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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LUNAR SAMPLE ANALYSIS PROGRAM

MICROPALEONTOLOGICAL STUDIES OF LUNAR SAMPLES

Proposal No. 90330

"A Search for Biogenic Structures in the Apollo 12 Lunar Samples"

by

J. William Schopf
Department of Geology
University of California, Los Angeles
Los Angeles, California 90024

January, 1971

Principal Investigator: J. William Schopf

Final Report

Prepared under Contract No. NAS9-9941

by

The Regents of the University of California
University of California, Los Angeles
Los Angeles, California 90024

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Manned Spacecraft Center
Lunar Receiving Laboratory
Houston, Texas

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A SEARCH FOR BIOGENIC STRUCTURES IN THE APOLLO 12 LUNAR SAMPLES

J. William Schopf

ABSTRACT

Optical and electron microscopic studies of rock chips and dust returned by Apollo 12, and of a petrographic thin section of microbreccia have yielded no evidence of lunar organisms. Terrestrial contamination of these samples by particulate organic matter is less than that typical of Apollo 11 samples.

A SEARCH FOR BIOGENIC STRUCTURES IN THE APOLLO 12 LUNAR SAMPLES

J. William Schopf

INTRODUCTION

The goal of this study has been to examine samples of lunar rocks and dust returned by Apollo 12 in search of morphologic evidence of present or former life on the moon. The rationale underlying these investigations has been discussed elsewhere[1].

SAMPLES STUDIED

The Apollo 12 samples investigated in this study consisted of the following: i) lunar fines (sample number 12001,36) from the selected sample container; ii) fines (12032,15; 12033,10; 12037,11; 12042,15) from the documented sample container; iii) fines (12023,16) from the lunar environment sample container; iv) rock chips from the exterior (12034,13) and interior (12034,22) of a microbreccia; and v) a polished petrographic thin section (12034,33) of a portion of the rock from which chips had been obtained. As a member of the Lunar Sample Preliminary Examination Team for the Apollo 12 mission, I also examined rocks, chips, fines and the two bioquarantine samples (one of which included portions of drive-tube core sample 12026 and the lowest portion of sample 12028, the deepest core recovered).

ANALYTICAL TECHNIQUES

Samples of the fines, placed on glass microscope slides either as free powder or dispersed in glycerine jelly, were studied with a light microscope at magnifications ranging from 4 to 1500 using normal and polarized transmitted light, phase-contrast optics, and reflected white and ultraviolet light. Similar optical microscopic studies were made of the chips and thin section of the microbreccia. Other samples of the fines and selected glass particles and rock fragments were coated with a thin gold-palladium film and studied with a scanning electron microscope at magnifications ranging from 30 to 30,000. Previous studies have demonstrated that acid maceration of lunar material does not provide additional significant information[1,2]; this destructive technique was therefore here omitted.

RESULTS AND SUMMARY

These investigations have yielded no evidence of living, recently dead or fossil microorganisms. In contrast with material returned by Apollo 11, which contained numerous cellulose fibers and other biogenic substances of terrestrial origin[1], the samples here studied appear to be essentially devoid of particulate organic contaminants. If organic contamination of other types has been equally minimal, there seems a strong possibility that much of the minute amount of total carbon (undifferentiated as to chemical species) detected

in the Apollo 12 samples[3] is of lunar origin. If this possibility can be further substantiated (e.g., by carbon isotopic analyses of the type developed by Kaplan and co-workers[4]), uncertainties as to the probable origin(s) and significance of organic materials found to be associated with Apollo 11 samples should be alleviated for Apollo 12.

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5. I thank Mrs. Carol Lewis and Mr. Bruce N. Haugh for assistance. This work was supported by NASA contract NAS 9-9941.

APPENDIX A

PUBLICATIONS OF THE PRINCIPAL INVESTIGATOR RESULTING FROM STUDIES SUPPORTED WHOLLY OR PARTIALLY BY NASA CONTRACT NAS9-9941

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Reprints Attached:

1. SCHOPF, J. W. 1970. Micropaleontological studies of lunar samples. Science 167:779-780.

2. PONNAMPERUMA, C., et al. 1970. Search for organic compounds in the lunar dust from the Sea of Tranquillity. Science 167:760-762.

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18. OEHLER, D. Z., and J. W. SCHOPF. In Press. Carbon isotopic studies of Early Precambrian sediments and early evolutionary processes. Program, Annual Meeting, Botanical Society of America, Edmonton, Canada (Abs).

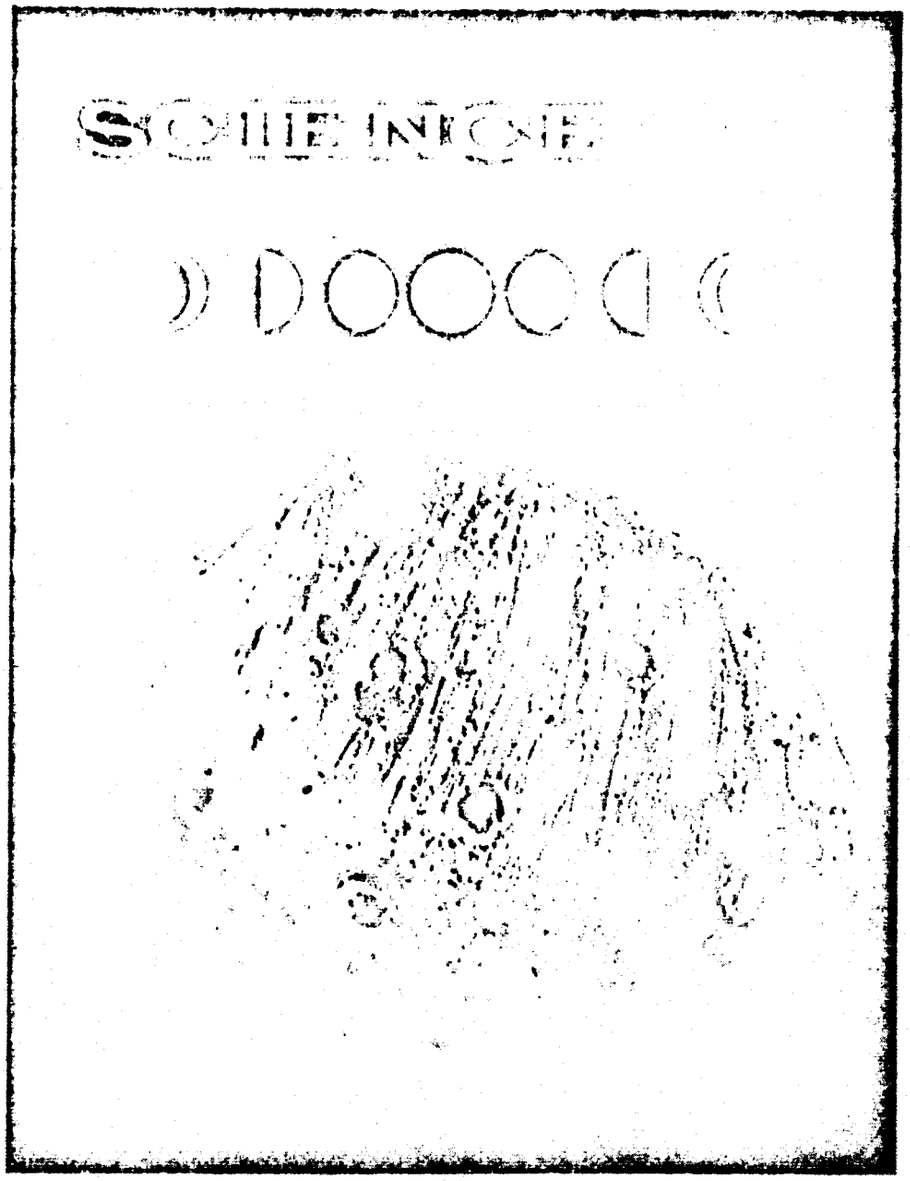
19. BLACIC, J. M., and J. W. SCHOPF. In Press. Late Precambrian microflora of the Bitter Springs Formation, central Australia. Program, Annual Meeting, Botanical Society of America, Edmonton, Canada (Abs).

ATTACHED REPRINTS

Reprinted from
30 January 1970, Volume 167, pp. 779-780

SCIENCE

Apollo 11 Lunar Science Conference



Micropaleontological Studies of Lunar Samples

J. William Schopf

Micropaleontological Studies of Lunar Samples

Abstract. *Optical and electron microscopic studies of rock chips and dust from the bulk sample box returned by Apollo 11 and of petrographic thin sections and acid-resistant residues of lunar material have yielded no evidence of indigenous biological activity.*

Although the present lunar environment is inimical to known biological systems, more favorable conditions may have existed in the geologic past. Urey (*1*) has suggested that the moon may have become "contaminated" with terrestrial organic matter early in the evolution of the earth-moon system. If this suggestion is correct, and if life became established, evidence of fossil organisms might be detectable in lunar rocks. It is even conceivable that such organisms might have been the progenitors of an extant biota, adapted to the harsh conditions of the lunar surface; such organisms probably could not survive in the terrestrial environment and therefore would not be recognized in studies designed to detect vital processes (such as metabolism, growth, and pathogenicity). The approach and techniques successfully used in Precambrian paleobiology (*2*), and the criteria developed to establish the indigenous and biogenic nature of Precambrian microfossils, seem well suited for the detection, characterization, and interpretation of any fossil or recently dead microorganisms that might occur in lunar materials (*3*).

In an effort to detect evidence of lunar organisms in the Apollo 11 samples, studies were made with a light microscope (L) at magnifications ranging from 4 to 1500, and, after the specimens had been coated with a thin gold-palladium film, with a scanning electron microscope (SEM) at magnifications ranging from 30 to 30,000. I examined samples as follows: (i) lunar dust (sample 10086,18 from the bulk sample box), divided into four size-fractions by sieving (>246 μm, 246 to 124 μm, 124 to 74 μm, and < 74 μm)—L and SEM; (ii) residue resulting from dissolution of lunar dust in hydrofluoric and hydrochloric acids—L; (iii) surfaces of rock chips from the exterior and interior of a microbreccia (sample 10002,54 from the bulk sample box), and fragments of these chips—L and SEM; (iv) petrographic thin sections of microbreccias (samples 10019,15, 10046,56, 10059,32, 10059,37, 10061, 27, 10061,28, and 10065,25)—L; (v) as a member of the Ames Lunar Sample Consortium, I studied (L) samples being investigated by Ponnamperuma *et al.* (*4*) (sample 10086, bulk A fines); (vi) as a member of the Lunar Sample Preliminary Examination Team for the Apollo 11 mission, I studied (L) rocks, chips, dust, and bioquarantine samples (including portions of both cores) (*5*).

Several thin sections (among them 10046,56, 10059,32, and 10061,27) contain elongate, spheroidal, spinose, or actinomorphic structures (Fig. 1) that superficially resemble terrestrial microfossils; many of these mineralogic "pseudofossils" are the result of partial devitrification of glassy inclusions. During preliminary studies at the Lunar Receiving Laboratory I detected birefringent organic fibers, a few microns in diameter, in the lunar dust and bioquarantine samples; a few similar fibers were noted in samples i and ii listed above, and in the mounting medium (but *not* within mineral grains) of several petrographic thin sections. With the exception of these terrestrial contaminants, apparently derived from lens tissue or similar substances, no biogenic materials were detected in these investigations.

Fig. 1. Optical photomicrograph showing actinomorphic pseudofossil, apparently produced by partial devitrification of the surrounding glassy matrix, in a petrographic thin section of a microbreccia (sample 10046,56); the scale represents 10 μm.

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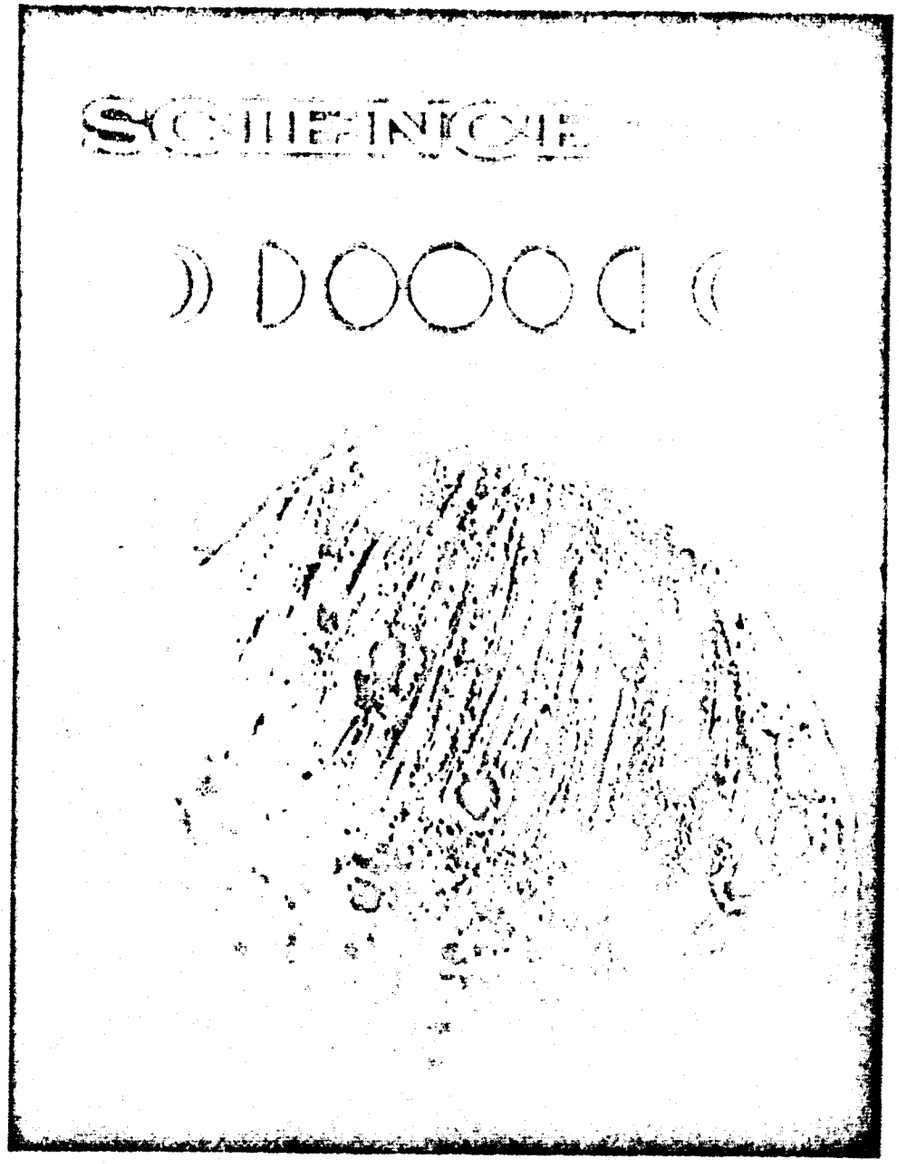
4 January 1970

Reprinted from
30 January 1970, Volume 167, pp. 760-762

SCIENCE

Apollo 11 Lunar Science Conference



Search for Organic Compounds in the Lunar Dust from the Sea of Tranquillity

Cyril Ponnamperuma, Keith Kvenvolden, Sherwood Chang, Richard Johnson, Glenn Pollock, Delbert Philpott, Isaac Kaplan, John Smith, J. William Schopf, Charles Gehrke, Gordon Hodgson, Irving A. Breger, Berthold Halpern, Alan Duffield, Konrad Krauskopf, Elso Barghoorn, Heinrich Holland and Klaus Keil

Search for Organic Compounds in the Lunar Dust from the Sea of Tranquillity

Abstract. *A sample of lunar dust was examined for organic compounds. Carbon detected in concentrations of 157 micrograms per gram had a $\delta^{13}C$ per mil (PDB) value of +20. Treatment with hydrochloric acid yielded hydrocarbons of low molecular weight, suggesting the presence of carbides. The gas chromatogram of the acylated and esterified derivatives of the hydrolyzate was similar to that obtained for the Pueblito de Allende meteorite. There were no detectable amounts of extractable high-molecular-weight alkanes, aromatic hydrocarbons, isoprenoid hydrocarbons, normal alkanes, fatty acids, amino acids, sugars, or nucleic acid bases. Traces of porphyrins were found, perhaps arising from rocket exhaust materials.*

A useful approach to the study of chemical evolution is the examination of organic matter in ancient rocks and sediments. The oldest known microfossils are about 3×10^9 years old, indicating that life was already well established at this period (*1*). The possibility, however, of finding rocks on the earth older than 3½ billion years appears to be small. On the other hand, the samples from the moon may give us some clues to prebiotic organic synthesis in the solar system (*2*).

This report contains the results obtained by a group of investigators established as the NASA Ames Research Center Consortium to analyze the sample labeled "10086 bulk A fines." Since this sample consisted of a relatively fine powder, no further grinding was undertaken before analysis.

Our analysis included an examination of the lunar material for total carbon, organic carbon, isotope fractionation, microfossils, and mineralogy. Sequential treatment of the sample by a benzene-methanol mixture, water, and hydrochloric acid provided extracts for examination by chromatographic and spectrometric methods (Fig. 1).

To monitor every stage of the analysis, parallel experiments were conducted on an interior sample from a 6-kg piece of the Pueblito de Allende meteorite (*3*), and a sand blank was prepared by heating a sample of Ottawa sand for 48 hours at 1000°C. To minimize contamination, the analyses were carried out in a clean laboratory ventilated with filtered air, and the entire sequence of solvent extractions of the lunar dust was accomplished in a single glass vessel.

Total carbon was determined by measuring the volume of CO_2 evolved when a 1-g sample was outgassed at

150°C at a pressure of less than 1 μm-Hg and burned at 1050°C. The values ranged from 140 μg/g to 200 μg/g. The most consistent values were between 140 and 160 μg/g. The comparable figure for a sample of the Pueblito de Allende meteorite was 3000 μg/g. The sand blank showed no detectable carbon.

The amount of carbon that could be converted into volatile carbon-hydrogen compounds was determined by pyrolyzing about 30 mg of the dust at 800°C in an atmosphere of hydrogen and helium (*4*). The resulting volatile compounds were estimated by a hydrogen flame ionization detector. The average value obtained was 40 μg/g. For a sample of the Pueblito de Allende meteorite this amounted to approximately 14 μg/g, and for the sand blank, 1 μg/g.

Isotope measurements on the total sample resulted in a $\delta^{13}C$ value of +20 relative to the PDB standard and the $\delta^{34}S$ of +8.2 relative to the Canyon Diablo meteorite. These figures are considerably higher than those generally reported for intact meteorites ($\delta^{13}C$, −4 to −20; $\delta^{34}S$, −2 to +2). A detailed account of these findings and their significance are described by Kaplan and Smith (*5*).

A portion (20 mg) of the sample was pyrolyzed from 80° to 300°C in the ion source of a CEC 110 high-resolution mass spectrometer. The analysis was repeated at 700°C with the high-resolution mass spectrometer (MS 9) at the Jet Propulsion Laboratory in Pasadena. Ions indicating the possible presence of formic acid, acetic acid, and SO_2 were found above the background concentration. However, no conclusive identification was possible. Carbon dioxide was identified in the pyrolysis products at 250°C to 750°C. Observations of dust, surfaces of the microbreccias, and thin sections of microbreccias made by light and electron microscopy yielded no evidence of indigenous biological structures (*6*).

To detect extractable organic compounds, 54.6 g of the lunar dust were treated with a mixture of benzene and methanol (9 : 1). Twenty-three percent of the extract was examined for porphyrins (*7*). Fluorescence excitation and emission spectra of these extracts are suggestive of porphyrins. Since similar spectral responses were observed in exhaust products from tests of the lunar descent rocket engines, it is possible that these pigments were formed from

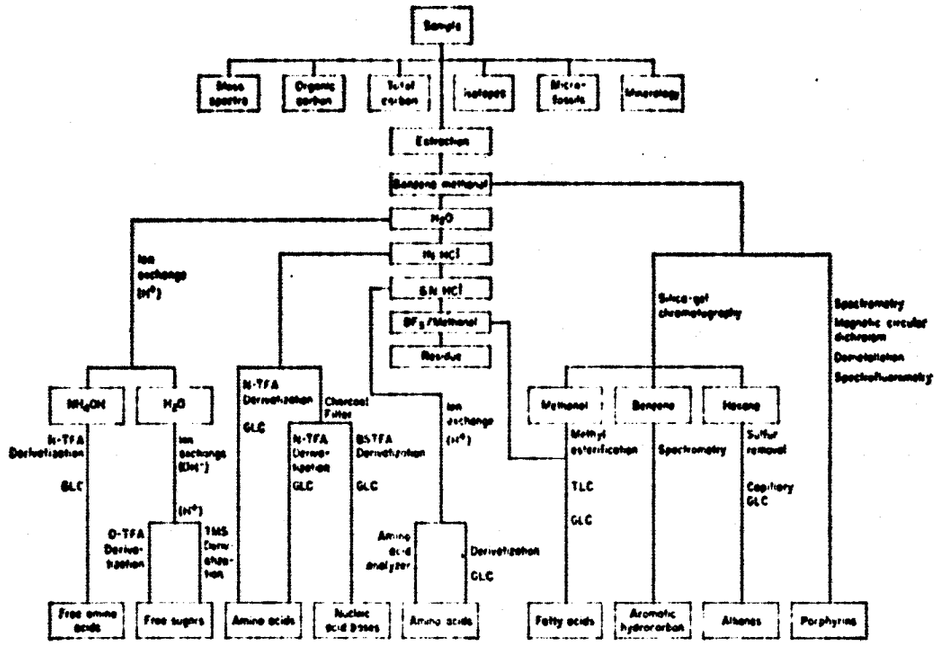


Fig. 1. Scheme of analysis.

components of the rocket exhaust (*8*). The amount of porphyrins detected was approximately 10^{-4} μg/g.

The remainder of the benzene-methanol extract was chromatographed on a silica-gel column and eluted with hexane, benzene, and methanol. Capillary gas-liquid chromatography of the hexane fraction showed that no single *n*-alkane from C_{12} to C_{32} was present at concentrations of 2×10^{-5} μg/g. The absorption spectrum of the benzene eluate showed bands at 224, 274, and 280 nm. Since these absorption bands were also present in the sand and solvent blanks, the presence of aromatics in the lunar sample cannot be inferred. The methanol eluate from the silica-gel chromatography was esterified and examined for fatty acids by gas-liquid chromatography. The C_{12} to C_{32} fatty acids were not detected at levels of 10^{-2} μg/g.

After treatment with benzene-methanol, the bulk fines were dried in a rotary evaporator and extracted with water. This extract was desalted and analyzed for free amino acids and carbohydrates by gas-liquid chromatography as *N*-trifluoroacetyl-*n*-butyl esters of amino acids, as trimethylsilyl derivatives of sugars, and as trifluoroacetyl derivatives of sugar alcohols. In the water extracts, the amino acids were not detected at a concentration of 10^{-5} μg per gram of sample. Sugars were not present at concentrations of 6×10^{-4} μg/g.

The residue, after the water extraction, was hydrolyzed with HCl. Hydrogen sulfide evolved during the hydrolysis was collected. The concentration was about 700 μg/g, with an average $\delta^{34}S$ value of +8.0. The 1*N* hydrolyzate was treated with Norite charcoal to absorb any bases that may have been present. The charcoal was extracted with formic acid, and the extract was treated with bis(trimethylsilyl)trifluoroacetamide and analyzed for the bases as trimethylsilyl derivatives. Purines and pyrimidine bases were not present at concentrations of 4×10^{-3} μg/g.

The hydrolyzate obtained after refluxing the sample with 6*N* HCl at 125°C for 19 hours was desalted and examined for amino acids by ion-exchange chromatography and gas chromatography of the *N*-trifluoroacetyl-*n*-butyl ester derivatives. Although as little as 2×10^{-3} μg/g could be detected by this method, none of the amino acids commonly found in protein appeared to be present.

However, in the HCl hydrolyzates several compounds were found which did not appear on the gas chromatogram unless the hydrolyzates were both esterified and acylated. These molecules were present in a similarly treated acid hydrolyzate of the Pueblito de Allende meteorite but not in the sand blank or the rocket exhaust material (Fig. 2). Organic compounds, as derivatives, appear to be present in both samples.

Since approximately 100 μg of carbon per gram of sample still remained to be accounted for, an attempt was made to determine whether some of the residual carbon was present as car-

bides. A fresh sample, outgassed in a vacuum at 150°C, was therefore hydrolyzed with 6*N* HCl in a sealed tube, and the resulting gases were distilled or extracted with *n*-hexane. Analysis by gas-liquid chromatography and mass spectrometry revealed the presence of C_1, C_2, C_3, and C_4 hydrocarbons. The total added up to almost 20 μg per gram of the lunar sample. A sample of Mighei meteorite and cohenite (Fe_3C) from the Canyon Diablo meteorite were similarly analyzed (Fig. 3), hydrocarbons being identified in each case.

Our examination of the Apollo 11 sample from the Sea of Tranquillity leads us to conclude that the concentration of carbon is about 157 μg per gram of sample. If we assume that the hydrocarbons generated from the acid hydrolysis come from carbides, the amount of carbon accounted for is approximately 20 μg/g. The isotopic compositions of carbon and sulfur are significantly different from the composition determined for other extraterrestrial samples. The $\delta^{13}C$ value of +20 relative to the PDB standard and the $\delta^{34}S$ value of +8.2 relative to the Canyon Diablo meteorite are unusual by comparison with both terrestrial and meteorite samples. Although the limits of detectability of our techniques were in the nanogram range, normal alkanes, isoprenoids, hydrocarbons, aromatic hydrocarbons, fatty acids, amino acids, sugars, and nucleic acid bases were not present at this level of concentration. There is a striking but yet unexplained similarity between the chromatogram of the compound that formed the derivative in the acid hydrolyzates of the lunar sample and of the Pueblito de Allende meteorite. These findings should be considered to be specific for a single surface sample from the Sea of Tranquillity. Samples from the highlands, or core samples, may be expected to yield different results.

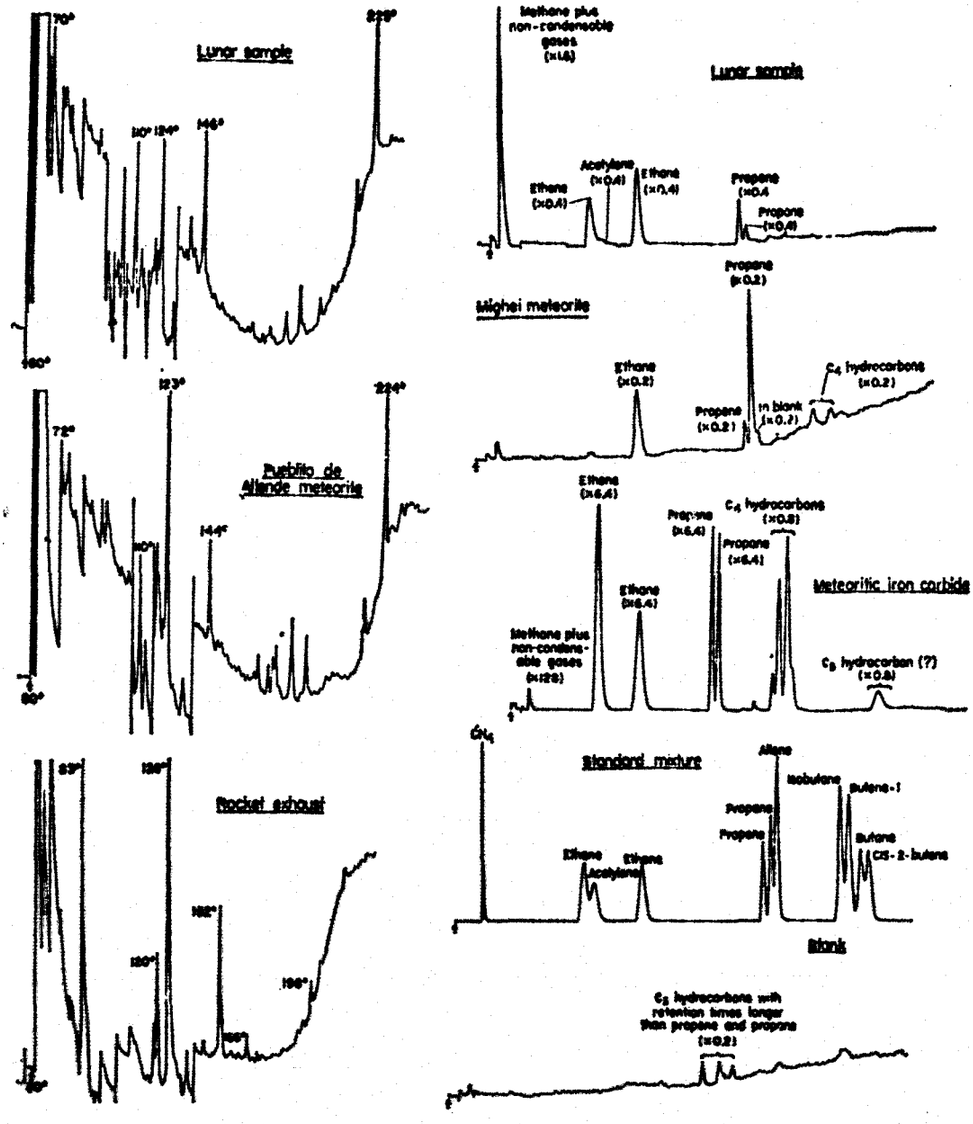


Fig. 2 (left). Gas chromatograms of *N*-trifluoroacetyl-*n*-butyl esters of 1*N* hydrolyzates of the Pueblito de Allende meteorite and the lunar sample, on a glass column (1 m by 6 mm), packed with 1.5 percent (by weight) OV-17, on heat-treated 80/100 mesh Chromosorb G, temperature programmed from 60°C to 250°C, at 4°C per minute. Vertical lines represent attenuation changes. Fig. 3 (right). Gas chromatograms of hydrocarbons from 6*N* HCl treatment of the lunar sample (0.1 g), Mighei meteorite (0.05 g), and Fe_3C (0.0014 g), on a stainless steel column (2 m by 3 m), packed with 150 mesh Poropack Q, programmed from ambient temperature to 150°C, at 10°C per minute. Standard mixture attenuated at × 160.

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5 January 1970

Proceedings of the Apollo 11 Lunar Science Conference, Vol. 2, pp. 1933 to 1934.

Micropaleontological studies of Apollo 11 lunar samples

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(*Received* 19 *January* 1970; *accepted* 20 *January* 1970)

Abstract—Optical and electron microscopic studies of rock chips and dust from the Bulk Sample Box returned by Apollo 11, and of petrographic thin sections and acid-resistant residues of lunar material, have yielded no evidence of indigenous biological activity.

ALTHOUGH the present lunar environment is inimical to known biological systems, more favorable conditions may have existed in the geologic past. UREY (1966) has suggested that the moon may have become "contaminated" with terrestrial organic matter early in the evolution of the earth–moon system. If this concept is correct, and if life became established, evidence of fossil organisms might be detectable in lunar rocks. It is even conceivable that such organisms might have been the progenitors of an extant biota, adapted to the harsh conditions of the lunar surface; such organisms probably could not survive in the terrestrial environment and therefore would not be recognized in studies designed to detect vital processes (e.g. metabolism, growth, pathogenicity). The approach and techniques successfully used in Precambrian paleobiology (SCHOPF, 1970), and the criteria developed to establish the indigenous and biogenic nature of Precambrian microfossils, seem well-suited to detect, characterize and interpret any fossil or recently dead microorganisms that might occur in lunar materials (SCHOPF, 1969).

In an effort to detect evidence of lunar organisms in the Apollo 11 samples, studies were made with a light microscope (L) at magnifications ranging from 4× to 1500× and, after coating specimens with a thin gold-palladium film, with a scanning electron microscope (SEM) at magnifications ranging from 30× to 30,000×. I examined the following samples: (i) lunar dust (sample 10086,18 from the Bulk Sample Box), divided into four size-fractions by sieving (>246 μ, 246–124 μ, 124–74 μ, <74 μ), L and SEM; (ii) residue resulting from dissolution of lunar dust in hydrofluoric and hydrochloric acids, L; (iii) surfaces of rock chips from the exterior and interior of a microbreccia (sample 10002,54 from the Bulk Sample Box), and fragments of these chips, L and SEM; (iv) petrographic thin sections of microbreccias (samples 10019,15, 10046,56, 10059,32, 10059,37, 10061,27, 10061,28, and 10065,25), L. (v) As a member of the Ames Lunar Sample Consortium, I studied (L) samples being investigated by C. PONNAMPERUMA *et al.* (1970) at the Ames Research Center (sample 10086, Bulk A Fines). (vi) As a member of the Lunar Sample Preliminary Examination Team, during the Apollo 11 mission I studied (L) rocks, chips dust and bio-quarantine samples (including portions of both cores) (LSPET, 1969).

Several thin sections (e.g. 10046,56, 10059,32 and 10061,27) contain elongate, spheroidal, spinose or actinomorphic structures (Fig. 1) that superficially resemble terrestrial microfossils; many of these mineralogic "pseudofossils" are the result of partial devitrification of glassy inclusions. During preliminary studies at the Lunar

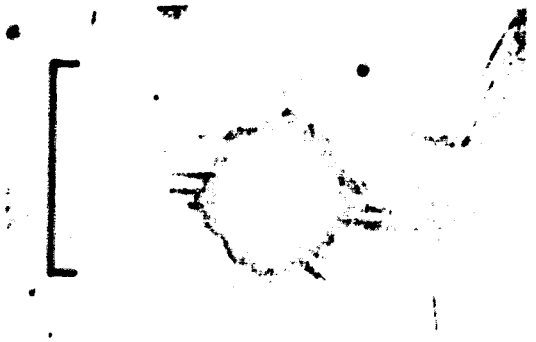

Fig. 1. Optical photomicrograph showing actinomorphic pseudofossil, apparently produced by partial devitrification of the surrounding glassy matrix, in a petrographic thin section of a microbreccia (Apollo 11 sample 10046,56); line for scale represents 10 μ.

Receiving Laboratory I detected birefringent organic fibers, a few microns in diameter, in the lunar dust and bio-quarantine samples; a few similar fibers were noted in samples (i) and (ii), above, and in the mounting medium (but *not* within mineral grains) of several petrographic thin sections. With the exception of these terrestrial contaminants, apparently derived from lens tissue or similar substances, no biogenic materials were detected in these examinations.

Acknowledgements—I thank Mrs. CAROL LEWIS for assistance, and G. OERTEL and J. CHRISTIE for suggestions. Supported by NASA Contract NAS 9-9941.

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eprinted from

PERGAMON PRESS
OXFORD NEW YORK LONDON PARIS

Geochimica et Cosmochimica Acta, 1970, Vol. 34, pp. 659 to 675. Pergamon Press. Printed in Northern Ireland

Extractable organic matter in Precambrian cherts*

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(*Received 5 November 1969; accepted in revised form 19 January 1970*)

Abstract—The concentrations of hydrocarbons and fatty acids, and the ratios of the stable isotopes of carbon and sulfur were determined for Precambrian cherts from the Gunflint Iron-Formation, the Paradise Creek Formation, and the Bitter Springs Formation. All three cherts are known to contain organically preserved microfossils. For comparison, studies were conducted on two fossiliferous Phanerozoic cherts (from the Rhynie Chert Beds and Serian Volcanic Formation) of comparable origin and geologic history. The highest concentrations of n-alkanes, pristane and phytane, and saturated and unsaturated fatty acids were generally recovered from the untreated surfaces of the samples; these compounds are primarily, and probably entirely, of recent origin. Extremely small concentrations (a few ppb) of similar compounds were extracted from interior portions of the Precambrian samples; although in part apparently indigenous to the sediments, these compounds are not demonstrably syngenetic with original sedimentation, and the major portion of these extracts also appears to be of relatively recent origin. Permeability and porosity measurements conducted on separate rock samples from the collection on which the organic studies were made, showed the presence of microfractures that could allow the passage of ground water under a pressure gradient. In the absence of chemical criteria firmly establishing the syngenetic nature of extracted organic constituents, such studies of Precambrian sediments may only provide ambiguous evidence of early biochemical processes.

Introduction

Paleontological evidence suggests that Precambrian time was characterized by gradually accelerating biological evolution (Schopf, 1969); the detection of chemical fossils in early sediments should serve to augment the morphological fossil record, possibly yielding evidence for the time of origin of major biochemical innovations. To date, however, organic geochemical studies have provided little evidence of early evolutionary development. In fact, no major differences between the extractable components of Precambrian and younger rocks have been demonstrated and, therefore, no specific chemical tests for "Precambrian origin" now exist.

The yields of extracts from Precambrian sedimentary rocks vary considerably. In the work here reported, the total yields of isolated material rarely exceed 0·1 ppm; it may be noted that these yields are two to three orders of magnitude lower than those previously reported from Precambrian cherts, including the well-known Gunflint chert (Oro *et al.*, 1965; Van Hoeven *et al.*, 1969) which we have here reinvestigated. Clastic sediments, however, may contain much greater amounts of extractable organic matter, and yields as great as 1500 ppm have been reported from Precambrian shales (Hoering, 1967). Since mobile fluids may migrate along bedding planes in shales, constituting a potential source of *in situ* contamination by materials of younger geological age, we have restricted this investigation to highly indurated, and relatively impermeable, carbonaceous cherts. We have studied five sediments

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of varying geological age known to contain well-preserved plant fossils in an attempt to relate the extractable constituents of these cherts to the biota extant during their deposition.

Pristane, phytane, normal paraffins and fatty acids have been previously reported from chert of the Gunflint Iron Formation by Oro *et al.* (1965) and Van Hoeven *et al.* (1969). Amino acids were isolated by Schopf *et al.* (1968) and Abelson and Hare (1968), and C^{13}/C^{12} ratios were measured by Hoering (1967) on the organic constituents. Amino acids were also identified in extracts from black cherts of the Bitter Springs Formation (Schopf *et al.*, 1968).

Several approaches have been used in the present study to differentiate between Precambrian organic matter and contaminants of more recent origin. Primary among these is an analysis of the effect of progressive particle size reduction on the nature and yield of the extracts obtained. The results of this analysis have been substantiated by replicate studies of three of the sediments investigated, and by a comparative study of cherts ranging in age from about $0{\cdot}2 \times 10^9$ yr to $1{\cdot}9 \times 10^9$ yr.

Description of Samples

The black, fossiliferous cherts selected for analysis were obtained from: (1) the Gunflint Iron Formation, Middle Precambrian, Ontario, Canada (ca. $1{\cdot}9 \times 10^9$ yr old); (2) the Paradise Creek Formation, Late Precambrian, Queensland, Aurtralia (ca. $1{\cdot}6 \times 10^9$ yr old); (3) the Bitter Springs Formation, Late Precambrian, Northern Territory, Australia (ca. $0{\cdot}9 \times 10^9$ yr old); (4) the Rhynie Cherts Beds, Lower Devonian, Aberdeenshire, Scotland (ca. $0{\cdot}39 \times 10^9$ yr old); and (5) the Serian Volcanic Formation, Upper Triassic, Sarawak, Borneo (ca. $0{\cdot}2 \times 10^9$ yr old).

All five cherts are black, waxy, and somewhat lustrous on freshly broken conchoidal faces, and all are noted for the cellularly preserved, permineralized plant fossils they contain. The cherts are composed predominantly of cryptocrystalline quartz and, except for the Triassic chert, have an organic carbon content of somewhat less than 1%; they appear to be chemical sediments displaying little diagenetic change. The three Precambrian sediments exhibit fine, irregular laminations reflecting the presence of stromatolitic algal mats; the younger cherts are more coarsely bedded and are thought to represent silicified peat deposits. The petrology of these cherts, and of associated sediments, indicates a general absence of metamorphism; the brown-to-amber color of the preserved organic matter, as seen in thin sections, presumably reflects a mild thermal history. The origin, lithology, mode of preservation of organic constituents, as well as the thermal history of the five deposits appear, therefore, to be quite similar.

The specimens of black chert from the Gunflint Iron Formation were collected by J. W. Schopf (June, 1968) from a stromatolitic horizon (the Lower Algal Chert Member) exposed on the northern shore of Lake Superior, about 6·4 km west of Schreiber, Ontario. A well-preserved microbiota, including 12 species of plant fossils, has been described from this locality (Barghoorn and Tyler, 1965). The chert samples from the Paradise Creek Formation were collected by J. W. Schopf and F. DeKeyser (May, 1968) from silicified stromatolites occurring in the upper third

of the formation, exposed on low hilltops about 13 km southeast of Lady Agnes Mine (72 km northeast of Camooweal, Queensland); organically preserved unicellular algae recently have been reported from these Late Precambrian stromatolites (LICARI *et al.*, 1969). The bedded carbonaceous cherts of the Bitter Springs Formation were collected by J. W. Schopf, R. Shaw and A. Magee (May, 1968) from the uppermost strata of the formation, exposed on a low ridge about 1·6 km north of the Ross River Tourist Camp (Love's Creek Homestead), 64 km east-northeast of Alice Springs, Northern Territory. Thirty species of algae, bacteria, possible fungi and other microorganisms have been described previously from the Bitter Springs cherts (SCHOPF, 1968).

Specimens of the Rhynie Chert (Old Red Sandstone), secured from the A"1 zone of KIDSTON and LANG (1917–1921) and containing numerous axes of the primitive vascular plants *Rhynia* and *Asteroxylon*, were obtained from E. W. R. Stollery (Portsoy Minerals, 12 Sandend, Portsoy, Banffshire, Scotland). The highly carbonaceous Triassic cherts of the Serian Volcanic Formation were collected by G. E. Wilford in the Penrissen region of West Sarawak (WILFORD and KHO, 1965), and were obtained for our study from E. S. Barghoorn; a variety of plant fossils, including dipteridaceous fern sporangia (GASTONY, 1970), are cellularly preserved in these cherts.

EXPERIMENTAL

Contamination controls

To monitor the level, nature and origin of contamination throughout the analytical technique, samples of powdered, freshly ignited firebrick (880°C; 12 hr) were subjected to the entire separation procedure including hydrofluoric acid treatment. These controls showed quite conclusively that, despite all precautions, some detectable contamination of the final products might be expected. In the case of the saturated hydrocarbons, the total contamination detected never exceeded $0{\cdot}1 \times 10^{-6}$ g; as much as $0{\cdot}4 \times 10^{-6}$ g of contaminating saturated and unsaturated fatty acids could be found in the final methyl ester fraction. When firebrick was omitted from these tests, however, the detected level of contamination was reduced by several orders of magnitude, presumably reflecting the effect of large surface areas in concentrating contaminants.

Recognizable laboratory contamination was finally reduced to an acceptable level (<1 ng/ml) by carefully distilling all solvents, by eliminating all organic materials (e.g. plastic, rubber, paper, etc.) from the experimental procedures, and by limiting the access of laboratory air.

The degree of contamination of the cherts in the geological environment prior to collection and laboratory analysis is more difficult to assess. To obtain some indication of the amount of *in situ* contamination, the untreated surface of each sample of chert was repeatedly extracted with a benzene/methanol solution. Details of this procedure are given below.

It should be noted that procedures to reduce the level of surface contamination of the rocks prior to extraction were deliberately avoided. Instead, an effort was made to collect and analyze those organic constituents readily extractable from accessible rock surfaces. Such material presumably contains the major portion of recent contamination, and a comparison of this fraction with materials extracted from the interior of the rock, and from acid-resistant organic residues, provides a basis for assessing the degree and depth of *in situ* contamination and for determining the origins of various extractable components.

Analytical procedure

Samples of the Gunflint, Bitter Springs and Rhynie cherts were examined in duplicate; single analyses were made of the Paradise Creek and Borneo cherts. For each extraction, individual pieces of the black cherts, each weighing at least 100 g, were taken as starting material; total sample weights ranged from 100 to 1300 g.

Solvent extractions

Three separate solvent extractions of organic matter from the cherts, at progressively smaller particle sizes, were made on each of the rock specimens analyzed.

(1) *Chips.* After brushing the surfaces of the specimens under running distilled water to remove loose or friable material, the samples were shattered by hammering, and those pieces 1–2 cm in size were collected. These chips were immersed in a solvent solution (30/70 methanol–benzene) in a covered beaker, boiled gently on a steam bath for 30 min, and then allowed to stand at ambient temperature for 24 hr. After decanting the solvent, the chips were washed three times with a hot solution of the same solvent, which was decanted into the original solvent extract. This fraction constituted the "extract of the chips."

(2) *Powder.* The chips were dried under cover at 60° and then immersed in a chromic/sulphuric acid solution overnight to oxidize any remaining surface contaminants. After repeated washing with distilled water, the chips were etched by immersion in 25% hydrofluoric acid for 2 hr; this treatment resulted in a loss of 6–8 per cent in weight, and effected the removal of previously extracted outer surfaces. Following washing and drying, the etched chips were ground in a shatter box mill (Spex Industries) for 4 min. Prolonged grinding was avoided in order to reduce possible contamination and formation of artifacts. Typically, the ground product consisted of the following powder:

$$88\% < 120 \text{ mesh};\ 8\% < 60 \text{ mesh} > 120 \text{ mesh};\ \text{and } 4\% > 60 \text{ mesh}$$

This powder was refluxed overnight in the benzene/methanol mixture, and the bulk of the solvent was decanted. After repeating this extraction twice with small quantities of solvent, the powder was transferred to a fritted funnel and washed several times with solvent. The washings and extracts were combined to form the "extract of the powder."

(3) *Acid-resistant residue.* The extracted chert powder was transferred to a covered Teflon beaker and dissolved in a minimum amount of 50% hydrofluoric acid (Baker-Analyzed Reagent). After 4 or 5 days when the reaction was complete, the acid-resistant organic residue was recovered by decantation of the acid followed by centrifugation. The resulting residue was generally composed of about 95% amorphous, brown-to-amber-colored organic matter, 2–4% organic microfossils and plant fragments and minor concentrations of insoluble minerals (e.g. pyrite, fluorite). Extraction of this water-washed and dried residue with the benzene/methanol solvent under reflux gave the third solvent extract.

Chromatography

The solvent extracts from the chips, powder, and acid-resistant residue were treated identically. Most of the solvent from each extract was removed by evaporation on a steam bath; the few remaining drops were removed under a stream of nitrogen at ambient temperature.

Alkanes were separated from the extracts by chromatography on pre-washed columns of silica gel and elution with hexane. The extracts resulting from further elution with benzene and methanol were combined and evaporated to near dryness, redissolved in benzene and the solution shaken with a 2% solution of sodium hydroxide to remove free fatty acids. The free acids were separated from the sodium hydroxide solution and converted to their methyl ester derivatives by treatment with diazomethane.

Hydrocarbons were identified by gas–liquid chromatography on S.E. 30 and P.P.E. (Polyphenyl ether) columns using an instrument equipped with a flame ionization detector. Identification was based on a comparison of the retention times of the individual components with those of authentic pristane, phytane and n-alkanes on the same columns and by coinjecting samples with known standards. Methyl esters of fatty acids were identified similarly, except that the P.P.E. column was replaced by a D.E.G.S. (diethylene glycol succinate) column, and saturated and unsaturated methyl ester derivatives were used for comparison.

For positive identification unsaturated methyl esters in the extracts were converted to saturated esters by reduction with hydrogen in the presence of platinum oxide at atmospheric pressure and ambient temperature. Peak shifts and peak height increases were then determined on the products.

The method of analysis enabled 5 ng of both n-alkanes and methyl ester derivatives of fatty acids to be unquestionably detected above noise level, and quantitatively resolved.

In the case of the Gunflint, Bitter Springs and Rhynie cherts, an additional procedure was introduced to recover bound fatty acids. Following benzene/methanol extraction of the chips, powder, and acid-resistant residue, fresh solvent was added and the solution was stirred while drops of hydrochloric acid were added until a pH of approximately 2·0 persisted for 30 min. After filtration, the bound acids were recovered from the solvent solutions, converted to their methyl ester derivatives, and identified by gas–liquid chromatography as described above.

C^{13}/C^{12} isotope ratios were measured on the CO_2 released by combustion of the acid-resistant organic residues following an adaptation of the method described by CRAIG (1953). δC^{13} values were measured in comparison with a PDB standard. S^{34}/S^{32} determinations were made on elemental sulfur dissolved in the benzene/methanol extracts of the acid-resistant residues; the sulfur was isolated by its reaction with freshly cleaned copper wire, to produce a black surface layer of copper sulfide. Strands of wire were added sequentially to the solution until the copper no longer turned black, indicating that dissolved sulfur had been completely removed from solution. The isotopic ratio of pyritic sulfur from the Gunflint chert was analyzed following the procedure described by KAPLAN *et al.* (1963). All δS^{34} values are based on the Canyon Diablo meteorite standard.

Permeability and porosity

Permeability and porosity measurements were made on the samples by Chevron Oil Field Research Company on 1-in. dia. cores. Permeability was determined from measurements of the flow rate of air through the core which was exposed to a pressure of 300 psi. Porosity was calculated from the weight of brine trapped within the core after an initial evacuation to 15 μmHg and a final exposure to a known brine at 1000 psi. The brine was forced into accessible voids.

No measurements were made on the Paradise Creek chert, since extensive fracturing within the available samples prevented the cutting of a suitable core.

Results and Discussion

Alkanes

The yields of alkanes obtained from solvent extraction of the cherts are summarized in Table 1; chromatograms of the extracts from the chips, powder, and acid-resistant residue from each chert are shown in Figs. 1 and 2.

Precambrian cherts

As is shown in Fig. 1, the extracts from chips of the three Precambrian cherts investigated contain very similar alkane suites. These similarities, and other features common to these three extracts, may be summarized as follows:

1. Relatively large extract yields, substantially greater than those detected in subsequent extractions, were obtained by immersing the freshly broken chips of chert in solvent for 24 hr. This distribution indicated that most of the soluble organic matter associated with these rocks is readily accessible and must, therefore, be present on the surface of the chips or in micro-fissures or pore systems of dimensions allowing penetration and extraction by benzene or methanol.

2. The ease with which the organic matter was extracted from the chips suggests that it is of relatively recent, rather than of Precambrian origin, since comparable interchange with mobile, organic materials must also have been possible in the geological environment.

3. In general, the extracts from the chips show a smooth distribution of n-alkanes with the maximum concentration occurring close to the C_{22} member. All three also exhibit a marked predominance of n-alkanes with an odd number of

Table 1. Total alkanes extracted from cherts

Chert	Borneo			Rhynie						Bitter Springs					
Age (yr)	0.2×10^9			0.37×10^9						0.9×10^9					
Sample wt. (g)	146			380			100			1100			200		
Extraction stage*	C	P	R	C	P	R	C	P	R	C	P	R	C	P	R
Total yield of alkanes (ppb)	17	19	7	1180	1640	2570	670	3500	3300	8	1	1	4	1	1
Carbon preference index (C_{27}–C_{33}) Odd/even	1·4	1·3	1·1	1·1	1·0	1·1	1·1	1·0	1·0	2·3	1·3	1·2	1·6	1·4	1·3
Pristane (% Alkanes)	1·1	1·1	—	4·0	3·5	6·7	—	2·5	6·4	3·2	+	—	+	—	—
Phytane (% Alkanes)	3·1	2·3	—	2·1	2·1	2·9	—	1·4	2·7	3·6	+	+	+	—	+
Pristane / Phytane	0·4	0·5	—	1·9	1·7	2·3	—	1·8	2·4	0·9	—	—	—	—	—

Chert	Paradise Creek			Gunflint					
Age (yr)	1.6×10^9			1.9×10^9					
Sample wt. (g)	1020			1300			300		
Extraction stage*	C	P	R	C	P	R	C	P	R
Total yield of alkanes (ppb)	21	1	2	26	2	1	22	6	1
Carbon preference index (C_{27}–C_{33}) Odd/even	1·2	1·2	1·0	1·4	1·2	1·2	2·0	1·3	1·2
Pristane (%Alkanes)	2·3	+	1·2	1·9	0·1	+	0·6	0·4	0·2
Phytane (% Alkanes)	4·7	2·5	2·0	2·3	0·2	+	1·3	0·6	0·4
Pristane / Phytane	0·7	—	0·7	0·5	0·5	—	0·5	0·7	0·5

* C = chips; P = powder, R = residue, + trace, — not detected.

carbon atoms for members of the homologous series above C_{27}. Values for the C.P.I. (Carbon Preference Index) (Bray and Evans, 1961) for C_{27} through C_{33} range from 2·3 to 1·2. In addition, the concentration of pristane is less than that of the phytane, with the ratio of these isoprenoids varying between 0·46 and 0·88 for the three samples.

Organic compounds from a variety of sources and at different stages of diagenesis almost certainly contribute to the extracts of the intact rocks. For example, the low ratio of pristane to phytane, similar to that in many crude oils, seems suggestive of a marine environment and considerable geologic age (Brooks and Smith, 1967). In contrast, the marked predominance of alkanes with odd number of carbon atoms in the range C_{32}–C_{36} in the Bitter Springs extract suggests contamination, possibly from a recent soil.

Disappearance of the odd-carbon number preference during diagenesis (assumed to occur with increasing age of burial) has been demonstrated for a very large number of Phanerozoic crude oils and coals (Bray and Evans, 1961; Brooks and Smith, 1967). The continued persistence of a CPI > 1 in n-alkanes of Precambrian age is not to be expected in view of the age unless the sediment had experienced an extremely mild thermal history or the alkanes had been protected from diagenesis in some very special fashion. The general abundance distribution of the alkanes found in the surficial extracts, however, appears to be similar to that found in solvent extracts of higher rank coals, indicating it is not primarily of recent origin.

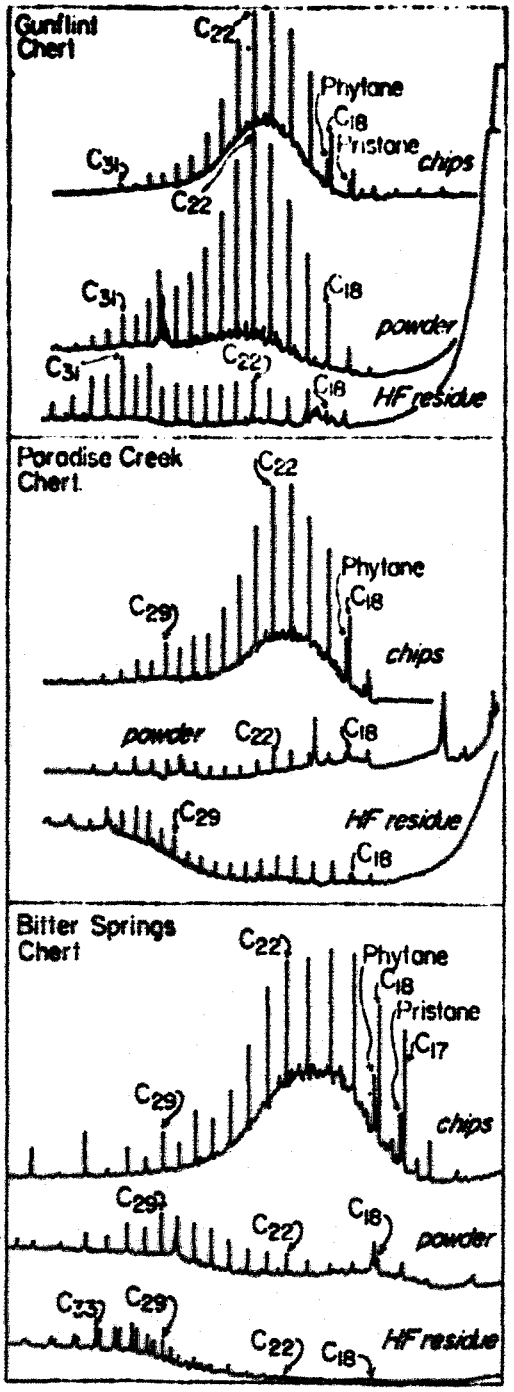

Fig. 1. Distribution of extractable alkanes in chips, powder and hydrofluoric acid residues from three Precambrian cherts.

In view of these considerations and the fact that this material is readily accessible to the exterior as demonstrated by solvent extraction, it seems most unlikely that any significant portion of the extracts from the chips consists of residues of Precambrian age. Although it is conceivable, of course, that some small fraction of these extracts is actually of Precambrian age, the occurrence of such material would be entirely obscured by the predominating constituents of relatively recent origin.

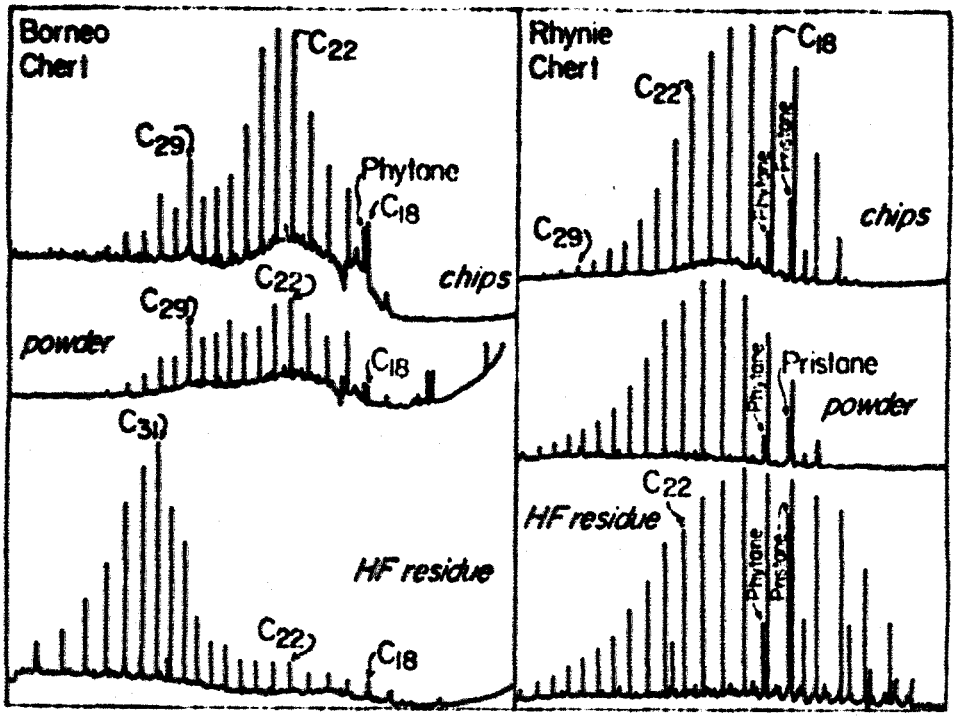

Fig. 2. Distribution of extractable alkanes in chips, powder and hydrofluoric acid residues from a Devonian and a Triassic chert.

Solvent extraction of the powder obtained by grinding the chips yielded small quantities of soluble material. The extracts from both the powdered Bitter Springs and Paradise Creek cherts were qualitatively different from those from the chips; in both cases the high concentrations of saturated hydrocarbons in the C_{22} region, and the associated "hump", were no longer in evidence (Fig. 1). The odd-carbon number preference in the longer chain n-alkanes was decreased noticeably although the relative concentration of higher molecular weight compounds increased. Pristane and phytane occurred in trace quantities only.

The extract from the powdered Gunflint chert, although in many ways resembling the corresponding extracts from the other Precambrian cherts, illustrated several unique features. The general distribution of the n-alkanes did not differ greatly from that in the extract from the chips; but the marked decrease in the concentrations of pristane and phytane relative to the total extract and, more significantly, to the C_{17} and C_{18} n-alkanes, was clearly demonstrated. It seems evident, therefore, that the major portion of these isoprenoid hydrocarbons must be located on surfaces, connected to the exterior, which facilitate their removal by solvents.

In all the Precambrian samples studied, yields of hydrocarbons from the extraction of organic residue remaining after treatment of the powder chert with hydrofluoric acid were very small, the greatest being some 2 ppb. At this level of recovery, the possibility of contamination is so high that the value of further investigation becomes doubtful. However, the yield in itself is of considerable significance since it demonstrates that the organic residues in richly fossiliferous Precambrian cherts, even when exhaustively extracted, yield only trace quantities of soluble organic compounds.

In all three Precambrian sediments, the material extracted from the chips differs significantly from that extracted from the acid-resistant organic residues (Fig. 1), strongly suggesting that the two extracts have different origins; whether the latter is of Precambrian age, however, is uncertain. Although the C.P.I. value approaches unity in the residue extracts, it is nevertheless significantly above unity (see Gunflint residue, Table 1) thus arguing against an age $> 10^9$ yr. Trace quantities of pristane and phytane were observed in extracts of the acid-resistant residues from the Gunflint and Paradise Creek cherts. In general, their concentration was lowest in these extracts but the pristane/phytane ratio was not significantly different from those of other extracts.

Phanerozoic cherts

Triassic cherts (Borneo). The extracts obtained from this chert (Fig. 2) were generally very similar to those from the Precambrian samples, although the yields of products were more equitably distributed between the three extracts, with a correspondingly larger portion of the total alkanes being recovered from the acid-resistant organic residue.

This latter fraction is of particular interest since a smooth distribution of n-alkanes exhibiting a maximum concentration at C_{31} has not been described in either biological products or their diagenetic derivatives. Presumably, such a distribution might arise from the fractionation of a crude oil with the higher molecular weight n-alkanes remaining behind in the residue. It is also possible that this material represents a laboratory contaminant or artifact. The marked similarity between these Triassic extracts and the corresponding fractions from the Precambrian cherts serves to strengthen the view that most of the latter originated during post-depositional times, and although in part apparently indigenous to cherts, they were primarily not syngenetic with Precambrian deposition. Although the carbon content of the Triassic chert was the highest of all the samples investigated (HF residue, 7·4%), the amount of extractable organic matter was surprisingly low.

Devonian chert (Rhynie). Yields from this sample were at least two orders of magnitude greater than the corresponding extracts from the older cherts; a strict comparison of the products obtained is, therefore, difficult. For example, if the yields and composition of alkanes reported from the Precambrian samples (and from the Triassic chert) were significantly influenced by contaminants, a similar level of contamination in the Rhynie extracts would not be detectable.

The close similarity in composition between the three fractions extracted from the Rhynie chert strongly suggests that the extracted materials have a common origin; the very high yields obtained from the acid-resistant residue seem to indicate that this fraction contains syngenetically emplaced organic matter. If so, diffusion of compounds from the organic material into the surrounding silica has apparently occurred. The concentrations of isoprenoid hydrocarbons relative to total alkanes, shown in Fig. 2 are consistent with this interpretation. The ratio of pristane to n-heptadecane in the extracts from the chips, powder and acid-resistant residue, increases progressively from 0·35 to 0·55 to 0·86; the phytane: n-octadecane ratio similarly increases. It seems apparent that the silicic matrix has acted as a molecular

sieve, preferentially retaining the isoprenoid molecules, which have a relatively large cross-sectional area, while allowing the outward diffusion of n-alkanes of corresponding chain length. It further indicates that when significant amounts of soluble materials are present they can be extracted from the kerogen by the procedure used.

The increase in the proportion of the lower molecular weight alkanes in the extract from the acid-resistant residue argues strongly against a significant loss of such hydrocarbons by evaporation or solution during the acid treatment.

The distribution of n-alkanes in the Rhynie chert is generally similar to that of high rank coals and mature crude oils; it seems unlikely, therefore, that the silicic matrix has served to protect the organic constituents from diagenetic alteration. In this respect, the ratio of pristane/phytane as well as concentrations of these isoprenoids, also indicate that the degree of diagenesis is quite advanced since similar values have been observed in coals of the highest rank only (Brooks *et al.*, 1969). The high content of fossil vascular plants in the Rhynie chert, and its origin as a silicified peat deposit suggest that features similar to those of coal might be expected.

Since the Triassic chert from Borneo yielded only trace quantities of soluble organic compounds and is substantially younger than the Devonian Rhynie chert, age alone cannot be the factor controlling the preservation of this material. Furthermore, these two sediments appear to be very similar in lithology and the mode of preservation of their organic constituents, and appear to have had similar origins and mild thermal histories. Differences in the amounts of extractable material obtained from the two cherts are not correlative with total carbon content, which points to differences in the diagenetic mechanisms not yet recognized. A comparison of the distribution of the alkanes extracted from the Triassic chert with those from the much older Precambrian chert does not reveal significant differences in the degree of geochemical maturation, as might be expected from on the great differences in age between these sediments.

Porosity and permeability of the host rock could be of the greatest significance in explaining differences in preservation of organic matter in cherts since they might control the early entrapment of organic compounds, and could certainly influence their subsequent elution and displacement by other materials. It seems possible that the rate of diffusion of isoprenoid hydrocarbons relative to n-alkanes could be controlled by pore size. Diffusion *outward* of these molecules previously associated with the insoluble organic residues of the Rhynie chert, and migration *into* the Gunflint chert from its surroundings, may be of this nature. Similar sieve effects have been suggested previously when it was noted that grinding of rock prior to extraction yielded extracts with an increased content of branched-chain alkanes (Meinschein, 1965).

Free fatty acids

Small quantities of free fatty acids were extracted from all three fractions of each chert investigated. Although the concentration of any individual acid never exceeded 111 ppb, there were marked variations in the concentrations detected.

Hexadecanoic acid was almost invariably the largest single component; the n-saturated C_{14} and C_{18} acids were also prominent, and significant concentrations of the mono-unsaturated n-C_{16} and n-C_{18} acids were usually observed.

The yields and distributions of the free acids (analyzed as their methyl ester derivatives) extracted from the various chert fractions are given in Table 2. In every case, unsaturated fatty acids were prominent in the chromatograms of the

Table 2. Distribution of free acids (ppb of dry sediment)

Carbon No.	11	12	13	14	15	16*	16	17	18*	18	19	20	21	22	23	24
Borneo																
Chips	1·1	1·6	5·4	9·6	5·8	2·6	32·0	1·4	4·6	28·2	—	2·6	—	60·2(2)	—	+
Powder	—	2·1	—	2·6	0·5	1·2	14·1	0·2	4·2	4·0	—	+	—	+	—	+
Residue	—	2·9	—	2·2	1·0	1·0	16·0	—	1·0	7·0	—	—	—	15·6(2)	—	+
Rhynie																
Chips	—	—	—	21·0	18·0	25·5	111·0	6·0	25·5	27·0	—	60·0(1)	+	+	+	+
Powder	—	—	—	—	—	+	+	+	+	+	—	—	—	+	—	—
Residue	—	2·6	1·0	5·2	2·2	1·0	16·0	2·0	2·0	6·0	+	+	+	+	+	+
Bitter Springs																
Chips	—	—	—	+	—	0·2	0·6	+	0·2	+	—	9·0(1)	—	—	—	—
Powder	—	—	—	+	+	+	0·1	—	+	+	—	—	—	—	—	—
Residue	—	1·2	—	5·0	0·9	2·0	20·0	+	5·2	9·6	—	+	—	—	—	+
Paradise Creek																
Chips	0·2	4·0	0·2	11·5	2·0	2·4	21·5	1·5	7·0	10·8	—	+	—	9·1(2)	—	+
Powder	—	+	0·2	0·4	0·2	0·2	2·0	0·1	1·0	0·9	0·2	0·2	0·1	0·1	+	+
Residue	0·2	5·0	0·2	22·7	7·2	5·0	61·2	5·5	10·1	64·0	—	1·5	—	1·0	—	2·0
Gunflint																
Chips	—	—	—	1·2	0·2	0·9	11·5	0·1	1·6	7·2	+	14·6(1)	—	—	—	—
Powder	—	—	—	+	+	+	2·0	+	0·1	0·1	—	—	—	—	—	—
Residue	—	+	—	0·4	0·1	0·4	5·5	+	2·1	2·2	—	0·1(1)	—	—	—	—

(1) and (2) Unidentified acids.
* Trace.
† Unsaturated acids.

freshly collected products; however, the concentration of these acids commonly decreased, or even completely disappeared, within a few days on storage of microgram quantities of these esters in sealed containers.

Reduction of these unsaturated esters with hydrogen in the presence of platinum oxide produced their saturated derivatives and confirmed the identity of the products. The products from the reduction of the unsaturated fatty acids extracted from the hydrofluoric acid-resistant residue of the Gunflint chert are given in Table 3.

Table 3. Hydrogenation of free acids from Gunflint residue

Carbon No.	Distribution as extracted (%)	Distribution after reduction (%)
C_{14}	0·5	9·4
C_{15}	1·6	0·4
C_{16} unsat.	11·4 } 71·6	—
C_{16}	60·2 }	71·2
C_{17}	1·1	0·4
C_{18} unsat.	14·4 } 25·3	—
C_{18}	10·8 }	27·7

Relatively high concentrations of unidentified fatty acids were present in extracts from the chips of all five cherts; the retention times of the methyl ester derivatives of these acids were slightly less than those of methylated C_{20} and C_{22} n-saturated acids. In Fig. 3 are shown typical chromatograms of the methyl ester derivatives obtained from extracts of the chert chips. These illustrate the high concentration of unsaturated acids and the distribution of the fatty acids detected in these extracts. This high degree of unsaturation indicates a much more recent origin than the Precambrian, and suggests that these free acids may be contaminants acquired during storage or extraction.

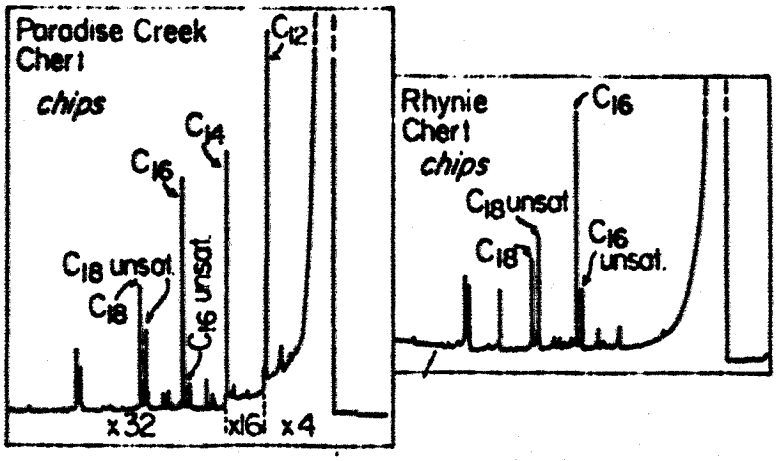

Fig. 3. Examples of free-fatty acid distribution in the chips from one Precambrian and one Devonian chert.

In many cases, the lowest yields of free fatty acids were obtained by extraction of the powdered cherts. Since this extraction was preceded almost immediately by treatment with chromic/sulphuric and hydrofluoric acids, a technique designed to produce a contamination-free surface, a small yield of free acids would be expected if they originated solely from laboratory contamination. Furthermore, the high yields of free acids usually obtained by extraction of the chips were to be expected, since the chips would contain the major portion of contaminants on their surfaces. In some cases, the yield of free fatty acids from extracts of acid-resistant residues was surprisingly high; this may be related to long exposures of the residues to the laboratory atmosphere during the treatment with hydrofluoric acid.

The similarity in composition between the free acids detected in all samples studied suggests that these compounds represent laboratory contamination, possibly of bacterial origin (Tornabene, 1967). If indeed this is the case, their presence may be partly attributable to the large weight of sample extracted. The purely mechanical difficulties in handling large quantities of powdered rock and the relatively long periods of time required to complete standard laboratory procedures (e.g. filtration, extraction, hydrofluoric acid maceration, etc.) in these samples may greatly increase the probability of contamination.

Bound fatty acids

The yields and distributions of fatty acids released from three of the cherts by acidification with hydrochloric acid are summarized in Table 4.

Table 4. Distribution of bound acids (ppb of dry sediment)

Carbon No.	11	12	13	14	15	16*	16	17	18*	18	19	20	21	22	23	24
Rhynie																
Chips	—	—	—	0·5	0·6	1·6	6·3	0·2	3·0	2·6	—	1·5(1)	—	3·6(2)	—	—
Powder	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Residue	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Bitter Springs																
Chips	—	—	—	+	—	—	5·0	—	—	—	—	7·5(1)	—	—	—	—
Powder	—	—	—	—	—	0·3	2·5	—	+	+	—	—	—	—	—	—
Residue	—	—	—	+	+	0·1	7·0	+	0·2	0·2	—	—	—	—	—	—
Gunflint																
Chips	—	—	—	+	+	+	44·8	+	+	2·7	—	+	—	—	—	—
Powder	—	—	—	+	+	+	11·0	—	+	+	—	+	—	—	—	—
Residue	—	+	—	0·1	0·3	1·0	16·8	0·3	2·5	1·8	—	+	—	1·2(2)	—	—

(1) and (2) Unidentified acids.
* Unsaturated acids.

Unlike the free fatty acids, the bound acids do not appear to exhibit a regular pattern of distribution. A degree of unsaturation similar to that found in the free acids was apparent in some extracts; in others, particularly those from the Gunflint chips and powdered chert, only saturated compounds were detected. A similar distribution of bound fatty acids from the Gunflint chert has recently been reported by VAN HOEVEN *et al.* (1969) who interpret the acids as being of probable Precambrian age, preserved by being bound to the chert matrix. Our results neither refute nor confirm this interpretation, but since the greatest yield of saturated acids was obtained from the chips, rather than from the powdered chert, and since unsaturated compounds were detected in the most interior, hydrofluoric acid-resistant residue, the evidence argues against these acids being preserved in the manner suggested.

Particular attention must be drawn to the stability of unsaturated fatty acids. A decrease in concentration of these compounds has definitely been observed on storage of microgram quantities of extracts in the laboratory. Presumably, oxidation reduction or polymerization reactions can effectively alter these unsaturated acids in solution; and the inability to demonstrate their occurrence should not be taken as a firm indication that they were not recently present.

Carbon and sulfur isotopes

Stable isotope data for δC^{13} and δS^{34} are presented in Table 5. The carbon values were measured on hydrofluoric acid-resistant residues, whereas the δS^{34} data were obtained on elemental sulfur extracted from these residues with a methanol/benzene solution. One pyrite sample, freed from the matrix of the Gunflint chert by hydrofluoric acid maceration, was also analyzed.

At first sight it would appear that an inverse correlation may exist between δC^{13} values and the age of the sample analyzed. HOERING (1967) also reports low values of δC^{13} for insoluble organic matter from several Precambrian sediments. Such enrichment in C^{12} is difficult to understand, since diagenetic and metamorphic processes acting on the sediment would result in liberation of isotopically light

Table 5. Ratios of the stable isotopes of carbon and sulfur in chert fractions

	δC^{13} HF Residue	δS^{34} Free sulfur
Gunflint*	−33·1	+19·5
Paradise Creek	−29·3	+1·4
Bitter Springs	−24·8	−0·3
Rhynie	−24·1	−17·3
Borneo	−23·4	−10·0

* δS^{34} of pyrite from this fraction was +14·4.

methane and other short-chained hydrocarbons and the remaining polymer should thus become enriched in C^{13} (Silverman, 1964). One possible explanation is that biosynthesis of the Precambrian organic matter may have occurred under higher partial pressures of CO_2 in acidic or mildly acidic environments. Growth under such conditions may result in a higher enrichment of C^{12} in the organic matter produced (Kaplan and Seckbach, 1970). An alternative explanation is that the insoluble organic fraction represents a high molecular weight polymer, formed by condensation of smaller, unsaturated molecules, that was subsequently metamorphosed during preservation. The δC^{13} values for the Bitter Springs, Rhynie and Borneo cherts are comparable to values characteristic of organic matter derived from both terrigenous and marine sources, and it is not possible to determine their probable origin based on these data alone (Silverman, 1964).

The sulfur isotopic measurements show a wide range in values. The δS^{34} value of sulfur extracted from the Gunflint chert is precisely that of present-day sea water sulfur (dissolved sulfate). The pyrite is 5·6‰ lighter, as is usual in co-existing sedimentary sulfur and pyrite (Kaplan *et al.*, 1963). Such a high value of δS^{34} is unusual for biogenic sulfur, and it seems more than a coincidence that it is identical to that of sea water sulfur. The most obvious explanation is that the Gunflint sulfur represents trapped sea water sulfate that was quantitatively reduced to hydrogen sulfide, followed by subsequent oxidation to elemental sulfur. If this interpretation is correct, it would indicate that connate water probably of marine origin or containing dissolved gypsum (presumably of relatively recent origin) has permeated the Gunflint cherts; such solutions might also carry organic contaminants.

The δS^{34} values for the Bitter Springs and Paradise Creek cherts are very similar to that characteristic of meteoritic sulfur. This suggests that the sulfur in these deposits is of igneous origin and that little or no biogenic fractionation occurred during the deposition of these Late Precambrian sediments. The sulfur present in these samples may have been dissolved in the water from which these primary cherts precipitated.

The two Phanerozoic cherts (Rhynie and Borneo) display δS^{34} values (−17·3 and −10·0) typical of biologically formed sulfur in present sediments. It seems likely that the sulfur in these two deposits is biogenic; the sulfur isotope ratios of the Precambrian samples provide no evidence for such an origin.

Permeability and porosity measurements

Permeability and porosity data for chert samples collected at the same locations and at the same time as those studied for organic components are given in Table 6.

Table 6. Permeability and porosity measurements on four chert specimens studied

		Permeability (μd)	Porosity (%)
Chert			
	Gunflint	190	0·44
	Gunflint	20	0·55
	Bitter Springs	220	0·62
	Bitter Springs	170	1·15
	Rhynie	650	4·01
	Rhynie	7	4·62
	Borneo	100	0·59
Sandstone		10^3–10^6	5–30
Limestone		10^3–2×10^4	1–15
Shale		$<10^3$	1–15
Granite		<1	

For comparison, ranges of permeability and porosity for sandstones, limestones, shales and granites measured in the same laboratory by identical procedure are also listed. The data show that the bedded cherts possess a finite permeability, not evident from microscopic examination, presumably resulting from microfractures in the matrix. The large variation in permeability measurements obtained for the Rhynie Chert samples is probably due to the presence of larger fissures in the more permeable specimen and may not be entirely representative of other rock samples from this formation. With the exception of the Rhynie chert samples, the porosity of the rocks measured was 1 per cent or less.

It can be seen from Table 6 that measured permeabilities range between 7–650 μd and fall in the general range of many shales. It is not known, of course, whether the microfracturing of these cherts occurred during burial at depth (from tectonic movements) or after exposure at the surface (from diurnal heating and cooling). In either event, if fracturing is present it could permit the entrance of solutions, and under hydrostatic pressure at depth by capillary action at the surface, or the entrance of particle-laden air through "breathing", under the influence of temperature changes.

The porosity is low for all chert samples measured with the exception of the Rhynie chert. The presence of pore spaces may therefore be important in the retention of relatively low-molecular-weight compounds.

Conclusions

The data presented here raise the same questions that previous studies have posed. Is it feasible to interpret the extractable organic constituents of very ancient sediments as evidence of the biochemical complexity and evolutionary status of the primitive biota? To answer this question a second, more fundamental problem must be considered: Can it be established that the extractable organic compounds in Precambrian sediments are syngenetic with original sedimentation? To approach this problem, we selected three, relatively impermeable, unmetamorphosed, primary Precambrian cherts, known from paleontological studies to contain well-preserved, syngenetically-emplaced, organic microfossils. For comparison, two Phanerozoic cherts of similar origin, lithology, and geologic history were also investigated. From

our studies of the extractable hydrocarbons and fatty acids of these sediments, we conclude that only traces of these compounds, in the range of a few ppb or less, are indigenous to the Precambrian cherts. Furthermore, there is no strong evidence to indicate whether this extractable material was emplaced at the time of sedimentation. Some portion of this organic matter may be a product of Precambrian biological activity, derived from the permineralized microorganisms organically preserved in these deposits; the results strongly suggest, however, that the majority of this extractable material is of post-depositional origin. This conclusion seems further supported by S^{34}/S^{32} measurements which, for the Gunflint chert, seem indicative of relatively recent contamination. The paucity of extractable compounds in these sediments may reflect an almost complete diagenetic conversion of the original organic materials to gases of low molecular weight and to insoluble polymers, a process analogous to that observed during coalification.

In view of these considerations and the studies of Abelson and Hare (1968), who have drawn comparable conclusions regarding indigenous, but not demonstrably syngenetic, amino acids in Precambrian cherts, it appears likely that unless chemical criteria clearly indicative of a "Precambrian origin" can be established, the extractable constituents of very ancient sediments will provide little or no interpretable evidence of early biological processes. As has often been concluded previously, we suggest that the key to the study of early biochemical evolution lies not in the analysis of extractable traces, but rather in the dominant insoluble kerogen-like fraction, and in particular, that material comprising organically preserved microfossils.

Acknowledgments—We thank Dr. Elso S. Barghoorn, Department of Biology, Harvard University, for partially defraying costs (through NSF Grant GA-1115) connected with the collection of specimens by J. W. Schopf from the Precambrian of Australia, and for providing the samples of Triassic chert used in the present study. We also gratefully acknowledge the field assistance provided in Australia by F. deKeyser and R. Shaw of the Bureau of Mineral Resources, and by A. Magee, Magellan Petroleum, Ltd. We wish to thank Mr. A. Timur, Chevron Oil Field Research Co., La Habra, California, for measurements of permeability and porosity on the cherts. The study was supported by NASA contracts NAS 9-8843 and NAS 9-9941.

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