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## Identification of Complex Aromatic Molecules in Individual Interplanetary Dust Particles

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Seventeen stratospherically collected particles—eight of which are classified as interplanetary dust particles (IDPs), seven of which are classified as probable terrestrial contaminants, and two of which have uncertain origins—were studied with a microprobe two-step laser mass spectrometer. Many polycyclic aromatic hydrocarbons (PAHs) and their alkylated derivatives were identified in two of the eight IDPs. The PAHs observed include a high-mass envelope not found in meteorites or terrestrial contaminants and prominent odd-mass peaks suggestive of nitrogen-containing functional groups attached to aromatic chromophores. In addition, the complexity of the IDP mass spectra has no precedence in previous studies of meteorite samples or their acid residues. Extensive checks were performed to demonstrate that the PAH signals are not caused by terrestrial contaminants.

Interplanetary dust particles consist of several distinctive types of primitive solar system materials that have similarities to and differences from meteorites (1). These particles have been proposed as the best vehicle for carrying potential organic matter to the primordial Earth's surface (2), but because of the technological difficulties associated with analysis of small particles (typically  $\leq 20 \mu\text{m}$  in diameter), only recently has it become possible to investigate the carbon chemistry of IDPs. Measurements made with a microprobe two-step laser mass spectrometer ( $\mu\text{L}^2\text{MS}$ ) (3, 4) show the presence of a rich mixture of nonvolatile, high-mass PAHs in two IDPs.

Several carbon-rich IDPs have been identified (5, 6), some with a carbon content greater than carbonaceous chondritic

meteorites (7–9), but no definitive measurements of specific organic molecules have been reported. Allamandola, Sandford, and Wopenka (10) have suggested that PAHs are present on the basis of Raman spectra and deuterium enrichments of individual IDPs; Wopenka reported that some particles show C–C vibrations characteristic of amorphous carbons and coals (11); and Swan, Walker, Wopenka, and Freeman (12) found infrared bands at 3.4  $\mu\text{m}$  characteristic of C–H stretches. Previous mass spectrometric studies of individual IDPs also have provided evidence for organics. Time-of-flight secondary-ionization mass spectrometry studies of a thinly sliced section of an IDP showed a faint signal with a high-mass envelope between 500 and 700 atomic mass units (amu) (13), although spectral interferences from silver ion attachment, fragmentation, and nonselective ionization prevented identification of the components of this envelope. Clusters of peaks separated by 14 amu indicate, however, the presence of methylene ( $\text{CH}_2$ ) units or the replacement of H by  $\text{CH}_3$ . This

evidence, like that of the vibrational spectroscopy, suggests that the carbon in IDPs is at least partially organic.

Laser microprobe studies have been performed on IDPs as small as 10  $\mu\text{m}$  (14, 15). The laser microprobe technique differs from the use of the  $\mu\text{L}^2\text{MS}$  in that the desorption and ionization are accomplished in the same step, thereby eliminating selectivity and promoting fragmentation. Trace amounts of organic material used in collection and curation (silicone oil, hexane, and freon) created serious interferences in the first studies (14), but later work that included background correction (16) minimized this problem. Nevertheless, no specific molecular information was obtained.

Our experimental procedure was as follows. Dust particles 2 to 50  $\mu\text{m}$  in diameter were collected from the stratosphere (altitude, 20 km) on "flags" mounted on the wings of the National Aeronautics and Space Administration's (NASA's) high-altitude ER-2 aircraft. The particle impact collector, which consisted of a surface coated with a thin film of viscous silicone oil, was examined postflight in a clean room, and particles were removed for further analysis (17, 18) (Table 1).

Elemental abundances were determined with a scanning electron microscope equipped with an energy dispersive x-ray detector (SEM-EDX). Particles denoted "chondritic" have Si, Mg, or Fe as the dominant element, contain Al (amounts less than that of Mg), as well as S, Ca, Cr, and Ni in variable proportions, and do not contain large proportions of K, Ti, or other elements not normally seen in the x-ray spectra of meteorite standards. Previous studies (19–22) have proven that many chondritic stratospheric particles are IDPs; by extrapolation, all chondritic particles are so classified. We also distinguished between probable terrestrial contaminants (TCs) (on the basis of, for example, their size or sporadic, large abundances on certain collectors) and particles for which other evidence suggests an extraterrestrial source and whose origin is thus uncertain.

The particles were crushed between quartz plates with apparatus at Washington University, and the material adhering to one of the plates was transferred to a KBr crystal mount for microscopic Fourier transform infrared spectroscopy (micro-FTIR) absorption measurements (23), micro-Raman scattering studies (10), or both. Material from the companion plate was transferred to a gold foil, and isotopic measurements were made with a modified Cameca IMS-3F ion probe (22). The SEM-EDX and ion microprobe results are presented elsewhere (24, 25). The relevant dust fragments were relocated on the KBr mounts and remeasured by micro-FTIR spectroscopy.

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py. Marks were also inscribed onto the KBr mounts to help locate the particles in the  $\mu\text{L}^2\text{MS}$ .

The KBr mount containing the particle was affixed to a ceramic sample platter at Stanford University. The  $\mu\text{L}^2\text{MS}$  described previously (3) has since been modified (26). The detection limits were in the subattomole ( $<10^7$  molecules) range (1 amol =  $10^{-18}$  mol) (27). Samples were introduced into the  $\mu\text{L}^2\text{MS}$ , and constituent neutral molecules of the sample were first desorbed with a pulsed infrared laser beam focused through a Cassegrain microscope objective to an analysis spot 40  $\mu\text{m}$  in diameter. In a second step, 25  $\mu\text{s}$  after the desorption laser pulse, PAHs in the neutral plume of desorbed material were preferentially ionized by a pulsed ultraviolet (UV) laser beam with 1 + 1 resonance-enhanced multiphoton ionization (REMPI). Resultant ions were extracted from the plume and injected into a reflectron time-of-flight mass spectrometer (28).

Positive detection of PAHs was obtained for two IDPs, Aurelian and Florianus. Both are certainly extraterrestrial, each has a

**Table 1.** Summary of particles studied on the U44 and U47 collectors.

| Particle number* | Name†      | $\mu\text{L}^2\text{MS}$ signal (%)‡ | Particle type§ |
|------------------|------------|--------------------------------------|----------------|
| U47-M1-2a        | Aurelian   | $\approx 100.0$                      | IDP            |
| U47-M1-7a        | Florianus  | 93.0                                 | IDP¶           |
| U47-M2-11e       | Anastasius | 3.6                                  | TC             |
| U47-M3-2a        | Commodus   | 4.1                                  | TC             |
| U44-M1-1         | Galba      | 1.5                                  | IDP            |
| U44-M4-1c        | Gratian    | 1.3                                  | IDP            |
| U44-M4-9a        | Jovian     | 7.3                                  | IDP            |
| U44-M6-1a        | Majorian   | 2.2                                  | IDP            |
| U44-M1-7g        | Nero       | 1.7                                  | IDP#           |
| U44-M2-3b        | Romulus    | 0.9                                  | IDP            |
| U44-M6-9a        | Glycerius  | 57.2                                 | UN**           |
| U44-M3-1         | Libius     | 2.1                                  | UN††           |
| U44-M1-6         | Caligula   | 78.2                                 | TC             |
| U44-M2-11a       | Antonius   | 3.7                                  | TC             |
| U44-M5-1a        | Decius     | 138.8                                | TC             |
| U44-M1-8b        | Otho       | 1.7                                  | TC‡‡           |
| U44-M3-5b        | Philip     | 6.0                                  | TC             |

\*The identification symbols denote the U2 collector flag, the nucleopore mount, and the number of the specific particle on the mount. †The nomenclature scheme devised by Stadermann, who originally selected the particles and made the isotopic measurements as part of his thesis work (25), is apparent to those familiar with the names of Roman emperors. ‡Integrated signal from 1 to 700 amu normalized to Aurelian. Values  $<10\%$  are not considered significant. §IDP, particle with chondritic composition; TC, particle that has major element composition and other properties indicative of terrestrial contaminants; UN, particle with uncertain origin. ||Deuterium enrichment  $\delta\text{D} = 771 \pm 85$  per mil. ¶ $\delta\text{D} = 1120 \pm 100$  and  $\delta^{15}\text{N} = 411 \pm 20$  per mil. # $\delta\text{D} = 244 \pm 68$  per mil. \*\*Na and Cl present, but  $\delta\text{D} = 441 \pm 93$  per mil. ††K-feldspar composition, but  $\delta\text{D} = 194 \pm 74$  per mil. ‡‡FeO.

chondritic elemental spectrum, and both have large deuterium enrichments. Furthermore, the  $^{15}\text{N}$  enrichment recorded for Florianus is among the largest recorded for an extraterrestrial object (24) (Table 1).

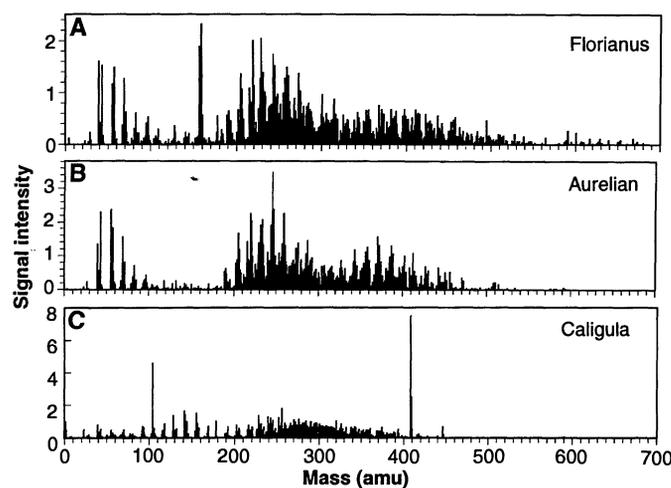
The  $\mu\text{L}^2\text{MS}$  results for Aurelian and Florianus were compared with those from a TC particle (Fig. 1). Laser shots made at locations on the KBr mount 100  $\mu\text{m}$  from the marked IDPs gave integrated signal intensities of less than 3% of the value for Aurelian and showed no evidence of PAHs. An integrated signal intensity less than 10% of the value for Aurelian was arbitrarily defined to mean that the material is devoid of PAHs. The mass spectra of both particles show three major mass envelopes: one near 60 amu; one at moderate mass, peaking at 250 amu; and one at high mass, peaking at 370 amu. In addition, Florianus shows a very weak fourth mass envelope that spans the range 580 to 670 amu (29). The moderate-mass envelope has the largest intensity, followed in decreasing order by the high and low envelopes. The low-mass envelope contains inorganic species, such as Na, K, and Al, that are easily ionized by the pulsed UV beam, as well as traces of hydrocarbon fragments ( $\text{C}_4\text{H}_x$ – $\text{C}_9\text{H}_x$ ). The presence of such hydrocarbon fragments is uncharacteristic of REMPI, which under our experimental conditions is a soft-ionization process for PAHs. The fragments may result from the decomposition of some other nonaromatic species in the desorbed plume or could be decompo-

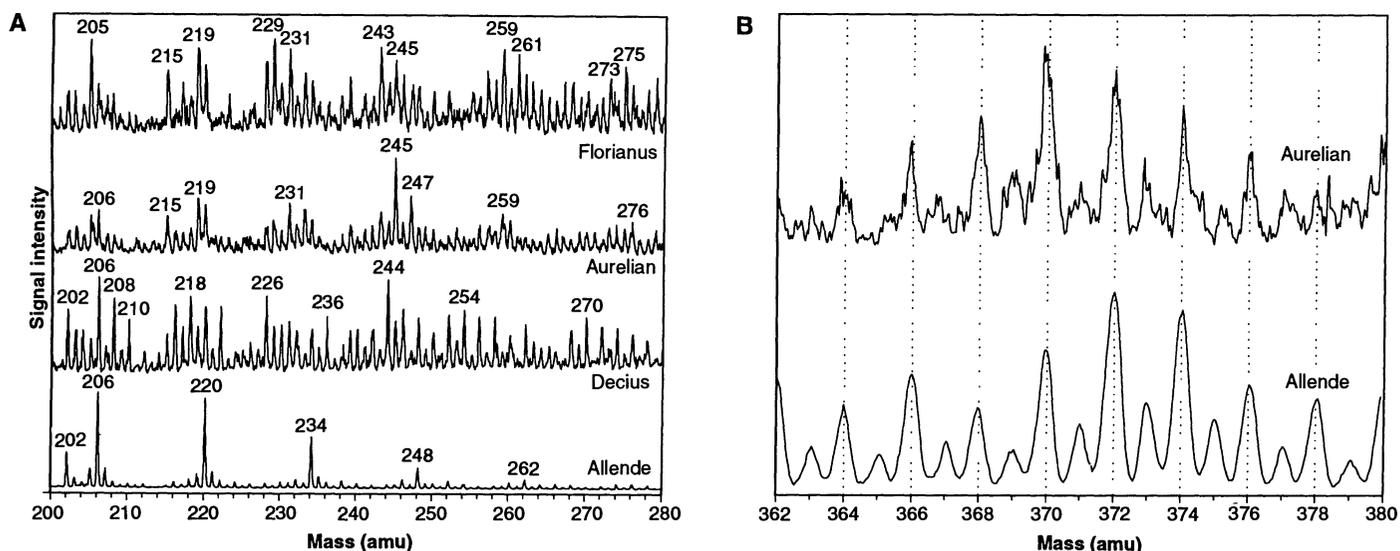
sition products of long-chain alkylated PAHs. The PAHs we observe in the upper-mass envelopes can be described by extensive alkylation to a degree far greater than we observe in chondritic meteorites.

The moderate-mass and high-mass envelopes contain signatures of PAHs and their alkylated derivatives, which are indicated by sequences of peaks separated by 14 amu as a consequence of successive addition of methylene ( $\text{CH}_2$ ) groups to the PAH skeletons. In striking contrast to those of meteorites, the  $\mu\text{L}^2\text{MS}$  spectra of the IDPs are dominated by odd-mass peaks in the moderate-mass envelope (Fig. 2A). In some cases, the odd-mass peaks might be accounted for by  $\beta$ -alkyl cleavage of extensively branched hydrocarbons adjacent to the aromatic chromophore, although this type of fragmentation has never been observed on meteorites. The presence of nitrogen would also explain the presence of dominant odd-mass peaks and is consistent with ion probe measurements of the particle that show a high nitrogen-to-carbon ratio (30). Owing to the weak photoionization cross section of nitrogen-containing heterocycles at 266 nm, we suggest the nitrogen is present in functional groups, such as CN or  $\text{NH}_2$ , attached to aromatic chromophores.

Even-mass species that dominate the high-mass spectra and the peaks separated by 2 amu (Fig. 2B) are familiar features that support the idea of successively dehydrogenated PAH species. This high-mass envelope constitutes roughly 30% of the total

**Fig. 1.** The  $\mu\text{L}^2\text{MS}$  spectra of the IDPs (A) Florianus and (B) Aurelian. Both have three mass envelopes. The lightest mass envelope contains inorganic species and traces of hydrocarbon fragments, whereas the two heavier mass envelopes show PAH signatures with distributions different from those seen in meteoritic samples. The peaks between 155 and 165 amu are the isotopomers (molecules made up of different isotopes) of the  $\text{K}_2\text{Br}^+$  cation, which are co-desorbed from the KBr mount. KBr is transparent to the IR laser beam, and these small clusters are produced from indirect heating of the KBr by an IR-absorbing particle (53). Florianus also has a fourth envelope in the mass range 580 to 670 amu. (C) The two-step mass spectrum of the TC particle Caligula has different mass envelopes, and strong peaks occur at 408 and 446 amu. The spectra are richer than the  $\mu\text{L}^2\text{MS}$  spectra of chondritic meteorites, which makes molecular identification more difficult. In common with meteorites, even-mass PAH skeletons—such as naphthalene (128 amu), phenanthrene (178 amu), pyrene (202 amu), chrysene (228 amu), benzopyrene (252 amu), and pentacene (278 amu)—were identified (54), and extensive alkylation series [up to (C-20)-alkyl-phenanthrene] for these skeletons are observed well into the high-mass envelope. Assignments for alkylation series peaks above 300 amu are complicated by overlap with larger PAHs, and their alkylation series, and are considered tentative.





**Fig. 2.** (A) Comparison of the  $\mu\text{L}^2\text{MS}$  spectra from the IDPs Florianus and Aurelian, the TC particle Decius, and the Allende (CV3) carbonaceous chondrite. Unlike the Decius and Allende spectra, the Florianus and Aurelian spectra are dominated by the odd-mass peaks indicated on the Florianus spectrum and are much more complex than that of the meteorite. The scale for each spectrum is not equivalent: Each spectrum is

normalized to the largest peak for the range shown. (B) Comparison of the two-step laser spectra in the high-mass region from the IDP Aurelian and the Allende (CV3) carbonaceous chondrite. The even-mass peaks separated by 2 amu and clustered into a 14-amu-wide subenvelope are similar for the two samples; however, the centroids of the subenvelopes are offset by 2 amu.

$\mu\text{L}^2\text{MS}$  signal, compared with typically <1% for chondritic meteorites.

In contrast to interior samples of meteorites, all IDPs are strongly heated during atmospheric entry. For example, a 10- $\mu\text{m}$  particle coming in at vertical entry is expected to reach temperatures of roughly 800 K for a few seconds during atmospheric deceleration at altitudes above 100 km (31). To assess possible atmospheric entry effects, we studied a sample of Allende (CV3) crushed to a grain size of less than 150  $\mu\text{m}$  and obtained spectra after various heating events (32). We conclude that the multimodal mass-envelope distribution and dominant odd-mass peaks seen in the IDPs were not produced during atmospheric entry.

With the exception of the peaks in the

Florianus spectrum at 155 to 165 amu and the fourth envelope, the IDP spectra show similar mass envelopes, although they differ in detail. These IDPs exhibit a relatively small abundance, particularly with respect to the alkylated homologs, of low-mass PAHs (between 78 and 192 amu) such as alkylbenzenes, alkyl-naphthalenes, and alkylphenanthrenes (Fig. 3), which is important because these compounds are well-documented components of meteorites (3, 33–36). Their depletion is consistent with evaporation of these lower mass, more volatile organic components during prolonged exposure in space, loss by heating during atmospheric entry, or both.

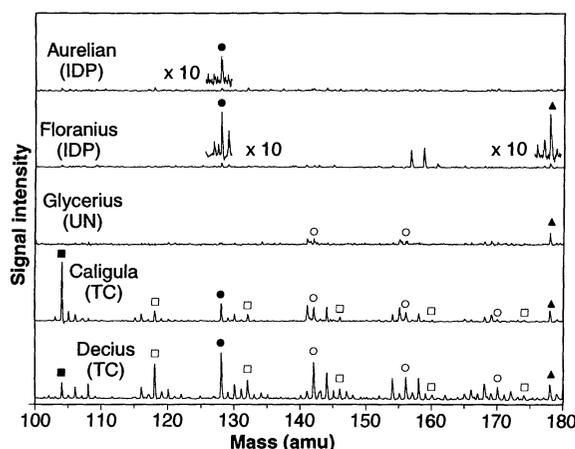
Extensive experiments have been carried out to ascertain that the PAH signa-

tures obtained from the IDPs Aurelian and Florianus are not artifacts caused by the wide-scale distribution of PAHs in the terrestrial environment (37) and the exceptional sensitivity of the  $\mu\text{L}^2\text{MS}$  instrument. During selection, curation, and analysis, particles were exposed to a laboratory environment, so airborne contamination was investigated with a clean, oxygen-ashed plate of a fine-grained silica substrate (Cab-O-Sil) as an exposure blank. The plate, which experienced an exposure history similar to that of the particles, was analyzed, and no PAHs were observed. Checks on the in vacuo environments were also performed, and no PAH contamination was found (38).

The silicone oil used as a collection medium for stratospheric particles contains no aromatic chromophores and therefore cannot be ionized; thus, it is essentially invisible to the  $\mu\text{L}^2\text{MS}$  technique. The oil may have become contaminated in the collection process, during which each collector samples some 80,000  $\text{m}^3$  of stratospheric air (17), but small beads of the oil from the U44 and U47 collectors placed onto Cab-O-Sil and analyzed in the  $\mu\text{L}^2\text{MS}$  chamber showed no signal above background. We removed the silicone oil from the collected particles by aspirating them over a nucleopore filter and washing them with xylene (22). Possible contamination from PAH impurities in the xylene was checked by two methods but proved negative (39).

We studied two particles previously identified as TCs from collector U47. The

**Fig. 3.** The  $\mu\text{L}^2\text{MS}$  spectra for the IDPs Aurelian and Florianus, an UN particle Glycerius, and two TC particles, Caligula and Decius. The strong presence of low-mass PAHs (between 80 and 190 amu) in the UN and TC particles, such as alkylbenzenes, (□) alkylstyrenes, (○) alkyl-naphthalenes, and alkylphenanthrenes, is in stark contrast to the Aurelian and Florianus spectra. (■) Styrene (104 amu), (●) naphthalene (128 amu), and (▲) phenanthrene (178 amu). The scales for all the spectra are equivalent; therefore, expansions of small peaks for the IDPs are plotted and annotated with the scaling factor. The peaks in the mass range 155 to 165 amu for the IDP Florianus are attributed to the isotopomers of  $\text{K}_2\text{Br}^+$  codesorbed from surrounding matrix.



first particle, Anastasius, was dominated by Si, O, and Al; the second, Commodus, by Ca, O, and Si. For neither did the ion probe reveal isotopic anomalies in H, N, C, or Mg. The total integrated yield of masses measured by  $\mu\text{L}^2\text{MS}$  are listed in Table 1; the mass spectra showed no evidence of PAHs. The fact that control particles exposed to the same environment as Aurelian and Florianus did not show abundant PAHs strongly supports the indigenous origin of the PAHs in the IDPs.

Of 13 stratospheric particles from collector U44, none of the six classified as IDPs gave significant PAH signatures. Thus, not all IDPs have large PAH concentrations. In addition, two TC particles, Caligula and Decius, gave large PAH signals. The mass spectra for these "terrestrial" particles (40) look similar to each other but are quite dissimilar to the spectra for the IDPs Aurelian and Florianus. These particles have low-mass PAHs (between 80 and 190 amu), such as alkylbenzenes, alkylstyrenes, alkyl-naphthalenes, and alkylphenanthrenes (Fig. 3), which are in stark contrast to the Aurelian and Florianus spectra. In addition, the mass envelopes are different, and strong peaks occur at 408 and 446 amu.

There has been indirect evidence of complex organic molecules in IDPs (1, 10–13, 16, 22) and a subset of comet Halley dust particles called CHONs (for carbon, hydrogen, oxygen, and nitrogen) (41–45). Moreover, PAHs have been found by  $\mu\text{L}^2\text{MS}$  in various meteorites and meteoritic acid residues (3, 34, 46–48). The mass patterns observed in Aurelian and Florianus, however, differ substantially from those of other extraterrestrial materials; the former are much richer and are dominated by odd-mass species in the mass range 180 to 340 amu.

Deuterium enrichments in IDPs, as well as in primitive meteorites, are known to be associated with carbonaceous matter (22, 49–51), and Aurelian and Florianus, the two IDPs that give large  $\mu\text{L}^2\text{MS}$  signals, also have the largest deuterium-enrichments of any of the IDPs studied. Similarly, the heavy nitrogen observed in ion probe measurements of Florianus may be carried by the molecules responsible for prominent odd-mass peaks in the  $\mu\text{L}^2\text{MS}$  spectrum of the particle. Many more particles must be studied by combined techniques to test these possible correlations.

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- A 50 Å thick layer of coronene ( $\text{C}_{24}\text{H}_{12}$ , 300 amu) was vapor deposited onto a glass substrate and analyzed with a 40- $\mu\text{m}$  desorption beam, defining an analysis volume of 30 fmol of coronene. The layer was removed in eight laser shots, which corresponds to about 6 amol per laser shot. This determines an upper limit to the ultimate detection sensitivity at 6 amol for the molecule coronene or 0.15 amol for the molecule phenanthrene ( $\text{C}_{14}\text{H}_{10}$ , 178 amu), accounting for the differing photoionization cross sections (52). The ion-extraction region was reconstructed before the analysis of the IDPs. Whereas the above sensitivity experiments were not repeated, micrometer-sized interior fragments of both the Murchison (CM2) and Allende (CV3) meteorites yielded well-resolved, single-shot mass spectra of PAHs. The total concentration of extractable PAHs in these meteorites has been estimated to be in the range of 15 to 28 parts per million [K. L. Pering and C. Ponnampuram, *Science* **173**, 237 (1971)].
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- Allende (CV3) grains both unheated and heated were prepared by C. M. O'D. Alexander and X. Gao. No increase in the proportion of odd-mass peaks was observed in any of the heated samples [flash heating (2 min) at 573 and 873 K in air and prolonged heating (24 hours) at 873 K under argon in a sealed platinum bucket]. The PAHs heavier than 350 amu were virtually unaffected, but the more volatile lower mass PAHs were reduced in abundance. Flash heating in air at 873 K reduced the total  $\mu\text{L}^2\text{MS}$  signal by two orders of magnitude, whereas prolonged heating in a closed, inert environment reduced the signal only by half.
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- The  $\mu\text{L}^2\text{MS}$  chamber is pumped by an essentially oil-free system: two turbomolecular pumps and a liquid nitrogen cryopump. Contamination checks for this chamber were previously reported (2). After cleaning, the particles were exposed to an SEM, whose chamber is pumped with diffusion pumps using Fomblin oil, a perfluoropolyether. Samples of Fomblin oil on Cab-O-Sil were studied by  $\mu\text{L}^2\text{MS}$ ; no PAH contamination was detected.
- First, a volume of xylene equivalent to that used to wash a particle (250  $\mu\text{l}$ ) was placed on a KBr mount, which was analyzed for PAHs after the xylene had evaporated. No evidence of contamination was observed. Second, five chondritic particles (Jovian, Majorian, Gratian, Galba, and Nero) from collector U44 were processed the same way, except that Jovian, Majorian, and Gratian were washed with xylene, and Galba and Nero were not. The spectra for all five particles are similar, and none shows a PAH signature.
- The particle Glycerius is not readily classified as either an IDP or a TC. Stadermann (25) reports a large deuterium enrichment ( $441 \pm 93$  per mil) in one of three pieces measured, which argues for an extraterrestrial origin; however, the other two pieces showed no enrichment. Moreover, the x-ray spectrum shows significant peaks at Na and Cl, and the particle is thus not "chondritic." In addition, the  $\mu\text{L}^2\text{MS}$  mass spectrum of Glycerius is similar to that of the terrestrial particles Caligula and Decius, particularly in the higher mass distributions, further indicating that Glycerius is probably a TC.
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 54. These identifications are based on extensive experience with standard samples and the fact that the UV laser is tuned to selectively photoionize aromatic molecules. Except for naphthalene, there are structural isomers for these assignments, and their contributions are uncertain. We do know, however, that the absorption cross section for phenanthrene and pyrene are 20 and 23 times stronger than that of their isomers anthracene and fluoranthene, respectively (52).  
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## The Effect of Changing Land Use on Soil Radiocarbon

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Most carbon budgets require greening of the terrestrial biosphere as a sink for some of the excess carbon dioxide produced by fossil fuel burning and deforestation. Much of this storage is thought to occur in soils, but running counter to this conclusion is the observation that cultivation has reduced the agricultural reservoir of soil humus. Radiocarbon measurements in agricultural soils lend support to this browning of agricultural lands. Moreover, the loss is from the fast cycling portion of the humus.

Soil contains about three times the amount of carbon that was present in the preindustrial atmosphere. This study uses soil radiocarbon measurements to explore the dynamics of soil carbon loss associated with agriculture, a significant source of atmospheric CO<sub>2</sub>.

In a survey of 1100 paired soil analyses (1), agriculturally modified topsoils averaged 25% less carbon than their native counterparts. As cultivated soil now contains about 180 gigatons of carbon (GtC) (2), this loss has added 60 GtC to the atmosphere and may have contributed as much as 0.5 GtC annually during the 1980s (3). There are a variety of reasons why disturbed soil might have less carbon than its native counterpart. These include reduction in the annual input of plant residues, increased decomposition as a result of elevated soil temperature, aeration, and extra moisture (4). In addition, plowing increases surface area, which accelerates soil carbon respiration (5). Although erosion is another way in which soil carbon could be lost from the profile, it should not change the

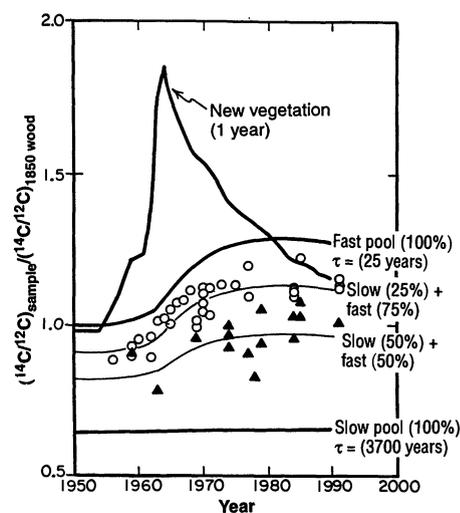
carbon concentration. Only the thickness of the topsoil would be diminished. Further, carbon losses from the soil due to erosion are much less than losses due to oxidation (4).

As we have shown in a previous paper (6), based on radiocarbon data, the carbon in soil can be divided into fast and slow turnover time pools. We suggest that the carbon lost from agricultural soils must have come from the fast cycling pool. If so, then this loss should be matched by a decrease in the <sup>14</sup>C/C ratio of bulk soil carbon. The logic is as follows: The evolution of radiocarbon in the surface of natural soil can be modeled by the assumption that 25% of the carbon resides in a slow-turnover pool with a <sup>14</sup>C/C ratio averaging 0.63 of that for preindustrial carbon (6). Because of its slow turnover, no significant bomb <sup>14</sup>C has entered this reservoir. The remaining 75% of the carbon resides in a fast turnover pool with a mean replacement time of 25 years. A 3:1 mix of these two end-members yields a time history that passes through the median of the available radiocarbon measurements on bulk carbon from uncultivated topsoil collected at various times and places over the globe (Fig. 1). If the 25% loss were to have come entirely from the fast cycling carbon pool, then the fast:slow proportions would be changed from a 3:1 mixture to a 2:1 mixture. Although agricultural soil has

a lower radiocarbon content than native soil, the deficiency is even greater than expected for a 25% loss (Fig. 1). Rather, the best fit curve corresponds to a 1:1 mixture of slow and fast cycling carbon pools. To accomplish this would require that two-thirds of the fast cycling carbon pool be lost (that is, 50% of the total carbon). In constructing these curves, for simplicity we have assumed that the carbon loss occurred largely before the nuclear era (1958 to the present). Were the calculation to assume, instead, that half was lost after 1958, the results would change only very slightly. The shape of the best fit curve through the cultivated soil suggests that the turnover time for the fast cycling carbon pool in cultivated soil carbon is 25 years, the same as for native soil.

The greater than expected <sup>14</sup>C/C reduction for mean cultivated soil may be, in part, the result of mechanical stirring by plowing. For most soils, the <sup>14</sup>C/C ratio decreases with depth, approaching values that are 30 to 50% lower than the pre-nuclear atmospheric ratio at the base of the profile. We attribute this drop to an ever-decreasing fractional contribution of the fast turnover carbon with depth. But, because plowing homogenizes only the upper 20 cm of soil, its impact would not be expected to be large.

Data on carbon content and <sup>14</sup>C/C ratio on a native soil from New Zealand (7) are



**Fig. 1.** Plot of radiocarbon versus time for the bulk carbon in topsoils (8). The natural soils (open circles) have higher radiocarbon values than the cultivated soils (solid triangles). The thick solid lines represent new vegetation, a fast (25-year turnover time) carbon pool's, and a slow (3700-year turnover time) carbon pool's responses to atmospheric bomb radiocarbon. The thin lines designate mixtures of fast and slow cycling carbon. A 75% fast and 25% slow mixture provides the best fit for the natural soils, but a 50% fast and 50% slow mixture provides the best fit for the cultivated soils.

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