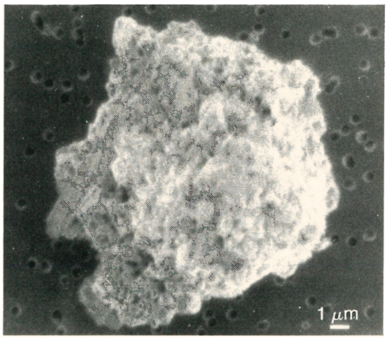
COMPLEX ORGANIC MOLECULES FOUND IN INTERPLANETARY DUST PARTICLES

Two research groups—one in Missouri that specializes in the identification and analysis of extraterrestrial particles, and one in California that has a long history of using laser technology to solve a range of problems—have combined their expertise to confirm the presence of polycyclic aromatic (benzene-skelton-containing) hydrocarbon molecules on interplanetary dust particles.[1] Frank Stadermann (now at the Technische Hochschule in Darmstadt, Germany), Patrick Swan and Robert Walker, in work done at the McDonnell Center for the Space Sciences at Washington University, Saint Louis, demonstrated that the particles were indeed extraterrestrial and classified them mineralogically. Then the microprobe two-step laser mass spectrometer, an instrument built by graduate students Simon Clemett and Claude Maechling in the laboratory of Richard Zare at Stanford University, provided evidence of the complex organic compounds: aromatic hydrocarbons composed of two or more six-carbon rings, and their alkylated (hydrocarbon-chain-containing) derivatives.

Zare and Walker note that the complexity of the mass spectra observed for the submillimeter particles is without precedent in the laboratory study of extraterrestrial material. And because the Earth accretes roughly 40 000 tons of interplanetary dust each year,[2] the observation that it carries elaborate organic compounds suggests that organic matter on our planet has its origins in interplanetary—or perhaps interstellar—space.

In the mid-1970s, at the urging of Walker and Don Brownlee (University of Washington, Seattle), NASA began a program, based at the Johnson Space Center in Houston, of collecting extraterrestrial particles picked up during U2 aircraft flights in the stratosphere. Dust particles stick to silicone-oil-coated collectors deployed when the aircraft reaches a cruising altitude of about 20 km.



Scanning electron micrograph of a 20-μm chondritic interplanetary dust particle named Florianus by Washington University researchers shows its porous, fluffy character. Florianus, which belongs to the subset of anhydrous dust particles, has large enrichments of deuterium and ^{15}N relative to terrestrial values.

Some of these particles have been shown, through a variety of characterization techniques, to come from interplanetary space. That these particles are samples of asteroids or comets, primitive bodies formed in the early solar system, is a prime motivation for studying them in the laboratory, explains Brownlee, a pioneer of the field. In addition, Brownlee, Walker and others suggest that interplanetary dust has probably carried organic matter to Earth since the early aeons of the solar system. The complexity of the organic molecules found on these particles has fueled the imaginations of many who ponder the role extraterrestrial matter may have played in the prebiological evolution of organic material on the primordial Earth.[3]

Most minerals found in the dust particles are also found in meteorites.[4] And many interplanetary dust particles and many meteorites have a "chondritic" elemental composition (similar to that of the Sun's photosphere). However, the tiny stratospheric dust particles, micrometeorites about 10 microns in diameter, are in many ways dissimilar to meteorites recovered from the surface of Earth. Both kinds of samples, notes Brownlee, represent biased, or "filtered," sets of extraterrestrial particles: Meteorites and dust particles each approach the Earth at high velocities (greater than 5 km/sec). The larger meteorites must be physically strong to survive atmospheric entry; those too fragile to withstand the high stresses produced by deceleration never make it to Earth. In contrast, dust particles have large surface-to-mass ratios and decelerate in the upper, tenuous regions of the atmosphere, so that even fluffy, porous particles can survive without fragmentation or excessive heating. In addition, meteorites and dust particles have different sources and probably reach the Earth by different transport mechanisms. According to Brownlee and Walker, meteorites are believed to be fragments of asteroids produced in collisions and put into Earth-crossing orbits by planetary gravitational perturbations. Dust also is produced in asteroid collisions, but the motion of the smaller particles is dominated by the Poynting–Robertson drag effect, which gradually (over the course of 10 000 years or so) causes their orbits to decay, allowing the dust to spiral in near-circular orbits to the Earth. Comets too produce dust, notes Walker: For example, meteor showers are associated with the orbits of specific comets.

Researchers have found that interplanetary dust particles consist of heterogeneous composites of microscopic mineral grains as small as 50 Å. Some are rich in carbon, but the molecular form of the carbon is not well known. Findings from early vibrational-spectroscopic studies of these particles by Lou Allamandola, Scott Sandford (NASA Ames Research Center) and Brigitte Wopenka (Washington University)[4] indicated the possible presence of microcrystalline domains of complex organic molecules—Raman scattering typical of the carbon–carbon vibrations in amorphous carbons and, in many particles, a noticeable fluorescence. Earlier mass spectrometric studies of interplanetary dust by Filippo Radicati di Brozolo and Ronald Fleming (Charles Evans and Associates, Redwood City, California)[5] showed clusters of peaks separated by 14 atomic mass units, suggesting the presence of methylene linkages (–CH3) in place of hydrogen groups (–H).

Zare, Walker and their coworkers say that the mass spectrometric measurements they have now reported[1] confirm these earlier suggestions of complex organic molecules in interplanetary dust particles. Chondritic meteorites often contain organic matter, and polycyclic aromatic hydrocarbons are common, found in diesel exhaust and emissions from coal firing as well as meteorites. Therefore, says Walker, it is not surprising that they exist in interstellar dust. "What *is* surprising," Walker notes, "and still not understood, is the fact that the organic molecules we see in the dust particles are different from those previously seen in meteorites." Another enigma is the observation of striking isotopic anomalies—large enrichments of deuterium relative to hydrogen, as much as ten times greater than one sees in terrestrial samples—in the particles in which Zare's group observed the organic molecules.

Proving extraterrestrial origin

It takes many steps to fully characterize the dust particles and substantiate their extraterrestrial origin. The particles' small size creates one of the larger obstacles to their study: One needs special experimental techniques to locate, handle and analyze bits of material (tens of nanograms) that can't be seen with the unaided eye. Optical microscopy is used to locate particles on the collectors, from which they are then plucked, placed on a nonreactive substrate and cleaned of the silicone oil used to trap them.

Walker's group uses several analytic techniques to characterize the particles and show that they are interplanetary dust and not some form of terrestrial contaminant. Scanning electron microscope images reveal the morphologies of particles. (See the figure on page 17.) Energy-dispersive x-ray analysis measures the particles' elemental composition and provides the first screening for extraterrestrial origin. If a particle's elemental makeup is chondritic, it is probably extraterrestrial. (Chondritic particles are those that contain largely Si, Mg, Fe and Al, along with S, Ca, Cr and Ni in appropriate proportions.) Chondritic particles frequently have other telltale signs of coming from interplanetary space: the presence of solar noble gases, fossil tracks from solar flares or large deuterium enrichments.

After the elemental screening, a member of the Washington University team crushes the particle and measures the infrared transmission spectra of some fragments and the isotopic characteristics of others. Those fragments destined for isotopic measurement are placed on gold foil for analysis in a device known as an ion microprobe, or secondary-ion mass spectrometer. In the ion microprobe, a 10–20-kV beam of primary ions impinges on the sample, sputtering secondary target ions, which are accelerated through a combination of electrostatic and magnetic fields, separating the ions by mass. If the ratios of certain isotopes in the particle—D:H and ^{15}N:^{14}N, for example—differ significantly from the range measured for terrestrial samples, then the particle is almost certainly extraterrestrial. In fact, Walker and Washington University researchers Ernst Zinner and Kevin McKeegan demonstrated years ago that about one-third of all the stratospheric particles of chondritic composition have large enrichments of deuterium.[6]

The remaining fragments are mounted on potassium bromide plates. Infrared measurements in the 3–15-μm-wavelength region identify the dominant silicate minerals present in the particle and classify particles into one of three known mineral subtypes. Before shipping the relevant fragments to Stanford for further study, Walker's group relocates them on the KBr mounts and inscribes the salt plates with tiny scratches to help the Stanford team find the dust fragments in their microprobe.

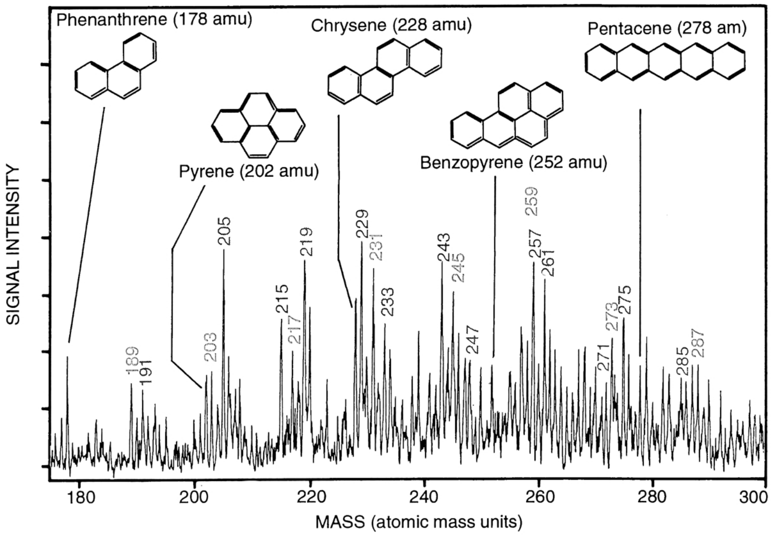
Finding organic molecules

The Stanford group places the KBr mounts in the vacuum chamber of their microprobe two-step laser mass spectrometer.[7] In the first step of the analysis a pulsed ir laser beam at 10.6 μm wavelength, focused through a Cassegrain microscope objective, desorbs molecules from the dust fragment, creating a neutral plume of molecules. In the second step, 25 μsec later, a uv laser pulse at 266 nm preferentially ionizes those molecules that absorb this wavelength, generally the aromatic hydrocarbons. The ions are extracted from the plume and injected into a reflectron time-of-flight mass spectrometer. The group records between 20 and 100 spectra for each particle.

The two-step laser microprobe offers high spatial resolution, high ion transmission, wide mass range and multichannel detection of all ion masses from a single laser pulse. And by separating the desorption and ionization processes, the two-step system avoids a significant drawback of one-step laser systems: the formation of a plasma in which the sample ions can react and decompose. Comparing his system to the one-step process, Zare notes: "We have good evidence that we are seeing the intact parent molecules. It's a kinder, gentler way to look at the substrate." And Brownlee says: "The [mass spectrometry] measurement itself is quite spectacular. They are pushing the state of the art to work on nanogram particles which contain only a small percentage of organic material."

The exceptional sensitivity of the microprobe two-step laser mass spectrometer and the ubiquity of polycyclic aromatic molecules pose difficulties for the experimenters, who must go to great lengths to convince themselves—and others—that the mass spectra obtained from the dust particles are not artifacts of terrestrial contamination. A blank plate of fine-grained silica that experienced an exposure history similar to that of the particles showed no evidence of the polycyclic compounds. The silicone oil used to collect the dust particles contains no chromophores (groups that absorb in the visible and uv regions); thus it is not ionized by the second laser pulse and is essentially invisible to the two-step laser mass spectrometer. However, the oil could have become contaminated, exposed as it is to a huge volume of stratospheric air in the collection process. Zare's group analyzed actual collection oil and observed no measurable mass spectrometric signal. The xylene used to wash the oil from the particles might also contain organic impurities, so it too was tested. Again, no contamination was found within the detection limits of the instrument. More convincing evidence is the fact that particles from the same collections identified as probable terrestrial contaminants did not show the organic signatures found in the interplanetary dust.

The Stanford team found that two of the dust particles, which were named Aurelian and Florianus, contain significant amounts of complex organic matter. The group also found that their mass spectra had some unusual characteristics. The spectrum of each of these two particles shows major groups of peaks, or "mass envelopes," near 60 amu, 250 amu and 370 amu. According to Zare the low-mass envelope probably contains inorganic species and hydrocarbon fragments that may be decomposition products of nonaromatic molecules or long-chain alkyl components of the polycyclic aromatic hydrocarbons. The higher-mass envelopes are characterized by series of peaks separated by 14 amu, indicative of methyl ($-CH_3$) or methylene ($-CH_2-$) groups, and provide evidence of polycyclic aromatic hydrocarbons with saturated hydrocarbon substituents. (See the figure on this page.) Zare's group has seen these traits in the microprobe two-step laser mass spectra of meteorites. The dust spectra, however, are more complex: The medium-mass envelopes of the dust fragments are dominated by odd-mass peaks, something not observed in meteorite spectra. The odd-mass peaks, explains Zare, could arise from the presence of nitrogen-containing cyano (–CN) or amino (–NH2) functional groups.



Mass spectrum of Florianus. The moderate-mass portion (shown here) of the microprobe two-step laser mass spectrum is dominated by odd-mass peaks and is much more complex than the spectrum of an ordinary or carbonaceous meteorite. Series of odd-mass peaks—beginning with masses 189, 191 and 215—are separated by 14-amu spacings, indicative of substitution of $-CH_3$ for –H on the periphery of the molecules. Researchers at Stanford and Washington Universities suggest that the odd-mass peaks arise from the substitution of nitrogen-containing groups for –H on the periphery. The molecular structures represent polycyclic aromatic hydrocarbons typically found in meteorite samples; note that these types of molecules do not dominate the spectrum.

Intriguing correlation

Also noteworthy is what was *not* seen in the mass spectra of the interplanetary dust: a peak near 720 amu, which is the mass of C_{60}, buckminsterfullerene. Many have speculated that the highly stable C_{60} molecule is abundant in interplanetary and interstellar space.[8] "We know we have the ability to detect C_{60} or C_{70} if it were there," says Zare, who has seen evidence of fullerenes in the mass spectra of soot from a candle flame. "There is no C_{60} in either of these two particles that we can detect."

Most intriguing, however, is a possible correlation between the isotopic anomalies and the presence of complex hydrocarbons. Aurelian and Florianus, the particles displaying the strongest mass spectroscopy signals, also have the largest deuterium and heavy-nitrogen enrichments of all the particles studied. In fact, says Walker, the ^{15}N enrichment of Florianus is among the largest recorded for an extraterrestrial object. Zare suggests that the heavy nitrogen measured in Florianus might be related to the molecules that produce the odd-mass peaks observed in the particle's mass spectrum. Walker wonders whether the observation of isotopic anomalies in these materials is coincidental or portentous. "Are the organic compounds uniquely associated with isotopic anomalies? Right now we're dealing with the statistics of small numbers. I'd like to go back to the laboratory and study a hundred particles to find the relationship, if any, between the organic compounds and the large isotopic anomalies in deuterium and nitrogen."

Washington University researchers had previously noted a link between deuterium enrichment and the presence of carbon in extraterrestrial material.[6] Now, says Walker, a tantalizing puzzle is elucidating the nature of the extraterrestrial compounds that carry deuterium. According to Brownlee, high deuterium-to-hydrogen ratios in extraterrestrial material may be associated with interstellar matter. The chemical dynamics of interstellar clouds, which are extremely cold (10 K), are driven by ion–molecule interactions, in which there is no kinetic barrier to reaction between an ion (such as D^+) and a molecule (such as HCN). The deuterated molecules have a smaller zero-point energy, and so even in the cold environment of the interstellar cloud, molecules are deuterium rich. Walker believes that some—or all—of the isotopically anomalous organic material could have formed in interstellar clouds or perhaps as circumstellar condensates similar to the circumstellar grains of silicon carbide and graphite found in meteorites.[9]

What kinds of molecules carry the deuterium? Could they be the polycyclic aromatic hydrocarbons Zare and Walker have found on Aurelian and Florianus? That is just what they would like to find out.

—Ellen J. Zeman

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