

included in the pores during synthesis and were then placed under dynamic vacuum conditions (10^{-5} torr) for 12 hours at 60°C to completely evacuate the pores (6). Thermogravimetric analysis confirmed that all of the guests were removed from the pores and revealed the thermal stability of all COFs beyond 450°C (figs. S43 and S46). Argon isotherms for COF-102 and COF-103 were recorded at 87 K from 0 to 760 torr (Fig. 4, A and B). COF-102 and COF-103 exhibit a classic type I isotherm characterized by a sharp uptake at the low-pressure region between $P/P_0 = 1 \times 10^{-5}$ to 1×10^{-2} , where P is gas pressure and P_0 is saturation pressure. The apparent surface areas calculated from the Brunauer-Emmett-Teller (BET) model were 3472 and $4210 \text{ m}^2 \text{ g}^{-1}$ for COF-102 and COF-103, respectively. The pore volume determined from the Dubinin-Radushkevich equation afforded values of $1.35 \text{ cm}^3 \text{ g}^{-1}$ (COF-102) and $1.66 \text{ cm}^3 \text{ g}^{-1}$ (COF-103). The BET surface areas of COFs exceed porous carbons ($2400 \text{ m}^2 \text{ g}^{-1}$) (11), silicates ($1300 \text{ m}^2 \text{ g}^{-1}$) (12), recently reported 2D COFs ($1590 \text{ m}^2 \text{ g}^{-1}$) (2), polymers of intrinsic microporosity ($1064 \text{ m}^2 \text{ g}^{-1}$) (13), and polymer resins ($2090 \text{ m}^2 \text{ g}^{-1}$) (14) and are comparable to some of the highest surface areas of MOFs [MOF-177 ($4500 \text{ m}^2 \text{ g}^{-1}$) (8) and MIL-101 ($4100 \text{ m}^2 \text{ g}^{-1}$) (15) (MIL, Matériel Institut Lavoisier)]. Calculation of pore size obtained from appropriately fitting density functional theory (DFT) models to the isotherms (figs. S48

and S52) yielded pore size distributions of COF-102 (11.5 \AA) (Fig. 4A, inset) and COF-103 (12.5 \AA) (Fig. 4B, inset) (16). Narrow distributions are obtained and are centered at values close to the pore diameters obtained from the crystal structures.

At the outset of this study, crystallization of 3D COFs (such as cross-linked polymers) was believed to be difficult, if not impossible, to achieve for both thermodynamic and kinetic reasons. This report demonstrates that this challenge can be met by striking a balance between these two competing factors and that the principles of reticular chemistry provide the basis for design and structure solution of the resulting materials.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/316/5822/268/DC1

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Figs. S1 to S56

Tables S1 to S6

References

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Direct Detection of the Asteroidal YORP Effect

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The Yarkovsky-O'Keefe-Radzievskii-Paddack (YORP) effect is believed to alter the spin states of small bodies in the solar system. However, evidence for the effect has so far been indirect. We report precise optical photometric observations of a small near-Earth asteroid, (54509) 2000 PH5, acquired over 4 years. We found that the asteroid has been continuously increasing its rotation rate ω over this period by $d\omega/dt = 2.0 (\pm 0.2) \times 10^{-4}$ degrees per day squared. We simulated the asteroid's close Earth approaches from 2001 to 2005, showing that gravitational torques cannot explain the observed spin rate increase. Dynamical simulations suggest that 2000 PH5 may reach a rotation period of ~ 20 seconds toward the end of its expected lifetime.

The Yarkovsky-O'Keefe-Radzievskii-Paddack (YORP) effect is a torque that can modify the rotation rates and obliquities of small bodies in the solar system; its causes are incident solar radiation pressure and the recoil effect from anisotropic emission of thermal photons (1). Several effects indicate that such a torque, as yet undetected, acts upon the surfaces of asteroids and meteoroids, and the YORP effect is the only realistic mechanism in these cases. A clear example of a YORP-evolved system can be seen within the Koronis asteroid family, formed by the catastrophic collisional disruption of a large parent

body at least 2 billion years ago. This event would presumably have resulted in random spin states for the daughter asteroids, but surprisingly, the larger members are divided into two distinct alignments (2). Theoretical modeling invoked YORP as a potential mechanism to explain the spin-vector alignments by eventually altering the spin rates and obliquities, with some asteroids becoming trapped in spin-orbit resonances (3).

Another likely manifestation of YORP torques is the evolution of orbital semimajor axes of small members of asteroid families toward extreme values, which is important for determining

their age (4). The evolving obliquity will have a direct bearing on the evolution of semimajor axes via Yarkovsky drift, a companion effect to YORP that is caused by a net force arising from emission of thermal radiation along the body's orbit and was recently detected for the first time (5). YORP is also an important component in models of the delivery of near-Earth asteroids from the main asteroid belt, as it leads to a Yarkovsky drift, forcing bodies into powerful perturbing orbital resonances (6).

Furthermore, there exists a distinct population of small, very-fast-spinning asteroids known as the monolithic fast rotators (MFRs) (7). If the orbits of such bodies are stable over million-year time scales, allowing YORP to significantly change the rotation rate, then the effect is highly

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likely to place these asteroids into this category. YORP could also cause small asteroids to spin up so fast that they are forced to morph into new shapes or even shed mass; perhaps such a progression would supersede tidal disruption and collisions as the main formation mechanism for binary asteroids in the planet-crossing population (8, 9). Conversely, YORP could act against the rotation direction to reduce the spin rate, leading to the very long rotation periods (>40 days) seen for some asteroids and possibly causing some of them to tumble. Despite its importance, there exists only indirect evidence for the presence of YORP on solar system objects.

Although the obliquity effect is too small to be detected with ground-based or even space-based instruments, changes in the rotation rate may be detected if very precise observations, such as high-quality asteroid light curves, are obtained over a long enough time span (10, 11). The small near-Earth asteroid (54509) 2000 PH5 (hereafter PH5) is one of the few known Earth co-orbitals in a near 1:1 mean-motion resonance with Earth. The characteristics of its horseshoe orbit result in periodic close Earth approaches, roughly every July and August, making it a good target for regular monitoring over yearly time scales. Here, we present results from long-term optical photometric monitoring of PH5 that reveal the YORP effect in action via an observed decrease in its sidereal rotation period, which is shown in our companion paper (12) to be in reasonable agreement with theoretical predictions for the effect. In (12), the optical data are analyzed alongside radar data to reconstruct a detailed shape model from which the expected YORP torques can be reliably assessed.

With a small radar-derived mean radius of ~57 m, any size-related YORP effect on PH5 is likely to be relatively high. Its fast spin period of 12.17 min makes it a very practical target for observations from Earth-based telescopes, because full and consecutive nights of observation are not required for accurate period determination. In 2 hours we could continuously sample the light curve over ~10 full revolutions, more than adequate for our purposes. This small size and fast rotation puts PH5 into the MFR asteroid group, so YORP may have been significantly affecting its spin rate for some time, and it is

Table 1. Evolution of the sidereal rotation period. There is partial overlap between successive data groups; however, the PAB corrections are performed on each biannual data group independently (13).

Date range of data group	Sidereal period (hours)*
28 Jul 2001–27 Jul 2002	0.20290046
27 Jul 2002–27 Aug 2003	0.20290020
29 Jul 2003–11 Sep 2004	0.20289985
12 Aug 2004–31 Aug 2005	0.20289941

*1 σ uncertainties are 10⁻⁸ hours.

reasonable to assume that it is still susceptible to YORP torques.

Our optical monitoring campaign began in 2001 and spanned ~4 years, with many observatories from various countries contributing telescope time. Because of the close approaches of PH5, the apparent brightness of the asteroid as

seen from Earth changed considerably over time scales of days to weeks. Therefore, as the integration time was restricted to 30 s to avoid rotational smearing of the light curve, a range of optical telescope apertures (0.65 to 8.2 m) was required to reach the desired signal-to-noise ratio in this time. The asteroid's rotational signature

Fig. 1. Light curve data from the 2002–2003 data group, folded to the best-fit sidereal period of 0.20290020 hours. The fortuitous near-constant viewing geometry throughout the observations ensured that the shape and amplitude variations in the light curve were small from one night to the next.

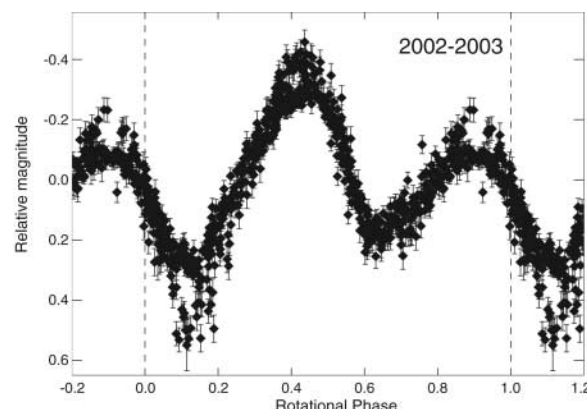


Fig. 2. Observed YORP effect on asteroid (54509) 2000 PH5. The sidereal rotation period P is steadily decreasing. For a solid YORP detection it is very important to confirm the existence of a trend, hence the need for repeated measurements over subsequent years. A linear trend is seen in $\Delta P/P_0 = (P - P_0)/P_0$ versus time, where $P_0 = 730.440756$ s (i.e., the nominal value from the 2002–2003 data group). Solid symbols represent the observed period change (the formal 1 σ uncertainty on the period is smaller than the plotted data points). The solid curve is a theoretical prediction for YORP strength computed from different shape variants of the asteroid and recalibrated by a factor of 0.16 to 0.38, as discussed in (12). Open circles (with 1 σ uncertainties) indicate the expected change of P during annual close encounters with Earth (arbitrarily offset for clarity), which is negligible relative to the observed period change.

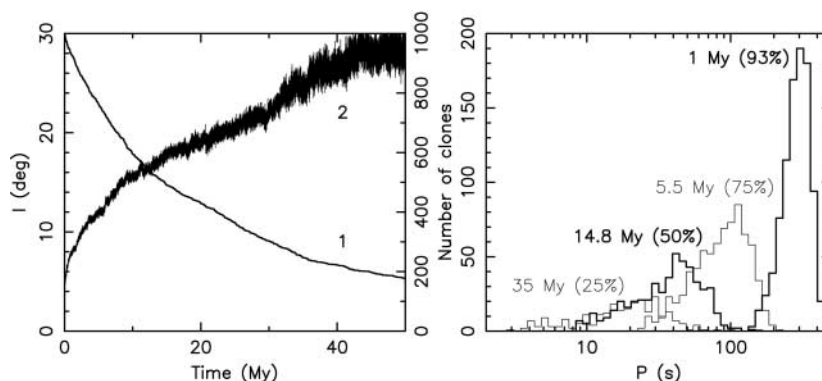
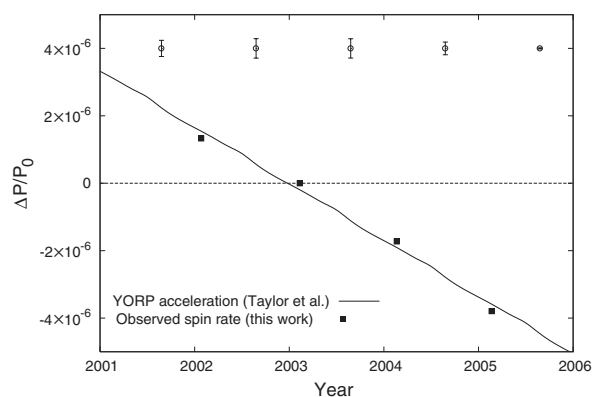


Fig. 3. Future orbital and spin evolution of asteroid (54509) 2000 PH5 from numerical integrations. Left: Number of surviving particles (right ordinate, curve 1) and median inclination I (left ordinate, curve 2) versus time. Right: Distribution of rotation period P values for the surviving particles after 1 My (93% of the population surviving), 5.5 My (75% surviving), 14.8 My (50% surviving), and 35 My (25% surviving). The spin-axis obliquity rarely drops below ~125°, and so YORP continues to increase the particle's rotation rate.

was extracted from each individual imaging data set (13), and the resulting light curves were grouped according to date; all the 2001 and 2002 light curves were taken together, then all the 2002–2003, 2003–2004, and 2004–2005 data, so that each data set had a 1-year time base. To find changes in the sidereal period, we shifted the observation times of the data points within each combined set by the established phase angle bisector (PAB) approximation (13, 14), which requires knowledge of the spin-axis orientation. Using a combination of radar data and our optical light curves, Taylor *et al.* (12) report that the pole position resides within 10° of (180° , -85°) in ecliptic coordinates (J2000).

Fourier analysis of the light curve modulation was then performed separately for each time-corrected data group (13) to determine the yearly averaged sidereal rotation periods (Table 1). The light curve amplitude changed little within any data set because of the nearly constant aspect angle of the asteroid throughout the observations. As a result of the asteroid's shape, there was also a pronounced asymmetry in the light curve that ultimately allowed unambiguous phasing of the data (Fig. 1). Sidereal rotation periods P were determined from 2001 to 2005 and were seen to decrease at a linear rate, with a fractional change of -1.7×10^{-6} ($\pm 9\%$) per year; that is, the asteroid has been increasing its rotation rate ω over these 4 years by $d\omega/dt = 2.0$ (± 0.2) $\times 10^{-4}$ degrees day $^{-2}$ (Fig. 2). This result was confirmed from analysis of the combined light curve and radar data in (12). Detailed dynamical simulations that used the shape model in (12) were performed that reproduced the close Earth approaches from 2001 to 2005, from which we can rule out Earth-tug effects as a potential mechanism for the observed sidereal-period decrease (Fig. 2) (13). Moreover, there is no reason for Earth tugs to be coherent, so uncorrelated positive and negative shifts in spin rate are possible in subsequent years. The reasonable agreement between observations and YORP simulations (12) and the fact that planetary tugs cannot account for the observed effect leaves YORP as the only viable cause.

The fast rotation of PH5 could imply that this asteroid underwent significant YORP evolution in the past. Indeed, its obliquity near 180° supports this idea because it is near one of the asymptotic YORP regimes (11, 15). Our result suggests that it would take $\sim 550,000$ years for YORP to double the rotation rate of PH5 in the future. From this value we may expect that YORP will cause structural changes, mass shedding, or even fission of this object at some point in the future, depending on its internal strength. To investigate this possibility, we ran a simulation that numerically propagated the orbit of PH5 and 999 close clones (13). We found a median dynamical lifetime before particle removal from the simulation, by solar or planetary impacts, of ~ 15 million years (My), a surprisingly long time scale (Fig. 3). The longest-lived clones of PH5 (about 6%) survived 100 My of orbital evolution.

In a second step, we numerically integrated the secular evolution of the spin state for each of these 1000 particles along their precise orbits (13), with the YORP strength set to our observed value. At 35 My, when 25% of the original clone population remained, the median rotation period was 19 s with a lowest extreme of 5 s (Fig. 3).

Our observational calibration of the YORP effect, in conjunction with orbital and spin integrations, demonstrates that asteroids like PH5 can attain extremely fast rotation rates. Our work also implies the possible existence of a population of 100-m asteroids with rotation periods of ~ 20 s, significantly faster than the most rapidly rotating asteroid of this size, 2000 WH10 with $P \sim 80$ s (16). Light curve observations to date are biased against the detection of such short periods, and hence the number of such bodies is unconstrained at present. If no such objects are found, then the most likely explanation is eventual significant mass shedding or rotational fission before they reach this value of P .

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Spin Rate of Asteroid (54509) 2000 PH5 Increasing Due to the YORP Effect

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Radar and optical observations reveal that the continuous increase in the spin rate of near-Earth asteroid (54509) 2000 PH5 can be attributed to the Yarkovsky-O'Keefe-Radzievskii-Paddack (YORP) effect, a torque due to sunlight. The change in spin rate is in reasonable agreement with theoretical predictions for the YORP acceleration of a body with the radar-determined size, shape, and spin state of 2000 PH5. The detection of asteroid spin-up supports the YORP effect as an explanation for the anomalous distribution of spin rates for asteroids under 10 kilometers in diameter and as a binary formation mechanism.

Theory predicts an evolution of the spin state of a small solar system body as a result of the absorption and asymmetric re-emission of sunlight, the so-called YORP effect. The resultant radiation torques are thought to realign the spin vector while changing the spin rate of the object (1). Lowry *et al.* (2) report an increase in the spin rate of 2000 PH5. Here we present, with radar and optical observations and modeling of 2000 PH5, the best

evidence to date that the YORP effect is responsible for changing the spin rate of an asteroid.

For objects with finite thermal conductivity, especially fast-rotating asteroids <1 km in diameter that lack regolith, YORP torques tend to force the spin vector to 0° or 180° obliquity (parallel or antiparallel to the orbit normal) and cause the spin rate to increase or decrease with equal probability (3) on time scales proportional to the square of the diameter D (1). Therefore, YORP may explain