als, such as activated carbons, are widely used in industry. In recent years, microporous organic polymers have been created that are chemically well defined, even though they are disordered and therefore possess a distribution of pore sizes.

One approach to microporous polymers involves tying polymer chains together with a large number of rigid bridges, to give "hyper-cross-linked" polymers (4, 5). Another approach starts with the design of the polymer backbone. By connecting rigid ladder-like components with units that force the backbone to twist or turn, it is possible to construct polymers that cannot pack together and fill space efficiently in the solid state. A variety of these "polymers of intrinsic microporosity" (PIMs) have been developed (6-8) (see the figure). Some are soluble and can be processed into useful forms such as membranes, whereas others are three-dimensional networks. They are commonly prepared by making use of a reaction that joins two aromatic rings together with a pair of oxygen bridges. This approach has the potential to generate polymers that are ordered in two or three dimensions, but in practice, amorphous materials are generally obtained.

Current theories suggest that to form a crystalline polymer network, the polymerization reaction must be reversible, so that it occurs under thermodynamic control. Yaghi's group set out to generate ordered polymer networks by making use of reversible condensation reactions of boronic acids. Using this approach, they first produced two-dimensional covalent organic frameworks that incorporate carbon-boron-oxygen linkages (see the figure) (9). A similar, but slightly easier, route to a two-dimensional covalent organic framework was taken by Lavigne and co-workers (10). But extending this concept to three-dimensional covalent organic frameworks is not trivial, because any given combination of building blocks could potentially give rise to an enormous variety of products. In their latest work (1), Yaghi's group drew on their experience of porous frameworks to select the most realistic targets and used a computer model to help predict the structures

that were likely to form. This helped them to design the synthesis and identify the products.

The results open a new chapter in the story of porous organic materials. It is likely that routes will now be found to a host of novel crystalline covalent networks. Their high porosity and controllable pore size, coupled with the versatility of organic synthesis, promises that this will be a rich and fruitful area of research.

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### PLANETARY SCIENCE

# **As Tiny Worlds Turn**

#### **David P. Rubincam and Stephen J. Paddack**

S unlight changes the rotation rate of an asteroid? The idea seems absurd, but on page 272 Lowry *et al.* (1) and on page 274 Taylor *et al.* (2) report observations that indicate sunlight is doing just that to the small asteroid 2000 PH5, and Kaasalainen *et al.* indicate the same is happening on 1862 Apollo (3). The mechanism is the Yarkovsky-O'Keefe-Radzievskii-Paddack effect, mercifully shortened to YORP. With YORP now on a solid foundation, we may be able to understand a number of strange observations involving small spinning asteroids and asteroid binary systems.

The saga of sunlight changing into spin began with Ivan Yarkovsky, a Polish engineer who realized more than a century ago that the infrared radiation escaping a body warmed by sunlight carries off momentum as well as heat (4). Point this heat in the right direction, and it will function like a rocket motor: Each infrared photon escaping the object carries away momentum, thanks to the relationship p = E/c, where p is the photon's momentum, E is its

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P. HUEY

CREDIT:

Sunlight

**Spinning in the Sun.** Sunlight speeds up rotation due to reflection off the vertical and slated faces of the wedges (blue arrows). Infrared radiation emitted by the faces also causes speed-up. If the body spins in the opposite sense, then YORP will slow it down.

energy, and c is the speed of light. By the principle of action-reaction, the object emitting the photon gets a kick in the opposite direction. (Yarkovsky knew nothing of photons and based his reasoning on the outmoded ether concept, but his idea survives the translation to modern physics.) Yarkovsky thrust is tiny, but space is Rotational force produced by sunlight may help explain the movement of small asteroids, unusual asteroid orbits, and asteroid pairs.

> so empty there is no friction to stop it. Moreover, because the Sun is always shining, the Yarkovsky effect goes on century after century with an inexhaustible supply of photonic fuel, profoundly altering the orbits of meter-sized meteoroids (5).

V. V. Radzievskii applied the photon thrust idea to rotation by imagining each face of a cubical meteoroid painted white on one half and black on the other; sunlight reflected by the white part pushes that area more than the black half, causing a torque, which changes the rotation rate ( $\delta$ ). His mechanism is weak because the black half, although it reflects little, makes up much of the difference by emitting infrared photons. Moreover, most small solar system objects have fairly uniform albedoes (that is, the fraction of light reflected) across their surfaces.

Building on this work, John A. O'Keefe and one of us (S.J.P.) at NASA realized that shape was a much more effective means of altering a body's spin rate than albedo and set about measuring spin changes in the laboratory. The idea was that light reflecting off of various angled surfaces on the object could

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alter its rotation. Thus YORP was born.

O'Keefe and Paddack imagined a body shaped rather like that shown in the figure: two wedges glued to a sphere. As the object rotates, the Sun shines on the vertical face of one wedge and the slanted face of the other. The momentum imparted in the direction of rotation by a photon bouncing off the vertical face is greater than that imparted by bouncing off the slanted face. As a result, there is a net torque, speeding up the object's rotation (7, 8). In addition, infrared radiation emitted by the faces also produces a torque, and infrared YORP probably dominates on small solar system bodies, which tend to be dark. To test this notion, Paddack actually used light (which simulated the Sun) to speed up objects that were magnetically suspended in a vacuum.

Paddack and Rhee applied the YORP effect as the cause of rotational bursting and eventual elimination from the solar system of small asymmetric particles. This may explain the puzzling deficiency in the numbers of small meteoroids (9).

O'Keefe's interest in the YORP effect came from a desire to show that tektites, mysterious glassy lumps found strewn across various regions of Earth, come from the Earth-Moon system (10); farther away, and they spend so long in space that they are spun up to bursting by centrifugal forces via YORP. O'Keefe believed tektites were belched out of lunar volcanoes. Although he was probably wrong about that—they are most likely created on Earth by giant impacts—and as yet there have been no observations of small celestial bodies being spun up to the bursting point, the YORP effect does have profound consequences for the spins of much bigger objects: asteroids. An object must have a certain sort of lopsidedness for YORP to work, and small asteroids, with their surfaces chiseled by impacts, often have the necessary asymmetry.

A 10-km asteroid might double its rotation rate in a few hundred million years, or have it cut drastically; the asteroid could even end up spinning in the opposite direction (11). Because the YORP time scale is proportional to  $R^2$ , where *R* is the radius, the spin rate of the asteroid PH5 with 57-m radius, already fast with its 12-min period, will double in just 600,000 years. Such rapid time scales argue for YORP being competitive or dominant compared with collisions for changing spin.

In addition to speeding up or slowing down rotation, YORP can alter the axial tilt and precession rate (the rate at which the axis moves) of asteroids (5, 12), so that the entire suite of YORP phenonema can send asteroids into interesting resonant spin states. Moreover, because the strength of Yarkovsky's original effect depends on spin speed and tilt, there should be feedback between orbit and spin evolution.

Most small asteroids are commonly believed to be rubble piles, so that they can change shape or even fission into two smaller piles as a result of YORP spin-up, helping explain the existence of binary asteroids. And if the body shown in the figure fissions into two wedge-like objects, for example, YORP might continue, so that the binary system orbitally evolves (13). As for further research, is YORP responsible for the Koronis family asteroids having roughly the same spin rate and spin axis orientation (14), or is some other mechanism at work? How precisely does an asteroid change shape or fission as it speeds up? Do asteroids slowed to tumbling ever speed up again? These questions await the future.

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### ECOLOGY

## A Positive Feedback with Negative Consequences

The ability to emit isoprene protects some plants from ozone damage, which may affect their future abundance.

**Manuel Lerdau** 

It has long been recognized that isoprene emissions from vascular plants play an important role in atmospheric chemistry (1-3). Recent advances (4, 5) suggest that these emissions—in conjunction with fossil fuel combustion and fertilizer application—may create a positive feedback loop, in which species-specific metabolism causes changes in tropospheric chemistry that in turn affect biological diversity and ecosystem metabolism.

About 1% of the carbon captured during photosynthesis by terrestrial ecosystems is

returned to the atmosphere as isoprene (6). Once in the atmosphere, isoprene can either ameliorate or aggravate ozone pollution, depending on the tropospheric concentrations of reactive nitrogen oxides. When nitrogen oxide concentrations (7) are high, isoprene oxidation leads to the net production of ozone, whereas isoprene oxidation at lower nitrogen oxide concentrations leads to the consumption of ozone (8). High nitrogen oxide concentrations occur in air masses that receive substantial inputs from fossil fuel combustion or fertilizer use. Anthropogenic changes in air chemistry thus alter the atmospheric impact of isoprene.

Isoprene is produced as the first end-product of the methylerythritol phosphate (MEP) pathway, which is responsible for all plastid-derived isoprenoids in plants (9). Upon synthesis, isoprene diffuses through the chloroplast membrane to the cytoplasm, through the cell membrane to the intercellular air space, and out through stomata (the pores in leaves through which water exits and carbon dioxide enters). Unlike many other organic volatile compounds produced by plants, isoprene is not stored in specialized structures in the plant (10).

We now understand much of the biochemistry of production and the physics of emission. Yet two crucial questions remain: Why do plants make isoprene? And why do only some plants make isoprene? Recent work by Loreto and co-workers attempts to answer these questions (4, 5). In a series of experiments, they exposed leaves to high, but environmentally

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