cay (as in remembering a sequence of numbers), the second curve reflecting perhaps the actual process of "consolidation" of the memory trace for longer-term storage and retrieval. Parenthetically, we have also found the apprehension levels of the animals (subjectively rated on a blind basis during the first 15 seconds before crossing the hurdle) to directly correlate with latencies for hurdle-crossing—for example, to be lowest approximately 5 minutes after the foot-shock stimulus.

From this framework it was of interest to determine the effects of strychnine and pentylenetetrazol on the biphasic response curve—that is, whether the agents accelerated the presumed "consolidation" process. Administration of strychnine (0.2 mg/kg) or pentylenetetrazol (3 mg/kg) 30 minutes before the first trial produced no change in the hurdle-crossing latency of animals not receiving a foot shock (Fig. 1). In animals receiving a foot shock, however, pretreatment with pentylenetetrazol completely prevented "memory" decay of the first phase and significantly increased the response latencies for all intervals of testing. Strychnine, in three separate studies with similar results (integrated in Fig. 1), produced comparable effects of lower magnitude. With both drugs, facilitation of one-trial learning appeared greater when administration preceded rather than followed the learning experience.

The dosage of pentylenetetrazol that facilitated one-trial learning in the mouse approximated 1/100th to 1/200th of the convulsant dose; thus facilitation cannot be readily ascribed to the mechanisms underlying its convulsant action. However, since other convulsants such as strychnine and picrotoxin also facilitate one-trial learning, such mechanisms cannot be ruled out entirely. Eccles *et al.* (*7*) have shown that the three agents differ significantly in their neurophysiologic modes of action: strychnine blocks postsynaptic inhibitory pathways, picrotoxin blocks presynaptic inhibition, and pentylenetetrazol blocks neither presynaptic nor postsynaptic inhibition. The excitatory effect of pentylenetetrazol on the nervous system seems rather to result from decrease in neuronal recovery time (*8*), without reference to inhibitory pathways; effects of small doses on behavior may derive from this acceleration of neuronal and synaptic transmission throughout the nervous system, as well as from possible specific regional effects on the brain that remain unknown.

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References and Notes

1. K. C. Lashley, *Psychobiology* **1**, 141 (1916).
2. J. L. McGaugh and L. F. Petrinovich, *Amer. J. Psychol.* **72**, 99 (1959).
3. R. A. Breen and J. L. McGaugh, *J. Comp. Physiol. Psychol.* **54**, 498 (1961).
4. J. L. McGaugh and L. F. Petrinovich, *Intern. Rev. Neurobiol.* **8**, 139 (1965), who refer to unpublished communications by Hunt and Krivanek and by McGaugh, reporting facilitation by pentylenetetrazol (10 to 24 mg/kg) of learning in rats and mice, respectively.
5. S. Irwin, *Federation Proc.* **23**, 102 (1964).
6. F. Wilcoxon and R. A. Wilcox, in *Some Rapid Approximate Statistical Procedures* (Lederle Laboratories, Pearl River, N.Y., 1964).
7. J. C. Eccles, R. Schmidt, W. D. Willis, *J. Physiol. London* **168**, 500 (1963).
8. C. Eyzaguirre and J. L. Lilienthal, Jr., *Proc. Soc. Exp. Biol. Med.* **70**, 272 (1949); J. Lewin and D. W. Esplin, *J. Pharmacol. Exp. Therap.* **132**, 245 (1961).

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Organic Matter in Carbonaceous Chondrites

In a recent article, Studier, Hayatsu, and Anders (*1*) report mass spectrometric analyses of volatile compounds from the Orgueil meteorite and interpret the results as due to the establishment of chemical equilibrium in the solar nebula. In a subsequent review article, the impression was given that this was a very definitive piece of work (*2*). We should therefore like to express our criticisms.

1) The analytical data are very approximate and are compared to theoretical data which are based on an improbable postulate. Mass spectrometric data on a complex mixture of carbonaceous compounds lead to an exceedingly complex spectrum of molecular fragments, and it is very difficult to sort out the possible compounds present. This was true when Nagy *et al.* (*3*) previously reported similar mass spectrometric analyses, and, in fact, the analytical data were severely criticized on these grounds by Anders (*4*). Studier *et al.* attempted in no way to present the original data and gave only their final results, expressing them only in very qualitative terms. The data as presented could hardly be expected to establish a quantitative agreement with any theory for the formation of these compounds. No attempt has been made to justify even the qualitative character of these analyses. Some of the criticisms that Anders directed against the previous work must be applicable to the work of Studier *et al.*, as well as any other similar mass spectrometric work on this material.

The qualitative analyses for some 16 compounds consisting only of positive and negative signs are compared with the corresponding calculated concentrations of Dayhoff, Lippincott, and Eck (*5*), which vary by a factor of 10^6 for those reported as present in the meteorites. Moreover, their equilibrium calculations were made on the assumption that graphite did not appear. This is an *ad hoc* assumption which we regard as doubtful. It seems improbable that chemical reactions producing very complex molecules such as benzene, naphthalene, anthracene, xylene, and others, could take place in spite of the fact that, under the postulated conditions, graphite is exceedingly stable thermodynamically (see Table 1). It is true that carbonaceous compounds persist on the earth through long periods of time, and possibly at 500°K, without graphite having appeared, but these compounds were not made by equilibrium processes but by the very nonequilibrium processes of living organisms. We object to the hypothesis of an *equilibrium* origin of the compounds in the *absence* of graphite. It would appear that very qualitative analytical data have been compared to a theory in which an arbitrary assumption, that is, the absence of graphite, is made.

2) The physical conditions and the composition of materials assumed by Studier *et al.* are improbable and difficult or impossible to attain in the solar nebula. They assume that a condition existed in the nebula with a high total pressure and a temperature of about 500°K, the constituents of the atmosphere being principally hydrogen, carbonaceous compounds, oxygen compounds, and nitrogen compounds, making a total pressure of one atmosphere, with hydrogen depleted very markedly from all estimates of solar abundances.

The relative atomic abundances of H:C:O in the sun are estimated to be 3000:1:3. Studier *et al.* postulate a mixture of 3 : 3 : 4. It is quite evident that if a mixture of H:C of 1 : 1 were used and no elemental carbon formed, only compounds of the composition $(CH)_n$, that is, C_2H_2, C_6H_6, and so forth, could be expected to be abundant. The addition of oxygen would complicate the problem but a suitable choice of temperature, pressure, and the ratio of H : C : O should make it possible to secure some proportion of aromatic compounds. But how was the solar ratio of these compounds modified to the ratio chosen? It is very difficult to understand how the hydrogen was driven out of the solar nebula to leave the other gaseous constituents behind, and also very difficult to understand how such high densities of the residual gas could exist anywhere in the solar nebula. The *un*depleted atmosphere which gave rise to this mixture must have been at a pressure exceeding 1 kb, if only H_2 is depleted. If other elements are assumed to have escaped, the required initial pressures are higher. These are very real difficulties (*6*).

Urey's (*7*) postulated solar nebula assumed about 2×10^{-6} g/cm^3 as the maximum density in the median plane of the solar nebula at one astronomical unit from the sun, and smaller densities at greater distances. The mass of the nebula was calculated to be approximately one-third of a solar mass. Of course, other assumptions can be made, but an increased density by even a factor of 1000, together with the removal of hydrogen gas from the nebula, would still leave a very low density in any solar nebula. It seems impossible to believe that any solar nebula could consist of material of the high density postulated by Studier *et al.*

It would seem that such densities could only be acquired on planetary bodies, and since the escape velocity of Ceres, the largest of the asteroids, is only 0.6 km/sec, it is quite obvious that gases of the density postulated could not exist on the surface of an object of this size.

Again, if hydrogen were depleted and pressures were low and the H : C : O ratio were 3 : 3 : 4, carbon would be present as carbon monoxide, predominantly, and carbon monoxide and hydrogen react in the presence of catalysts to give hydrocarbons. But how was the ratio established?

3) Studier *et al.* discard the idea that the processes that produced the carbon compounds in these meteorites occurred on the surface of a planetary body. We, on the other hand, believe that a planetary body of some considerable mass, that is, lunar or larger, is the most probable place of origin. Here carbon, nitrogen, and water could have been separated from the hydrogen gas, and temperatures and pressures could have assumed moderate values. Also, solar radiation could have been available for the promotion of these sluggish reactions of carbon compounds. It will be interesting to observe what kinds of material come back with the Apollo mission from the moon.

Studier *et al.* also suppose that their compounds originating in the nebula accumulated on the earth and served as the basic material from which life evolved. The percentages of carbonaceous compounds and of water in the Orgueil meteorite are very much larger than they are in the earth as a whole. Hence the proportion of the carbonaceous meteoritic materials captured by the earth and presumably produced in the nebula must have been a very small fraction of the total. But how could this happen in an enormous nebula? What differentiated some small fraction of the total nebula? It was proposed many years ago by Aston that the greater loss of rare gases from the earth, than of carbon and oxygen, occurred because of the formation of relatively nonvolatile compounds of carbon and oxygen within the solid materials of the earth. We suspect that the carbonaceous chondrites are incidental material from the surface of a planetary object and thus constitute only a small fraction of the total material, that a nebula with the postulated properties is improbable, and hence that Aston's hypothesis is relevant.

4) In discussing the difficult problem of the carbonaceous materials in the carbonaceous chondrites, most of us are assuming that a possible important source for the compounds that appear to be of biological origin is contamination by microorganisms after the arrival of these objects on the earth, and this is certainly a very important point that must always be considered. In our opinion, the conclusions as to whether these compounds in meteorites, which appear to be of biological origin, are preterrestrial or not is not definitely decided as yet, though it is a natural reaction on the part of all scientists, including ourselves, to question seriously whether they are not of terrestrial origin. But, of course, one also may expect that the compounds studied by Studier *et al.* may have been produced by biological organisms after the object arrived at the earth. Compounds of the kind discussed are similar to those found in petroleum, coal, or carbonaceous materials in sediments, which, of course, are residues and decomposition products of biological origin. We may expect that the benzene and other compounds investigated by Studier *et al.* were perhaps produced by contaminating terrestrial

Table 1. Calculations of concentrations in moles per mole of total carbon for point C in report of Dayhoff *et al.* (*5*), including graphite.* Hydrogen, 30 atoms per hundred; carbon, 30 atoms per hundred; oxygen, 40 atoms per hundred; 500°K; ~ 1 atmosphere, total of HCNO compounds.

Compound	Moles per mole of total carbon: Based on pressures reported by Dayhoff *et al.* (no graphite)	Moles per mole of total carbon: Based on pressures recalculated with graphite activity = 1 (½ of C is graphite)
H_2	1.3×10^{-4} (0.86×10^{-4})*	3.80×10^{-3}
O_2	$< 10^{-38}$	2.5×10^{-42}
N_2	0.50	0.50
H_2O	7.9×10^{-5}	.463
CH_4	0.24	.0388
CO_2	.66	.455
CO	5.3×10^{-3}	2.73×10^{-5}
NH_3	1.1×10^{-7} (1.4×10^{-7})*	5.37×10^{-5}
C_2H_6	2.3×10^{-5}	1.69×10^{-8}
C_2H_4	5.7×10^{-9}	5.62×10^{-14}
HCN	1.4×10^{-10} (1.7×10^{-10})*	6.59×10^{-14}
C_6H_6	6.6×10^{-4}	3.9×10^{-25}
$C_6H_5CH_3$	not reported	1.1×10^{-28}
$mC_6H_4(CH_3)_2$	9.4×10^{-8}	6.7×10^{-33}
$C_{10}H_8$	1.4×10^{-4}	$\sim 1 \times 10^{-31}$
$C_{14}H_{10}$	2.9×10^{-5}	$\sim 1 \times 10^{-37}$

* By correspondence with Dayhoff we have learned that their calculations contain small errors due to incorrect standard free energies of the elements hydrogen and nitrogen. Concentrations recalculated with corrected standard-state free energies for hydrogen and nitrogen are given in parentheses. These values were in error by 0.38 kcal per mole. The computed concentrations for all other compounds are unaffected. Our computed concentrations, when graphite is precipitated (column 3), are very close to point A of Dayhoff *et al.*, just below the "graphite line."

organisms with about the same certainty that we can assume that optically active compounds, porphyrins, hydrocarbons, and so forth, that have been investigated by other scientific workers looking for evidence of biological materials, were produced by such organisms.

5) Studier *et al.* point out that possibly the compounds produced in the nebula by the process which they discussed are indeed the materials which led to the evolution of life, rather than compounds produced on the surface of the earth by the action of physical processes, which owe their origin directly or indirectly to solar radiation. It is very likely that any carbonaceous material available from any source whatsoever may have contributed to the evolution of living things, but it is a strange hypothesis that an organism evolved on material produced by pseudo-equilibrium processes in the solar nebula and then, after a living organism had evolved, it derived its free energy for its metabolic processes from the sun during all the subsequent eons of time. It would seem to us more likely that living organisms have used the sun as their source of free energy both during the period of evolution and the subsequent history of the earth.

In order to secure nitrogen compounds suitable for the evolution of living organisms on earth, some nonequilibrium process is needed, as Dayhoff *et al.* noted. It is thus natural to argue that some energetic process capable of producing nitrogen compounds was available, and this same process would probably produce hydrocarbons of great variety. These would also be unstable with respect to graphite and hydrogen, but would persist, nonetheless, at terrestrial or lower temperatures for long periods of time, as they have in terrestrial petroleum and coal deposits. These unstable compounds would supply an energetic mixture suited to the evolution of life. In this way, life probably did evolve on the surface of the earth.

We also have searched for equilibrium processes to account for these compounds and have been unable to postulate any reasonable source of this kind. Again we note that both the inorganic and organic compounds in the Orgueil meteorite are similar to those which, aside from the sorting effects produced by running water and the absence of amino acids, may be expected to have been present on the primitive earth, that biological organisms are very ubiquitous on the earth, and that contamination by these organisms must be guarded against in all investigations. We believe that the carbon compounds detected by Studier *et al.* and other investigators could have been produced only by high-energy radiations, or, in some instances, by living organisms of either terrestrial or possibly extraterrestrial origin.

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References

1. M. H. Studier, R. Hayatsu, E. Anders, *Science* **149**, 1455 (1965).
2. "Research facilities and programs," in *Physics Today* **18**, 84 (Nov. 1965).
3. B. Nagy, W. G. Meinschein, D. J. Hennessy, *Ann. N.Y. Acad. Sci.* **93**, 658 (1962).
4. E. Anders, *ibid.*, p. 651.
5. M. O. Dayhoff, E. R. Lippincott, R. V. Eck, *Science* **146**, 1461 (1964).
6. E. Öpik, in *Origin of the Solar System*, R. Jastrow and A. G. W. Cameron, Eds., (Academic Press, New York, 1963).
7. H. C. Urey, *Monthly Notices Roy. Astron. Soc.*, in press.

10 December 1965

Studier, Hayatsu and Anders (*1*), analyzing the organic matter in samples of the Orgueil, Cold Bokkeveld, and Murray meteorites, interpreted their results in terms of a very interesting hypothesis regarding the formation of organic compounds under equilibrium conditions (*2*) in a "solar nebula." While we do not wish here to take issue with this thesis, we would like to record some observations on the experimental data presented in its support.

1) Studier *et al.* report the first identification of sulfonic acid esters, and note that "a definite identification was made from the infrared spectrum"—which, unfortunately, was not further specified. A few peaks from the mass spectra of these "sulfonates" are given, namely, *m/e* 355, 281, and 207, without showing, however, how ions of such nominal mass could be formed from methyl esters of sulfonic acids. This omission is somewhat disturbing, particularly since Beynon (*3*) and Biemann (*4*) have listed and interpreted the peaks mentioned above as those characteristic of the mass spectra of silicon oil compounds, common sources of contamination. Also, one should note that the strong infrared absorption bands for alkyl sulfonic acid esters and silicon compounds occur in similar regions of the spectrum such that a positive identification by infrared spectroscopy might be difficult; of course, an infrared spectrum only then constitutes definite proof for a given compound after it has been demonstrated the sample is indeed pure and uncontaminated by other species which may give rise to analogous intense absorption bands.

2) Studier *et al.* list a series of compounds, assigning very definite molecular compositions and structures to them. It might be questioned whether a time-of-flight mass spectrum on a complex mixture permits such a definite identification of molecular species since, in fact, an elemental composition cannot be determined for a single nominal mass peak with a low-resolution instrument, but must be deduced from the fragmentation patterns of the substances in question. Several compounds listed in Table 1 of their article (*1*) display very similar fragmentation patterns, and the assurance with which these compounds are identified and distinguished from each other in a mixture seems quite remarkable. Too great a reliance on the low-resolution mass spectral data of mixtures may lead to ambiguities, as suggested above, and thus cast doubt on the correctness of the identification of the remaining substances listed. These questions could probably be satisfactorily resolved by the presentation of more extensive data and analysis of fragmentation patterns in terms of the compounds thought to be present. Such a presentation might also shed some light on the "prominent unidentified peaks" in the spectra of the three meteorites, the mention of which seems of somewhat dubious value, particularly since the reader is not told what the prominent identified peaks were. In the absence of further data, one might assign the "prominent peaks" at *m/e* 58 and 72, for instance, to molecular ions, for the corresponding C_4 and C_5 alkanes; whereas, *m/e* 69, 71, 95, 97, and 113, to name a few, might simply be unsaturated or saturated alkyl fragments.

3) D. P. Stevenson and P. A. Wadsworth (Shell Development Company, Emeryville, California) have kindly informed us that they have found chlorinated hydrocarbons in a sample of the Felix meteorite, one of which, polychloronaphthalene, could be identified by high-resolution mass spectrometry as a material known to be a synthetic component of wax extenders used in the 1930's. Information of this sort, when coupled with the ambiguous

identification noted under our point 1, above, and the lack of original data in the paper by Studier *et al.* tend to foster skepticism and uncertainty in the reader, such that a very careful scrutiny of the reported results would be desirable in order to eliminate the possibility that some of the compounds found might represent similar contaminants.

4) The results of Studier *et al.* seem to be at variance with several recent reports (for example, those of Oro, Nagy *et al.*, and Hoering, *5*) on the identification of saturated aliphatic hydrocarbons in meteorites. Studier *et al.* report the finding of "only subordinate amounts" of saturated alkanes (tentatively identified in the Orgueil and Cold Bokkeveld; not found in the Murray—see *1*, Table 2), except for methane, and such lack of agreement can only give rise to the question as to the completeness of the analysis presented. In this connection, it may be instructive to outline results obtained by the Shell group (*6*) from the analyses of two different specimens of the Murray meteorite (1.2 g from the Harvard Collection via Brookhaven; 0.2 g from M. Calvin, University of California, Berkeley). The larger sample was extracted with hexane to yield several parts per million of saturated hydrocarbons in the C_{10} to C_{30} range. Portions (20 mg per trial) of the smaller specimen were examined by direct introduction to the source of a high-resolution mass spectrometer (C.E.C. 21-110 employing photographic plate recording), taking 5 to 10 high-resolution mass spectrograms as the sample was heated to 250°C. Only elemental sulfur (S_n), carbon disulfide, sulfur dioxide, benzene, toluene, methyl mercaptan, and a series of olefins of low molecular weight ($\leqq C_5$) were detected. Analogous results were obtained upon direct introduction of samples of the Precambrian Kalgoorlie Slate. It would appear, therefore, that arguments and conclusions based on the results obtained by a particular technique for the case of a single meteorite specimen assume an untenable position in the light of apparently conflicting data from other specimens and techniques. The argument that Green River Shale samples were run as checks on the technique and, since aliphatic hydrocarbons were identified in these, their presence would have been noted also in the meteorite samples, is somewhat less than convincing, since the Green River Shale contains such an abundance of hydrocarbons (1 percent of shale by weight) (*7*) that failure to identify them would have been astounding indeed.

5) Since the hypothesis of Studier, Hayatsu, and Anders presupposes that the mixture of organics found today is representative of the sample produced in the solar nebula, it is interesting to note that Anders has repeatedly argued (*8*) that the long exposure of organic material to radioactivity and radiation might result in extensive transformation of the compounds present such that the composition found might be "several steps removed" from that of the original mixture. The results presented are now interpreted to indicate that radiation damage has occurred to a minor extent, although one might indeed wonder whether the authors' qualitative data really provide any basis for a meaningful estimation of the degree of radiation-induced fragmentation.

Some results reported by Biemann and Hayes (*9*) are also pertinent in this connection. These authors, using similar experimental techniques (namely, direct volatilization and fractionation of organic matter into the ion source of a high-resolution mass spectrometer), have found compounds of considerably greater complexity (up to *m/e* 250) among samples taken from a core of the Murray meteorite. Near-surface specimens were richer in oxygenated compounds than the respective inner core cuttings, an indication that secondary (possibly terrestrial) chemical transformations such as oxygenations (dehydrogenation?) may have altered the organic composition to a considerable degree. Anders, in criticizing (*8*) earlier work (of Nagy *et al.*, *5*), has argued that sulfur contained in meteorites may cause extensive dehydrogenation upon heating the sample. Although we ourselves do not subscribe to this view, the "overwhelming predominance" of aromatics reported calls for a more explicit consideration of this question by Studier *et al.*

6) Finally, some clarification and elaboration upon the claimed "overwhelming preponderance of aromatic over aliphatic hydrocarbons" in the three meteorites would seem desirable, since, after close inspection of the results of Studier *et al.* (*1*, Table 1) this preponderance might not be particularly obvious to the unbiased reader. For instance, in the case of the Murray sample, the only aromatic compound found is benzene, whereas at least three non-aromatic substances (methane, butene, and "alcohols") are reported for the same sample (and according to the table in comparable abundance). Likewise, the yield of aromatic hydrocarbons from the Cold Bokkeveld does not appear "overwhelming" (benzene, toluene, dimethyl ethyl benzene, and dichlorobenzene, in varying amounts) when compared with the abundance of non-aromatic hydrocarbons and the identification of seven homologous aliphatic chlorocarbons, leaving, thus, only the sample of the Orgueil with a (not very striking) predominance of aromatic compounds.

Indeed, both on the basis of the number of different compounds identified in the three samples and the relative abundances assigned to them in the table of Studier *et al.*, one might be inclined to argue that non-aromatic substances are the preponderant species. For example, a count of the plus signs of their Table 1 (denoting abundance) assigned to the aromatic substances versus those given to aliphatic molecules (assuming that a plus denotes approximately the same relative abundance throughout the table—as stated in its heading) would produce the intriguing result of 21 plus signs for the aromatics versus 27 plus notations for the aliphatics (not counting the "tentatively" identified alcohols and aliphatic and alicyclic hydrocarbons). Applying such a treatment to the qualitative abundance ratios listed in the table might be considered unjustified, but in that case it would be of some interest to learn the exact experimental data upon which the conclusion of a great predominance of aromatic species appears to rest, particularly also the manner in which relative abundances of given compounds were determined from the mass spectra of mixtures.

It is thus apparent that the reported data of Studier, Hayatsu, and Anders are far too inconclusive and qualitative to provide meaningful support for any hypothesis on the origin of organic matter in meteorites. The findings of Russian workers (*10*) that the non-extractable matter in meteorites (the major amount of the total organic material) consists of aromatic polymers supports the view that, in general, aromatic compounds are indeed the preponderant species. This fact alone, however, does not require formation of this material under equilibrium conditions, since terrestrial kerogen (undoubtedly not an endowment from a solar nebula) also occurs largely as an aromatic polymer and it may, of course, have been formed simply by the degradation and transformation of biological polymers, for example, lignin.

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References

1. M. H. Studier, R. Hayatsu, E. Anders, *Science* **149**, 1455 (1965).
2. M. O. Dayhoff, E. R. Lippincott, R. V. Eck, *Science* **146**, 1461 (1964).
3. J. H. Beynon, *Mass Spectrometry and Its Application to Organic Chemistry* (Elsevier, Amsterdam, 1960), p. 421.
4. K. Biemann, *Mass Spectrometry, Organic Chemical Applications* (McGraw-Hill, New York, 1962), pp. 171–172.
5. J. Oro, data presented at the Meeting for the Analysis of Organic Matter in Carbonaceous Chondrites, Washington, 19 April 1965; B. Nagy, W. G. Meinschein, D. J. Hennessy, *Ann. N.Y. Acad. Sci.* **93**, 25 (1961); T. Hoering, data presented at the Meeting for the Analysis of Organic Matter in Carbonaceous Chondrites, Washington, 19 April 1965.
6. Private communication, A. Polgar, D. P. Stevenson, P. A. Wadsworth, Shell Development Company, Emeryville, California (see reports of NASA contract, No. NASw 438).
7. G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, W. Richter, M. Calvin, in *Advances in Organic Geochemistry*, vol. 2, in preparation.
8. E. Anders, *Ann. N.Y. Acad. Sci.* **93**, 651 (1962); *Proc. Lunar Planetary Colloq.* **2**, No. 4 (1964).
9. K. Biemann and J. Hayes, data presented at Meeting for the Analysis of Organic Matter in Carbonaceous Chondrites, Washington, 19 April 1965.
10. A. P. Vinogradov and G. P. Vdovykin, *Geokhimiya* **1964**, 843 (1964).

3 December 1965

Our reply will be keyed numerically to the points raised by Urey and Lewis (U) and Burlingame and Schnoes (B).

U-1, B-2, B-6) The experimental results described in our forthcoming paper (*1*) dispose of Urey and Lewis' principal criticisms. Complex aromatic molecules such as benzene, naphthalene, and so forth, whose formation was considered "improbable," do in fact form in a matter of seconds under the conditions postulated in our previous paper (*2*), even though they are metastable with respect to graphite. Kinetic inhibition of graphite formation, likewise called an improbable assumption, is now an established experimental fact.

We share Urey and Lewis' high regard for Anders' criticism (*3*) of the mass spectrometric work of Nagy *et al.* (*4*). However, this criticism does not apply to our work, owing to fundamental differences in technique. Nagy *et al.* attempted a *quantitative* analysis of a complex, *unfractionated* mixture, whereas we limited ourselves to a *qualitative* analysis of a simpler mixture that had been extensively *fractionated.* Our samples consisted mainly of light aromatics rather than aliphatics; aromatics give simple spectra with large parent ion peaks, and their identification is straightforward. By careful fractionation we often obtained samples consisting of essentially pure species. Since the time-of-flight instrument permits simultaneous observation of the entire mass spectrum, we were able to establish from a comparison of fractionally distilled samples which peaks were covariant and thus belonged to the same species.

Our critics also reproach us for "not present[ing] the original data" and expressing our results "only in very qualitative terms." As to the former, we have merely followed the example of other authors, our critics included (*5*); we know of no journal that would welcome a manuscript accompanied by 400 Polaroid photographs. Of course, we shall gladly furnish details to any interested scientist. As to the latter criticism, we too believe that what is ponderable should be measured. Our conclusions hinged primarily on two observations:

(i) Methane was more abundant than ethane by a factor of at least 1000; alkanes from C_3 to C_5 were undetectable.

(ii) From C_6 on up, aromatics were far more abundant than their aliphatic counterparts. Burlingame and Schnoes asked for a "clarification and elaboration" of this finding, which we are glad to provide herewith. C_6 occurs as benzene, not hexane; C_7 occurs as toluene, not heptane; C_8 occurs as xylene, not octane; and so forth. Ergo, preponderance of aromatics.

The first of these observations is quantitative, and is thus exempt from Urey and Lewis' criticism. Such extreme ratios are uniquely characteristic of equilibrium in the C–H–O system. Neither we nor our critics have been able to come up with a nonequilibrium process that favors methane over its congeners with such extreme selectivity, and we thus adopt the working hypothesis that some features of the meteorite distribution are due to equilibrium.

The second observation is admittedly qualitative, but can nonetheless be interpreted with little ambiguity, since the effect discovered by Dayhoff *et al.* (*6*) is an exceedingly gross one. For each temperature and pressure there exists a sharply defined carbon content ("asphalt threshold") above which the abundance of aromatics rises by factors of 10^{20} to 10^{30}, until they become major constituents of the system. Now, if the high methane/ethane ratio is taken to be symptomatic of equilibrium, then the very detectability of aromatics shows that equilibrium was established on the carbon-rich side of the asphalt threshold. Even a qualitative method suffices to distinguish between concentrations differing by factors of 10^{20} to 10^{30}.

U-2) Nowhere in our paper did we suggest anything as untenable as a solar nebula at 500°K and 1 atm. The essential point is that the asphalt region discovered by Dayhoff *et al.* is a perfectly general phenomenon in the entire P-T range investigated by her (300° to 1000°K, 10^{-6} to 300 atm), not a singularity at 500°K and 1 atm. True, their only illustrative example ("distribution C") happened to be calculated for 500°K and 1 atm, but since it was typical of the asphalt region in general, our reference to this particular distribution did not imply that the meteorite organics must likewise have formed at 500°K and 1 atm.

That the selective depletion of hydrogen was an embarrassment to our hypothesis was frankly and explicitly conceded in our paper. Meanwhile, this stumbling block has been removed, as the experiments in our forthcoming paper show (*1*). Even in a gas of cosmic composition, hydrocarbons and other organics form metastably by the reaction of CO and H_2, catalyzed by meteoritic dust. The further evolution of this primary distribution into a quasi-equilibrium mixture is described in our paper (*1*). Having abandoned the troublesome assumption of hydrogen depletion, we see no need to defend it against Urey and Lewis' criticism.

Urey and Lewis note that the proportion of organic matter in the earth must have been smaller than that in the carbonaceous chondrites, and ask how such differences could have arisen "in an enormous nebula." This is hardly a paradox. The carbon and metal content of meteorites varies greatly from class to class and so does the density of the planets (*7*). Comets are still richer in carbon. Apparently, appreciable chemical fractionations occurred during the accretion of the asteroids and planets. Hence there is no a priori reason why material from the asteroid belt and the earth should contain the same amount of organics. Modern theories on the origin of the solar system and the meteorites show in detail how such differences could have arisen (*8*).

U-4, B-3) Urey and Lewis propose ". . . that the benzene and other compounds investigated by Studier *et al.* were perhaps produced by contaminating terrestrial organisms . . .," while Burlingame and Schnoes attribute the chlorinated hydrocarbons to terrestrial contamination. Having repeatedly alerted others to the danger of contamination, we are not entirely unaware of the problem. Contamination may possibly have affected our results to some degree, but we believe that our technique discriminates more successfully than any other against surficial contaminants. The volatiles evolved only from freshly ground samples, not from unbroken fragments or a powder that had been ground 10 years earlier. Often they were observed only when mineral grains were broken up under vacuum after preliminary degassing at 100°C. Terrestrial contaminants should be located mainly at accessible surface sites, not in the interior of mineral grains.

These arguments aside, it does not seem likely that the volatiles observed by us were produced by terrestrial bacteria. We are not aware of terrestrial organisms whose metabolic products include noble gases, hydrogen, SO_2, chlorobenzene, sulfonic acid esters, and xylene. As for the chlorinated hydrocarbons, it is a well-established fact that the carbonaceous chondrites contain indigenous, organically bound chlorine. It is not clear how this chlorine is to be accounted for if the chlorocarbons detected by us are dismissed as contaminants. Industrial use alone is not prima facie evidence of contamination. By this argument one could exclude not only all simple organic chlorine compounds but also meteoritic hydrocarbons, nickel-iron, graphite, diamonds, and so forth.

It seems to us that contamination problems experienced by others may have little bearing on our work.

U-5) We do not recognize as our own the "strange hypothesis" imputed to us ". . . that *an organism evolved* [italics ours] on material produced by pseudo-equilibrium processes in the solar nebula and then, *after* a living organism had evolved [*sic*; italics ours], it derived its free energy for its metabolic processes from the sun during all subsequent eons of time." We merely suggested that equilibrium processes may have contributed a significant part of the prebiological organic matter on earth, and thus shortened the chemical evolution stage, but we never claimed that Miller-Urey reactions could be dispensed with altogether. Several eminent authors, such as Oparin, Hoyle, Calvin, and Lederberg have previously suggested that processes other than Miller-Urey reactions may have contributed to the earth's endowment of prebiological organic matter. We regret that our suggestion should have caused offense.

In the final paragraph of their paper, Urey and Lewis propose that the organic compounds in meteorites detected by us " . . . could have been produced only by high-energy radiations, or, in some instances, by living organisms of either terrestrial or possibly extraterrestrial origin." We did, of course, consider high-energy radiation, and rejected it only because of its extreme nonselectivity. It accounts for neither the high methane-ethane ratio, nor the absence of propane, butane, and pentane, nor the predominance of aromatics, nor the high ratio of straight-chain to branched alkanes. All of the numerous experiments with high-energy radiation performed to date have yielded precisely the opposite trends: light alkanes always accompany methane; aliphatics dominate over aromatics; complex aromatics such as coronene are undetectable; branched alkanes vastly outnumber straight-chain isomers. If a way is ever found to produce the meteoritic distribution of organics by high-energy radiation, we shall gladly reconsider the situation. However, the experiments described in our forthcoming paper (*1*) show that the meteorite distribution can be produced with extraordinary ease by near-equilibrium processes, as predicted in our first paper. Perhaps this fact should not be disregarded altogether in the present debate.

B-1) It is not likely that we mistook silicones for sulfonic acid esters. The infrared spectrum of our chromatographed extract showed a peak at 1365 cm^{-1}, in a region where sulfonic esters but not silicones absorb strongly. The mass spectrum differed significantly from published silicone spectra, failing to show the characteristic isotopic pattern of silicon noted by Biemann. To settle this question we will gladly repeat our experiment on another Orgueil stone. However, the main thesis of our paper is in no way dependent on the identity of this compound.

B-2) We can only reiterate our previous statement: lighter alkanes other than CH_4 were undetectable. The unidentified peaks at *m/e* 58 and 72 were not accompanied by fragment peaks of the appropriate mass number or intensity and hence were not due to butane and pentane. We had no trouble recognizing the peaks from 69 to 113 as alkyl fragments from the several families of aliphatics listed as "tentatively identified" in our Table 1. But we are not prepared to offer definite identification of individual compounds in these families.

B-4, -5, -6) We do not wish to reply to Burlingame and Schnoes' remaining criticisms. It is not profitable to argue with critics who question one's ability to make a simple qualitative judgment of one's own data.

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References and Notes

1. M. H. Studier, R. Hayatsu, E. Anders, "Origin of organic matter in early solar system. I. Hydrocarbons," Enrico Fermi Inst. preprint 65-115 (1965). This work was also presented at the autumn meeting of the National Academy of Sciences, Seattle, Washington, 12 October 1965.
2. ———, *Science* **149**, 1455 (1965).
3. E. Anders, *Ann. N.Y. Acad. Sci.* **93**, 651 (1962).
4. B. Nagy, W. G. Meinschein, D. J. Hennessy, *ibid.* **93**, 25 (1961).
5. W. G. Meinschein, E. S. Barghoorn, J. W. Schopf, *Science* **145**, 262 (1964); G. Eglinton, P. M. Scott, T. Belsky, A. L. Burlingame, M. Calvin, *ibid.*, p. 263.
6. M. O. Dayhoff, E. R. Lippincott, R. V. Eck, *ibid.* **146**, 1461 (1964).
7. H. C. Urey, *The Planets* (Yale University Press, New Haven, 1952); ———, *J. Geophys. Res.* **66**, 1988 (1961); ——— and H. Craig, *Geochim. Cosmochim. Acta* **4**, 36 (1953).
8. R. Jastrow and A. G. W. Cameron, Eds., *Origin of the Solar System* (Academic Press, New York, 1963); A. G. W. Cameron, *Icarus* **1**, 13 (1962); J. Wood, *ibid.* **2**, 152 (1963); E. Anders, *Space Science Rev.* **3**, 583 (1964).
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