

systems indicate synchrony of the two events, but comparison between the two systems would suggest discrepancies unless errors in decay constants (and standards for the  $^{40}\text{Ar}/^{39}\text{Ar}$  method) are considered. Thus, the ages for the Permian-Triassic boundary are  $251.4 \pm 0.4$  million years ago ( $^{206}\text{Pb}/^{238}\text{U}$ ) and  $250.0 \pm 4.4$  million years ago ( $^{40}\text{Ar}/^{39}\text{Ar}$ ), clearly not statistically resolvable. Neglecting uncertainty in  $^{40}\text{K}/^{40}\text{Ar}$  data for the  $^{40}\text{Ar}/^{39}\text{Ar}$  standard, which compounds decay constant error, only decreases the absolute error to  $\pm 3.6$  million years.

The precisely known decay constants for  $^{238}\text{U}$  and  $^{235}\text{U}$ , as well as the existence of internal reliability criteria in the U-Pb systems (9), offer a "gold standard" for geochronology and cosmochronology. Normalization of other radioactive systems' decay constants to those of  $^{238}\text{U}$  and  $^{235}\text{U}$ , either directly or indirectly by comparison with the  $^{207}\text{Pb}/^{206}\text{Pb}$  system (10), provides advantages over disintegration counting in experimentally difficult cases such as the

low-energy  $\beta$  decay of long-lived radionuclides. Naturally, such normalizations require propagation of the decay constant errors in  $^{207}\text{Pb}/^{206}\text{Pb}$  ages (see above) and demonstrated absence of nonanalytical (that is, "geologic") errors but in principle can yield improved accuracy for many decay constants (those for  $^{87}\text{Rb}$ ,  $^{147}\text{Sm}$ ,  $^{176}\text{Lu}$ , and  $^{187}\text{Re}$ , for example).

Reconciliation of increasingly precise results from different dating methods is forcing geochronologists to confront systematic errors. Twenty-one years ago, Steiger and Jäger (3) stated that decay constants "will be reviewed by the subcommission from time to time so as to bring the adopted conventional values in line with significant new research data" (p. 359). It might be added that increased communication between geochronologists and nuclear chemists and physicists would be desirable. Additionally, evaluation of  $^{40}\text{Ar}/^{39}\text{Ar}$  standards has never been formally undertaken by any international organization and is overdue.

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## PERSPECTIVES: OPTICAL PHYSICS

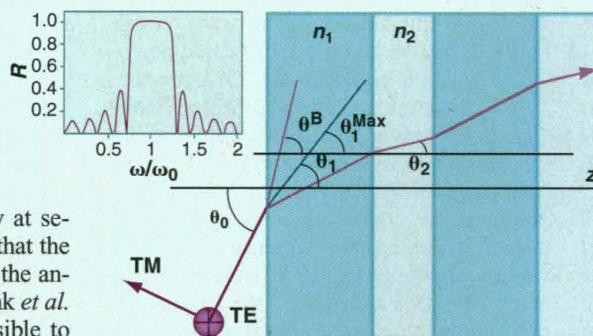
## Mirror on the Wall: You're Omnidirectional After All?

Jonathan P. Dowling

Every once in a while somebody comes up with an important new idea that, in hindsight, is so clear and obvious you could kick yourself for not having thought of it first. The mirror reported last week in *Science* and developed by Joannopoulos and his colleagues at the Massachusetts Institute of Technology is just such an idea (1). Dielectric mirrors are a special type of reflector carefully constructed out of thin layers chosen to create unusually high reflectivity at selected wavelengths. The problem is that the reflectivity is extremely sensitive to the angle at which light hits the mirror. Fink *et al.* (1) have now shown that it is possible to construct a periodic, multilayer, thin-film dielectric mirror that is highly reflective over a broad range of wavelengths at all angles—even up to  $90^\circ$  off axis (see figure).

Consider in the figure a light ray propagating through a periodic dielectric stack, entering at an angle of incidence  $\theta_0$ . On axis ( $\theta_0 = 0$ ), the fraction of radiant ener-

gy,  $R$ , reflected from the stack will look like the graph in the inset, which shows a broad frequency range over which the thin-film stack is highly reflective. (The



**A different angle.** A light ray refracting and propagating through a multilayer thin-film stack. There are two polarization modes shown, indicating the TE mode with the electric field vector polarized parallel to the first interface plane ( $s$  polarized) and the TM mode with the magnetic field parallel to the plane ( $p$  polarized). If the difference between the incident index  $n_0$  and that of the first layer  $n_1$  is large enough, then the external light ray cannot couple to the internal mode at Brewster's angle inside the stack—where  $p$ -polarized light would otherwise propagate all the way through without reflection. (Inset) Reflectivity ( $R$ ) of a five-layer thin-film stack as a function of frequency.

graph was generated assuming a quarter-wave stack of indices of refraction  $n_1 = 1$  and  $n_2 = 2$  with five periods.) Midgap corresponds to a quarter-wave reference frequency  $\omega_0$ . Dielectric mirrors made in this fashion can be made much more reflective and much less lossy than metal mirrors, and so they have many applications, such as in microcavity laser physics for the construction of high-gain, vertical-cavity, surface-emitting lasers (2) and the construction of lossless optical transmission filters (3).

The first problem with these mirrors is that the broad reflection band shifts to higher frequencies  $\omega$  as a function of incident angle,  $\theta_0$ . The reflection bandwidth  $\Delta\omega/\omega_0$  (where  $\omega_0$  is the center frequency of the mirror) is proportional to the difference between the indices of refraction of the layers,  $n_1$  and  $n_2$ . The question is, can one make  $\Delta\omega/\omega_0$  so big that one runs out of angle before one runs out of reflection band (photonic band gap)? The conventional wisdom was no, because of the "Brewster window" problem, which I now describe.

There are two independent light polarization modes to consider in this problem: TE (transverse electric) modes ( $s$  polarized) and TM (transverse magnetic) modes ( $p$  polarized) where the electric or the magnetic field vector, respectively, is parallel to the dielectric interface (shown in the figure). On axis, the reflection band for both polariza-

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tions is the same. However, off axis ( $\theta_0 > 0$ ), they are substantially different. To make a true omnidirectional dielectric mirror, one wants to have a broad reflection band that survives for all angles and for both polarizations. The *p*-polarized band was thought to always have a hole or "window" at Brewster's angle,  $\theta^B$ , where *p*-polarized light propagates from an  $n_1$  to an  $n_2$  layer, and from an  $n_2$  to an  $n_1$  layer without any reflection (3). Once light gets into the multilayer film at  $\theta^B$ —regardless of the frequency—it will propagate unimpeded; there is a hole in the reflection band at that angle. It is somewhat ironic that even Joannopoulos himself once implied that it was impossible to make a one-dimensional (1D) omnidirectional reflector in his own book with Meade and Winn (4). Their proof actually showed that there is no om-

nidirectional photonic band gap in an infinite 1D, periodic, layered structure. However, all physical 1D structures are finite, and this offers the way out.

The real reflection coefficient  $R_{12}$  at a  $n_1$  to  $n_2$  interface is identically zero for Brewster's condition,  $\theta_1^B = \arctan n_2/n_1$ . Now in the figure, we see that the overall incident angle  $\theta_0$  has a full domain  $[0, \pi/2]$ . However, the corresponding range of the refracted angle  $\theta_1$  is restricted by Snell's law ( $n_0 \sin \theta_0 = n_1 \sin \theta_1$ ) to the interval  $[0, \theta_1^{\max}]$ , where  $\theta_1^{\max} \equiv \arcsin n_0/n_1$ . If  $\theta_1^{\max} < \theta_1^B$ , then incident light from the outside can never couple to the Brewster window. That is the trick, and it is easy to do by making  $n_0/n_1$  sufficiently large. Now we make sure that  $n_1$  and  $n_2$  are just right so that we run out of angle  $\theta_0$  before we run out of bandwidth, and voila, we have the

omnidirectional reflector of Fink *et al.* (1).

An omnidirectional dielectric reflector—unlike metal—is nearly totally lossless and can be engineered to have extremely high reflectivities. Applications in the optical wavelength range are as solar and thermoelectric power sources and laser microcavities. In the microwave regime, the structure would find uses as an antenna substrate or in high-power microwave sources—where lossy metals just will not do.

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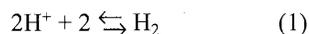
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#### PERSPECTIVES: BIOCHEMISTRY

## Biological Hydrogen Production: Not So Elementary

Michael W. W. Adams and Edward I. Stiefel

Hydrogenase is the name given to the family of enzymes that catalyze what is seemingly one of the simplest possible chemical reactions, the interconversion of the smallest molecule, hydrogen gas ( $H_2$ ), and its elementary particle constituents, two protons and two electrons:



Representatives of most prokaryotic genera, as well as a few eukaryotes, metabolize hydrogen gas and contain hydrogenase (1). The enzyme was discovered in the 1930s, its requirement for iron was established in the 1950s (2), and, in the 1980s, many, but not all, hydrogenases were shown to contain nickel as well as iron (3). Nickel-iron varieties are usually found in microorganisms that consume hydrogen, whereas those that typically produce hydrogen contain iron-only enzymes. The nature of the catalytic sites in hydrogenases has been subject to intense study and conjecture (4). On page 1853 of this issue, Peters *et al.* report their use of x-ray crystallography to provide the first structural glimpse of the iron-only hydrogenase from the hydrogen-producing,

anaerobic bacterium *Clostridium pasteurianum* (5). The resolved array of five iron-sulfur clusters includes the very special "H cluster," which almost certainly is the catalytic site. With an unprecedented nuclearity of six, the H cluster contains two strikingly organometallic iron atoms, with metal-carbon bonds supplied by diatomic ligands, thought to be carbon monoxide (CO) or cyanide (CN<sup>-</sup>) (or both).

Hydrogen gas, a mainstay of the chemical industry (6) and much discussed potential fuel (7), is central to the life forms that inhabit virtually all anaerobic environments, including lake sediments, deep-sea hydrothermal vent sites, and the human intestine (1, 8, 9). Hydrogen is produced by fermentative organisms, such as clostridia, which degrade (oxidize) sugars and other organic matter, through pyruvate, to carbon dioxide and acetate (see figure). To sustain this process, oxidized electron carriers, such as the protein ferredoxin, must be regenerated so that the next sugar molecule can be degraded. With the humble proton as the electron acceptor, ferredoxin is oxidized through the production of hydrogen gas by hydrogenase.

Hydrogen seldom escapes anaerobic ecosystems. In fact, in humans and various animals, hydrogen in the breath is used to monitor intestinal malfunction (8). Depending on the environment, various types of hydrogen-consuming anaerobes obtain energy by using the electrons from hydro-

gen to produce methane or acetate from carbon dioxide, sulfide from sulfate, ferrous from ferric iron, or nitrogen and nitrite from nitrate. Hydrogen is also used to reduce carbon dioxide to cellular building blocks and, in some cases, to reduce nitrogen to ammonia. Any hydrogen that reaches aerobic environments is consumed by bacteria that obtain energy using the reaction of hydrogen and oxygen to produce water (1). Indeed, metabolic hydrogen interdependence may have driven the evolution of the original eukaryotic cell (10).

The hydrogen-evolving hydrogenase of clostridia, first purified almost 30 years ago (11), is now revealed as a mushroom-shaped molecule of 60-kD mass (5). Its single subunit contains the five distinct iron-sulfur clusters, covalently attached to the protein, that had been previously identified by spectroscopic and biochemical studies (4). Four of these are "conventional," one  $Fe_2S_2$  cluster and three  $Fe_4S_4$  clusters. Their spatial arrangement (see figure) implicates them in interprotein and intraprotein electron transfer to the fifth center, the H cluster.

Hydrogenase receives electrons from pyruvate oxidation (catalyzed by an enzyme that contains at least two  $Fe_4S_4$  clusters) through ferredoxin (which contains two  $Fe_4S_4$  clusters). Indeed, electrons from pyruvate oxidation may wend their way through at least seven iron-sulfur clusters before they reach yet another iron-sulfur center, the H cluster. This multitude of iron-sulfur centers brings to mind the proposals of Wächtershäuser for an iron sulfide-based primordial metabolism as the prelude to cellular life (12).

The complexity of the molecular machinery that has evolved in hydrogenase

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