Application of Two-Step Laser Mass Spectrometry to Cosmogeochemistry: Direct Analysis of Meteorites

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Polycyclic aromatic hydrocarbons in C1, C2, and C3 carbonaceous chondrites and in some ordinary chondrites have been directly analyzed by two-step laser desorption/laser multiphoton ionization mass spectrometry, a selective and sensitive method requiring only milligram samples. At the ionization wavelength of 266 nanometers, parent ion peaks of polycyclic aromatic hydrocarbons dominate the mass spectra. Quantitative analysis is possible; as an example, the concentration of phenanthrene in the Murchison meteorite was determined to be 5.0 parts per million.

ORGANIC COMPOUNDS IN METEORites are key to understanding abiotic synthetic reactions, the cosmochemical cycle of carbon, and the role these processes may play in biogenesis. Although it was demonstrated over a century ago that some meteorites contain carbonaceous material, partly in the form of organic compounds (*1*), their analysis has posed an extreme challenge because of the limited sample amount available combined with possible contamination and chemical modification during sample storage and processing (*1, 2*). In general, many grams of meteorite material are required and their chemical analysis is laborious, often involving a series of extraction, purification, and identification steps (*1, 3*). We report here a new method for the direct analysis of meteorites, which is nondestructive from a mineralogical standpoint and requires only milligram quantities of meteorite material. It is based on two-step laser desorption/laser multiphoton ionization mass spectrometry in which the first laser thermally desorbs primarily intact neutral molecules from the sample surface and a second laser causes "soft ionization" of selected classes of compounds, permitting their identification in a time-of-flight (TOF) mass spectrometer (*4, 5*). We have applied this method to a variety of meteorites for the detection of polycyclic aromatic hydrocarbons (PAHs). We are able to identify and quantitate PAHs in a number of meteorites for which there was little or no previous information about their PAH content.

It has been well established that C1 and C2 carbonaceous chondrites contain a vast assortment of organic molecules (*3, 6*), including amino and carboxylic acids, alkyl and aromatic hydrocarbons, purines, and a high molecular weight polymer that resembles kerogen, the most abundant organic component on the earth. Other meteorite types contain only trace amounts or are totally devoid of organic carbon. Recently, attention has focused on the need for the direct detection of PAHs because their presence has been implicated in interplanetary dust particles (*7*) as well as in the interstellar medium (*8*). This surmise was based on the Raman spectra of meteorites and interplanetary dust particles (*7*) and the infrared emission bands of interstellar grains (*8*). Although these techniques provide evidence for the presence of PAHs, they do not yield any compositional or quantitative information. Our technique enables us to determine directly the PAH content and composition of such samples in a rapid, highly selective, and sensitive manner.

The two-step laser methodology has been described previously (*4, 5*). In the first step, the pulsed output of a CO_2 laser (10.6 μm; 30 mJ/pulse; 10-μsec pulse width; 6-Hz repetition rate) is focused onto a small spot (≈1 mm diameter) on the meteorite sample (Fig. 1a). The infrared (IR) radiation is readily absorbed by the meteorite minerals and causes the ejection of intact neutral molecules from their surfaces in a rapid laser-induced thermal desorption process (Fig. 1b). The fact that desorption dominates over decomposition in rapid laser heating processes has been demonstrated for many molecular adsorbates (*4, 5, 9*). The sample can be rotated by a stepping motor in order to expose fresh surface to the desorption laser. After an appropriate time delay (≈130 μsec), the fourth harmonic of a neodymium:yttrium-aluminum-garnet (Nd:YAG) laser (266 nm; 2.5 mJ/pulse; 10-nsec pulse width; 6-Hz repetition rate) is used to induce 1+1 resonance-enhanced multiphoton ionization (REMPI) of the desorbed molecules in an interaction region about 5 mm from the surface (Fig. 1c). With our present ionization wavelength, aromatics are selectively ionized, although with varying efficiencies for different compounds. REMPI causes soft ionization so that the parent ions of the desorbed aromatic compounds almost exclusively dominate the mass spectrum (*4, 5, 9, 10*). One of the characteristics of our method is the spatial and temporal separation of the desorption and ionization processes; this gives us more control than in one-step desorption/ionization processes. We estimate that our total ionization efficiency is about a factor of 100 to 1000 greater than that of methods where ions are directly produced on a surface. The laser-generated ions are mass-separated in a reflectron TOF system (mass resolution = 500) and detected with a microchannel plate array (Fig. 1c). Usually, data from 100 laser shots were averaged as the sample was rotated, although a complete mass spectrum can be obtained from a single shot.

For sample preparation, a small portion of pulverized meteorite was well mixed with a drop of glycerol (used as a binder) and then pressed into a 7-mm diameter pellet. No extraction or further sample treatment was required. The sample pellet was mounted on the tip of a 12-mm diameter teflon rod that was directly introduced into the source region of our TOF mass spectrometer through a vacuum interlock without breaking high vacuum (10^{-7} torr) of the system. Sample introduction takes about 1 minute and the spectrum can be recorded immedi-

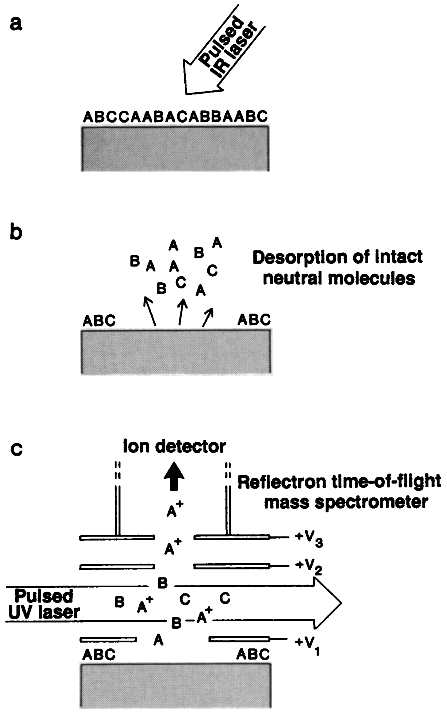

Fig. 1. (**a**) Laser-induced rapid heating of a sample by a CO_2 laser pulse; (**b**) thermal desorption of intact neutral molecules from the surface; (**c**) 1+1 resonance-enhanced multiphoton ionization of aromatic compounds by an ultraviolet (UV) laser pulse serves as an efficient, selective, and soft ionization process. The ions produced are extracted by an electric field and mass-analyzed in a reflectron TOF mass spectrometer.

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ately thereafter. For the purposes of quantitation, an aliquot of a 30 ng μl^{-1} solution of phenanthrene (Aldrich Chemical Company) in CH_2Cl_2 was added to 100 mg of the dry meteorite powder. These spiked samples were then processed as described above after evaporation of the solvent.

Our selection of meteorites includes C1, C2, and C3 carbonaceous chondrites and some ordinary chondrites (*11*). Figure 2 shows the laser desorption/multiphoton ionization mass spectra obtained from the Murchison meteorite, a meteorite that is our most pristine sample as far as terrestrial contaminants are concerned. The selection of 266 nm as an ionization wavelength enables us to detect aromatic compounds in these meteorites, in particular the PAHs, but not in general other organics that either have too high an ionization potential or fail to absorb efficiently this wavelength. The dominant masses of 128, 178, and 202 in Fig. 2 correspond to naphthalene, phenanthrene/anthracene, and fluoranthene/pyrene, respectively, which is consistent with the PAH analyses of Murchison reported previously by means of conventional wet chemistry coupled with combined gas chromatography/mass spectrometry (*12*). It is striking that the spectra of the three samples are so similar in their PAH composition, even though the samples came from different parts of the meteorite. The relative amounts of the same compound in the samples can be directly estimated from the peak heights and the scaling factors. The differences in the relative PAH abundances can be attributed to the well-known inhomogeneous distribution of organics within the whole meteorite (*1*). In the "Murchison #1 outside" sample, which includes part of the fusion crust, the PAHs are only somewhat less concentrated than in the other two samples, indicating that there was no extensive decomposition and alteration of PAHs during atmospheric entry of the Murchison meteorite. We observe no masses in the 500–atomic mass unit range characteristic of porphyrins, although such compounds have been shown to be readily detected at this wavelength (*5*). This confirms their absence, at least at the parts per billion level (*13*).

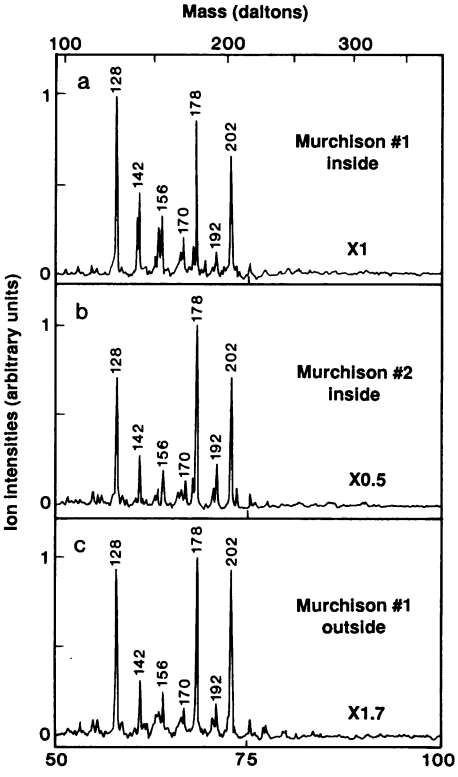

Fig. 2. Laser desorption/multiphoton ionization TOF mass spectra of (**a**) Murchison #1 inside, (**b**) Murchison #2 inside, and (**c**) Murchison #1 outside. The masses were calibrated by analyzing several known molecular weight compounds. Possible mass identifications are: 128, naphthalene; 142, methylnaphthalene; 156, C_{12}-alkylnaphthalene; 170, C_{13}-alkylnaphthalene; 178, phenanthrene/anthracene; 192, methylphenanthrene; and 202, fluoranthene/pyrene. The scaling factors are normalized to the spectrum of Murchison #1 inside.

Figure 3 shows the mass spectra of some other meteorites we studied. Each meteorite appears to have its own unique distribution of PAHs. Particularly noteworthy is Ivuna (Fig. 3a), a C1 chondrite, which apparently contains mostly phenanthrene/anthracene and their alkylated forms in considerably higher concentrations than the other meteorites. Both bicyclic and tetracyclic compounds are present only at much lower concentrations in this meteorite. Allende (Fig. 3e), a C3 chondrite, has a weak PAH signal compared to other meteorites, which is consistent with a low level of carbon (0.3%) and other organics found in the Allende meteorite (*14*). The C2 carbonaceous chondrites Murray, Mighei, and Haripura (Fig. 3, b, c, and d) contain in addition to the masses found in Murchison some heavier masses that correspond to increasing alkylation of naphthalene and phenanthrene/anthracene. Two possible reasons for this observation may be put forward. Terrestrial PAHs, which incidentally are not biosynthetic products (*15*), show a high degree of alkylation (*16*) and thus the extra masses in the other C2 meteorites may indicate the presence of terrestrial PAH contamination. This seems doubtful, however: the ordinary

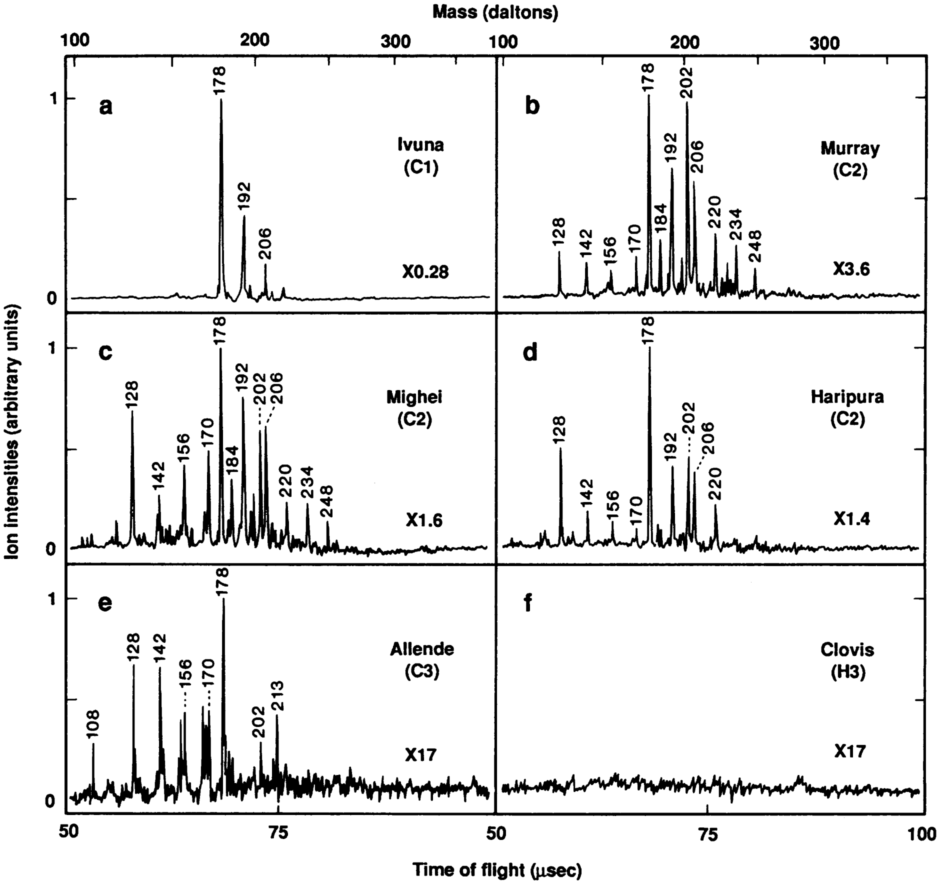

Fig. 3. Laser desorption/multiphoton ionization TOF mass spectra of (**a**) Ivuna, (**b**) Murray, (**c**) Mighei, (**d**) Haripura, (**e**) Allende, and (**f**) Clovis. The dominant masses other than those in Fig. 2 are tentatively identified as: 184, C_{14}-alkylnaphthalene; 206, C_{16}-alkylphenanthrene/C_{16}-alkylanthracene; 220, C_{17}-alkylphenanthrene/C_{17}-alkylanthracene; 234, C_{18}-alkylphenanthrene/C_{18}-alkylanthracene; and 248, C_{19}-alkylphenanthrene/C_{19}-alkylanthracene. The scaling factors are normalized to the spectrum of Murchison #1 inside (Fig. 2a).

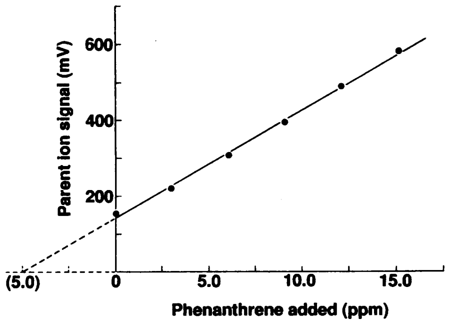

Fig. 4. The ion intensity for mass 178 of the Murchison #1 inside sample spiked with various amounts of a known phenanthrene solution (30 ng μl^{-1}). Extrapolation to an ion intensity =0 yields a phenanthrene concentration in the unspiked sample of 5 $\mu g\ g^{-1}$ or 5 ppm.

chondrite Clovis (Fig. 3f) shows no PAH components (*17*) and it should be just as susceptible to terrestrial contamination as the carbonaceous chondrites. Another possible explanation for the presence of more alkylated PAHs is that these C2 meteorites were heated more extensively than others sometime throughout their history, since the high extent of alkylation of PAHs has been attributed to the thermal cracking of the "organic polymer" (*3, 18*).

For quantitation we spiked the Murchison #1 inside sample with various amounts of phenanthrene. Figure 4 plots the phenanthrene parent ion peak heights versus the amount of phenanthrene added to the sample. The linearity is excellent. The calculated concentration of phenanthrene for the unspiked Murchison meteorite sample is 5.0 parts per million (ppm). Pering and Ponnamperuma (*12*) previously reported that Murchison contains 3 to 5 ppm of phenanthrene.

The relative abundances of different PAHs are not determined because of different ionization efficiencies. However, from the relative ion intensities in different spectra we found that the concentration of PAHs is in the order of Ivuna > Murchison ≈ Haripura ≈ Mighei ≈ Murray > Allende. This sequence is similar to the order of the carbon content of the various carbonaceous chondrites (*11*). We can assume that the desorption efficiencies are similar for the various carbonaceous chondrites and conclude that Ivuna contains roughly 15 to 20 ppm of phenanthrene/anthracene. The other C2 chondrites have abundances similar to Murchison. Allende has ≈0.5 ppm of phenanthrene/anthracene. This is close to the detection limit (with a signal-to-noise ratio of 2) of our system, which is calculated to be about 0.3 ppm, corresponding to 2 fmol per laser shot. Ordinary noncarbonaceous chondrites, like Clovis (and the Chinese meteorite Jilin, which we also analyzed), are devoid of PAHs, at least at the sensitivity of our system.

One CO_2 laser shot desorbs PAHs from approximately 1 μg of a sample and can produce a complete mass spectrum. Thus, we believe that the two-step laser methodology has particular promise as a tool in cosmogeochemistry because the technique is well suited to the analysis of samples available only in limited amounts.

REFERENCES AND NOTES

1. See B. Nagy, *Carbonaceous Meteorites* (Elsevier, Amsterdam, 1975), for a comprehensive review of this early research.
2. J. M. Hayes, *Geochim. Cosmochim. Acta* **31**, 1395 (1967); P. G. Stoks and A. W. Schwartz, *ibid.* **45**, 563 (1981); J. L. Bada *et al.*, *Nature (London)* **301**, 494 (1983).
3. E. Anders and R. Hayatsu, *Top. Curr. Chem.* **99**, 1 (1981).
4. F. Engelke, J. H. Hahn, W. Henke, R. N. Zare, *Anal. Chem.* **59**, 909 (1987).
5. J. H. Hahn, R. Zenobi, R. N. Zare, *J. Am. Chem. Soc.* **109**, 2842 (1987).
6. F. Mullie and J. Reisse, *Top. Curr. Chem.* **139**, 83 (1987).
7. L. J. Allamandola, S. A. Sandford, B. Wopenka, *Science* **237**, 56 (1987).
8. L. J. Allamandola, A. G. G. M. Tielens, J. R. Barker, *Astrophys. J.* **290**, L25 (1985).
9. R. Tembreull and D. M. Lubman, *Anal. Chem.* **58**, 1299 (1986); *ibid.* **59**, 1003 (1987); *ibid.*, p. 1082; J. Grotemeyer, U. Boesl, K. Walter, E. W. Schlag, *Org. Mass Spectrom.* **21**, 595 (1986); J. Grotemeyer *et al.*, *ibid.*, p. 645; J. Grotemeyer *et al.*, *J. Am. Chem. Soc.* **108**, 4233 (1986).
10. D. A. Lichtin, L. Zandee, R. B. Bernstein, in *Lasers in Chemical Analysis*, G. M. Hieftje, J. C. Travis, F. E. Lytle, Eds. (Humana Press, Clifton, NJ, 1981), pp. 125–141.
11. The meteorites analyzed were: Ivuna (C1, Tanzania, 1938, 3.9%); Murchison (C2, Australia, 1969, 2.1 to 2.5%); Murray (C2, United States, 1950, 2.8%); Haripura (C2, India, 1921, 4.0%); Mighei (C2, U.S.S.R., 1889, 2.5%); Allende (C3, Mexico, 1969, 0.3%); and Clovis (H3, United States, found 1960–61, 0.2%). The type of meteorite, the date of fall, and the percentage of carbon are given in parentheses and were taken from (*1*); E. A. King, Jr., E. Schonfeld, K. A. Richardson, J. S. Eldridge, *Science* **163**, 928 (1969); B. Mason, *Handbook of Elemental Abundances in Meteorites* (Gordon & Breach, New York, 1971); J. A. Wood and S. Chang, *The Cosmic History of the Biogenic Elements and Compounds, Special Paper 476* (National Aeronautics and Space Administration, Washington, DC, 1985). Three separate Murchison samples were investigated: an inside and outside portion of the original sample analyzed by K. A. Kvenvolden *et al.*, *Nature (London)* **228**, 923 (1970), and a second inside piece obtained from D. J. Macdougall who also kindly supplied the other meteorites with the exception of Allende which was provided by K. A. Kvenvolden.
12. J. Oró *et al.*, *Nature (London)* **230**, 105 (1971); K. L. Pering and C. Ponnamperuma, *Science* **173**, 237 (1971); M. H. Studier *et al.*, *Geochim. Cosmochim. Acta* **36**, 189 (1972); B. P. Basile, B. S. Middleditch, J. Oró, *Org. Geochem.* **5**, 211 (1984).
13. The ionization efficiency for porphyrins at 266 nm is very high (*5*), which implies that they should have been detectable if they were present at parts per billion levels.
14. J. R. Cronin and C. B. Moore, *Science* **172**, 1327 (1971); M. H. Studier *et al.*, *Geochim. Cosmochim. Acta* **36**, 189 (1972); J. R. Cronin, S. Pizzarello, J. S. Frye, *ibid.* **51**, 299 (1987).
15. A. Hase and R. A. Hites, *Geochim. Cosmochim. Acta* **40**, 1141 (1976).
16. R. E. Laflamme and R. A. Hites, *ibid.* **42**, 289 (1978).
17. We must caution that the lack of PAHs in ordinary chondrites may be the result of a difference in the desorption efficiencies for this type of meteorite in comparison to carbonaceous chondrites.
18. R. Ishiwatari and K. Fukushima, *Geochim. Cosmochim. Acta* **43**, 1343 (1979).
19. We thank K. A. Kvenvolden and D. J. Macdougall for generously supplying the meteorites from their collections, as well as M. Wing for preparing the pulverized samples. Partial financial support by NSF (CHE 85-05926) and the California Space Institute (University of California) is gratefully acknowledged.

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Cooperative Hunting in Harris' Hawks (*Parabuteo unicinctus*)

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Coordinated hunting by several individuals directed toward the capture and sharing of one large prey animal has been documented convincingly only for a few mammalian carnivores. In New Mexico, Harris' hawks formed hunting parties of two to six individuals in the nonbreeding season. This behavior improved capture success and the average energy available per individual and enabled hawks to dispatch prey larger than themselves. These patterns suggest that cooperation is important to understanding the evolution of complex social behavior in higher vertebrates and, specifically, that benefits derived from team hunting are a key factor in the social living of Harris' hawks.

Cooperative hunting, when individuals coordinate actions such that the probability of successful capture of one large prey item that is shared among all participants is increased, has been reported almost exclusively for social mammalian carnivores (*1*). All species that exhibit social hunting behavior also live in groups (*2*), but most investigators have argued that

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