for one of the original steps in the evolution of life. Earlier biochemical and genetic data provided clues about critical components of the active site, particularly the universally conserved rRNA residues A1492 and A1493 (*8*, *9*). However, it is the work of the Ramakrishnan group that identifies the precise contacts in decoding: Nucleotides A1492 and A1493 flip out to probe the minor groove of the codon-anticodon double helix, checking for Watson-Crick pairing of the first two base pairs. More flexibility is allowed the third codon-anticodon base pair, consistent with Crick's wobble hypothesis (*10*) that less stringent base pairing at this position accounts for how a single tRNA species can bind to more than one codon. Two additional participants include ribosomal protein S12, which contacts A1492, and G530, which flips from the *syn* to *anti* conformation to contact both the codon-anticodon double helix and A1492. Both S12 and the 530 loop have a long history in translational fidelity, and now we know why.

Once the crystal structure of the decoding region was resolved, the authors could address the question of how antibiotics such as paromomycin induce misreading of the genetic code. Residues A1492 and A1493 flip in a fashion similar to that occurring during decoding, although G530 is unmoved. Apparently, by paying part of the energetic cost of flipping the A residues, paromomycin facilitates binding of near-cognate tRNAs. This result must be particularly gratifying to pioneers such as Julian Davies and Walter Gilbert who, in 1964 along with the late Luigi Gorini (*11*), proposed that decoding occurred at an active site that distinguished between cognate and near-cognate tRNAs, and suggested that decoding could be perturbed by antibiotics such as paromomycin.

Both the Noller and Ramakrishnan manuscripts are landmark contributions to the understanding of ribosome structure and function. Francis Crick's Adaptor molecule (tRNA), first proposed by him to the RNA Tie Club in 1955 (*12*), has assumed its rightful place in the ribosome—bridges, wobble, and all. Our appetites have been whetted, and we now look forward to seeing crystal structures representative of different conformations of the dynamic ribosome.

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PERSPECTIVES: INTERSTELLAR CHEMISTRY

Tunneling Reactions in Interstellar Ices

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Light essentially cannot penetrate dense interstellar clouds, and temperature inside dark clouds is kept at about 10 K. About 120 interstellar molecules have been observed by millimeter and submillimeter spectroscopy in such dark clouds. It is becoming increasingly clear that gas-phase ion-molecule reactions—the dominant processes in diffuse interstellar clouds—are less important in dense clouds. Instead, chemical reactions on cosmic dust grains play an important role (*1*). Interstellar ices, which grow on solid dust particles in cold, dense clouds, also become the substrates for various chemical reactions. Recently, the Infrared Space Observatory (ISO) has provided much information about interstellar and cometary ices (*2*).

Unfortunately, direct observations of the solid-phase chemistry of dense clouds are difficult to come by. In the absence of direct evidence, we have to resort to laboratory studies. A wealth of data has been gathered on gas-phase ion-molecule reactions, but investigations on solid-phase reactions of various molecules remain scarce (*3*), although there have been experimental studies of molecular hydrogen formation on the surface of cosmic dust analogs (*4*).

Because of their high mobility in solids, hydrogen atoms are believed to play a particularly important role in the chemical evolution of dense clouds. Because of their wave nature (*5*) and their low atomic weight, hydrogen atoms can "tunnel" through seemingly insurmountable barriers. In a solid, a hydrogen atom can be visualized as a quantum liquid that creeps quickly from one site to another and participates in tunneling reactions wherever it encounters a suitable reactant.

The horsehead nebula. This well-known astronomical feature is part of a much larger dust cloud. It looks dark because of absorption of light by the dust. Starlight illuminates the nebula's background, causing hydrogen there to fluoresce. Thus, the "head" is silhouetted.

CREDIT: NASA

Ammonia and formaldehyde are implicated in the origin of life. They are examples of molecules whose interstellar abundances are difficult to explain by gas-phase reactions alone (*6*). It has been suggested (*7*) that the substantial abundance of formaldehyde and methanol in the diffuse envelopes of dark clouds can be explained by consecutive hydrogenation reactions of CO molecules trapped on dust grains with hydrogen atoms:

$$CO \rightarrow HCO \rightarrow H_2CO \rightarrow H_2COH \rightarrow CH_3OH$$

In a recent laboratory simulation of cosmic grain chemistry at cryogenic temperatures (*8*), formaldehyde was formed when a solid CO film was deposited on a cold silicon substrate and then reacted with hydrogen atoms at 10 K. The rather high energy barrier of 4.1 kcal/mol (*9*) for the reaction H + CO → HCO suggests that the reaction proceeds through a tunneling process. No CH_3OH could be detected, indicating that the addition reaction of H atoms with H_2CO to form CH_3OH is practically forbidden (*10*). These results suggest that interstellar ices may indeed play a role in the formation of interstellar saturated molecules.

The formation of saturated hydrocarbons in the interstellar medi-

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um is unlikely to proceed entirely through gas-phase ion-molecule reactions because positively charged carbon species (carbonium ions) cease to react with H_2 before they are fully saturated. Observation of saturated hydrocarbons in dense clouds, either frozen on grains or as gases, would thus provide strong evidence that reactions on grains play major roles in interstellar chemistry.

Comets bear some similarity to interstellar ices in dark clouds, and insights gained into their chemistry can therefore provide some clues for the chemistry taking place in dark clouds. Most of the time, comets orbit far from the sun, allowing them to remain virtually unchanged since the origin of the solar system (*11*). The high-resolution infrared telescope on Mauna Kea, Hawaii, detected the hydrocarbons C_2H_2, C_2H_6, and CH_4, along with CO and H_2O in comet Hyakutake. Comet Hale-Bopp was observed at wavelengths from 2.4 to 195 μm with the ISO when the comet was about 2.9 astronomical units from the sun (*12*). The gas-phase abundances of C_2H_2 and C_2H_6 were found to be about the same, at about 0.5% of the abundance of H_2O (*12*).

C_2H_4 was not detected by infrared spectroscopy in these comets despite the relatively strong intensities of the related molecules C_2H_2 and C_2H_6. The abundance of C_2H_4 is generally observed to be low in the solar system; for example, C_2H_4 is missing in Saturn and its moon Titan, where other hydrocarbons with two carbon atoms are common. To find out why, we must consider the channels through which these molecules form.

There are several gas-phase channels for the formation of C_2H_2 (such as $C^+ + CH_4 \rightarrow C_2H_3^+ + H$ and $C_2H_3^+ + e^- \rightarrow C_2H_2 + H$). The presence of C_2H_2 in comets is therefore reasonable. C_2H_6 may form by consecutive hydrogenation of C_2H_2 trapped in cometary ice, $C_2H_2 \rightarrow C_2H_3 \rightarrow C_2H_4 \rightarrow C_2H_5 \rightarrow C_2H_6$, with C_2H_4 as an intermediate. We have found that when solid C_2H_2 was reacted with H atoms at 10 K, C_2H_6 was the only product; no C_2H_4 could be detected (*8*). This finding is in accord with the observation of comets Hyakutake and Hale-Bopp. C_2H_4 is absent because the addition reaction $H + C_2H_2 \rightarrow C_2H_3$ is the rate-controlling process and the subsequent reactions to form the final product C_2H_6 proceed much faster than the initial one. A model of gas-grain chemistry in dense clouds correctly predicted that the grain surface concentrations of C_2H_2 and C_2H_6 are much greater than that of C_2H_4 (*13*).

Usually, chemical reaction rates decrease with decreasing temperature. We found, however, that in the reaction of hydrogen atoms with solid C_2H_2, C_2H_4, C_2H_6, CO, and SiH_4, the product yields increased drastically with decreasing temperature. The rate of reaction of hydrogen with C_2H_2 to form C_2H_6 increased by about four orders of magnitude when the reaction temperature was decreased from 50 to 10 K.

Such a negative temperature dependence of the rate constants for tunneling reactions has been predicted (*14*). The argument runs as follows: The many-body reactant-substrate and product-substrate interactions produce a dense spectrum of vibrational energy levels. The quasi-continuous set of vibrational levels of the reactant-substrate system acts as a dissipating channel and promotes the forward reaction (*15*). This becomes more favorable at lower temperature because thermal fluctuations are suppressed.

The fact that the temperature in dark clouds is kept at about 10 K is thus crucial for the chemical evolution in dark clouds. If the temperature of the molecular clouds were higher, the rate of chemical evolution would be slower because of the decrease of the rates of the tunneling reactions.

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PERSPECTIVES: PALEOCLIMATE

CO_2 and Climate Change

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Geologists have long known that on time scales of tens of millions of years, intervals of continental glaciation were interspersed with times of little or no ice. The magnitude of warmth during these warm intervals is impressive. At times during the Cretaceous [about 65 to 145 million years ago (Ma)], duck-billed dinosaurs roamed the northern slope of Alaska. Deep and bottom waters of the ocean, now near freezing, could reach a balmy 15°C.

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In the 1980s, a convergence of results from paleoclimate data and geochemical and climate models suggested that such long-term variations in climate were strongly influenced by natural variations in the carbon dioxide (CO_2) content of the atmosphere (*1*). Lately, some geochemical results have raised concerns about the validity of this conclusion. CO_2 concentrations over the past 65 million years appear to have reached low levels well before the most recent phase (the past 3 million years) of Northern Hemisphere glaciation. This is especially true for times of elevated temperatures at about 50 to 60 Ma and 16 Ma, when CO_2 was apparently low (*2–4*). A study spanning the Phanerozoic (the past 540 million years) also suggests some decoupling between times of predicted high CO_2 and some climate indices (*5*).

In light of these results, it is important to reevaluate the validity of the assumed CO_2-climate link. Here we address this issue by comparing estimates of Phanerozoic CO_2 variations (*6*) and net radiative forcing with the continental glaciation record (*7*, *8*) and low-latitude temperature estimates (*5*) (see the figure).

Estimates of CO_2 variations are based on carbon cycle modeling and on geochemical proxies. Modeled oscillations in CO_2 (see panel A in the figure) result from an interplay of outgassing and weathering changes due to, for example, uplift of mountains. The large downward trend in CO_2 reflects the appearance of vascular land plants about 380 to 350 Ma, which accelerated silicate weathering and created a new sink of more bacterially resistant organic matter (lignin) in marine and nonmarine sediments. CO_2 proxy estimates (panel A) (*9*) are based on indices whose variations correlate with atmospheric CO_2—paleosols (fossilized soils), marine sedimentary carbon, the stomata of fossil leaves, and the boron isotopic composition of carbonate fossils. There is good first-order agree-

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