evolution is one of the most successful approaches toward achieving these goals (*5*). This method is a laboratory-based, accelerated version of natural evolution. Mutants with beneficial properties are advanced to subsequent rounds of mutagenesis in an iterative quest for the ideal enzyme. This approach has proven fruitful for altering the substrate scope for numerous target enzymes. For example, Arnold *et al.* evolved P450$_{BM3}$ to selectively hydroxylate ethane, a much smaller molecule than the natural fatty acid substrate, to afford ethanol (*6*). Directed evolution has also been used to identify thermally stable enzyme mutants (*7*) or variants that function effectively in organic solvents (*8*).

These accomplishments have advanced the field of enzymatic catalysis. However, many continue to overlook the utility of enzymes compared to the endless modes of reactivity that can be probed and discovered by synthetic chemists. With a specific function ingrained in a protein's native design, is it possible to completely re-engineer its function through iterative mutagenesis of its corresponding gene?

To access a totally new form of catalysis requires more than just library screening of a target enzyme. This feat demands a funda-

mental understanding of the enzyme's structure and function combined with chemical intuition. In a pioneering study, Wilson and Whitesides used an oversized protein ligand to create a chiral environment around a metal complex. These artificial metalloenzymes, with biotin-tethered metal complexes bound to streptavidin, catalyzed asymmetric hydrogenation reactions (*9*). The power of this approach was recently expanded by Hyster *et al.*, who used biotinylated rhodium(III) complexes with streptavidin mutants for asymmetric C–H activation. The study demonstrated the influence of key second sphere residues on the reactivity and selectivity of the enzyme (*10*).

Although progress has been made to optimize the native function of enzymes, the ability to leverage an individual active site to catalyze a new type of reaction remains a greater challenge. To achieve this goal, Coelho *et al.* selected diazoester carbene precursors as their cyclopropanation reagent. These compounds form metallocarbenoids with metals such as Rh, Ru, Cu, Co, and Fe (*11*). From the metallocarbenoid intermediate, cyclopropanation occurs through the transfer of the carbene to a double bond.

Coelho *et al.* screened 92 structurally and functionally diverse P450$_{BM3}$ mutants from a larger library. They found five candidates,

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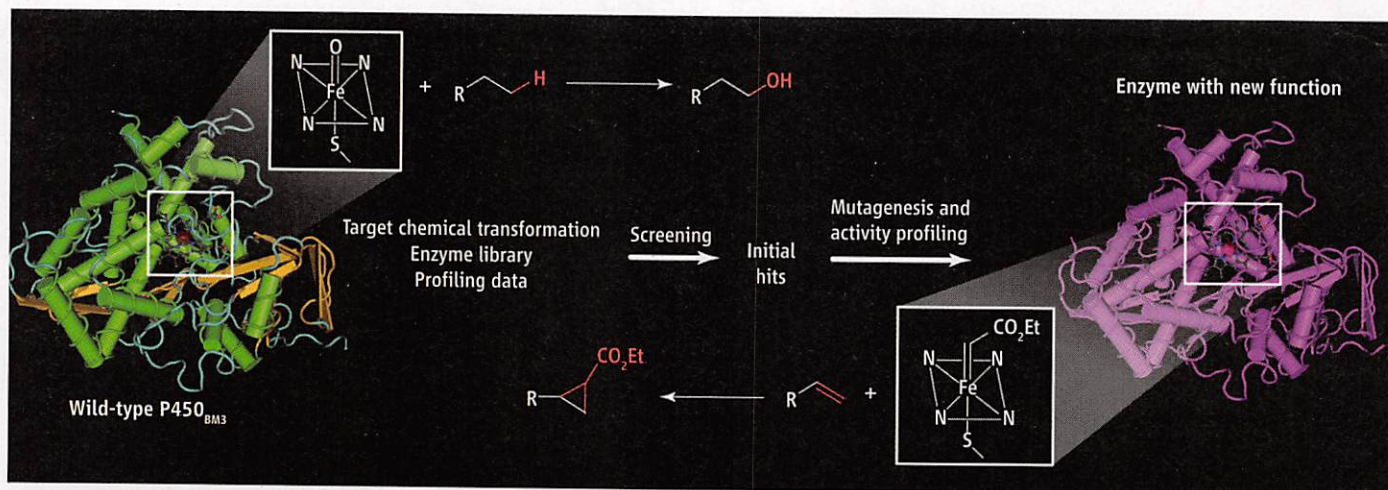
Biomimicry in reverse. The natural P450 monooxygenase enzyme catalyzes C–H bond oxidation. Through judicious choice of enzyme and substrate followed by directed evolution, Coelho et al. have re-engineered this protein to perform a different catalytic reaction, namely cyclopropanation.

which they evolved further to a suite of diastereo- and enantioselective cyclopropanation catalysts that can favor either a cis- or trans-cyclopropane product.

An existing library of P450$_{BM3}$ variants and information on the native functionality of these proteins facilitated this impressive example of engineering new enzyme reactivity. Pairing library screening with additional information on structure and function provides an appealing model for streamlined, directed evolution efforts. For example, Fasan et al. recently reported the devel-

opment of P450 enzymes for the regio- and stereoselective oxidation of the human antimalarial drug artemisinin. The authors performed first-sphere active-site mutagenesis, followed by high-throughput screening with a panel of model compounds; they then used the reactivity data to predict substrate scope and to drive further protein evolution efforts (12).

These studies show that translating classical synthetic chemical transformations into versatile chemoenzymatic reactions is ripe for expansion. However, going from a promising idea on paper to an efficient enzymatic transformation remains a formidable challenge. Drawing on multiple sources of information—such as computational modeling, x-ray structural data, reactivity profiles, and high-density library design derived from iterative mutagenesis

and screening—will be essential for building a wide variety of new functions into nature's complex catalysts.

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MATERIALS SCIENCE

Polymer Rigidity Improves Microporous Membranes

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> Microporous membranes with rigid polymer chains have high gas permeability but can separate gas molecules of slightly different sizes.

G as separation with membranes has been commercialized for more than 30 years, and includes processes such as the production of nitrogen (N_2) from air and the removal of carbon dioxide (CO_2) from natural gas. Commercial membranes have been largely derived from poly-

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mers with moderately rigid chains that pack closely to create small intermolecular spaces (or "free volume") that impart moderate to high gas selectivity. However, their relatively low gas permeability slows down the separation processes. Microporous organic polymers (MOPs) (1–3) offer higher permeability, but the polymer chains must be made sufficiently rigid to maintain good selectivity. On page 303 of this issue, Carta et al. (4) describe a soluble, highly rigid MOP, from which a highly permeable membrane with

good selectivity was fabricated. For example, oxygen (O_2) and N_2 have only a 5% difference in kinetic diameters (which are related to the smallest effective dimensions of the gases), but the gas throughput of the smaller O_2 molecule is very much higher through their membrane.

Gases are separated by first pressurizing gas mixtures in contact with the membrane; each component sorbs (dissolves in it) and diffuses (passes through the free volume) through it at different rates with a character-