fuse and fluidize the entire overlying surface layer. These motions, which would be most intense in the central region delimited by the explosion crater, would ensure the hydrodynamic collapse of the crater into an elevated mound, which would then subside to form the familiar ring system in the surrounding fluidized region. The radial extent of fluidlike motions, according to this model, would be limited to that radius where the initial peak shock pressure had degraded to the order of the ambient hydrostatic pressure at the top of the elastic layer (~ 2 kb). This limit, which scales like the cube-root of explosion energy, is shown (Fig. 1) as a reasonable bound to the observed ring systems.

After generation of the rings and the restoration of hydrostatic equilibrium, I suggest that relatively slow isostatic collapse of the rings was prevented, or mitigated, by more rapid resolidification of the perfused rubble-fluid matrix within the surface layer, where the rapid heat transfer to the solid phase would occur during the period of fluidization (20 to 80 minutes). However, I expect that the central region, being relatively enriched with injected material, would remain plastic for a much longer time, and hence would be in quasi-isostatic equilibrium with the plastic region below. Eventual cooling by conduction through the surface would result in a solid layer of somewhat higher density whose strength-weight ratio would increase roughly as the square of its thickness, possibly resulting in a self-supporting structure. Subsequent smaller impacts into such a structure, before complete subsurface freezing had occurred, would be expected to produce the partially flooded craters characterized by Archimedes and Plato within the central basin of Mare Imbrium.

While the foregoing model invokes hydrodynamic and thermodynamic processes on a scale totally beyond human experience, none of them is mysterious, and most of them are amenable to experiment or calculation. The extreme fluidity necessary to sustain surface waves and the enormous heat transfer rates required to freeze them are well-known properties of fluidized liquid-solid systems (*9*). Numerical methods for the analysis of explosive cratering have already been applied to hypervelocity impacts into homogeneous material (*10*). Their extension to the proposed multilayer model would be of great interest. If the epoch of mare formation occurred during the moon's cooling phase, at least the predicted 50-km discontinuity should still be detectable by seismic refraction in regions outside the maria; if mare formation occurred during the heating phase, I would expect to find the discontinuity at some shallower depth.

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Acidic Components of Green River Shale Identified by a Gas Chromatography–Mass Spectrometry–Computer System

Abstract. *A system consisting of a gas chromatograph coupled to a mass spectrometer and computer has been used to characterize the extractable acidic components of Green River shale. This system accumulates mass spectra at every point of the gas chromatogram in a permanent form which permits one to observe mass spectra of minor as well as major constituents. One minor component, whose identification was confirmed by synthesis, was 6,10,14-trimethylpentadecanoic acid.*

Within the past few years, the utilization of gas chromatography for separation and of mass spectrometry for identification has led to significant advances in the characterization of organic mixtures isolated from geological sources. In most of these cases after collection the fraction is introduced into the mass spectrometer; the use of a system in which a gas chromatograph is directly coupled to a mass spectrometer (GC-MS) eliminates the tedious collection of the sample. This technique, which requires a mass spectrometric scan whenever a fraction of interest emerges from the gas chromatograph, still results in an inefficient and rather subjective selection of part of the total material. We have, therefore, explored the possibilities inherent in our recently developed GC-MS computer system (*1*), which permits automatic, continuous (every 4 seconds) recording of the mass spectrum of the effluent of the gas chromatograph. The computer not only serves as a digital recording system, but it can, after appropriate programming, also aid in the interpretation or identification of the large number of spectra thus obtained (about 400 spectra for a gas chromatogram ½ hour in duration).

The major advantage of such a system is that all the information inherent in a GC-MS system is accumulated in permanent form at once, and mass spectra are obtained at every point of the chromatogram rather than only for major or well-resolved components.

Table 1. Minor constituents identified in gas chromatogram of extracted acidic components of Green River shale (Fig. 1).

Label on Fig. 1	Identification
a	Methyl 2,6-dimethylheptanoate
b	2,6,10-Trimethyldodecane*
c	Tetradecane*
d	2,6,10-Trimethyltridecane*
e	Methyl 9-methylpentadecanoate
f	Pentadecane*
g	Hexadecane*
h	Dimethyl octanedioate†
i	2,6,10,14-Tetramethylpentadecane*
j	Heptadecane*
k	2,6,10,14-Tetramethylhexadecane*
l	Nonadecane*; and dimethyl pentanedioate
m	Dimethyl tridecanedioate; and methyl 2,6,10-trimethylhexadecanoate†
n	Methyl 16-methylheptadecanoate
o	Dibutyl phthalate‡
p	Dimethyl tetradecanedioate
r	Dimethyl pentadecanedioate
t	Dimethyl hexadecanedioate
v	Dimethyl heptadecanedioate†
w	Dimethyl octadecanedioate†
x	Dimethyl nonadecanedioate†

* Incompletely removed major component of the neutral fraction of total extract. † Identification tentative. ‡ Artifact also present in procedure blank.

This aspect is particularly important for the identification of minor, insufficiently resolved compounds.

An example of the application of this approach is the investigation of the acidic fraction of Green River shale. The major components of this extract (long-chain fatty acids and isoprenoid acids) have been identified (*2*), but the detection of small amounts of 6,10,14-trimethylpentadecanoic acid [the alleged absence of which (*3*) would seem to corroborate the origin of these isoprenoid acids from phytol by consecutive α-oxidations] was made possible with the system described here.

The acid fraction was obtained (*4*) by extraction of a powdered sample of Green River shale (*5*) (previously extracted with water, dilute sodium carbonate, and dilute hydrochloric acid, respectively) with a mixture of benzene and methanol (1 : 1). The extract [5 percent (by weight) of the total shale] was separated into acidic, basic, and neutral components soluble in methylene chloride (0.55, 0.015, and 2.0 percent of the total shale, respectively). The acids were converted to methyl esters by treatment with diazomethane, and 0.2 mg of the resulting ester mixture was injected into the GC-MS computer system. Figure 1 shows the "total ionization plot" generated by the computer plot of the total intensity of each consecutive mass spectrum recorded (*1*).

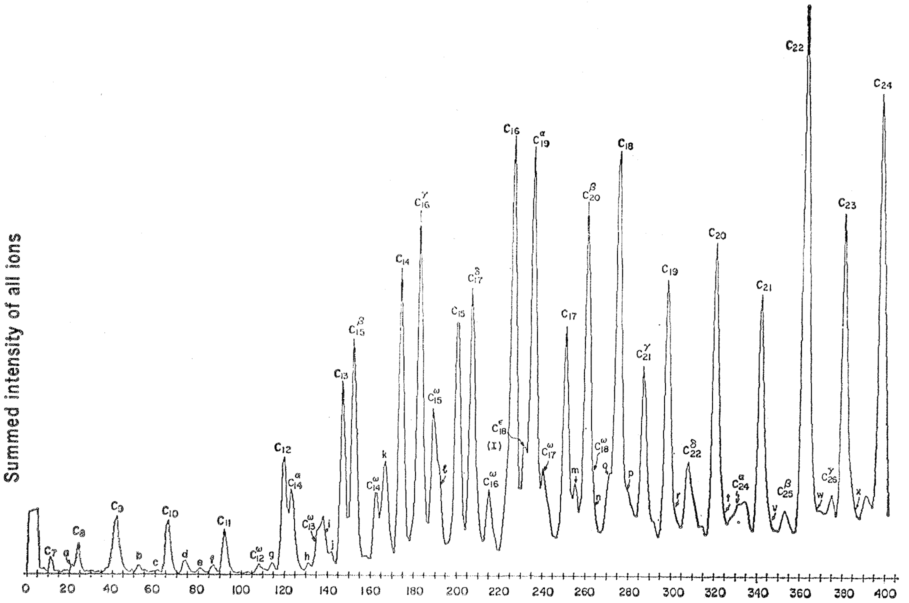


Fig. 1. Total ionization plot of a portion of a gas chromatogram of extracted acidic components in Green River shale. Conditions of the gas chromatograph were: glass column (12.7 × 0.32 cm); silicon gum rubber (OV-17), 3 percent on Gas Chrom Q; programmed from 75° to 300°C; helium carrier gas with a flow rate of 20 ml min^{-1}. (C_x) represents the methyl esters of saturated, straight-chain carboxylic acids containing x carbon atoms (not counting the methoxy carbon); ($C_x^{\alpha-\epsilon}$) represents methyl esters of isoprenoic acids containing x total carbon atoms (not counting the methoxy carbon) with the first methyl branch at position α to ϵ to the carboxyl group; (C_x^{ω}) represents the methyl esters of an isocarboxylic acid containing x carbon atoms. (Isoacids are fatty acids with a single methyl substituent on the penultimate carbon atom.)

For identification, we used a computer routine (*6*) to compare a selected number of spectra (particularly those representing discrete maxima, shoulders, and the front and back of apparently symmetrical peaks in the chromatogram) with mass spectra of authentic substances stored on magnetic disks. All the unbranched monocarboxylic esters listed in Table 1 were identified either directly, if their authentic spectrum was in our collection, or by the combination of computer results (which also list similar spectra in addition to identical ones) and gas chromatographic behavior.

The esters of the isoacids (fatty acids with a single methyl substituent on the penultimate carbon atom) were identified on the basis of their mass spectra (which are very similar to those of the isomeric unbranched acids) and their retention time (slightly less than that of the unbranched acids) (*7*). The esters of the isoprenoid acids were recognized as 2-, 3-, 4-, or 5-methyl-substituted esters—in the case of the ester of the C_{21} isoprenoid acid, a computer search indicated a 4,8,12-trimethyl-substituted ester, methyl 4,8,12-trimethyloctadecanoate being the only spectrum (*8*) of that type in our library.

All these compounds had been identified previously in the acidic extract of Green River shale [in the case of the esters of the isoacids, this experiment represents mass spectrometric confirmation of their previous identification on the basis of infrared spectral data (*9*)].

For the mass spectra (scans Nos. 230 to 233 are shown in Fig. 1; scan No. 232 is shown in Fig. 2) recorded during the emergence of the small peak just ahead of the methyl ester of norphytanic acid, the computer comparison indicated a close similarity to the spectrum of methyl octadecanoate. Since that compound emerges much

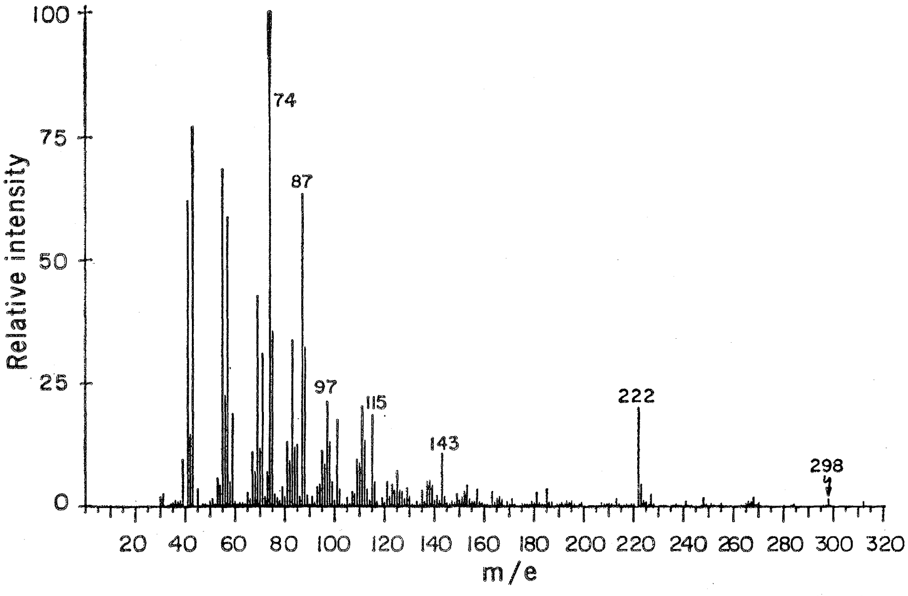


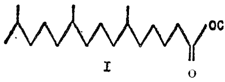
Fig. 2. Mass spectrum No. 232 recorded during the gas chromatogram shown in Fig. 1.

later (around scan No. 265), the substance in question must be an isomer, branched in such a way as to substantially reduce its retention time in the gas chromatograph. A particularly conspicuous peak in the mass spectrum of this fraction is found at *m/e* 222, corresponding to a loss of 76 mass units from the molecular ion of a C_{18} methyl ester.

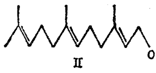
Another portion of the ester mixture had been injected into an identical gas chromatograph coupled to a double-focusing mass spectrometer (*10*), and about 30 exposures were taken during the gas chromatogram to provide high-resolution mass spectra for the identification of any of the components. Measurement of the accurate mass of the line at *m/e* 222 in the exposure taken during the emergence of the fraction in question indicated a composition of $C_{16}H_{30}$.

This is compatible with the assumption that this is a fragment ion (loss of $C_3H_8O_2$) of the methyl ester ($C_{19}H_{38}O_2$) of the C_{18} acid. The two-step loss of CH_3OH and C_2H_4O is indeed a characteristic fragmentation process for methyl esters containing an alkyl substituent at C-6 but no substituents on C-2 through C-5 (*7, 11*). The short retention time requires a polysubstituted chain, and, since the mass spectrum did not show any evidence for large substituents, a trimethyl substitution pattern would be most plausible. In view of the preponderance of isoprenoid compounds in this mixture, it was likely that this acid would also have an isoprenoid skeleton. There is a peak at *m/e* 213 which could be interpreted as cleavage at C-10, the next branching point, but it would be dangerous to use this as a convincing argument. The evidence was sufficient, however, to warrant the synthesis of the methyl ester of 6,10,14-trimethylpentadecanoic acid (I) for comparison.

For this purpose farnesol (II) was hydrogenated to hexahydrofarnesol, which in turn reacted with phosphorus tribromide to form hexahydrofarnesyl bromide. The Grignard reagent prepared from this bromide was then coupled with methyl acrylate (*12*) to yield the desired ester I. The resulting mass spectrum compared well with that in Fig. 2.



I

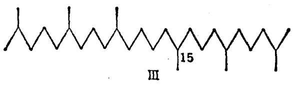


II

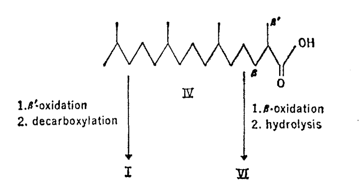
Furthermore, coinjection of the synthetic ester on a support-coated open tubular gas chromatographic column resulted in superposition of its emergence with the fraction tentatively identified as methyl 6,10,14-trimethylpentadecanoate (I).

The occurrence of structure I in Green River shale is particularly important, not only because it was not found before, but because its alleged absence (*3*) might be interpreted as a confirmation of the hypothesis that the isoprenoid acids in this source are derived from polyisoprenoids of the head-to-tail type by consecutive loss of adjacent carbon atoms, a sequence which could not lead to compounds containing a series of four unsubstituted carbon atoms. The hydrocarbon 2,6,10-trimethyltetradecane found in Antrim shale (*13*) could result from decarboxylation of 6,10,14-trimethylpentadecanoic acid.

As biological oxidations could have occurred before the organic material had become integrated in the sediment (*14*), there are thus two possible pathways for the formation of an ester with the substitution pattern of structure I. It could be formed either by oxidation at C-15 of a functionalized squalane skeleton (III) or, alternatively, by β-oxidation of an acid derived from a pure head-to-tail isoprenoid such as norphytanic acid (IV), which has two β-carbon atoms. If oxidation occurs at the methyl carbon (at β′), it would lead to an α-alkylmalonic acid which could decarboxylate to the free acid of structure I.

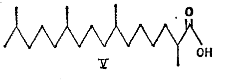


III



IV

If oxidation of a compound of the squalane type were indeed involved, the next larger acid would be structure V. Searching the mass spectra recorded at that area of the gas chromatogram where this compound would be expected to emerge (near the isomeric C_{20} isoprenoid ester), we found no significant peak at *m/e* 88, which is the most abundant ion expected for the methyl ester of structure V.



V

Thus the second hypothesis is more plausible if one invokes both β-oxidation and α-oxidation to account for all other acids. This is indeed the case, at least in the human body where phytanic acid undergoes α-oxidation to norphytanic acid (IV) which then suffers β-oxidation to give 4,8,12-trimethyltridecanoic acid (VI) (*15*). Oxidation of the methyl β-carbon atom is probably much less favored and leads to a minor product which might have gone undetected in the human body.

The examples discussed above demonstrate the usefulness of an integrated gas chromatograph, mass spectrometer, and computer system for the rapid and exhaustive analysis of complex mixtures in a single experiment. Such a system is even more useful in investigations which produce a series of related mixtures, all of which must be analyzed in detail, a task difficult to accomplish with manual, discontinuous techniques, and individual interpretation of each spectrum. For this reason previous work has centered on individual peaks or selected groups in each particular chromatogram (*2, 3, 13*).

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