

the calcite lattice in relation to the orientation of the diatom.

A few samples of carbonated diatoms were placed in water and subjected to an HCl-H₂O gradient on a microscope slide. As the HCl concentration increased, the "diatoms" effervesced with a violence that fortunately could be controlled to some extent by the gradient. The deterioration could be observed continuously under the microscope. Immediately after the bubbles had ceased to develop and all traces of birefringent material had been destroyed, an ethereal skeleton could be seen as a relic of the fine reticulate structure. This skeleton existed in this form for only a few seconds and then collapsed into a mass that appeared to be structureless. It was evidently unstable in the acid environment that exposed it.

The formation of pseudomorphs preserving the submicroscopic morphological detail of the parent is evidently feasible in the laboratory even when the main components have been completely changed, as from hydrated silica to calcium carbonate. The final composition and crystal structure bear no ion exchange or topotactic relationship to the original material. In the case of the particular pseudomorphing reaction reported here, the siliceous phase itself provides the site for the reactions between lime, silica, and carbon dioxide.

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References

1. C. Frondel, *Bull. Am. Mus. Nat. Hist.* **67**, 389 (1935).
2. M. C. Ball and H. F. W. Taylor, *Miner. Mag.* **33**, 467 (1963); G. W. Brindley and J. Zussman, *Am. Miner.* **42**, 461 (1957); L. S. Dent and H. F. W. Taylor, *Acta Cryst.* **9**, 1002 (1956); J. A. Gard and H. F. W. Taylor, *Am. Miner.* **43**, 1 (1958); L. S. Dent Glasser and F. L. Glasser, *Acta Cryst.* **14**, 818 (1961); A. L. MacKay, paper presented at the Proceedings of the Fourth International Symposium on the Reactivity of Solids, Amsterdam, 1961; H. F. W. Taylor, *Acta Cryst.* **8**, 440 (1955); *Adv. Sci.* **1964**, 17 (1964).
3. R. B. Peppler, *J. Res. Natl. Bur. Stand.* **54**, 208 (1955); E. P. Flint, H. F. W. Taylor, L. S. Wells, *ibid.* **21**, 617 (1938).
4. J. P. Miller, *Am. J. Sci.* **250**, 192 (1952); D. Langmuir, *Geochim. Cosmochim. Acta* **32**, 835 (1968).
5. R. I. Harker, *Miner. Mag.* **34**, 232 (1965).
6. H. W. Harvey, *J. Mar. Biol. Ass. U.K.* **31**, 475 (1953); E. G. Jorgensen, *Physiol. Plant.* **8**, 840 (1955); W. Einsele and J. Grim, *Z. Botan.* **32**, 545 (1938).
7. L. H. N. Cooper, *J. Mar. Biol. Ass. U.K.* **30**, 511 (1952).
8. E. Rogall, *Planta* **29**, 279 (1939).
9. H. K. Henisch, *Crystal Growth in Gels* (Pennsylvania State Univ. Press, State College, 1970).
10. G. Donnay and D. L. Pawson, *Science* **166**, 1147 (1969).

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Aromatic Hydrocarbons in the Murchison Meteorite

Abstract. Polynuclear aromatic hydrocarbons in the Murchison meteorite have been identified by the combined techniques of gas chromatography and mass spectrometry. The distribution of the aromatic compounds suggests that they are the products of a high-temperature synthesis.

The formation of complex organic molecules from simple compounds is considered an important cosmochemical process. Evidence for the types of molecules that are important during the early stages of chemical evolution is being obtained from laboratory simulation experiments involving such simple components as methane, carbon monoxide, water, and ammonia (1); from radio astronomical observations (2); and from analysis of the organic matter indigenous to meteorites (3).

Aromatic hydrocarbons may be an important class of primitive organic molecules: they are the major product formed from simple gases such as methane and carbon monoxide at high temperatures (4, 5), and they may be present in interstellar space (6). A variety of aromatic hydrocarbons have been reported to be present in carbonaceous chondrites (3), but lack of precise identification coupled with the ever-present question of contamination

renders the significance of much of this work somewhat equivocal. The recently fallen Murchison meteorite provides a new opportunity to characterize these compounds, since our preliminary analysis indicates that the organic matter in it is indigenous and relatively free from terrestrial contamination (7). We have now found in this meteorite 14 polynuclear aromatic hydrocarbons whose identity has been established by gas chromatography and mass spectrometry. We have further established the molecular weight of nine additional compounds by mass spectrometry.

Two pulverized meteorite samples were extracted with a mixture of benzene and methanol (9 : 1, by volume) and the recovered extracts (I and II) chromatographed on columns of silica gel, as previously described (7). The benzene fraction from one sample, referred to here as in the preliminary report (7) as sample II, was evaporated

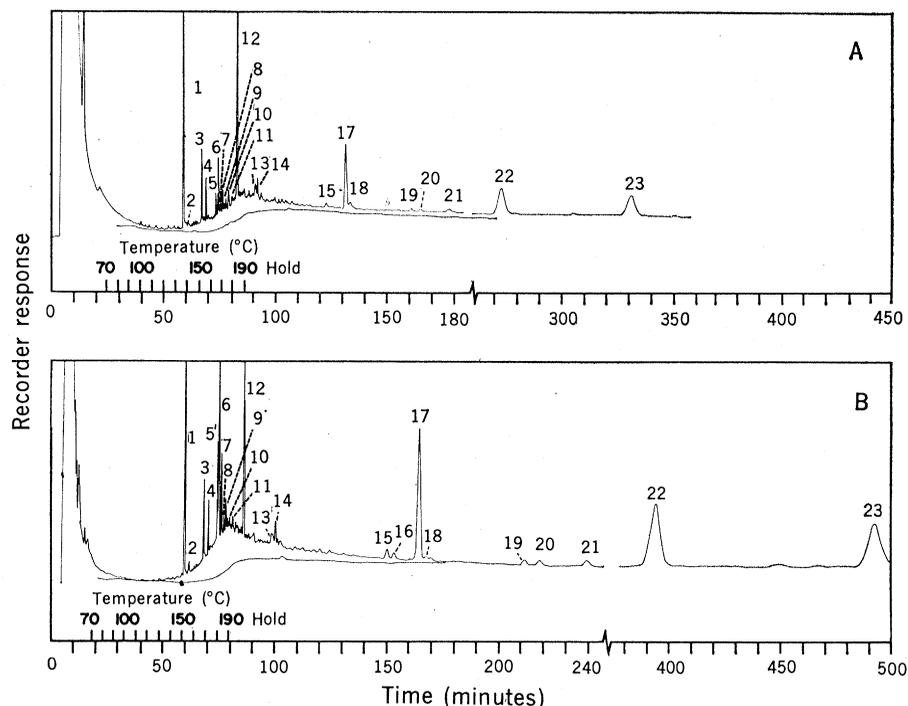


Fig. 1. Gas chromatograms of the aromatic hydrocarbons isolated from the Murchison meteorite sample I (A) and sample II (B). Analytical conditions were as follows: 15.2-m support-coated open tubular polyphenyl ether column (Perkin-Elmer Corp.) in a flame-ionization gas chromatograph (Perkin-Elmer 880); helium flow rate, 3 ml/min; attenuation, $\times 50$. Differences in retention times between the two chromatograms may be due to a slight oxidation of the column when it was unintentionally exposed to air for a period of time while being transferred from the Perkin-Elmer to the Loenco gas chromatograph.

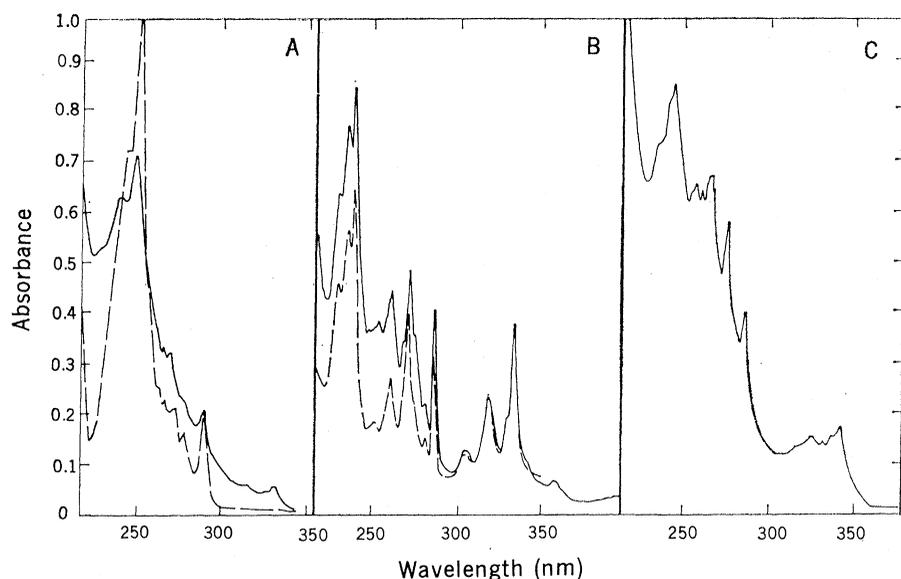


Fig. 2. Ultraviolet spectra of the eluates from the thin-layer bands of the benzene fraction of the Murchison meteorite sample II. (A) Band 2 (—) and phenanthrene standard (----). (B) Band 3 (—) and a standard composed of equal weights of fluoranthene and pyrene (----). (C) Band 4.

to about 100 μ l, and 20 percent was injected onto a support-coated open tubular polyphenyl ether column in a combined gas chromatograph (Loenco 160X) and mass spectrometry (Consolidated Electrodynamics 491) system. The mass spectra were recorded for all gas chromatographic peaks. The column was transferred to a gas chromatograph

(Perkin-Elmer 880). Standards, selected on the basis of mass spectral data, were coinjected with the benzene fraction. Generally, the molecular ion is the most dominant ion in the mass spectrum of a polynuclear aromatic hydrocarbon, and for many of the minor compounds in this sample as well as the second sample, it is the only

ion of measurable intensity. When there were sufficient compounds present to yield ion fragments as well as a very intense molecular ion, mass spectra were compared with those of the corresponding standards.

The remainder of the benzene fraction of sample II was applied to an alumina thin-layer plate, and the plate was developed in hexane. Six bands were distinguishable under light from a long-wavelength ultraviolet lamp: band 1, nonfluorescent, pale yellow, $R_f = 0.73$ to 0.34; band 2, pale purple, $R_f = 0.27$ to 0.34; band 3, blue, $R_f = 0.19$ to 0.27; band 4, yellow, $R_f = 0.11$ to 0.19; band 5, nonfluorescent, colorless, $R_f = 0.11$ to 0.07; and band 6, nonfluorescent, yellow, $R_f = 0.07$ to 0.00. These bands were eluted with benzene. The eluates from bands 1 through 4 were analyzed by gas chromatography, those from bands 3 through 6 were analyzed by direct probe in the mass spectrometer, and those from bands 2 through 4 were analyzed on a spectrophotometer (Cary 14).

The second sample, referred to here as in the preliminary report (7) as sample I, was examined by the same procedure. Because less material was present, thin-layer chromatography was not attempted. Instead, the material remaining after analysis by gas chromatography-mass spectrometry was injected onto a DC-430, 30.5-m capillary column in a gas chromatograph (F&M 5750). Under the conditions used, this column completely resolved the polynuclear aromatic isomers chrysene and triphenylene, whereas pyrene and compounds of lower molecular weight emerged very early as an unresolved series of peaks. Control blanks were analyzed in parallel with the meteorite.

Figure 1 shows the chromatograms corresponding to the two meteorite fractions and their blanks. The amount of aromatic compounds, roughly estimated from the gas chromatographic peaks alone, is about 15 μ g per gram of meteorite sample I and about 28 μ g per gram of meteorite sample II. Table 1 summarizes the identification of the gas chromatographic peaks.

Seven compounds were present in the benzene fraction in amounts large enough to yield identifiable mass spectra. On the basis of this evidence and results from the coinjection of standards, these compounds are identified as naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthene, phenanthrene, fluoranthene, and pyrene. Seven other compounds, present in

Table 1. Aromatic hydrocarbons in the Murchison meteorite. The corresponding gas chromatograms and ultraviolet spectra are shown in Figs. 1 and 2, respectively. Letters in parentheses refer to the method of identification: (a) complete fragmentation pattern; (b) molecular ion only, with an M-15 peak if a methyl substituent is present; (c) coinjection of standard; and (d) ultraviolet spectrum.

Gas-liquid chromatography peak No.	Amount present (μ g/g)		Molecular weight	Compound
	Sample I	Sample II		
1	1.12	6.40	128	Naphthalene (a, c)
2	0.05	0.20	132	?
3	0.32	1.60	142	2-Methylnaphthalene (a, c)
4	0.32	1.00	142	1-Methylnaphthalene (a, c)
5	Trace	0.50	152	? (Not acenaphthylene or biphenylene)
5'	0.30	Trace	180	? (Not stilbene)
6	0.64	1.20	154	2,6-Dimethylnaphthalene (b, c)
			156	Biphenyl (b, c)
7	0.24	0.20	156	Dimethylnaphthalene (b)
8	0.005	0.50	156	1,3-Dimethylnaphthalene (b, c)
9	?	0.20	168	Diphenylmethane (b, c)
10	0.003	0.30	156	1,4-Dimethylnaphthalene or 2,3-dimethylnaphthalene, or both (b, c)
11	0.002	0.40	170	C-3 naphthalene* (b)
12	1.12	5.80	154	Acenaphthene (a, c)
13	0.07	0.30	168	? (Not a methylbiphenyl)
14	0.08	0.40	166	Fluorene (b, c)
15	0.24	0.40	184	C-4 naphthalene† (b)
16	0.16	Trace	184	C-4 naphthalene† (b)
17	2.56	4.80	178	Phenanthrene (a, c, d)
18	0.05	0.10	178	Anthracene (c)
19	0.11	0.20	192	Methylphenanthrene (b)
20	0.11	0.20	192	Methylphenanthrene (b)
21	0.11	0.20	192	1-Methylphenanthrene (b, c)
22	3.70	4.90	202	Fluoranthene (a, c, d)
23	3.30	4.90	202	Pyrene (a, c, d)

* A naphthalene with three carbon atoms as substituents. † A naphthalene with four carbon atoms as substituents.

smaller amounts, yielded mass spectra in which only the molecular ion and an M-15 peak (if a methyl substituent was present) were evident. On the basis of this evidence and results from the coinjection of standards, these compounds are tentatively assigned the structures 2,6-dimethylnaphthalene, 1,3-dimethylnaphthalene, diphenylmethane, 1,4-dimethylnaphthalene or 2,3-dimethylnaphthalene, or both, fluorene, and 1-methylphenanthrene.

Molecular ions were obtained for nine other compounds, but standards were not available to enable us to establish their identities. In a few cases, tentative structural assignments were made on the basis of molecular weight and the presence or absence of an M-15 peak. It was also possible to rule out several possible compounds as responsible for these unknown peaks by the coinjection of standards. In this manner, it was established that peak 5' is not *trans*-stilbene, peak 5 is not acenaphthylene or biphenylene, and peak 13 is not a methylbiphenyl.

Gas chromatography of the eluates from the thin-layer bands showed that all of the compounds appearing in the chromatograms in Fig. 1 were contained in the first three thin-layer bands. The eluate from band 1 contained compounds from naphthalene up to phenanthrene, the eluate from band 2 contained phenanthrene and its methyl homologs, and the eluate from band 3 contained fluoranthene and pyrene. Ultraviolet spectra of the eluates from bands 2 and 3 helped to confirm the presence of phenanthrene, fluoranthene, and pyrene (Fig. 2, A and B).

Direct probe analysis of the eluate from band 4 produced a mass spectrum with a major molecular ion at a mass-to-charge ratio m/e of 228 and minor molecular ions at m/e 242, 244, 254, 256, and 258 whose total intensity was less than half that of m/e 228. These mass spectral data suggest that this band may be primarily chrysene or one of its isomers, and the R_f value of band 4 is identical with that of a chrysene standard. However, the ultraviolet spectrum of the eluate from band 4 does not resemble that of any of the chrysene isomers (Fig. 2C). Furthermore, gas chromatography of this eluate on the DC-430 column showed that a group of at least 12 peaks of almost equal intensity emerge in the region between the triphenylene and chrysene peaks. There was insufficient material to enable us to obtain mass spectra of these peaks, whose total in-

tensity amounted to less than 1 percent of that of phenanthrene (Table 1).

The distributions of aromatic compounds in the two Murchison samples are different. For instance, there are more compounds of higher molecular weight relative to those of lower molecular weight in sample I than in sample II; the unidentified peak 5' does not appear in sample II; and peak 5 does not appear in sample I. The degree of inhomogeneity in the distribution of organic matter within the whole meteorite is not known.

The composition of both aromatic fractions is relatively simple if we consider the number of aromatic and alkyl aromatic compounds possible. In both samples there is a noticeable lack of long- or even short-chain alkyl-substituted aromatic compounds. By far, most of the sample is composed of unbranched, polynuclear compounds containing an even number of carbon atoms. In these respects the Murchison aromatic compounds are similar to those produced by the pyrolysis of methane (4). This similarity suggests that the aromatic compounds in this meteorite may be the product of an essentially thermal, high-temperature synthesis.

The simple composition of the aromatic fractions contrasts with the apparent complex composition of the aliphatic hydrocarbon fractions reported earlier (7), but the significance of this difference in complexity is not clear. Future work should include an exploration of the various synthetic conditions which might duplicate those that led to the formation of the Murchison hydrocarbons.

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References and Notes

1. E. Gelpi, J. Han, D. W. Nooner, J. Oro, *Geochim. Cosmochim. Acta* **34**, 965 (1970); C. Ponnampuruma, *N.Y. State J. Med.* **70** (No. 10), 1169 (1970).
2. P. Swings and L. Haser, *Atlas of Representative Cometary Spectra* (University of Liège Astrophysical Institute, Louvain, 1956); L. E. Snyder, D. Buhl, B. Lukerman, P. Palmer, *Phys. Rev. Lett.* **22**, 679 (1969).
3. J. M. Hayes, *Geochim. Cosmochim. Acta* **31**, 1395 (1967).
4. J. Oro and J. Han, *Science* **153**, 1393 (1966).
5. M. H. Studier, R. Hayatsu, E. Anders, *Geochim. Cosmochim. Acta* **32**, 151 (1968).
6. F. M. Johnson, *NASA SP 140* (1965), p. 229; B. Donn, *Astrophys. J.* **152**, L129 (1968).
7. K. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnampuruma, I. R. Kaplan, C. Moore, *Nature* **228**, 5273 (1970).
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Glycerinated Muscle Fibers: Relation between Isometric Tension and Adenosine Triphosphate Hydrolysis

Abstract. *The isometric tension of glycerinated muscle fibers and the adenosine triphosphatase activity of homogenates were determined as a function of the concentration of adenosine triphosphate without the addition of divalent cations. These two phenomena are not parallel; large tensions can be developed with negligible hydrolysis of adenosine triphosphate. It is concluded that the large negative free energy change of the hydrolysis is not required for shortening or development of tension.*

In "living" muscle and in the model glycerinated muscle fiber system adenosine triphosphate (ATP) is hydrolyzed during some stage of the contractile process (1). The necessary catalysis is provided by the fibrous protein myosin acting as an enzyme. The specific role and function of ATP in this process has not been established definitely (2), and two widely divergent views have evolved (3). One argument is that the large negative free energy change which accompanies the ATP hydrolysis is the direct cause of shortening or tension development. Hence, it is claimed that the two processes

are directly coupled with one another (4). Alternatively, it has been proposed that the intact ATP induces contractility, with hydrolysis taking place subsequently (5).

When the contractile process is mediated by Mg^{2+} or Ca^{2+} , there is a striking lack of parallelism between shortening and enzymatic activity (6). Bowen (6) has reported that although Mg^{2+} accelerates the ATP-induced shortening of myosin threads and glycerinated muscle fibers the dephosphorylation is retarded. The introduction of Ca^{2+} results in the opposite effect; shortening is retarded, but