rock samples. These results led to the slip-weakening model, in which friction was assumed to decrease as slip on the fault increased. The key model parameter was the slip-weakening distance (the amount of slip required to reduce friction at high speeds). This phenomenological model avoided the difficult question of the origin of friction.

Mechanical studies of rocks in the late 1970s provided the first experimental evidence that steady-state friction indeed decreased logarithmically with slip rate. Friction also depends on several parameters representing the state of the slipping surface (*3*). In these experiments, designed to understand friction at low slip rates, the slip-weakening distance is very small, on the order of a fraction of 1 mm.

In the past 15 years, seismologists were able to study in detail several major earthquakes in the United States, Japan, Turkey, and Taiwan. The slip-weakening distances inferred for these events were several orders of magnitude longer than those observed in rate-and-state friction experiments. A simple scaling argument explains the long slip distances. Earthquakes are similar for a broad range of scales, at least from magnitudes of about 4 to 8; the single scaling variable appears to be the length of the fault. If this is the case, then slip-weakening distances must scale with earthquake size; otherwise, either large earthquakes would all propagate with rupture speeds higher than that of shear waves, or small events could never occur because of the high frictional resistance of the faults. Han *et al.* find that slip weakening occurs on scales on the order of a meter, a value that is very close to the slip-weakening distances observed in earthquakes of magnitude around 7. A numerical simulation of the Landers earthquake of 28 June 1992 in California (see the figure) required slip weakening distances of several tens of centimeters, similar to those observed by Han *et al.*

The experiments by Han *et al.* show that friction is very sensitive to slip rate. Large slip-rate weakening favors the creation of rupture pulses instead of long cracks. In pulses (*4*), slip occurs in a narrow zone that follows the rupture front; this is a very efficient way to propagate seismic slip while maintaining a high average stress on the fault. The results reported by Han *et al.* may also help to explain the "San Andreas Fault paradox": There is no observed increase in heat flow near the fault, which means either that the fault is very weak during slip, producing very little heat, or that friction is high but heat is evacuated by fluid flow (*5*).

The experiments also raise several questions. The most obvious is that they were done at a fixed slip rate, whereas earthquakes are intrinsically transient phenomena, with slip rate increasing from zero to speeds on the order of 1 m/s when the rupture front arrives, finally decreasing to zero as the fault heals. It remains unclear whether the friction law derived in this work applies to transient slip of short duration.

By far the most important question concerns scaling. Han *et al.* carried out their experiments at confining pressures of 7.3 MPa. Will the same friction law apply at the much higher confining pressures that prevail in seismogenic zones? Seismic data have shown that slip rates are proportional to stress drop (the difference between the static and dynamic friction). Stress drops in the experiments were on the order of 7 MPa at the confining pressure of 13 MPa. Extrapolating to the depths where earthquakes occur, this implies stress drops at least an order of magnitude greater than those observed. Furthermore, the experiments were done on marble; the results may be different for the silicate rocks found at 10 km depth.

Thermal weakening is not the only mechanism that may reduce friction at high slip rates; melting (*6*) is another example. Furthermore, direct application of the results reported by Han *et al.* actual fault zones depends on the assumption that slip is concentrated on a narrow band. Recent experiments on sand have shown (*7*) that slip bands tend to form outside the main slip zones as fault zones evolve toward large accumulated slip. We are only at the beginning stages of a fresh understanding of fast frictional processes in earthquakes.

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PLANETARY SCIENCE

Titan's Organic Factory

Sushil Atreya

Researchers have identified molecules in the atmosphere of one of Saturn's moons that are responsible for its smog-like haze.

Since its discovery by Christiaan Huygens in 1655, Saturn's large moon Titan has intrigued scientists, not the least because its surface is blanketed by thick haze. This haze plays an important role in warming Titan's nitrogen atmosphere, preventing its condensation and subsequent removal. However, the most important aspect of Titan's haze may be its composition. It has long been suspected that the haze results from complex organic molecules, perhaps even prebiotic molecules (*1*). Now, close flybys of Titan by the Cassini spacecraft reveal that such molecules may indeed be forming. On page 870 of this issue, Waite *et al.* (*2*) report identification of benzene, along with both positively and negatively charged organic ions. Heavy molecules formed from these ions eventually produce Titan's upper haze layers and are expected to contribute substantially to the total haze content of the atmosphere.

Unlike the other moons in the solar system, Titan has a massive atmosphere, consisting of 95% nitrogen and 5% methane. Chemical processes are initiated by the break-up of these gas molecules by solar radiation and charged particle collisions (see the figure). Even though Titan receives only 1% of the solar ultraviolet flux that Earth does, and is bombarded by charged particles from Saturn's magnetosphere only some of the time, this energy is sufficient for photochemistry to proceed efficiently. Simple hydrocarbons—such as ethane, acetylene, and diacetylene—and nitriles, such as hydrogen cyanide (HCN) and cyanogen (C_2N_2) form readily. Somewhat

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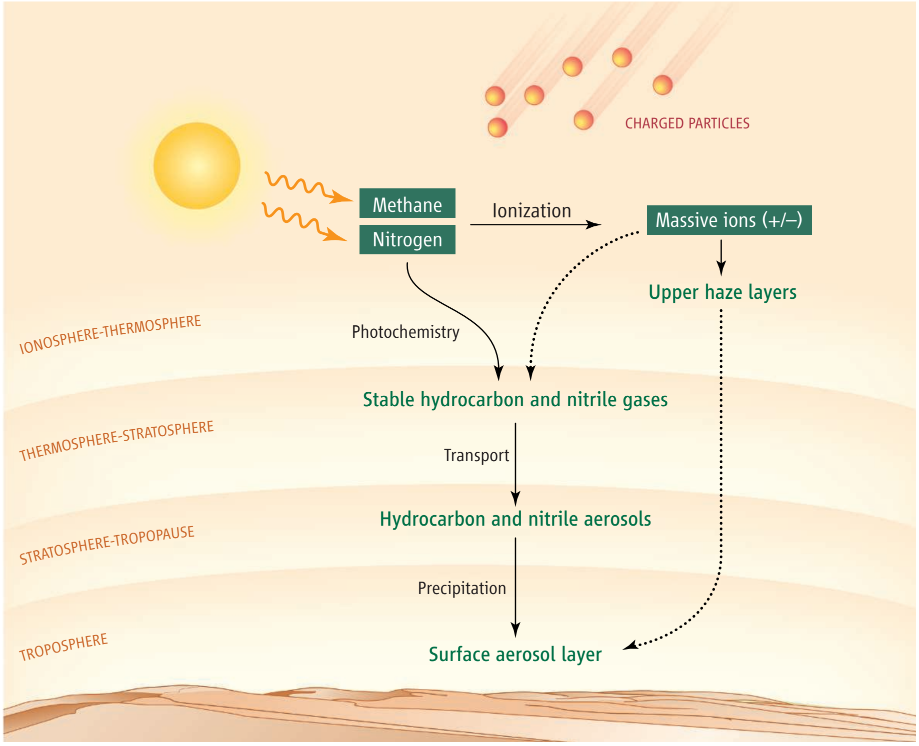
more complex molecules such as propane, butane, polyacetylenes, and cyanoacetylene follow from these simpler units (*3*). Researchers believed that the haze seen on Titan by Voyager 1 and Voyager 2 during 1980–1981 was the result of condensation of many of these molecules and polymers of polyynes and HCN (*3*), somewhat similar to the formation of urban photochemical smog on Earth.



Haze formation. Ultraviolet radiation from the sun and charged particles from Saturn's magnetosphere initiate photochemical reactions of nitrogen and methane in Titan's ionosphere-thermosphere region (~1000 km altitude) and these reactions can extend into the lower stratosphere (~200 km). The hydrocarbon and nitrile products begin condensing below ~200 km down to the tropopause (~40 km). These aerosols eventually precipitate out of the troposphere and accumulate on Titan's surface together with aerosols from the upper layers. [Adapted from (*12*)]

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That is where things stood until a tentative detection of a few parts per billion of benzene (C_6H_6) by the Infrared Space Observatory (ISO) in 2003 (*4*). Wilson *et al.* proposed recombination of propargyl (C_3H_3) molecules (which are derived from acetylene) with each other to explain the observations (*5*). Benzene is key to the formation of polycyclic aromatic hydrocarbons (PAHs) through a continued sequence of hydrogen atom removal and acetylene addition (*6*, *7*). Conversion from gas phase to particulates occurs when the PAHs reach a high mass of about 2000 daltons (1 dalton is the atomic mass unit equal to 1/12 the mass of the carbon atom), and ultimately soot forms, like the exhaust from diesel trucks. PAHs were predicted in laboratory simulation experiments of Titan (*8*), and models showed PAH polymers to be the largest contributors to Titan's haze (*9*).

The conventional photochemical process leading up to PAHs begins with the dissociation of methane some 600 to 800 km above Titan's surface. However, measurements with the Ion Neutral Mass Spectrometer (INMS) on Cassini (*2*) show that benzene must be forming in the thermosphere-ionosphere region also, well above Titan's normal photochemical regime. Moreover, the benzene is found to be at a concentration of parts per million, some 1000 times as high in mole fraction as the stratospheric value from the ISO and the Cassini Composite Infrared Spectrometer. Thus, the benzene abundance in the (lower density) thermosphere is comparable to its abundance in the (higher density) stratosphere.

What is the cause for this high benzene concentration? A previously neglected mechanism of ion-molecule reactions seems to be at work. Although charge-exchange reactions to produce simple one- and two-carbon ions, such as CH_5^+ and $C_2H_5^+$ were known in the past (*10*), no one recognized that the chemistry in the ionosphere could proceed to more complex molecules. Waite *et al.* (*2*) show that heavier ions, including $C_6H_7^+$ are formed through a sequence of subsequent charge-exchange reactions of the above ions with ambient neutral molecules such as acetylene and diacetylene. Benzene results from electron recombination of $C_6H_7^+$ in the ionosphere. The ion-molecule reactions proceed much more efficiently than those between neutrals in the atmosphere below. This can explain why the ionospheric benzene mole fraction is enormous. With so much benzene around, a large production of PAHs in the ionosphere cannot be far behind.

The detection reported by Waite *et al.* of heavy positive ions up to 350 daltons and negative ions up to 8000 daltons by Cassini Plasma Spectrometer (CAPS) (*2*) implies that ion-molecule reactions may be producing more complex ions than just $C_6H_7^+$ even as the PAHs form and grow in Titan's ionosphere. However, there is no way to positively identify the composition of such molecules from the CAPS spectra. Chemical models do not help either, because the appropriate laboratory chemical kinetics data are lacking. Thus, to conclude that the ions seen by CAPS are massive organic molecule precursors to haze or haze itself is speculative. However, considering the likely chemical pathways to the formation of such molecules, the unexpectedly large mole fraction of benzene in the ionosphere, the presence of haze layers at high altitudes, and the total atmospheric aerosol content, this speculation may be close to reality.

The picture emerging from the work of Waite *et al.* and previous studies is that both the ionosphere and the neutral atmosphere below play important roles in the formation of complex organic molecules. These molecules are precursors to haze. Very few molecules survive condensation below Titan's cold tropopause (70.4 K). As a result, aerosols have been snowing down onto the surface of Titan over the past 4.5 billion years. If left alone, they could accumulate to a depth of hundreds of meters. However, the rain of methane is expected to wash some of the deposit into lake beds or river basins. Nevertheless, relatively large quantities are expected to survive intact on the surface.

The combined CAPS and INMS observations (*2*) allow a glimpse of the composition of these aerosols. Unfortunately, their low concentrations mean that chemical identification of the more complex of these molecules is beyond the capability of most instruments. Yet there is hope for detection of complex species on the surface where the

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atmospheric aerosols accumulate. Indeed, the Huygens Gas Chromatograph Mass Spectrometer (part of a probe launched from the Cassini spacecraft) found Titan's surface material to be a rich mixture of molecules (*11*). The Huygens team has made a tentative identification of benzene and cyanogen among other volatiles, even though the same molecules are not yet seen in the mass spectra during descent, most likely due to their low abundance in the atmosphere below 146 km where the data were taken.

A complete chemical analysis of the surface material, including isotopes, should be a key focus of any future missions to Titan. This is because Titan's surface composition is expected to reflect to a large extent the composition of molecules originating from its atmosphere and ionosphere, but in substantially greater concentration than that in their production region. Who knows, we may yet find those elusive prebiotic molecules.

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CELL SIGNALING

The Art of the Soluble

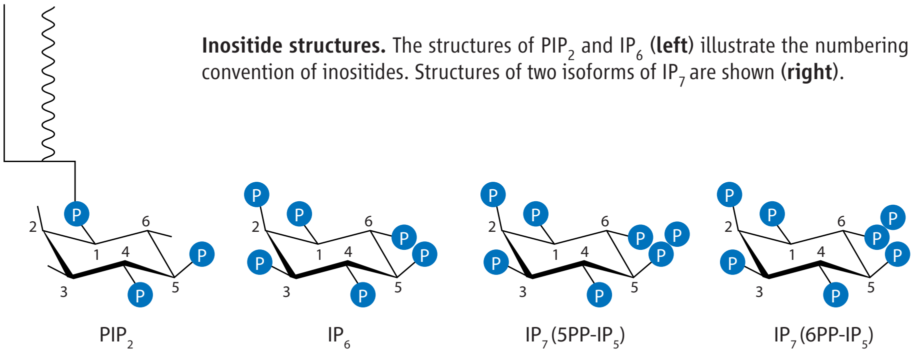
Robin Irvine

New information about the synthesis and function of inositol phosphates shows that they may have wider and more important effects than previously realized.

Since the 1980s, inositol lipids have captured more attention than inositol phosphates as important cellular signaling molecules, even though it was an inositol phosphate—inositol 1,4,5-trisphosphate (IP_3)—that was assigned a definitive cellular function first (*1*). Two papers recently published in *Science* (*2*, *3*) and one that appears in this issue (*4*) go a long way toward redressing this balance and establish (*4*) a new relationship between the lipids and their soluble counterparts.

In most eukaryotic cells, IP_3 is phosphorylated by a sequence of enzymes (kinases) to produce inositol hexakisphosphate (IP_6; see the figures) (*5*, *6*). Remarkably, phosphorylation does not stop there but continues to produce mono- and bis-pyrophosphorylated inositol phosphates [properly called PP-IP_5 and $(PP)_2$-IP_4, but loosely termed IP_7 and IP_8, respectively]. A number of potential functions have been assigned to IP_7, including DNA recombination, vacuolar morphology, gene expression, protein phosphorylation, and telomere length (*6*).

One way in which such functions for IP_7 have been determined is by studying the phenotypes resulting from deletion of *Kcs-1*, the gene that encodes IP_6 kinase in the budding yeast *Saccharomyces cerevisiae*. However, the recent *Science* paper by Mulugu *et al.* (*2*) shows that we've been aware of only half the IP_7 story. The authors revisited a puzzling finding that yeast lacking *Kcs-1* still make IP_7 (*7*). The great investigative strength of yeast is the ability to manipulate its genetics, but sometimes you have to do things the hard, biochemical way. Mulugu *et al.* combined both approaches, forging through protein purification and then a screen of 40 potential yeast proteins, to identify a second, novel IP_6 kinase. This enzyme turns out to be encoded by a gene that, in the fission yeast *Schizosaccharomyces pombe*, is functionally linked to a protein complex (ARP) and the actin cytoskeleton to control cell shape and integrity.



Inositide structures. The structures of PIP_2 and IP_6 (**left**) illustrate the numbering convention of inositides. Structures of two isoforms of IP_7 are shown (**right**).

This new IP_6 kinase (called Vip1 in *S. cerevisiae* and Asp1 in *S. pombe*) is found in all eukaryotes and has a kinase domain and a phosphatase domain, the latter of which has an unknown role. Mulugu *et al.* used elegant structure-based threading software to identify key residues in the enzyme that they then mutated to generate forms lacking kinase activity. They show that it is indeed the ability of Vip1/Asp1 to make IP_7 that is essential to its contribution to yeast cellular integrity, growth, and morphology.

But why are there two IP_6 kinases? Mulugu *et al.* show by nuclear magnetic resonance that each kinase makes a different IP_7 isomer. Kcs-1 makes 5PP-IP_5, but Vip1 synthesizes 4/6PP-IP_5—that is, IP_7 with a pyrophosphate in the 4 or 6 position. Although 4PP-IP_5 and 6PP-IP_5 cannot be distinguished by nuclear magnetic resonance (*5*), it is likely to be 6PP-IP_5, the form identified in the slime mold *Dictyostelium discoideum* (*8*). This discovery enabled the researchers to solve another long-standing mystery—the identity of an IP_7 kinase that makes IP_8. When added together, the two IP_6 kinases synthesized IP_8 in vitro. In short, either IP_6 kinase can make IP_8, but each needs the right substrate—an IP_7 made by the other kinase.

Another important function for IP_7 comes out of the accompanying *Science* paper by Lee *et al.* (*3*). Budding yeast stop growing when deprived of phosphate, a result of the inactivity of a cyclin/cyclin-dependent kinase (CDK) complex that con-

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