

AN INVESTIGATION OF THE CARBONACEOUS MATERIAL IN THE ORGUEIL, MURRAY,
MOKOIA, AND LANCÉ CARBONACEOUS CHONDRITIC METEORITES

A Thesis

Presented to
the Faculty of the Department of Chemistry
College of Arts and Sciences
University of Houston

In Partial Fulfillment
of the Requirement for the Degree
Master of Science

by
Joseph Charles Raia
January 1966

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DEDICATION

This thesis is dedicated to my wife, Saana, and my parents for their continued support and neverfailing encouragement.

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ABSTRACT

The Orgueil Murray, Mokoia and Lancé carbonaceous chondritic meteorites were analyzed for their amino acid content employing methods similar to those used to isolate amino acids from terrestrial sediments. An automatic ion-exchange chromatographic technique indicated that only the Murray meteorite sample contained ninhydrin positive compounds identified as common protein amino acids. The other meteorites studied contained either no detectable amounts of these type acids or only trace amounts, these being considered to have arisen during the analysis. Available data indicated that the amino acids detected in the Murray were not indigenous to the meteorite sample, but originated from terrestrial contamination acquired since its fall.

The bulk of the carbonaceous material in the Orgueil meteorite, which exists as a relatively intractable, insoluble substance, was subjected to analysis by physical and chemical methods. X-ray diffraction and elemental compositional data suggested that the material may be structurally similar to terrestrial carbonaceous materials such as lignitic coals and coaly type kerogens. Oxidative degradation of the meteorite material produced a complex mixture containing components whose identification could not be ascertained. Preliminary paper chromatographic and infrared data however did indicate that compounds possessing carboxylic acid, aromatic, hydroxy aromatic, ester, and ether structures may be present.

Soluble aromatic hydroxy compounds were searched for in ether extracts of the Orgueil meteorite using methods which have been used to extract phenolic substances from terrestrial sediments. Sensitive paper chromatographic methods failed to detect any such compounds in the meteorite sample.

A possible origin for the insoluble, carbonaceous material was suggested on the basis of data presently available.

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I.

INTRODUCTION

INTRODUCTION

NATURE OF METEORITES

I. Definition, Origin, and Classification

The solar system contains various forms of solid matter. In addition to the sun, this for the most part consists of the nine major planets, the minor planets or asteroids, numerous comets, and a multitude of so-called minor bodies (1). Among these minor bodies are objects ranging in size from the smallest dust particles to many tons; such objects large enough to survive passage through the earth's atmosphere are known as meteorites (2).

Meteorites are generally considered to have originated from a common parent material similar originally to that of the primeval solar nebula from which the rest of the solar system was formed. The chemical composition of this material has been described by Latimer (3) and also by Urey (4). At present, there are three principal theories regarding the size of meteorite parent bodies; these are (1) planetary size, (2) two successive generations, one of lunar size and one of asteroidal size, and (3) asteroidal size (5). None of these, however, seems to account completely for all of the data presently available on meteorites.

Some 1500 meteorites are known to have reach Earth from extraterrestrial space. These have beenpredominantly either metallic or stony, or partially metallic and partially stony. As a result, meteorites are generally classified as follows (2):

A. Aerolites or stones: These consist essentially of silicate minerals (mainly olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, and orthopyroxene, $(\text{Mg,Fe})\text{SiO}_3$,

with small amounts of nickel-iron alloy, averaging 90% Fe and 10% Ni). The stones are divided into two major groups termed chondrites and achondrites respectively, according to the presence or absence of spheroidal aggregates of silicate mineral about 1 mm in diameter, called chondrules.

B. Siderolites or stony-irons: These meteorites average approximately 50% nickel-iron and 50% silicate mineral.

C. Siderites or irons: These are predominantly nickel-iron alloy with small amounts of minerals.

Each of the above main groups are further classified on the basis of similarities in mineralogy and chemical composition. The carbonaceous chondrites comprise a distinct subgroup of stony meteorites and some of their features will now be briefly described.

II. The Carbonaceous Chondrites

The carbonaceous chondrites constitute a class of meteorites numbering about thirty (see Table I). These stony meteorites were all seen to fall and were recovered soon afterwards. Their friable nature along with their close resemblance to organic rich terrestrial soils upon being weathered, make them very unlikely as finds. The unique property of these meteorites is their high carbon content (0.5%-6%); most other meteorites contain only traces of carbon [0.1-100 parts per million (6)]. Wiik (7) has determined the chemical composition of eleven carbonaceous chondrites and has divided them into three subgroups (Type I, Type II, and Type III) based on mean values of certain constituents present. Certain trends present themselves as one examines the

TABLE I
THE CARBONACEOUS CHONDRITES

Name	Date of Fall	Mass Preserved (kg)	Wiik's Grouping
1. Alais, France	1806, Mar. 15	6	I
2. Al Rais, Arabia	1957, Dec. 12	0.16	II
3. Bali, Cameroon, Africa	1907, Nov. 22	0.05	?
4. Bells, Texas, U.S.A.	1961, Dec. 10	0.3	II
5. Boriskino, U.S.S.R.	1930, Apr. 20	1.34	II
6. Cold Bokkeveld, South Africa	1838, Oct. 13	3	II
7. Cresent, Oklahoma, USA	1936, Aug. 17	0.08	II
8. Erakot, India	1940, Jun. 22	0.11	II
9. Felix, Alabama, U.S.A.	1900, May 15	3	III
10. Grosnaja, U.S.S.R.	1861, Jun. 28	3.3	III
11. Haripura, India	1921, Jan. 17	0.5	II
12. Indarch, U.S.S.R.**	1891, Apr. 7	2.7	III
13. Ivuna, Tanganyika	1938, Dec. 16	0.7	I
14. Kaba, Hungary	1857, Apr. 15	3	III
15. Karoonda, S. Australia	---	---	---
16. Lancé, France	1872, July 23	52	III
17. Mighei, U.S.S.R.	1889, Jun. 18	8	II
18. Mokoia, New Zealand	1908, Nov. 26	4	III
19. Murray, Kentucky, USA	1950, Sep. 20	12.6	II
20. Nawapali, India	1890, Jun. 6	0.06	II
21. Nogoya, Argentina	1879, Jun. 30	4	II
22. Orgueil, France	1864, May 14	10	I
23. Ornans, France	1868, Jul. 11	6	III
24. Pollen	---	---	---
25. Renazzo, Italy	1824, Jan. 15	5	II
26. Santa Cruz, Mexico	1939, Sep. 3	0.5	II
27. Simonod, France	1835, Nov. 13	?	?
28. St. Caprais, France**	1883, Jan. 28	0.14	?
29. Tonk, India	1911, Jan. 22	0.01	I
30. Vigarano, Italy	1910, Jan. 22	16	III
31. Warrenton, Missouri, USA	1877, Jan. 3	1.6	III

* Most of the data in the table was obtained from Briggs and Mamikunian (8).

**There is doubt that these are carbonaceous chondrites in the true sense.

data on members of each subgroup. For example, the amount of carbon and water present generally decreases from Type I to Type III, while the amount of silicate mineral increases. Type I carbonaceous chondrites contain no chondrules [according to Mueller (9) Type I contain microchondrules] and have been considered by some to be the most primitive type of chondritic meteorites (10,11,12).

The carbon present in these meteorites appears to be predominantly organic in nature; this in no way refers to its origin (i.e. biogenic or not), but merely to its classification in the chemical sense (8). Of the total organic matter present, only about 25% has thusfar been extracted by organic and aqueous solvents; some 75% of the carbonaceous material remains as a black, coal-appearing, insoluble material (8).

The literature review which follows will present the reported findings regarding the nature of each of these two major organic fractions of the carbonaceous chondrites.

ORGANIC COMPOUNDS IN CARBONACEOUS CHONDRITES - A REVIEW OF THE LITERATURE

I. Early Investigations. The occurrence of solid bodies falling from the sky goes back to antiquity. Early Greek, Latin and Chinese historians wrote of such phenomena and records of meteorite falls can be found in sources dating back to the 14th century B.C. (1). A detailed list of the oldest falls of meteorites is contained in a book by Mukhin (13).

Meteorites in ancient times were objects of religious worship rather than of scientific investigation (1). Indeed for the most part the scientific community rejected the notion of extraterrestrial bodies reaching the

Earth. This view was prevalent even as recent as the beginning of the last century. A detailed report presented by J. B. Biot to the Paris Academy of Sciences in 1803, describing a meteorite shower near the town of L'Aigle, France, was probably the first scientific recognition of the reality of meteorite occurrences (2).

Following Biot's investigation, however, meteorites soon won the attention of several prominent scientists of the nineteenth century. Early studies consisted largely of chemical analysis and circumstances of falls, but by the end of the century mineralogical and internal structural studies were being made (2).

Berzelius (14) was perhaps the first to demonstrate the presence of organic compounds in carbonaceous meteorites. He observed that the Alais contained a water soluble organic substance which upon heating became brown and evolved a tarry odor. The meteorite residue on being heated produced carbonic acid and a brown gaseous substance which evaded identification by this scientist.

Wöhler (15,16,17,18) and Harris (19) investigated the Kaba and Cold Bokkeveld meteorites. They were able to isolate a hydrocarbon-type crystalline compound which was soluble in alcohol and ether. Wöhler maintained that the "ozocerite-like" substance in the Kaba was of organic origin (20).

Berthelot (21,22) made oxidation studies of the organic matter in Orgueil with potassium chlorate and fuming HNO_3 . He found no evidence for so-called graphitic acid (mellitic acid); with hydriodic acid, however, paraffinic hydrocarbons were produced. Smith (23,24) made similar studies

using the same oxidizing agent and found that graphite containing iron meteorites, unlike the carbonaceous chondrites, produced graphitic acid and at a much more rapid rate than terrestrial graphites. This investigator isolated from the Orgueil and Alais an organic crystalline compound which he considered perhaps similar to a sulfhydrocarbon represented as $C^4H^6S^4$.

Cloez (25,26) studied the bulk of the carbonaceous material in Orgueil after demineralizing the meteorite with boiling HCl and KOH. He considered this material to be neither graphite nor amorphous carbon, but confusingly similar to terrestrial humus-type substances (2).

A detailed review of nineteenth century studies may be found in Cohen's book Meteoritenkunde (27).

II. Modern Investigations. From 1890-1950 very little is reported in the chemical literature concerning organic compounds in carbon chondrites. Mueller (28) appears to be the first contemporary to pursue such studies. Following Mueller's work, however, and concomitant with the emphasis on space exploration, a renewed interest in these meteorites has taken place. Since the beginning of this decade numerous reports have appeared in the scientific literature regarding the presence and origin (i.e., biogenic or not) of organic compounds in carbonaceous meteorites. The following discussion of the literature is divided into the sections indicated in view of the vast number of individual compounds reported.

A. Studies of the extractable organic material

1. Hydrocarbons: The first detailed study of the hydrocarbons in these meteorites was done by Nagy et al. (29). Hydrocarbons obtained by distilling solid samples of the Orgueil were analyzed by mass spectroscopy; saturated hydrocarbons distilled from 250-400°C were detected

in parts per thousand of solid meteorite. Similarities in the mass spectral pattern of hydrocarbons from the Orgueil, recent sediments, and butter (an animal product), led these investigators to suggest a biogenic origin for these compounds.

Anders (30) has criticized the work of Nagy and co-workers on ten points. He questioned the origin proposed for these hydrocarbons rather than their actual indigenous presence. Perhaps the strongest point advanced by Anders is the possibility of a selective type non-biogenic synthesis which could have produced a hydrocarbon distribution observed for the Orgueil [Wilson (31) has made interesting studies along these lines.] Nagy and coworkers defend their position on each of the criticisms proposed (30).

Sztrokay et al. (32) studied organic material from the Kaba by infrared spectroscopy and found evidence for paraffinic hydrocarbons and perhaps aliphatic sulfur compounds. Vdovykin (33) extracted the Groznaya and Mighei successively with several organic solvents obtaining 0.0965% of so-called bituminous material from the Groznaya and 0.1573% from Mighei. Luminescence and infrared analysis of this material indicated the presence of aliphatic saturated hydrocarbons. Kaplan et al. (6) have determined the presence of hydrocarbons in organic solvent extracts of several carbonaceous chondrites. NMR and infrared spectra indicated the presence of aliphatic, aromatic, and alkene compounds.

Meinschein (34) has compared the mass spectral pattern of aromatics in benzene extracts of Orgueil to those of aromatics from recent and ancient terrestrial sediments and from crude oil. The meteorite aromatics were found to be similar to recent sediments, which unlike ancient sediments

and crude oil, consisted predominantly of phenanthrenes, chrysenes, and pyrenes.

Meinschein, Nagy, and Hennessy (35) extended their earlier work on meteorite hydrocarbons by making a detailed study of benzene-methanol extracts of Murray and Orgueil. The extracted material was fractionated by silica gel column chromatography using four different organic solvents as eluates. Ultraviolet, infrared, and mass spectroscopic analysis of the fractions revealed the presence of various hydrocarbons. Paraffins, non-condensed naphthenes, condensed naphthenes, alkyl benzenes, and condensed aromatics such as naphthalene, phenanthrene, pyrene, and chrysene were detected. These workers showed that saturated hydrocarbons isolated from the Orgueil and Murray have infrared spectra, molecular weight ranges, and mass spectrometric cracking patterns which resemble those of sedimental saturated hydrocarbons; the relative amounts of hydrocarbons in benzene extracts of Orgueil were very similar to those in terrestrial marine sediments. These findings have led the authors to a most interesting conclusion; in their words: "...lacking another experimentally established explanation, we propose that the amounts and composition of the benzene extracts of the Murray and Orgueil are evidence for biological activity in the parent body of these meteorites."

The most extensive work on the paraffinic hydrocarbons in carbonaceous chondrites has been done by Oró et al. (36). Some sixteen carbonaceous chondrites (Wiik Types I, II, III) and several other meteorites were extracted with benzene-methanol and the extracts fractionated by silica gel chromatography using a method similar to that used by Meinschein and coworkers (35).

The high molecular weight hydrocarbons present in the n-heptane chromatographic fractions were analyzed by gas chromatography and gas chromatography-mass spectrometry. All meteorites contained paraffinic hydrocarbons in varying amounts (1 ppm - 415 ppm) and distribution. Normal and isomeric alkanes from $C_{15} - C_{25}$ ($C_{19} - C_{21}$ hydrocarbons predominated) were found in the Orgueil, Murray, and Mokoia meteorites. Two saturated polyisoprenoid hydrocarbons, pristane and phytane (known to be degradation products of chlorophyll) were found in practically all of the meteorites studied. Strikingly similar hydrocarbon chromatographic patterns were observed for practically all the meteorites of Type II and some of Type III indicating a common origin for the hydrocarbons. The distribution of paraffin hydrocarbons in some of the meteorites were found to be similar to that of precambrian rocks some 2×10^9 years old. Terrestrial materials considered as possible contaminants, such as kerosene, varnish, furniture wax, ligroin, crude oil, lubricating oil, linseed oil and mineral oil were also analyzed. Only varnish and crude oil gave chromatographic patterns similar to the meteorites. Although from quantitative considerations, it appeared unlikely that these materials could account for the hydrocarbons detected, it was suggested that other terrestrial materials having a similar composition to that given by the varnish-alkanes may act as contaminants. The possibility of an abiogenic process accounting for their results also could not be eliminated.

More recently Oró, Tornabene, and Nooner (37) have made interesting contamination studies in hope of elucidating the origin of the hydrocarbons in meteorites. Bacteria isolated from a sample of the Murray meteorite

were cultivated and analyzed for paraffinic hydrocarbons by gas chromatography, and gas chromatography-mass spectrometry. Normal alkanes and saturated polyisoprenoid hydrocarbons were identified which qualitatively and quantitatively resemble those found in the Murray. This appears to be the first experimental evidence that the hydrocarbons in the carbonaceous chondrites may be due to terrestrial microorganisms.

2. Organic Acids. The presence of acidic functional groups in extracts of carbonaceous meteorites has been determined by infrared analysis by several investigators (6,33,35,38,39). For most meteorites definite absorptions occur at 3400 cm^{-1} , 2960 cm^{-1} , 2930 cm^{-1} , 790 cm^{-1} , and 750 cm^{-1} . This has been interpreted to be the result of a mixture of compounds possessing aromatic, carboxylic, aliphatic, and phenolic groups (8).

a. Fatty acids: Nagy and Bitz (40) have detected long-chain fatty acids of chain lengths $C_{14} - C_{30}$ in the Orgueil; a predominance of even carbon numbered acids resembling ancient terrestrial sediments were observed. The acids were extracted by a benzene-methanol solvent, saponified and esterified. Urea adduction was used to separate the unbranched chain esters. Gas chromatography revealed the presence of $125\text{ }\mu\text{g}$ of esters per gram of meteorite. The authors claim these compounds to be indigenous but make no definite conclusions about their origin. It should be mentioned that Meinschein (35) has failed to detect any appreciable amounts of fatty acids in benzene fractions of chromatographically fractionated benzene-methanol extracts of Murray and Orgueil using mass spectroscopy. Similarly Kaplan et al. (6) have also been

unable to find evidence for the presence of these compounds in combined extracts of several carbonaceous chondrites, including the Orgueil; the method of analysis in this case was not specifically stated. These findings however do not discredit the work of Nagy and Bitz since their methods of isolation and analysis were not identical to those used by Meinschein, and Kaplan and co-workers.

b. Hydroxy Acids and Phenols: Mueller (28) deduced on the basis of composition and solubility properties that the extracted resinous material from the Cold Bokkeveld consists largely of organic acids having N, S, and halogen substitutions. He considered it to be similar to terrestrial dopplerite (a calcium salt of humic acids). Significance was given to the presence of organic chlorine in the extracted material, since this element is virtually absent in terrestrial bitumens. Others (6,8) however, have cautioned that the presence of chlorine may be due to the extraction method, since chloroform was used.

Alkali soluble hydroxy acids have been reported to be present in several carbonaceous meteorites (8,41). However, Kaplan et al. (6) were unable to detect phenolic compounds in acetone-benzene extracts of several meteorites by NMR and sensitive chromatography methods. Also, Nagy et al. (29) found no spectroscopic evidence for hydroxyl or carbonyl containing molecules in a CS₂ extract of Orgueil. Kaplan and co-workers, however, did observe a variety of diazonium sensitive compounds in combined HCl hydrolysates of Orgueil, Murray, Mokoia, and Felix. Four compounds were similar in chromatographic R_f values to m-hydroxybenzoic, p-hydroxybenzoic, p-hydroxyphenylacetic, and vanillic acid. It was considered possible,

however, that diazonium sensitive amines could account for these observations. It is not entirely clear from the paper of Kaplan and associates as to whether or not the HCl hydrolysates analyzed had been desalted, and, if so, to what extent. This however is a very important point in view of the findings of Steelink et al. (42). These investigators have shown that iron, nickel, and cobalt salts possess paper chromatographic and ultraviolet absorption properties confusingly similar to phenols, and have advised caution concerning deductions made about the presence of phenols in materials of high mineral content.

c. Amino Acids: The presence of amino acids in carbonaceous meteorites is quite controversial at present. Some investigators have reported evidence for these compounds while others have failed to detect them.

Calvin and Vaughan (41) analyzed the Murray and were unable to find amino acids. Briggs (38) found no detectable amounts in hot water extracts of Mokoia, and Nagy et al. (39) found benzene-methanol extracts of Orgueil to contain no amino acids.

Degens and Bajor (43), however, have reported both free and combined (i.e. those freed by HCl hydrolysis of the meteorite) amino acids in the Murray and also in a non-carbonaceous chondrite, the Bruderheim. Using paper chromatography most of the amino acids common to proteins were detected in the Murray in a concentration of 50 μg per gram of meteorite. These authors found no relationship between the amino acid content and organic carbon content in these meteorites. These compounds were considered to originate via non-biogenic synthesis, terrestrial contamination, or both.

Kaplan, Degens, and Reuter (6) have made the most extensive search for amino acids in carbonaceous chondrites. They have examined eight carbonaceous chondrites, five non-carbonaceous chondrites, and one achondrite using paper chromatography. Common protein amino acids were identified in all meteorites studied. The amounts detected (free plus combined) ranged from 30 $\mu\text{g/g}$ to 500 $\mu\text{g/g}$. Generally, the carbonaceous chondrites contained greater amounts than did the non-carbonaceous meteorites. These researchers consider the bulk of the acids to be indigenous but of a non-biogenic origin.

Anders et al. (44) has made a similar finding for hydrolyzed water extracts of Orgueil which compares quantitatively with the results of Kaplan and co-workers. Vallentyne (45) has analyzed the Orgueil and the Holbrook non-carbonaceous chondrite using an automatic amino acid analyzer that is based on the principle of ion exchange chromatography. HCl hydrolysates of these meteorites contained a total of 27.6 $\mu\text{g/g}$ and 20.4 $\mu\text{g/g}$ for the Holbrook and Orgueil, respectively. The total amino acids found in Orgueil were less than half of that reported by Kaplan and co-workers. Important from the standpoint of contamination possibilities was the observation that samples of ordinary dust hydrolysates contained amino acids in a concentration about a thousand times higher than detected in the meteorites; also very interesting in this respect was the finding that a sample of hand picked sand displayed an amino acid pattern that is very similar to that of the meteorites. No definite conclusion was made by Vallentyne as to the origin of the amino acids detected, but terrestrial contaminants were considered to be at least partly responsible for the results obtained.

The possibility of contaminating a given sample with amino acids by handling it in the laboratory during the course of its analysis has been investigated by Hamilton (46) and also by Oró and Skewes (47). These investigators have shown that simple hand contact with glassware or other apparatus could result in significant contamination at the micromolar level by the amino acids that are present on human hands. In their study, Oró and Skewes have examined the amino acids on the fingertips of seven individuals using an automatic amino acid analyzer. An essentially identical chromatographic pattern, both qualitatively and in terms of relative abundance, was observed in each case, suggesting that the composition of free amino acids on human hands is essentially constant. These observations have led these investigators to question the reported findings regarding amino acids in meteorites, as there was good agreement both qualitatively and quantitatively between the amino acids detected on fingertips and those found in meteorite analyses.

3. Organic Bases: Calvin and Vaughan (41) have reported the presence of ultraviolet absorbing material in a water extract of Murray. The absorption characteristics of this substance were sensitive to changes in pH and appeared to be similar in some respects to the pyrimidine, cytosine. Oró (48) has suggested, however, that the ultraviolet absorbing material was not indigenous to the meteorite but present in the ion exchange resin used in the analytical procedure. He has shown that the resin itself contained material with identical spectral characteristics as the substance reported present in the Murray. The results of Kaplan et al. (6) are in agreement with this in that they have failed to find conclusive spectroscopic

evidence for the presence of purines and pyrimidines in aqueous extracts of several carbonaceous chondrites, including Murray.

Briggs (38) examined hot water extracts of Mokoia and reports the presence of a substance which reacts with purine staining reagents (silver chromate- HNO_3 ; and silver nitrate-bromphenol blue); this substance however does not correspond in R_f value to any known purine.

Hayatsu (49) in an attempt to clarify the question of organic bases in meteorites has searched for organic nitrogen compounds in Orgueil, specifically avoiding the use of ion exchange resins in the analytical procedure. Using primarily spectroscopic and chromatographic methods he reported the presence of purines, amino derivatives of sym-triazine, and substituted guanidines in HCl extracts. Compounds identified were melamine (40 $\mu\text{g/g}$), ammeline (28 $\mu\text{g/g}$), adenine (15 $\mu\text{g/g}$), and guanine (20 $\mu\text{g/g}$). The author considers the presence of melamine and ammeline to indicate an abiotic origin, since these compounds have no known biological significance. There was no indication that this researcher ran procedural blanks in the study, however, and therefore these results are not without question.

Briggs and Mamikunian (8) have detected low concentrations of urea and acetaminde in the meteorites they have studied. Likewise, Vallentyne (45) tentatively identified a substance to be urea in acid hydrolysates of Orgueil.

4. Carbohydrate: Degens and Bajor (43) using paper chromatography detected free and combined sugars in Murray and also in the Bruderheim non-carbonaceous meteorite. Glucose and mannose were found

free and combined in both meteorites and Murray was also found to contain arabinose. Bruderheim contained a total sugar concentration of 20 $\mu\text{g/g}$ while Murray contained 70 $\mu\text{g/g}$. These authors made the same conclusion for the origin of these compounds as they did for the amino acids detected (see page 12).

Kaplan et al. (6) also used paper chromatography to analyze stony meteorites for sugars. Most meteorite samples contained only trace amounts or none at all. Several, however, (Hvittis, Murray, Orgueil, Mokoia) had sugars ranging from 5-26 $\mu\text{g/g}$, which were somewhat lower levels than that found by Degens and Bajor. Glucose, mannose, arabinose, and xylose were identified. These authors favor a non-biogenic origin for these compounds.

5. Pigments: The only report of pigment material in carbonaceous meteorites is that of Hodgson and Baker (50). Kaplan et al. (6), Degens (51), and Nagy et al. (39) were unable to find evidence for such substances in the meteorites that they have studied. Hodgson and Baker used silica gel column chromatography to fractionate benzene-methanol extracts of the Orgueil meteorite. The n-hexane-benzene and benzene fractions contained a component absorbing at 410-412 m μ . The chromatographic and absorption characteristics of this material were very similar to esterified vanadyl porphyrins of terrestrial ancient sediments and petroleum. The concentration was in the range found for terrestrial rocks (0.01 parts per million of meteorites). Limited data available for possible contaminants such as dust, soils, and recent sediments indicated that these substances contain chlorins and porphyrins with chlorins predominating. Chlorins however were virtually absent in the meteorite

sample and the authors concluded these as unlikely contaminants. A biogenic origin was suggested on the basis of data presently available.

6. Optical Activity: Enzyme-dependent biochemical processes occurring in living matter are the only known sources of naturally occurring optically active compounds (39). Because of this many researchers have looked for optical activity in the carbonaceous meteorites in hope of elucidating the origin of the organic compounds present.

Mueller (28) was perhaps the first to analyze extracts from these meteorites for optical activity. Using an instrument of sensitivity 0.02° , he was unable to detect activity in extracts of Cold Bokkeveld. Briggs (8) has reported a similar finding for the soluble fractions of Mokoia and Haripura.

Amino acid fractions from meteorites have received particular attention for possible optical activity in view of the almost exclusive presence of L-amino acids in terrestrial organisms. But polarimetric measurements employing instruments as sensitive as 0.0005° have failed to detect any activity in amino acid fractions from several meteorites (6,45,52).

The only positive indication of optical activity yet reported was that of Nagy and coworkers (39). These investigators made a spectropolarimetric study of saponified benzene-methanol extracts of three different stones of the Orgueil. A small but reproducible laevorotation ($-0.023^\circ \pm 0.005^\circ$) was observed. Identically prepared fractions of possible contaminants such as dust, pollen, soil, wax, and alga, either showed no rotation or was slightly dextrorotatory at the same wavelength. These authors concluded that the rotation observed was real and evidence for biological activity

either indigenous to the meteorite or perhaps due to terrestrial contamination. Hayatsu (52) however was unable to confirm these findings. He failed to detect any activity in the Orgueil above that found in optically inactive controls. He considers the results obtained by Nagy's group to be instrumental artifacts caused by (1) scattered depolarized light from colloidal particles present in the samples examined, (2) reduced instrument sensitivity due to low transmittance of the solutions, or (3) a combination of both of these. Nagy (53), however, in a second report maintained that Hayatsu's objections are not valid since the latter employed a significantly different process to extract the meteorite thus allowing for the optically active material to be missed.

B. Studies of Non-extractable Organic Material

The bulk of the carbonaceous material present in carbon chondrites exists as an insoluble, intractable substance. This material can be isolated in a manner similar to that used for terrestrial kerogens. Generally this is done by removing soluble organics with organic solvents followed by removal of mineral matter by treating the residue with hydrochloric and hydrofluoric acids. The insoluble, coal-like nature of this material makes its analysis very difficult. As a result, very little definitive data has appeared in the literature regarding the exact chemical nature of this substance.

Mueller (28) studied this fraction of Cold Bokkeveld by x-ray diffraction. Obtaining no evidence for graphite, he suggested that it is similar to the extractable organic fraction (i.e., a humic acid type substance) though richer in carbon and perhaps containing amorphous carbon.

Briggs and Mamikunian (8) have found insoluble organic material occurring as translucent flakes of micron size in the meteorites that they have studied. Based on the optical characteristics of this material and on its density, they suggest it to be a very high molecular weight hydrocarbon polymer. Kaplan et al. (6) also consider this fraction to be a highly polymerized organic substance. Their conclusion was based principally on the fact that it did not appear to be graphite since it proved to be amorphous to x-rays, and on the nature of organic material freed by HCl hydrolysis of the meteorites studied. This group, however, did not exclude the possibility that it could be amorphous carbon.

Vdovkin (54) detected characteristic absorptions in the infrared region for this material which indicated an aromatic structure associated with polar functional groups. Vinogradov and Vdovkin (55) made a similar observation for the so-called "high molecular weight organic substance" in several carbonaceous chondrites. Infrared studies indicated that this fraction consisted of a condensed aromatic carbon skeleton having peripheral polar groups such as OH and COOH.

Very recently, electron spin resonance spectroscopy has been employed to detect possible free radicals in this fraction of the meteorite organics. It is known that free stable organic radicals exist in such terrestrial natural macromolecules as wood, lignins, and humic acids (56). The existence of such radicals in these polymers is considered to be evidence for their biogenic origin (57,58).

Villee et al. (59) detected a small ESR signal which could be attributed to the carbonaceous matter in Alais and Cold Bokkeveld. Similar

results have been obtained for the high molecular weight substance in Mighei (55,60). Duchesne, Depireux, and Litt (61,62) have concluded a biogenic origin for the carbonaceous matter in the meteorites they have studied based on the similarities of its ESR spectra to that of coal.

Schulz and Elofson (63) have used this method to study the Orgueil meteorite. The ESR response as a function of temperature of carbonization of the insoluble material was found to be very similar to that observed for terrestrial coals and kerogens. The possibility of trace contaminants producing the effect was ruled out by quantitative considerations. Even though a biogenic origin for this substance appeared plausible to these workers, they made note of the fact that synthetic insoluble organic polymers exist which behave in a similar manner.

III. Summary

The presence of organic compounds in carbonaceous chondrites has been known since the first half of the nineteenth century. The lack of adequate tools for analysis however prevented early investigators from obtaining any truly definitive data as regards the identity of the organic compounds present. In recent times, however, more detailed analyses of these meteorites have been possible and, as a result, a vast number of organic compounds have been reported to be present.

Hydrocarbons from these meteorites have been identified and in many cases found to be identical or very similar to those of biological significance. Some investigators have postulated an extraterrestrial biogenic origin for these compounds, while others have proposed a non-

biogenic origin. Recent contamination studies, however, have indicated that terrestrial contaminants, including microorganisms, could account for the hydrocarbons detected.

Organic acids (fatty acids, phenols, amino acids) have also been reported to be in the meteorites. Other studies however have indicated that many of these compounds are either terrestrial contaminants or artifacts. Organic bases (purines and pyrimidines), sugars, pigments, and optical activity have also been reported to be present, but this data is either inconclusive or questionable.

The bulk of the carbon in these meteorites has been suggested to be either so-called amorphous carbon, or a highly condensed macromolecule. Available data indicates that it is not graphitic. Some investigators have suggested that the material is of biogenic origin based on similarities of certain of its properties to those of terrestrial biogenic materials such as coal. Others, however, have noted that certain abiogenic materials may possess similar properties.

STATEMENT OF THE THESIS PROBLEM

Meteorites, as natural existing matter are, in their own right, important objects for scientific study. The organic matter in the carbonaceous chondrites, however, adds special significance to the study of this class of meteorites, for a knowledge of the nature and origin of this material could provide valuable information regarding the possible presence or absence of extraterrestrial life.

The foregoing review of the literature has revealed how little is known concerning the nature of the carbonaceous material in these meteorites. Indeed, not even 5% of the organic matter present has been identified (8).

The present investigation was thus undertaken in an attempt to clarify the controversial status of the reported presence of meteoritic amino acids and to gain further knowledge as to the chemical nature and origin of the bulk of the carbonaceous material in carbonaceous chondrites. The study consisted of the following two aspects:

- (1) An analysis for amino acids in the Orgueil, Murray, Mokoia, and Lancé carbonaceous chondrites.

- (2) A constitutional analysis study of the non-extractable carbonaceous material in the Orgueil carbonaceous chondrite.

II.

EXPERIMENTAL AND RESULTS

EXPERIMENTAL AND RESULTS

ANALYSIS FOR AMINO ACIDS IN THE ORGUEIL, MURRAY, MOKOIA, AND LANCÉ CARBONACEOUS CHONDRITES

I. INTRODUCTION

The universal presence of proteins and their amino acids in all living matter implicitly points out the very important role that these substances play in living processes. This fact has led several investigators to examine carbonaceous chondrites for amino acids with the hope of gaining information as to the possibility of biological activity in the meteorite parent bodies. As pointed out in the Introduction, some have reported the presence of amino acids in meteorites, but others have failed to detect them. The very low concentration levels reported by those who claim their presence, however, makes it very difficult to exclude completely the possibility that these compounds are the result of terrestrial contamination.

This study was thus undertaken in an attempt to establish if amino acids are present in certain carbonaceous chondrites, and, if so, to provide evidence which would establish their origin.

II. METHODS

1. Extraction and Isolation Procedures: The following meteorite samples (Table II lists the source of each sample) were analyzed for amino acids: Orgueil (2.0g), Murray (2.0g), Mokoia (2.0g) and Lancé (1.0g). The procedure is summarized in Figures 1 and 2. It involved an initial extraction of the

SCHEME FOR THE ISOLATION OF AMINO ACID FRACTIONS FROM THE
METEORITE SAMPLES

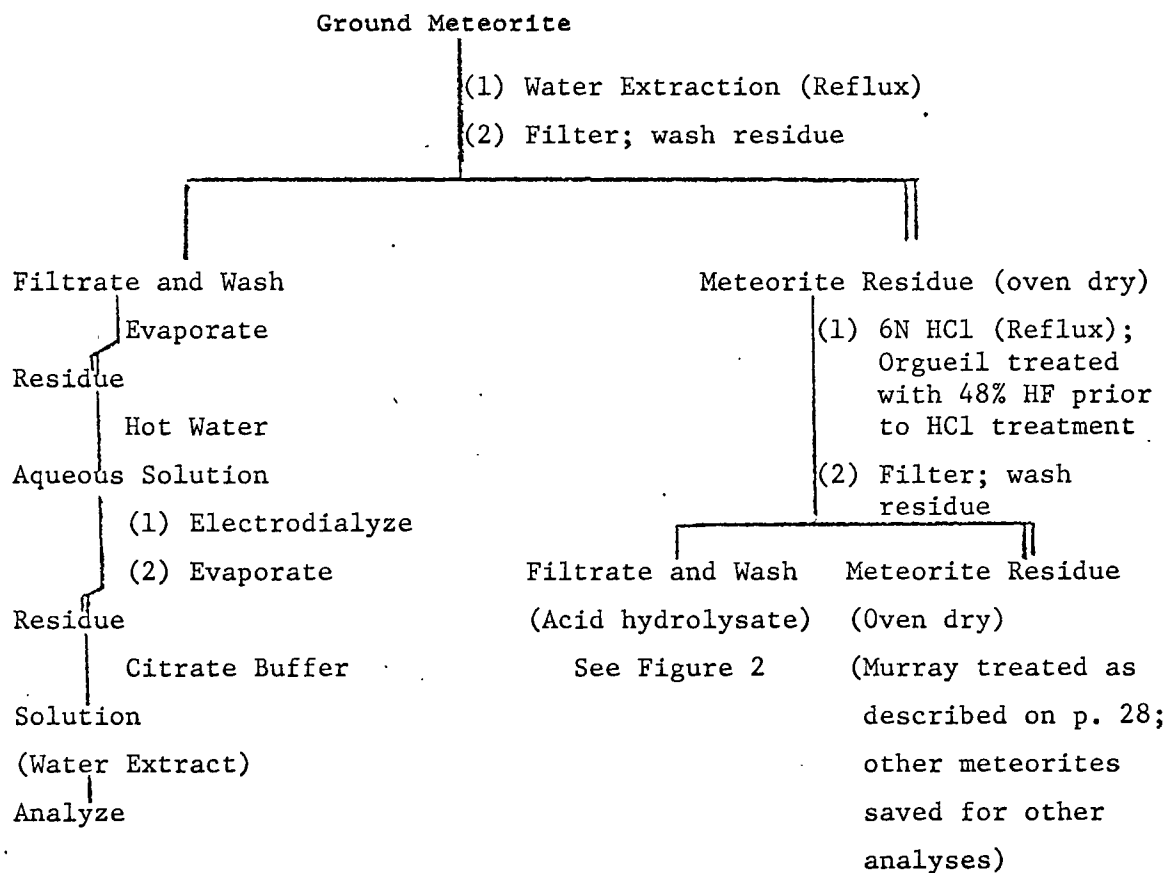


FIGURE 1

SCHEME FOR THE ISOLATION OF AMINO ACID FRACTIONS FROM THE ACID HYDROLYSATES OF THE METEORITE SAMPLES

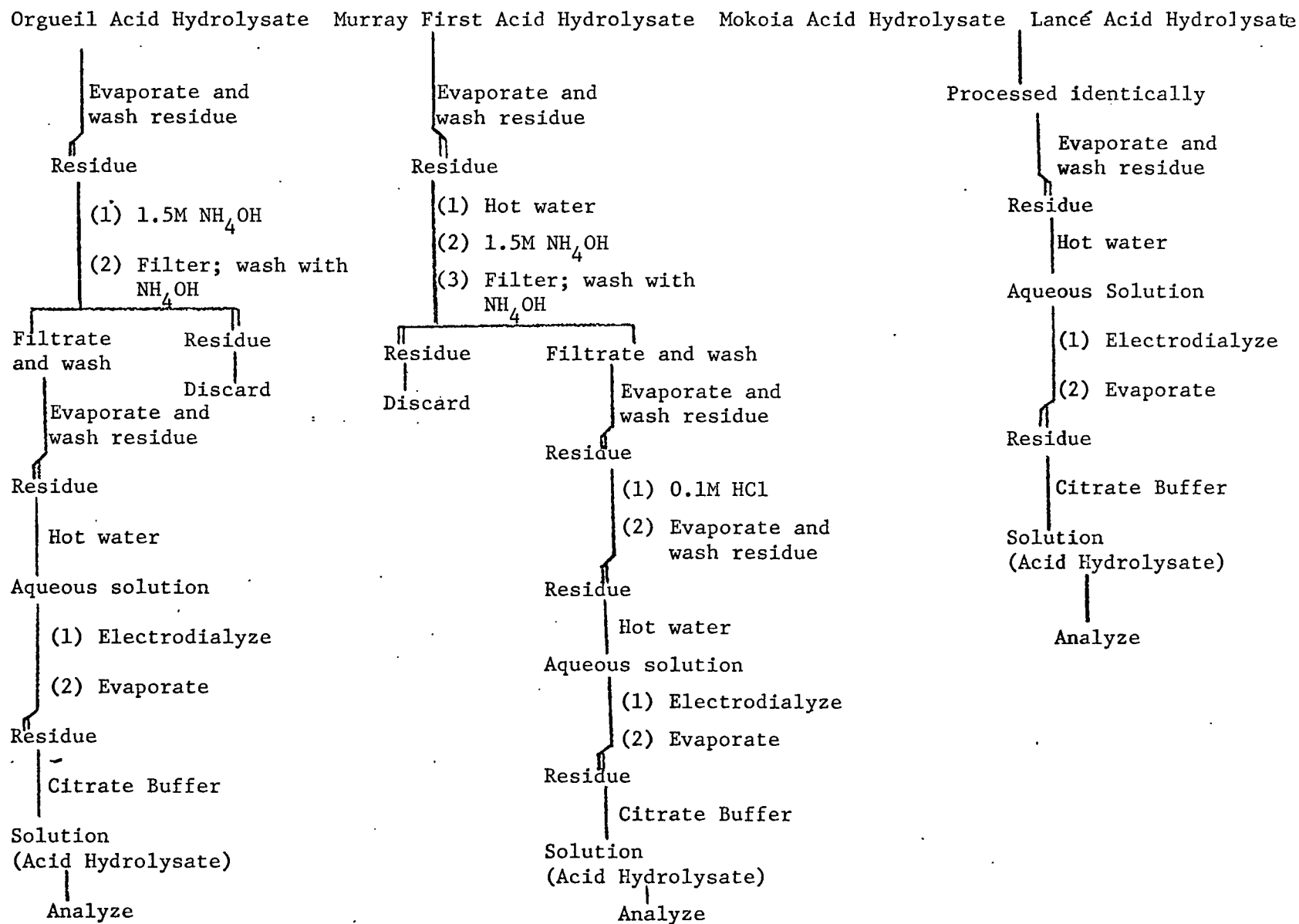


Figure 2

TABLE II
DATA ON METEORITE SAMPLES ANALYZED

Meteorite	Wiik Classification	Source	Condition
Orgueil, France	Type I	A. Cavaillé; Museum of Natural History, Montauban, France	Pulverized, small pieces
Murray, U.S.A.	Type II	E. P. Henderson; Smithsonian Institute, U.S. National Museum, Washington, D. C.	Whole fragment
Mokoia, New Zealand	Type III	C. B. Moore; Arizona State University and Nininger Meteorite Collection, Tempe, Arizona	Whole fragment
Lancé, France	Type III	G. Kurat; Mineralogy Petrography Division, Museum of Natural History, Vienna, Austria	Whole fragment

finely ground and weighed meteorite sample with 100 ml of distilled water for 8 hrs. in a reflux apparatus (a Soxhlet type extractor was used for the Orgueil sample). The aqueous extract was filtered through a sintered glass funnel and the meteorite residue washed with water and dried in an oven at 80-85°C. The dried meteorite was then refluxed for 20 hrs. with 150 ml of 6N HCl (for Orgueil, the meteorite was treated with 25 ml. of 48% HF prior to HCl hydrolysis; the HF was removed by evaporation over a steam bath). The amber colored, hydrolyzed mixture was filtered in the same manner as above and the remaining meteorite residue dried in an oven at 80-85°C. and saved for other analyses. The pooled water extract and washings was concentrated to dryness by vacuum distillation at 40-45°C using a rotating flash evaporator. In all cases the residue of the water extract was dissolved in 12 ml of hot distilled water and the inorganic salts removed from the aqueous solution by electrodialysis, as will be described later.

There was slight variation in the isolation procedure of the HCl hydrolysates for the different meteorites studied (Figure 2). In the case of Mokoia and Lancé identical procedures were followed. The filtered hydrolysate was concentrated to dryness by vacuum distillation at 45°C. and the residue washed three times by adding distilled water to the sample, taking it to dryness each time by vacuum distillation. The washed residue was dissolved in 15 ml. of hot distilled water and the inorganic salts removed from the resulting solution by electrodialysis.

The Orgueil HCl hydrolysate was concentrated and washed as just described. However, the washed residue was then taken up in 40 ml of

1.5M NH_4OH and the precipitated iron hydroxides removed by filtration through a sintered glass funnel; the colorless filtrate was concentrated by vacuum distillation at 45°C . and washed with water as described previously until no odor of ammonia was detected. The washed residue was dissolved in 10 ml. of hot distilled water and desalted by electrodialysis.

The Murray HCl hydrolysate was also concentrated as described in the above. Then the washed residue was taken up in 15 ml. of hot distilled water and 25 ml. of 1.5M NH_4OH was added to the aqueous solution. The precipitated iron hydroxides were removed by filtration as in the case of Orgueil, and 15 ml. of 1.5M NH_4OH was used to wash the precipitate. The pooled alkaline filtrate and washings was concentrated to dryness at 45°C . by vacuum distillation and washed until no odor of ammonia was detected. 10 ml. of 0.1M HCl was then added to put any amino acids in their acid form, and the excess HCl removed by distillation and washings as described earlier. The washed residue was then dissolved in 12 ml. of hot distilled water and the solution desalted by electrodialysis.

In the case of Murray only, the meteorite residue remaining after HCl hydrolysis was dried in a vacuum dessicator over phosphorous pentoxide and then treated with 25 ml. of 48% HF for one hour at room temperature. The HF was removed by evaporation over a steam bath, the residue being washed twice with distilled water, evaporating off the water each time. The washed residue was hydrolyzed for 20 hrs. with 150 ml. of 6N HCl. The filtered hydrolysate was concentrated in the same manner as described for Mokoia and Lancé, and then desalted by electrodialysis.

2. Method of Desalting: Both the water extracts and HCl hydrolysates contained inorganic salts; the acid hydrolysates being especially rich in these compounds. A relatively high concentration of inorganic salts in an aqueous solution is known to interfere with its chromatographic analysis, and thus a desalting step is usually necessary before analysis. Previously, ion-exchange resins have generally been used to desalt amino acid fractions from meteorites (6,45,64). It has been shown however that ion-exchange resins themselves contain amino acids (65,66); in order to avoid contamination from this source an alternative method, electro-dialysis, was used in this procedure. This method has been described earlier by Consden and coworkers (67) and the recovery has been determined to be relatively high for most of the common amino acids (68).

An RSCo Electric Desalter (Model 1930) was used to electro-dialyze the amino acid fractions isolated as described above. The procedure consisted of adjusting the voltage between the two electrodes so that the solution to be desalted conducted initially a current of 0.6 amps; when the current decreased to 0.2 amps, the sample was considered adequately desalted. The sample was then removed from the desalter, concentrated to dryness over a steam bath and dissolved in 1.5 ml. (2.0ml for the Lancé hydrolysate) of sodium citrate buffer of pH 2.2 and analyzed. Samples having high salt concentrations were difficult to desalt by this method; in some cases, as long as 4 hrs. was needed to adequately remove the inorganic material.

3. Blanks: In order to determine the extent of contamination arising during the analytical procedure, two procedural blanks were run as

controls (runs processed through every step of the procedure but containing no meteorite sample). One of these was processed in a manner identical to the Orgueil sample (Blank 1) and the other to the Murray (Blank 2); there was no blank run for the second acid hydrolysate of Murray.

4. Method of Analysis: The desalted water extracts and acid hydrolysates, which had been dissolved in citrate buffer, were each analyzed by the method of ion-exchange column chromatography using a Beckman Model 120 B Amino Acid Analyzer. Identifications were made by comparing the retention times of ninhydrin positive compounds from the meteorites to those from a standard amino acid solution containing the common protein amino acids in a concentration of 1 μ M/ml respectively; this method thus also allowed for a quantitative study to be made. Table III gives the amount of sample analyzed for each meteorite studied.

III. RESULTS AND DISCUSSION

Only the Orgueil and Murray meteorite samples were found to contain ninhydrin positive compounds which have elution times corresponding to those of common protein amino acids; neither the Mokoia nor the Lance meteorite samples contained detectable amounts of common protein amino acids (see Figures 3 and 4).

The low-level of amino acids detected in the Orgueil sample most reasonably have their source in contamination acquired during the experimental procedure (the broad peak of chromatogram 2 in Figure 3 was due to a malfunction in the instrument). This is clearly indicated by the results of the analysis of procedural blank 1 (Figure 3). The chromatogram

FIGURE 3

CHROMATOGRAMS OF THE WATER EXTRACTS AND ACID HYDROLYSATES OF THE
ORGUEIL, MURRAY, MOKOIA AND LANCÉ METEORITES AND OF BLANK 1

(1) cysteic acid, (2) urea, (3) aspartic acid, (4) threonine,
(5) serine, (6) glutamic acid, (7) glycine, (8) alanine,
(9) valine, (10) methionine, (11) isoleucine, (12) leucine,
(13) tyrosine, (14) phenylalanine, (15) lysine, (16) histidine,
(17) ammonia, (18) arginine

*This peak was due to a malfunction in the instrument

Note: The wavy lines in this figure are due to the fact that the
original chromatograms were hand traced.

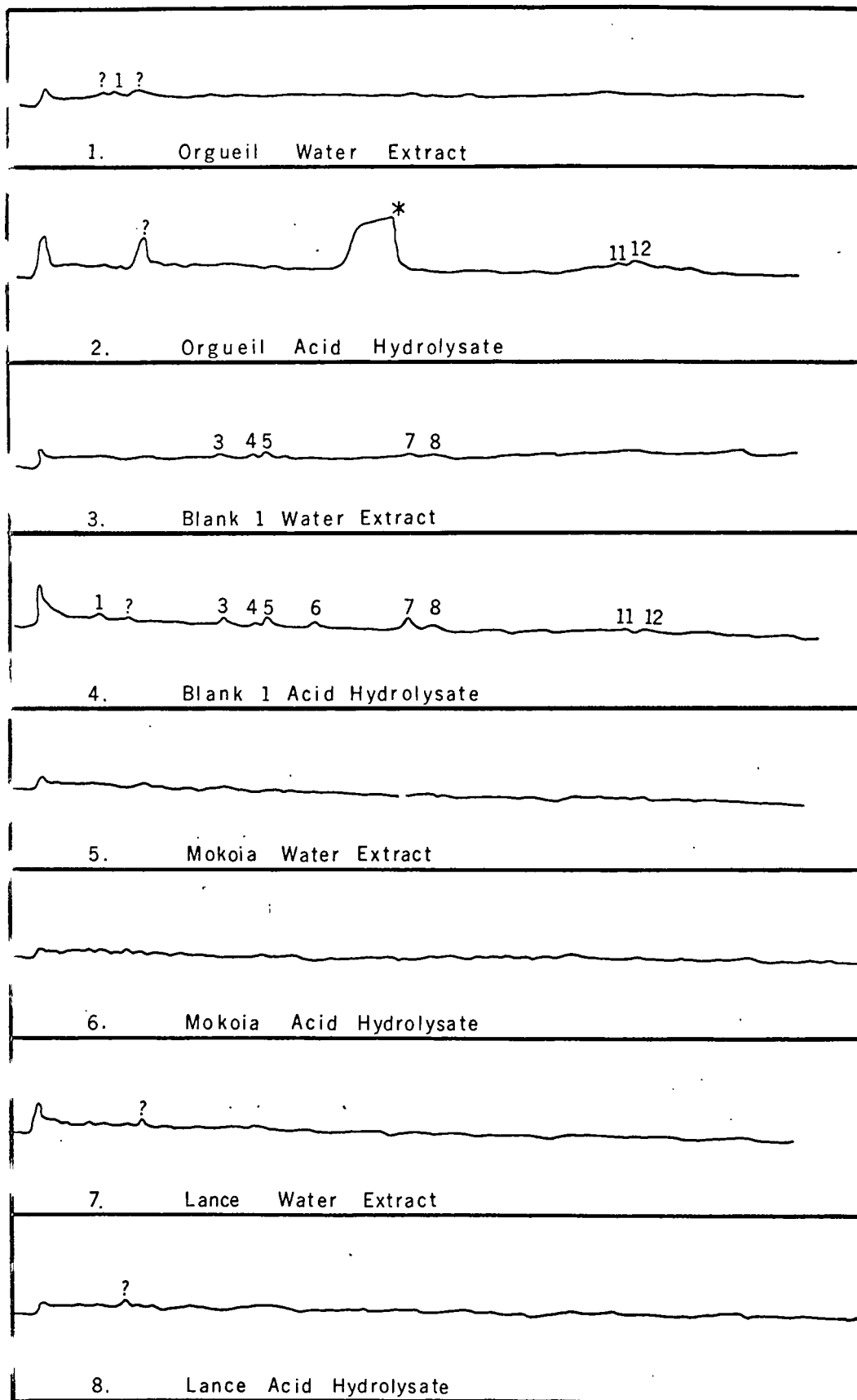


FIGURE 4

CHROMATOGRAMS OF THE WATER EXTRACTS AND ACID HYDROLYSATES
OF THE MURRAY METEORITE AND OF BLANK 2

Peaks numbered as in Figure 3

Note: The wavy lines in this figure were due to the fact
that the original chromatograms were hand traced.

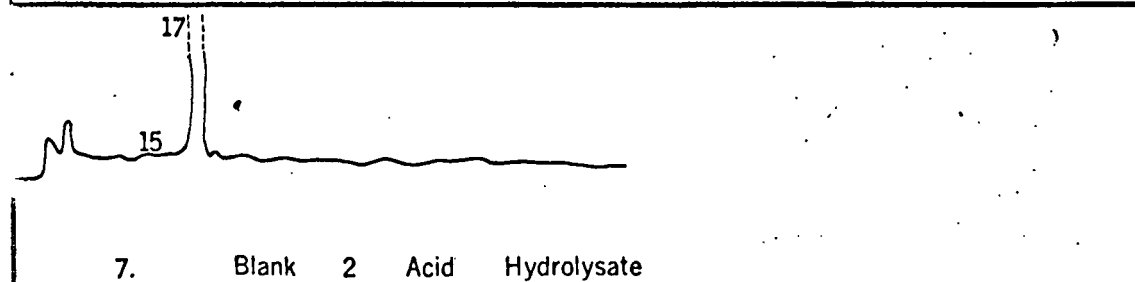
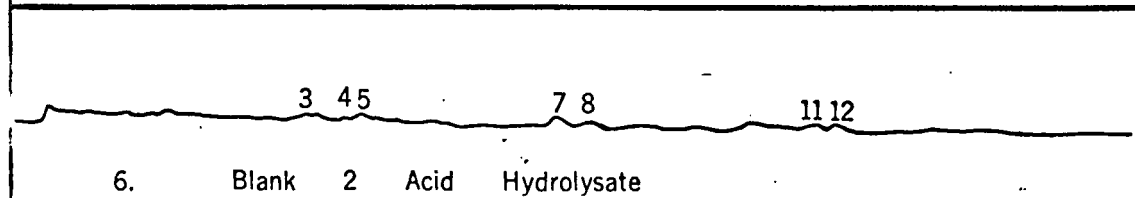
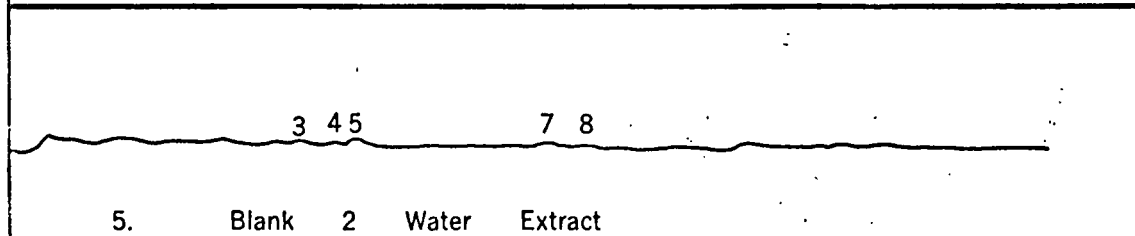
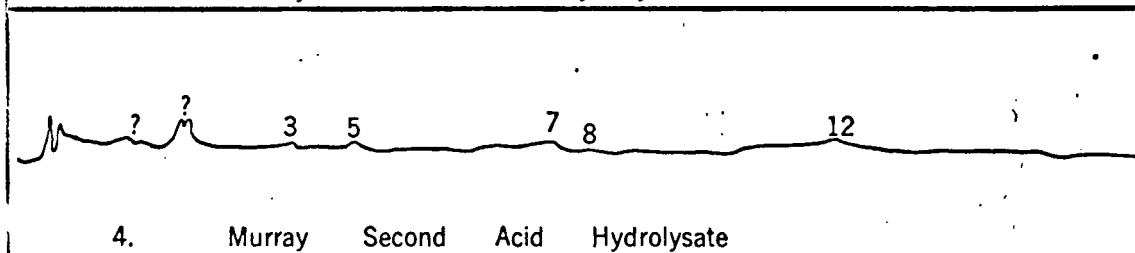
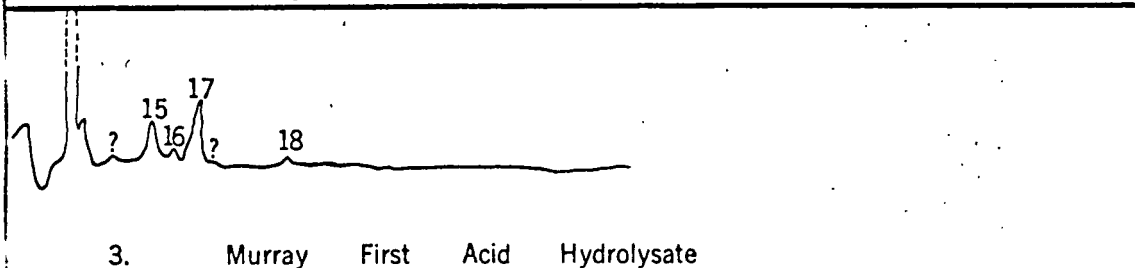
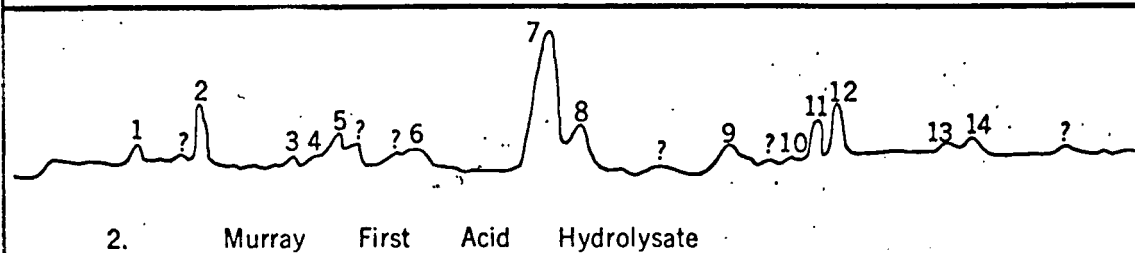
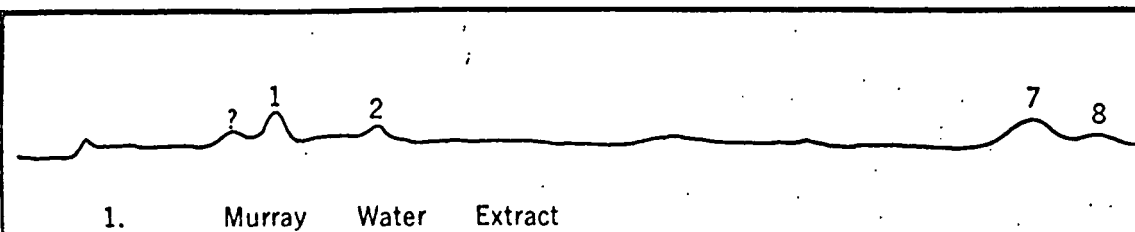


TABLE III
AMOUNT OF SAMPLE TAKEN FOR ANALYSIS ON THE AUTOMATIC
AMINO ACID ANALYZER

(Values shown represent the volume of buffer solution containing
either the water extracted or acid hydrolyzed material from the
respective meteorite samples)

Meteorite Sample	Volume of Sample Analyzed (ml.)	
	Water Extract	Acid Hydrolysate
Orgueil	0.45	0.30
Murray	0.70	0.70 (first hydroly- sate) 0.30*(first hydroly- sate) 0.70 (second hydroly- sate)
Mokoia	0.65	0.70
Lancé	0.70	0.70
Blank 1	0.70	0.70
Blank 2	0.70	0.70 0.30*

* This analysis was for basic amino acids only; the basic amino acids are analyzed on a separate column from that used to determine the acidic and neutral amino acids.

shows that more amino acids were present in the blank than in the meteorite sample; the explanation for this is the fact that more than twice as much blank sample was analyzed than meteorite sample, and also that greater care was probably exercised in processing the meteorite sample than this particular blank. The amino acid pattern of the blank resembles closely that of free amino acids present in the epidermal cells of human fingers (47), and the contaminants probably arise from this source. It should be pointed out here (as discussed in the Introduction) that even when great care is taken to avoid any possible contamination during the analysis of a given sample, simple hand contact with glassware or other experimental apparatus could contaminate a sample with sufficient amino acids to be detected at the micromolar level (46,47).

The Murray meteorite as can be seen in Figure 4 definitely contains common protein amino acids and in a concentration that is well above that detected in the corresponding procedural blank. The amounts of individual amino acids per gram of meteorite are shown in Table IV. A total amino acid content of 37.2 μg per gram of meteorite was found in the acid hydrolysate following the initial water extraction of the sample; only 2.0 μg were detected in the corresponding blank. In the order of decreasing abundance, the most abundant amino acids present were: glycine, alanine, lysine, proline (the accuracy of this value is questionable), leucine, serine, histidine, and arginine. The total content agrees well with that found by Kaplan *et al.* (6), who found 35.7 μg of combined amino acids per gram of Murray. The relative abundance of the individual amino acids are in some agreement, but in the present case, more of the

TABLE IV

AMOUNTS OF INDIVIDUAL AMINO ACIDS PRESENT IN THE FIRST ACID HYDROLYSATE

OF THE MURRAY METEORITE SAMPLE AND IN THE CORRESPONDING BLANK

(Values shown represent $\mu\text{g/g}$ of meteorite and $\mu\text{g/sample}$ of blank)

	Sample	
	Murray	Blank 2
Urea	0.67	0
Asp	0.40	0.13
Thr	0.60	0.05
Ser	2.0	0.32
Glu	1.3	0.15
Pro*	3.3	0
Cit		
Gly	9.4	0.30
Ala	4.1	0.09
Val	1.4	0
Met	0.30	0
Ileu	1.8	0.13
Leu	2.8	0.30
Tyr	0.54	0
Phe	1.5	0
Lys**	4.1	0.60
Orn		
His	1.9	Trace
Arg#	1.7	0
Total†	37.2	2.0

* This peak contains proline and also citrulline

**This peak contains ornithine and also lysine

It is possible that the desalting method may have converted any arginine present to ornithine (68)

† This value represents total less urea

basic amino acids are present. The results of the Orgueil, Mokoia, and Lancé analyses are however in complete disagreement with these investigators since they have reported a total amino acid content per gram of meteorite of 112 μg , 73.2 μg , and 528 μg (combined only), for the Orgueil, Mokoia, and Lancé, respectively. Vallentyne (45) reported a much lower value of 20.4 $\mu\text{g/g}$ for the Orgueil sample that he analyzed. Contamination studies, however, make some of these results questionable (45,46,47).

Chromatogram 1 of Figure 4 shows that the water extract of Murray also contained appreciable amounts of compounds tentatively identified as glycine, alanine, urea, and cysteic acid (the broad absorption peaks and late elution times are the results of an unintentional change in the recorder speed). A quantitative determination of these compounds was not made. Chromatogram 4 of the same Figure shows the results of the analysis of the second acid hydrolysate of Murray (following hydrofluoric acid treatment) and indicates that essentially all of the amino acids had been removed from the meteorite by water extraction and acid hydrolysis, and that virtually none were entrapped within the silicate minerals of the meteorite.

The high concentration of ammonia in the first acid hydrolysate of Murray (and also in the corresponding blank), is an artifact which can be attributed to the NH_4OH which was used in the procedure. Also interesting to note is the relatively high concentration of urea in the meteorite sample and its virtual absence in the corresponding blank (urea, however, has been identified in hand contaminated samples (46,47)).

Despite the low levels of amino acids found in the procedural blanks, contamination possibilities pose a paramount problem in establishing if the amino acids detected in the Murray are indigenous or not. The work of Hamilton (46) and of Oró and Skewes (47), as mentioned earlier, has demonstrated how extremely easy it is to contaminate a given sample at the micromolar level. Quantitatively speaking, both the level of amino acids and the relative concentrations of individual amino acids found in the Murray, are quite comparable to that associated with handling contamination as described by Oró and Skewes. Table V gives the ratios of prominent amino acid pairs of the Murray sample and the two blank samples analyzed in this study; for comparison, ratios of the same pairs of amino acids found in contamination and other meteorite studies as given by Oró and Skewes (47) are included. The serine/alanine ratio is somewhat lower in this study than in the others, but when the standard deviations are taken into account, the values are more comparable.

Contamination from terrestrial microorganisms may also be quite possible, especially in view of the porous nature of carbonaceous chondrites. In this regard, it is very interesting that recent analyses for viable organisms in samples of Orgueil, Murray, and Mokoia taken from the same fragments from which the samples here analyzed for amino acids were obtained, gave results which correlate very well with the present findings. Oró and Tornabene (69) have shown that the Murray and Mokoia samples contained an average count per gram of meteorite of 6,000 and 1,800 bacteria respectively, these being lower limit values. The Orgueil sample contained no viable organisms, and not all of the Mokoia

TABLE V
RATIOS OF AMINO-ACID PAIRS FROM METEORITE ANALYSES AND FROM
CONTAMINATION STUDIES

Sample	Ser/Thr	Gly/Ala	Ser/Ala
1) Murray Acid Hydrolysate ¹	3.8	2.7	0.41
2) Blank 2 Acid Hydrolysate ²	6.6	3.1	2.2
3) Blank 1 Acid Hydrolysate ³	2.7	1.4	0.53
4) Average of Above 1), 2), & 3)	4.4	2.4	1.0
5) Handling Contamination (Average) ⁴	5.4	2.1	3.6
Standard Deviation	0.77	0.37	0.38
6) Other Meteorite Analysis (Average) ⁵	4.7	1.6	2.1
Standard Deviation	2.0	1.7	2.4

^{1,2,3}Present Study

⁴Average of 10 values taken from Or6 and Skewes (47)

⁵Average of 15 values (12 values for Ser/Thr) taken from Table III of Or6 and Skewes (47)

samples gave viable counts, suggesting a heterogeneous distribution of bacteria throughout the meteorite fragment. An organism of bacterial size weighs on the order of 10^{-11} grams (70) and may have a protein content of from 12.5%-87.5% (71). Assuming a high protein content for the bacteria found in the Murray, about 0.05 μ g of amino acids per gram of meteorite could be accounted for by the 6,000 bacteria reported to be present. In spite of the upper limit taken for protein material, this is probably a reasonable estimate in view of the lower limit of viable organisms considered. Admittedly, this amount of bacteria could by no means account for the concentration of amino acids detected in the Murray; nevertheless, it does not appear improbable that much higher concentrations of amino acids could be attributed to remnants from once-living bacteria which may have been deposited in the Murray over the years. The relatively high content of glycine, alanine, and lysine may in part be accounted for by such occurrences since it is known that these amino acids account for a major amount of the amino acid constituents found in certain bacterial cell walls (72). Furthermore, according to Oró and Tornabene, the viable count determined was only 3%-25% of the number of non-viable bacteria which have been observed in other meteorites.

A CONSTITUTIONAL ANALYSIS STUDY OF THE NON-EXTRACTABLE CARBONACEOUS MATERIAL IN THE ORGUEIL CARBONACEOUS CHONDRITE

I. INTRODUCTION

As pointed out in the Introduction, the exact chemical and structural nature of the non-extractable organic material in the carbonaceous

chondrites has not yet been determined. The data presently available indicates that structurally this material is not graphitic, but more like the heteropolymers which constitute terrestrial humic and kerogen type substances.

This study was thus undertaken in an attempt to provide informative, experimental data which would contribute towards elucidating the constitution of this major fraction of the meteorite organics. The study was limited to the Orgueil meteorite, and consisted of the following: (1) analysis of the non-extractable carbonaceous material, per se, and (2) analysis of extractable organics for compounds of structural significance. The former of these consisted of elemental and x-ray diffraction analyses, and analyses of the degradation products formed on oxidation of the non-extractable material. The latter of the above was limited to analysis for aromatic hydroxy compounds, since these substances appear to be associated with the suggested precursors of the heteropolymers described above (73,74).

II. METHODS

1. Analysis of the Non-Extractable Carbonaceous Material

a) Isolation Method: The non-extractable material was isolated (see Figure 5) from the soluble organic and inorganic substances in the meteorite by a chemical technique very similar to that described by Forsman for the isolation of kerogens from terrestrial sedimentary rocks (74). A 5.5 g sample of the Orgueil meteorite (see Table II for

SCHEME FOR THE ISOLATION OF THE NON-EXTRACTABLE CARBONACEOUS
MATERIAL IN THE ORGUEIL METEORITE

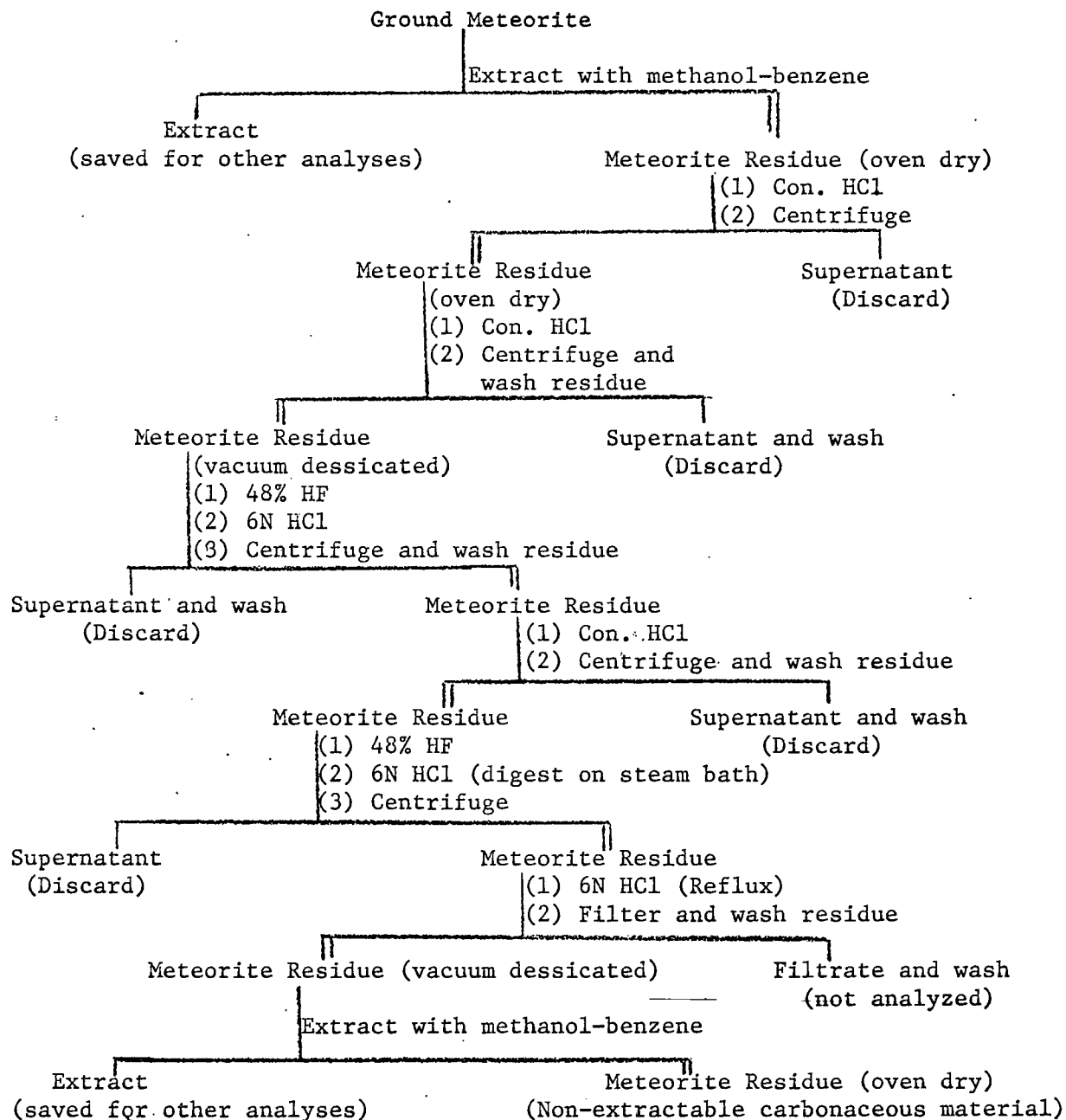


FIGURE 5

source) was ground to a fine powder in a mortar and pestle and extracted for 8 hours with 50 ml. of a mixture of methanol-benzene (1:3V/V) in a Soxhlet type extractor. The meteorite residue remaining from extraction was then dried in an oven at 120-130°C (the extract was saved for other analyses). To the dried meteorite was added 100 ml of concentrated hydrochloric acid in portions, the mixture being stirred at room temperature for a half hour. The mixture was then centrifuged and the supernatant removed by decanting; 50 ml more of concentrated hydrochloric acid was added to the remaining meteorite residue, and the mixture stirred for three hours at room temperature. The hydrochloric acid was again removed by centrifuging and decanting, after which the residue was washed with water and vacuum dessicated over phosphorous pentoxide. A 50 ml volume of 48% hydrofluoric acid (Mallinckrodt) was then added to the dried residue and stirred for 3 1/2 hours; to this mixture was added 50 ml of 6M hydrochloric acid and the resulting mixture then stirred for two hours. Again the supernatant was removed by the centrifuge method and the residue washed with water. A 125 ml volume of concentrated hydrochloric acid was then added to the residue and the mixture stirred for a half hour; the acid was again removed as before. The residue was washed with water and vacuum dessicated once again over phosphorous pentoxide. A 30 ml volume of 48% hydrofluoric acid was next added to the dried residue, and the resulting mixture digested on a steam bath for a one hour. Following this treatment, the sample was allowed to cool, and stirred for 1 hour at room temperature. The acid solution was removed as before, and the meteorite residue was next refluxed with 100 ml of 6M hydrochloric acid for 20 hours; the resulting

acid solution was removed from the meteorite residue by filtration using a sintered glass funnel. After being washed with water the meteorite residue was dried in a vacuum dessicator as before. Finally, the dried meteorite sample was extracted once again with a 50 ml volume of methanol-benzene for 8 hours, and then dried in an oven at 120-130°C. This dried sample is hereafter refereed to as the non-extractable carbonaceous material.

b) Degradation Methods: Analysis of the non-extractable carbonaceous material as such (in its relatively intractable state) is very limited. Conversion of this material to more soluble products, however, would make its analysis more amenable. This approach has proved quite valuable in constitutional analysis studies of similarly insoluble, terrestrial substances, and oxidation as a method of degradation has been extensively used in studies of coal and kerogen (75,76,77,78,79).

Two different oxidation methods were used in the present study and each is described below.

(i) Alkaline potassium permanganate oxidation: Alkaline potassium permanganate has been widely used to degrade compounds of known composition and type (80,81,82,83). Available data indicates that the oxidation reactions are predominantly degradative and are not complicated by secondary reactions such as polymerization, which may occur in pyrolytic degradations (84). Based on these facts, this reagent was selected in the present study, using a procedure similar to that described by Robinson and co-workers (84).

The scheme for the following procedure is given in Figure 6; 0.05 g of the non-extractable material, isolated as described above, was mixed with 0.20 g of potassium permanganate (Baker Reagent Grade), 0.09 g of sodium hydroxide (Fischer Reagent Grade), and 10 ml of distilled water. These proportions provided for every one part carbon, six parts potassium permanganate and two parts of sodium hydroxide; this was based on the assumption that the non-extractable material was about 75% carbon (see page 56 for true percentage of carbon). This mixture was refluxed for 1 1/2 hours, during which time the reaction mixture had changed in color from purple to brown due to the formation of manganese dioxide. The reaction mixture was then filtered through a sintered glass funnel, and the meteorite residue washed with 15-20 ml of 1M sodium hydroxide, followed by distilled water; it was then dried in an oven at 100°C, and the filtrate and washings pooled. Each of these two fractions were further processed as described below.

The dried meteorite residue, which also contained the manganese dioxide produced in the oxidation reaction, was extracted with 15 ml of 1M sodium hydroxide for 12 1/2 hours using a reflux apparatus; the mixture was then filtered as described before, and washed with 35 ml of 1M sodium hydroxide followed by water (the remaining meteorite residue was saved for other analyses). The filtrate and washings were combined, adjusted to a pH of about 2 with 10 ml of 6N sulfuric acid, and concentrated over a steam bath; upon being concentrated, a flocculant red-brown precipitate separated from the acid solution. This substance was isolated and washed (a total of 40 ml of 0.1M HCl containing 1 mole KCl per liter was used) by

SCHEME FOR THE ISOLATION OF THE PERMANGANATE OXIDATION PRODUCTS

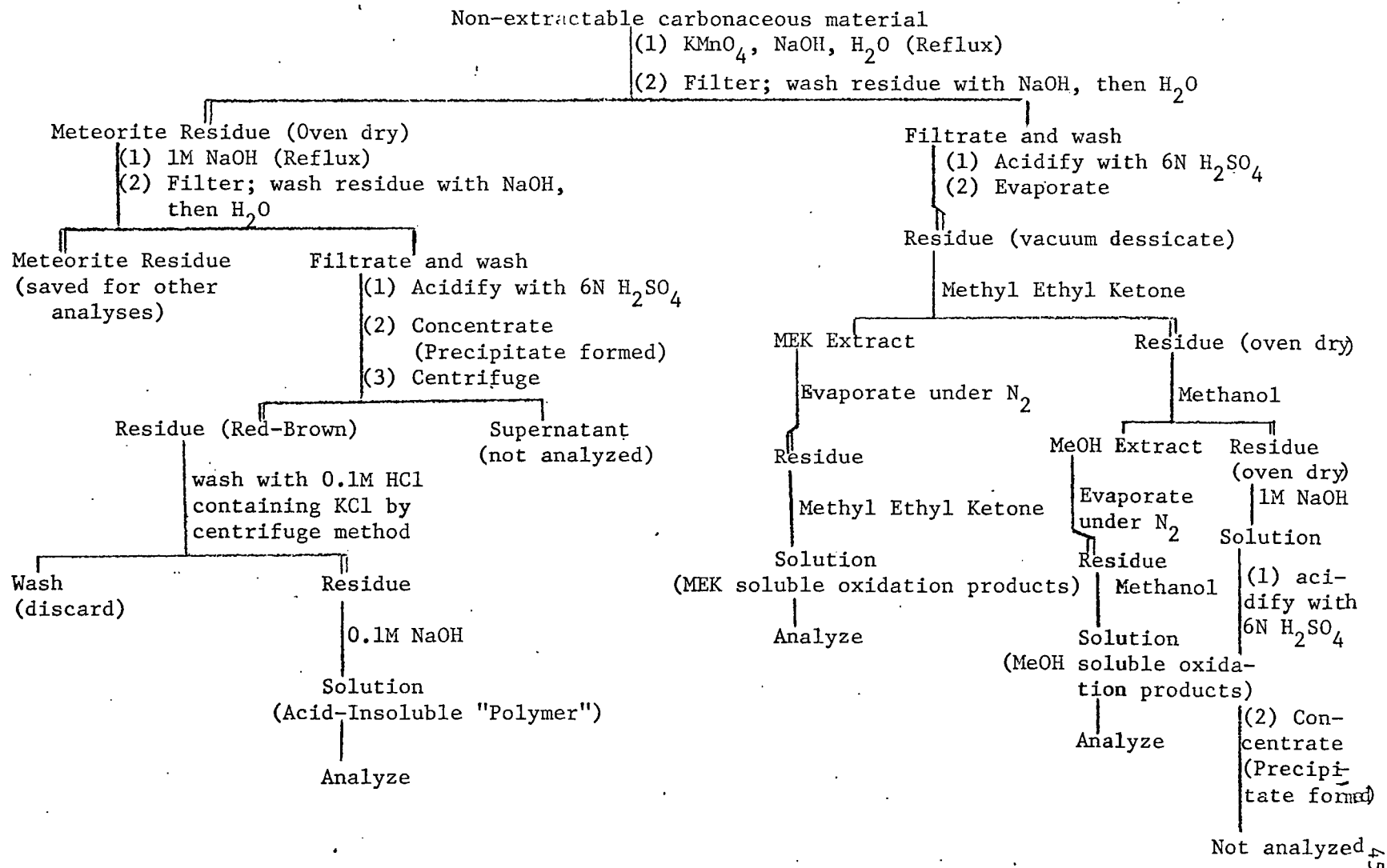


FIGURE 6

the centrifuge method. The washed precipitate was dissolved in 3 ml of 0.1M sodium hydroxide, and is hereafter referred to as the acid-insoluble "polymer".

The pooled filtrate and washings described in the paragraph preceding the one above, was adjusted to a pH of about 2 with 5 ml. of 6N sulfuric acid, and evaporated to dryness on a steam bath (upon being concentrated a red-brown precipitate was observed which appeared identical to that described above). The resulting residue was dried further in a vacuum dessicator over phosphorous pentoxide, and then ground to a fine powder in a mortar and pestle. The powdered material was placed in an extraction thimble having a sintered glass disc and extracted as described below.

A 55 ml volume of methyl ethyl ketone (MEK) (Matheson, Coleman and Bell: B.R. 79-80°C) was poured over the sample in the thimble in 15 ml portions and collected in a beaker; each 15 ml portion was recycled several times. The resulting extract was transferred to a small vial, using 3 ml of MEK to complete the transfer and concentrated to almost dryness under a stream of purified nitrogen at 25°C; the residue was dissolved in 2.5 ml of MEK for analysis. This sample is hereafter referred to as MEK soluble oxidation products.

The residue remaining in the thimble from the MEK extraction was oven dried and again extracted in a manner similar to that just described, but using 55 ml of methanol (MeOH) (Matheson, Coleman and Bell, Spectrograde); the extracted material was then dissolved in 2.5 ml of methanol for analysis. This sample is hereafter referred to as MeOH soluble oxidation products.

A procedural blank was run beginning with the permanganate oxidation step (i.e., the blank was not processed through the isolation procedure described on page 40). The blanks are hereafter referred to as MEK soluble blank, and MeOH soluble blank respectively.

The residue remaining in the thimble from the above methanol extraction was then treated with 25-35 ml of 1M sodium hydroxide; essentially all of the material appeared to dissolve. The resulting solution was acidified with 6N sulfuric acid and concentrated on a steam bath. Again, a flocculant red-brown precipitate, as described previously, precipitated from the acid solution. This material was not, however, combined with the acid-insoluble "polymer" obtained previously.

(ii) Nitric Acid Oxidation: Nitric acid has also been used to oxidize carbonaceous materials, though less extensively than alkaline permanganate (75,76,77). The use of nitric acid allows for a much less involved procedure in the recovery of reaction products, and any excess acid is easily removed by vacuum distillation. The use of this reagent in the present study is described as follows.

To 0.02 g of the non-extractable material (isolated as described previously) was added 10 ml of concentrated nitric acid (Baker Reagent Grade, S.G. 1.4), and the mixture was refluxed for 6 hours. During the reflux period, the mixture acquired a brown-gold color and the undissolved, originally black, meteorite material became dark brown, much if it having been solubilized. After oxidation, the reaction mixture was evaporated to dryness at 50°C by vacuum distillation, using a rotating flash evaporator. The residue was washed with distilled water to remove residual

nitric acid (the water being removed each time by vacuum distillation); 5 ml of distilled water was then added to the brown-gold residue to form a brown-gold aqueous solution. This sample, hereafter referred to as HNO_3 oxidation products, also contained the undissolved, brown meteorite material.

A procedural blank was run beginning with the nitric acid oxidation step; this sample is hereafter referred to as HNO_3 oxidation blank.

c) Methods of Analysis

(i) Elemental Composition: Elemental analysis of the non-extractable carbonaceous material was performed by Huffman Microanalytical Laboratories (Wheatridge, Colorado); oxygen was determined by the Unterzaucher method and nitrogen by the Dumas method.

(ii) X-ray Diffraction: The powder method was used to obtain the x-ray diffraction pattern of the non-extractable carbonaceous material. A Norelco Diffractometer and Wide Range Goniometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) was used for the analysis. The sample was prepared for analysis as follows: a few milligrams of the material was ground to a fine powder in a mortar and pestle and placed on an ordinary glass slide; a few drops of ethyl acetate was added forming a film of the meteorite material. The ethyl acetate was allowed to evaporate at room temperature and the sample then analyzed.

(iii) Infrared and Ultraviolet Spectrophotometry: A 2 μl aliquot of the 0.1M NaOH solution containing the acid-insoluble "polymer" (see page 46) was diluted to 3 ml with 0.1M NaOH and analyzed using a Beckman DB Spectrophotometer.

The HNO_3 oxidation products were analyzed by infrared spectrophotometry using a Baird-Atomic Spectrophotometer. Prior to analysis water was removed from the sample (described on page 48) by vacuum dessication over phosphorous pentoxide. A few milligrams of the dried sample was ground in contact with carbon disulfide (Matheson, Coleman and Bell, Spectrograde) in a mortar and pestle. The carbon disulfide solution was then placed in an Irtran-2 cell of 1 mm pathlength and analyzed.

(iv) Paper Chromatography: Ascending paper chromatography was used to analyze the products from both the permanganate and nitric acid oxidations of the non-extractable carbonaceous material. An aliquot of the solution to be analyzed was spotted on Whatman No. 1 Chromatography Paper by means of a micropipette, and the chromatogram was then developed in one or more of the following solvents (See Table VI for the details of each analysis): (a) Ethyl acetate-acetic acid-water-sodium acetate (100:50:50:0.1 g) referred to as (EAWS); (b) Ethanol-buffer (7:3) referred to as (EB); buffer consists of ammonia and ammonium carbonate, 1.5N with respect to each other; (c) Ethanol-ammonium hydroxide-water (190:4:6), referred to as (EAW); (d) Propanol-formic acid-water (100:40:40), referred to as (PFW); (e) Propanol-formic acid-water-sodium formate (100:40:40:0.1 g) referred to as (PFWS); (f) Butanol-pyridine-water (140:30:30), referred to as (BPW).

After being developed in the appropriate solvent(s), the chromatogram was allowed to dry in a forced draft hood. Any ultraviolet absorbing or fluorescing material was detected by scanning the dried chromatogram with an ultraviolet lamp ($\lambda = 2537 \text{ \AA}$). An acridine spray reagent (85)

TABLE VI

DATA ON THE PAPER CHROMATOGRAPHIC ANALYSIS OF THE POTASSIUM PERMANGANATE
AND NITRIC ACID OXIDATION PRODUCTS

Figure	Sample Analyzed	Sample Designation in Figure	Developing Solvent	Spray Reagent
9	15 μ l MEK Soluble Oxidation Products	U-MEK	EAWS	Acridine
	15 μ l MEK Soluble Blank	B-MEK		
	15 μ l MeOH Soluble Oxidation Products	U-MeOH		
	15 μ l MeOH Soluble Blank	B-MeOH		
10(1)	35 μ l MeOH Soluble Oxidation Products	U-MeOH	First, EAWS Second, PFW	Acridine
10(2)	35 μ l MeOH Soluble Blank	B-MeOH	First, EAWS Second, PFW	Acridine
10(3)	35 μ l MEK Soluble Oxidation Products	U-MEK	First, EAWS Second, PFW	Acridine
10(4)	35 μ l MEK Soluble Blank	B-MEK	First, EAWS Second, PFW	Acridine
11(1)	50 μ l Acid-Insoluble "Polymer"	U-"Polymer"	EAW	Acridine
11(2)	50 μ l Acid-Insoluble "Polymer"	U-"Polymer"	EAW	Paranitraniline
	15 μ l Gallic Acid	S-G		
13(1)	50 μ l HNO ₃ Oxidation Blank	B-HNO ₃	EAWS	Acridine
	50 μ l HNO ₃ Oxidation Products	U-HNO ₃		
	20 μ l HCl and HNO ₃ Standard	S-HCl-N		
	20 μ l Mellitic Acid Std.	S-Ml		
	20 μ l Oxalic Acid Std.	S-O		
13(2)	50 μ l HNO ₃ Oxidation Products	U-HNO ₃	EAWS	Acridine
	20 μ l Malonic Acid Std.	S-M		
	20 μ l Succinic Acid Std.	S-S		

TABLE VI CONTINUED

DATA ON THE PAPER CHROMATOGRAPHIC ANALYSIS OF THE POTASSIUM PERMANGANATE
AND NITRIC ACID OXIDATION PRODUCTS

Figure	Sample Analyzed	Sample Designation in Figure	Developing Solvent	Spray Reagent
14(1)	50 μ l HNO ₃ Oxidation Blank	B-HNO ₃	First, EAWS Second, PFW	Acridine
14(2)	50 μ l HNO ₃ Oxidation Products	U-HNO ₃	First, EAWS Second, PFW	Acridine
14(3)	50 μ l Mellitic Acid Standard	S-Ml	First, EAWS Second, PFW	Acridine
14(4)	50 μ l 1,2,4,5 Benzene-carboxylic Acid Standard	S-Bc	First, EAWS Second, PFW	Acridine
14(5)	50 μ l 1,2,3 benzenetri-carboxylic Acid Standard	S-B	First, EAWS Second, PFW	Acridine

15	100 μ l HNO ₃ Oxidation Products	U-HNO ₃	EAWS	Acridine
	100 μ l HNO ₃ Oxidation Products	U-HNO ₃	EAWS	Parani-
	μ l 2,4,6 trihydroxy benzoic acid Standard	S-T		traniline

was used to detect compounds possessing carboxyl groups (0.1 g/100 ml of Absolute ethanol); the acridine forms a yellow colored complex with such functional groups. A paranitraniline spray reagent was used to detect aromatic hydroxyl groups; the preparation of this reagent is described later (see page 54).

Solutions of the following compounds were prepared as standards: 1,2,3 benzene tricarboxylic acid (1%)(Aldrich Chemical Co.); 1,2,4,5 benzene carboxylic acid (.5%)(Aldrich Chemical Co.); citric acid (1%); gallic acid; malonic acid (1%)(Nutritional Biochem. Corp.); mellitic acid (2%)(Aldrich Chemical Co.); oxalic acid (Fisher); succinic acid (1%) (California Foundation for Biochemical Research); 2,4,6 trihydroxy benzoic acid (1.2%)(Aldrich Chemical Co.).

2. Analysis of Extractable Organics for Aromatic Hydroxy Compounds

a) Extraction Method:

(i) First Ether Extract: 2.0 g of the Orgueil meteorite (see Table II for source) was ground to a fine powder in a mortar and pestle; 50 ml of anhydrous ether (Baker Reagent Grade) was added to the meteorite sample and shaken for 13 hours at 20°C. The shaken mixture was centrifuged and the ether extract removed by decanting; the residual meteorite material was then reextracted with 25 ml. of ether for 30 hours at 20°C. The extracts were each evaporated to dryness under purified nitrogen at 20°C (fine yellow crystals were deposited from the ether extracts upon evaporation; these were identified as elemental sulfur).

The extracted material from each ether extraction was taken up in 95% ethanol and combined. The resulting solution was then evaporated

to dryness under nitrogen and dissolved in 1 ml of 95% ethanol. This sample is hereafter referred to as first ether extract.

A procedural blank was run in a manner identical to the above; the blank is hereafter referred to as first ether blank.

The meteorite residue remaining from the first ether extraction was subjected to further extraction (ii and iii below) according to a method similar to that described by Degens and Reuter (64)..

(ii) Second Ether Extract: A 3:1 slurry of water and meteorite [residue from (i) above] was made, and 0.1 ml of 6M hydrochloric acid and 1.5 g of sodium chloride then added. The resulting mixture was extracted with three successive 20 ml volumes of anhydrous ether by shaking for 1 hour, 3 hours, and 3 hours respectively. The ether extract was removed from the aqueous mixture each time by the centrifuge method. The three 20 ml extracts were then pooled and concentrated to dryness under nitrogen at 20°C. Upon evaporating, yellow crystals were deposited as in the first ether extraction described above; this material was assumed to be elemental sulfur.

The ether extracted material was then taken up in 2 ml of 95% ethanol; this sample is hereafter referred to as second ether extract.

A procedural blank was run which is hereafter designated as second ether blank.

(iii) Third Ether Extract: The meteorite-aqueous mixture from the above described ether extraction was placed under nitrogen at 20°C for 15 minutes in order to remove any residual ether. This aqueous mixture was then refluxed with 25 ml of 6M hydrochloric acid for 4 hours.

The resulting mixture was adjusted to a pH of about 2 with 10 ml of 13% sodium hydroxide, and 10.3 g of sodium chloride then added.

The resulting mixture was shaken with a total of 45 ml of ether and the ether layer decanted. The ether extract was evaporated to dryness under nitrogen at 25°C. The extracted material was dissolved in 2 ml of 95% ethanol and this sample is hereafter referred to as third ether extract.

A procedural blank was run for this sample also, and is designated as third ether blank.

b) Method of Analysis: Ascending paper chromatography was used to analyze the ether extracted material. The procedure followed was essentially the same as that described earlier. The developing solvents employed were the following: (a) benzene-acetic acid-water (125:72:3) referred to as (BzAW); (b) butanol-acetic acid-water (200:50:250), referred to as (BAW); (c) isopropanol-acetic acid-water (160:20:20), referred to as (IpAW). Table VII gives the details of each analysis.

A paranitraniline spray reagent was used to detect the aromatic hydroxy compounds; the reagent was prepared as described by Smith (85) as follows: 0.8 g of paranitraniline was dissolved in a solution of 22 ml of concentrated hydrochloric acid and 475 ml of water; just before use, 10 volumes of the paranitraaniline solution was mixed with 0.2 volumes of 5% sodium nitrite in an ice bath and then 10 volumes of 10% sodium carbonate was added.

A standard was prepared containing the following inorganic substances (0.1 g of each dissolved in 6 ml of 95% ethanol): Sulfur (sublimed; National

TABLE VII
DATA ON THE PAPER CHROMATOGRAPHIC ANALYSIS OF THE ETHER
EXTRACTED MATERIAL

Figure	Sample Analyzed	Sample Designation in Figure	Developing Solvent	Spray Reagent
17	500μl First Ether Extract	U-1	BzAW	Paranitraniline
	500μl First Ether Blank	B-1		
	500μl Second Ether Blank	B-2		
	500μl Second Ether Extract	U-2		
	500μl Third Ether Extract	U-3		
	500μl Third Ether Blank	B-3		
	50 μl Inorganic Standard	S		

18(1)	100μl Third Ether Blank	B-3	BAW	Paranitraniline
	100μl Third Ether Extract	U-3		
18(2)	25 μl Inorganic Standard	S	BAW	Paranitraniline

Package Drugs, Inc.); magnesium sulfate heptahydrate (Recrystallized; Reliable Brand); ferric chloride hexahydrate (Mallinckrodt Analyzed Reagent); ferrous chloride $4\text{H}_2\text{O}$ (Baker Reagent Grade). This standard is hereafter referred to as inorganic standard (S).

III. RESULTS AND DISCUSSION

1. X-Ray Diffraction Analysis. Figure 7 shows the x-ray diffraction spectrum of the non-extractable carbonaceous material. No evidence for graphite was obtained and the material appeared to possess no crystalline form (graphitic substances display a strong intensity signal at an incidence angle, 2θ , of 26.5°). This observation was in agreement with that of Mueller (28) and Kaplan et al. (6), who examined the Cold Bokkeveld and Mokoia meteorites, respectively.

The only significant signals occurred at incidence angles of 18.5° and 35.7° ; these correspond to d-spacings of 4.79–4.82 Å and 2.51–2.52 Å, respectively, and are most probably due to residual mineral matter which was not removed by the hydrochloric-hydrofluoric acid treatment. The featureless spectrum, however, indicates the effectiveness of the acid treatment in removing most of the inorganic materials.

2. Elemental Analysis. The results of elemental analysis of the non-extractable carbonaceous material are given in Table VIII. The major elements found to be present were carbon, oxygen, hydrogen, sulfur and nitrogen. The relatively high content of sulfur is very interesting, and the question arises as to whether or not the sulfur is present as a chemically bonded constituent of the carbonaceous material. This

X-RAY DIFFRACTION SPECTRUM OF THE NON-EXTRACTABLE CARBONACEOUS MATERIAL IN THE ORGUEIL METEORITE

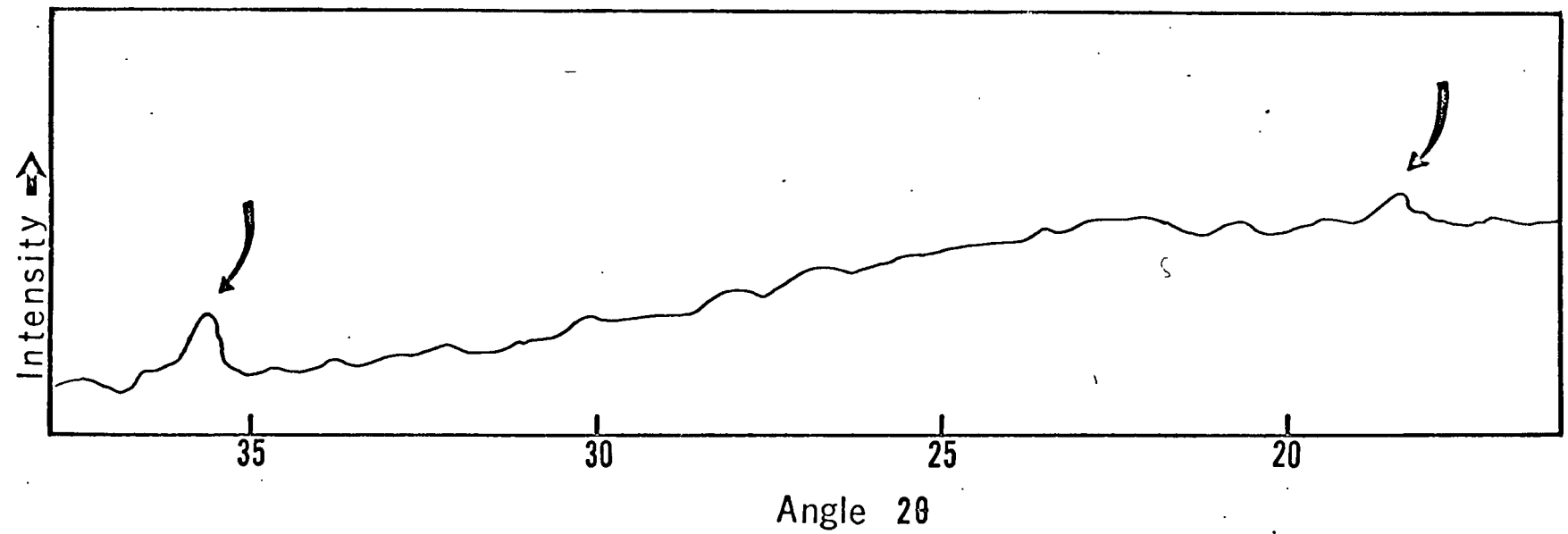


FIGURE 7

TABLE VIII
ELEMENTAL COMPOSITION OF THE NON-EXTRACTABLE CARBONACEOUS MATERIAL
IN THE ORGUEIL METEORITE

Element	%
Carbon	70.39
Hydrogen	4.43
Oxygen*	9.80
Nitrogen**	1.59
Sulfur	6.91
Chlorine	1.22
Fluorine	1.25
Residue (C-H)	4.58

* Determined by the Unterzaucher method

**Determined by the Dumas method

question could not be answered by the present study, however, since the effectiveness of the methanol-benzene in extracting the inorganic sulfur present was not determined [no doubt some, or perhaps most, of the sulfur is inorganic, but it is noteworthy that Dancy and Giedroyc (86) have reported evidence for sulfur being an integral part of the Kimmeridge kerogen].

The presence of chlorine and fluorine (Table VIII) is also very interesting. As pointed out in the Introduction, Mueller (28) found chlorine to be present in the carbonaceous material of the Cold Bokkeveld and suggested that it was present as organic chlorine. Kaplan *et al.* (6) however, has cautioned that this may have been an artifact arising from the chlorinated organic solvents which had been used to treat the material. The equal amounts of chlorine and fluorine found in the present study suggest that these elements may be artifacts since hydrochloric and hydrofluoric acids were used in the isolation procedure.

The relatively low ash value of 4.58% again indicates, as did the x-ray results, the effectiveness of the isolation method in removing the inorganic minerals.

Despite the fact that elemental composition can provide only a very crude picture of structure, it nevertheless does allow for certain comparisons and correlations to be made. Indeed, carbon, hydrogen, and oxygen relationships are often very informative to the organic geochemist in the classification of naturally occurring carbonaceous substances. The compositional data obtained in the present study has been used in a similar manner in an attempt to obtain correlations between the meteorite material and certain terrestrial carbonaceous materials.

Table IX gives the hydrogen/carbon ratio of the meteorite material as determined in the present study, and also shows the hydrogen/carbon ratios of several terrestrial substances as reported by Swain (73). The meteorite has a ratio in the range of that of kerogen and lignite. This is very interesting in view of the work of Schulz and Eloffson (63) who suggested that the insoluble material of the Orgueil was similar to coals and kerogens on the basis of ESR studies of the material.

A very interesting observation presents itself if the compositional data of the meteorite material and various kerogens are further compared. Forsman (74) has plotted carbon, hydrogen, and oxygen percentages of various kerogens, as obtained from the literature, on a triangular compositional diagram. Figure 8 shows the upper part of the triangle; the compositional data for the Orgueil, as obtained in the present study, has been inserted into the diagram for the purpose of comparison. The sum of the C, H, O coordinates of a particular point totals 100 in all cases (i.e., the C, H, O values have been normalized so that their sum is 100%). Also indicated on the diagram are the generalized environments of deposition, and the results obtained, regarding the presence or absence of benzenoid acids, upon oxidation of seven of the kerogen samples.

The essential features of the diagram are the three regions designated "coals", "coaly oil shales", and "non coaly oil shales". Nearly all of the kerogens fall within the areas described by these bands. As discussed by Forsman, this and other data indicates that there are perhaps three structurally different types of kerogens occurring in sedimentary rocks.

CARBON, HYDROGEN, OXYGEN COMPOSITIONAL DIAGRAM OF TERRESTRIAL KEROGEN (74)

AND OF THE NON-EXTRACTABLE CARBONACEOUS MATERIAL IN THE ORGUEIL METEORITE

ENVIRONMENT
 • MARINE
 + NON MARINE
 • UNKNOWN

OXIDATION
 ○ BENZENOID
 △ NON BENZENOID
 • NOT ANALYZED

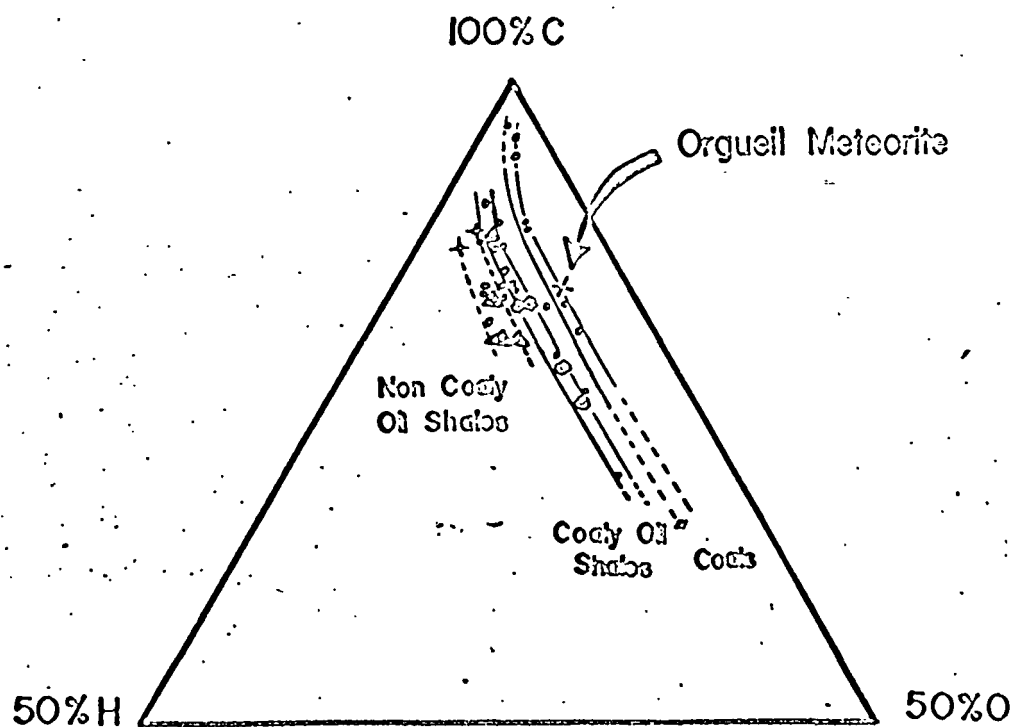


FIGURE 8

TABLE IX
HYDROGEN/CARBON RATIOS FOR ASPHALTS, KEROGEN, COALS AND
THE ORGUEIL METEORITE

Substance	Atomic H/C Ratios
Natural Asphalts*	1.24-1.60
Kerogen from Shales and Dolomite*	0.68-0.90
Lignite*	0.7-1.0
Bituminous Coal*	0.5-0.7
Orgueil (Non-Extractable Carbonaceous Material)**	0.76

* Values taken from Table IX of Swain (73).

**Value obtained in this study.

Those lying within the coal band (this band was determined from published data on the C, H, O contents of a large number of coals) appear to have properties similar to coal and probably have a similar aromatic type structure; those comprising the "non coaly oil shale" kerogens apparently possess more open-chain structures and it was found that three members of this group, upon oxidation, produced no benzenoid acids; kerogens of the "coaly oil shale" group appear to have properties intermediate between the coaly and non coaly kerogens (five kerogens from the "coaly oil shale" group were oxidized, and each produced benzenoid acids).

Inspection of Figure 8 reveals that the non-extractable carbonaceous material of the Orgueil has a C, H, O composition that places it very nicely in the coal band. If the analogy that has been made between the coaly type kerogens and coals (74), can also be made for the meteorite material, this data suggests that the non-extractable material of the meteorite may be structurally similar to coal. Such a picture would be compatible with other recent studies of this fraction of the meteorite organics, as discussed in the Introduction.

Although as yet there is not sufficient data to determine if a correlation exists between elemental composition and depositional environment (marine or non-marine) of kerogens, it is noteworthy that the kerogens which fall within the coal band have been isolated from rocks deposited in a near-shore marine environment (the non-coaly oil shale kerogens are from rocks deposited under both marine and non-marine conditions) (74). This is especially interesting in view of the aqueous environment postulated for the Orgueil parent body (87), and of the similarity in relative

hydrocarbon content between the Orgueil and terrestrial marine sediments (35).

The compositional data obtained in this study also provides information regarding the possibility of the non-extractable carbonaceous material being similar to amorphous carbon. Mueller (28) suggested that the carbon of the Cold Bokkeveld may be present to some extent in such a form, while Kaplan et al. (6) found no conclusive evidence for or against this possibility in the meteorites they studied.

"Amorphous" carbon (there is no truly amorphous carbon), an allotropic form of elemental carbon, may be derived from organic material of plant or animal origin. Carbon black and acetylene black are examples of "amorphous" carbon which, however, may be obtained non-biogenically. Mantell (88) has presented compositional data of various carbon blacks which show these substances to possess the following compositions: Carbon, 92-99% (a few have percentages between 80-90%); hydrogen, 0.5%-1.0%; nitrogen, 0.02%-0.09%; and oxygen, 2.5%-7.0%. Acetylene black also contains a relatively high carbon content (99%), and resembles either carbon black or lamp black in most of its properties (lamp blacks have compositions comparable to carbon blacks) (88). Comparison of this data to that obtained for the meteorite indicates that the meteorite material is notably lower in carbon content, and distinctly higher in both hydrogen and nitrogen content; the oxygen percentages, however, appear to be comparable.

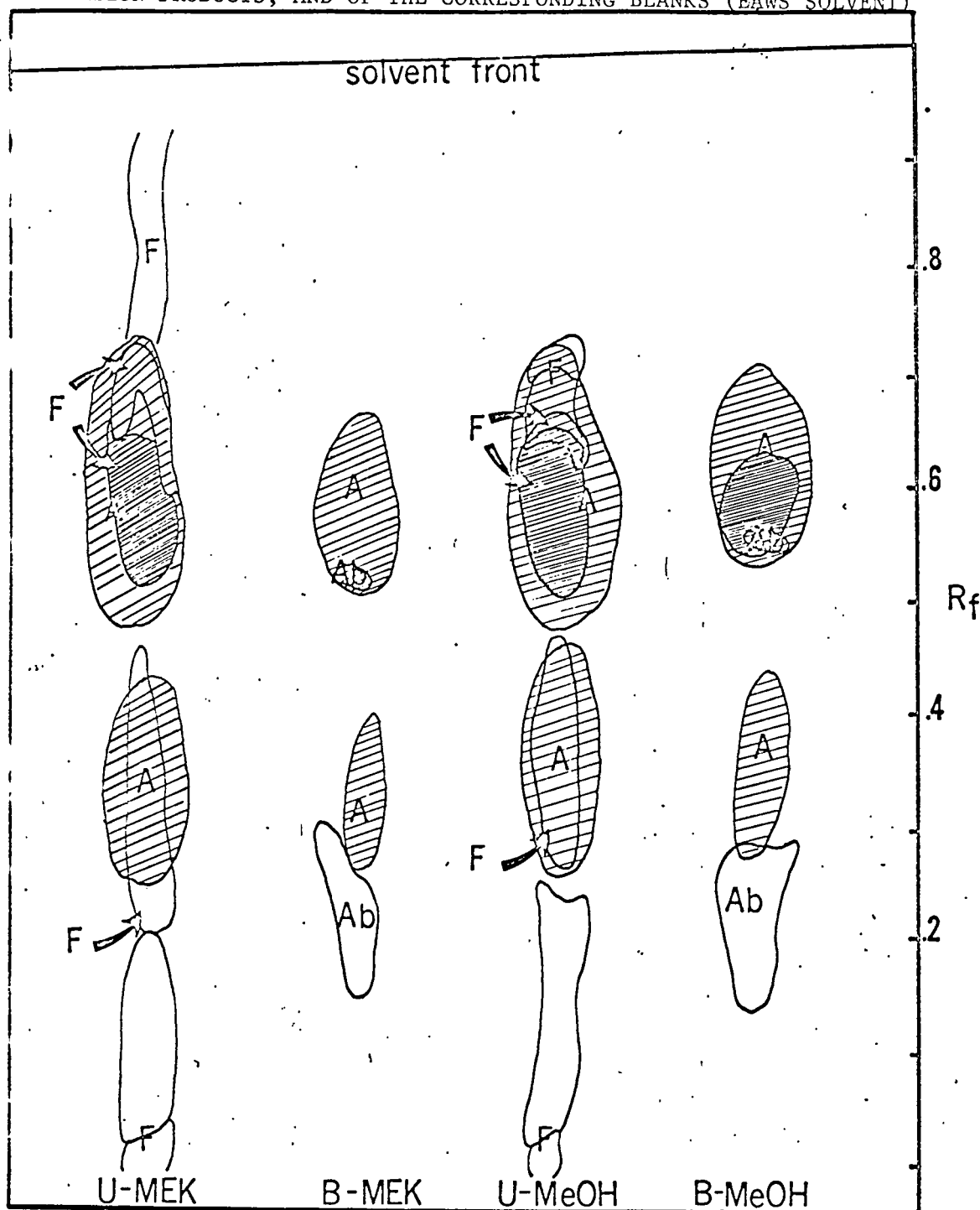
3. Analysis of Potassium Permanganate and Nitric Oxidation Products

a) Permanganate Oxidation Products: Figure 9 shows the MeOH (U-MeOH) and MEK (U-MEK) soluble oxidation products contained no acridine positive components (i.e., substances containing acidic functional groups) which did not also appear in the corresponding procedural blanks. The acridine positive compounds present are probably due to the acids used in the oxidation procedure. The oxidation products did however contain fluorescing materials, which absorbed ultraviolet light and which were absent in the respective blanks (Figure 9). The very weak ultraviolet absorbing regions which appeared only in the blank samples were apparently artifacts since they did not appear in chromatograms (2) and (4) of Figure 10.

Two dimensional chromatography (Figure 10) revealed distinct differences between the MEK soluble and MeOH soluble oxidation products, which were not apparent in the one dimensional chromatogram. The MEK soluble material contained several fluorescing compounds which were absent in the corresponding blank, and the MeOH soluble material, though apparently much less complex, contained an acridine positive component (R_f in EAWS: 0.68-0.75) which did not appear in the MeOH soluble blank.

At first sight it may appear that the results of oxidation do not support the inferences made from the compositional data discussed in the previous section. No definite conclusion can be made on the basis of the permanganate oxidation results; however, since it is quite possible that the time allowed for oxidation was not sufficient to degrade the carbonaceous material to the point of acid production. In support of this

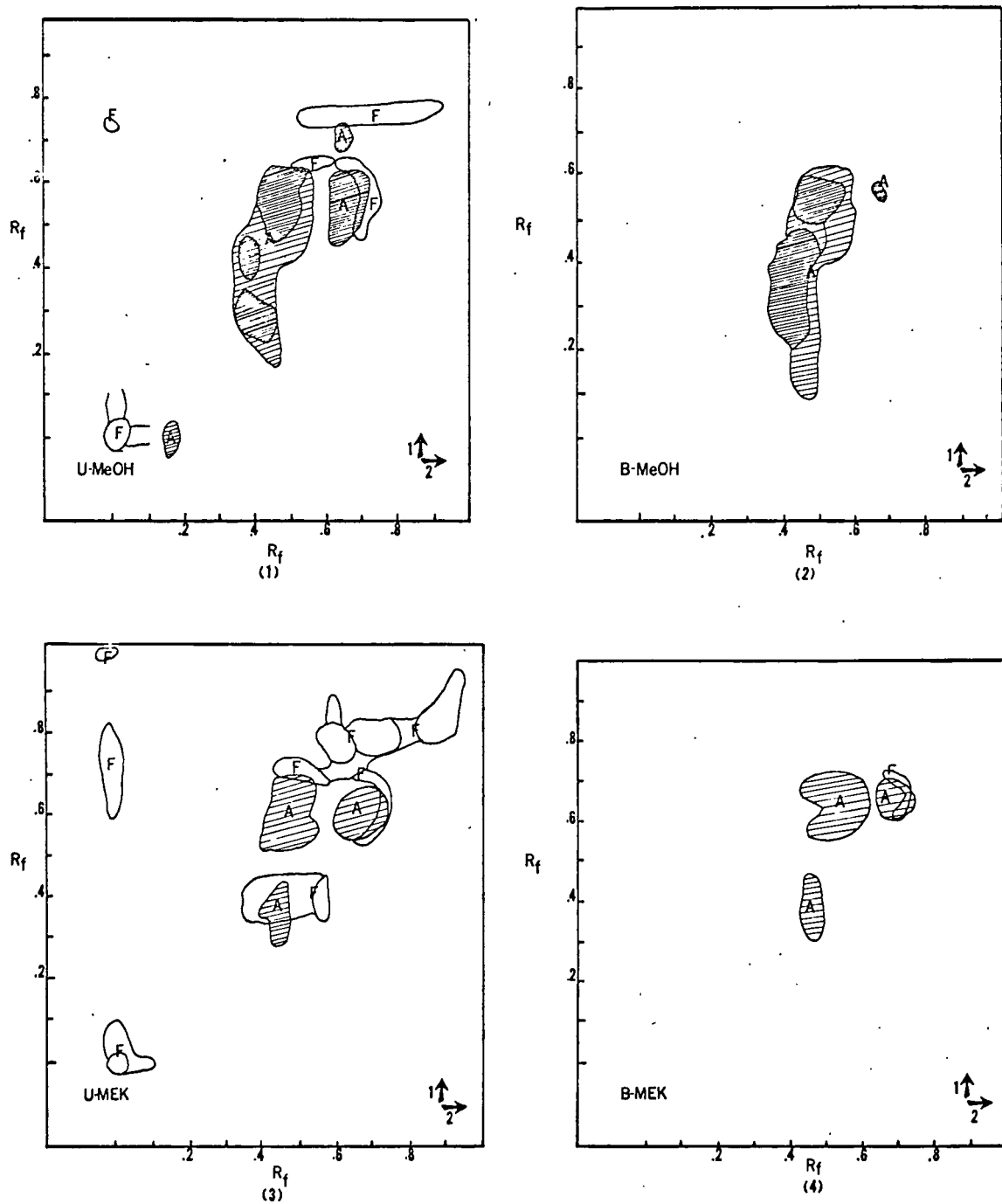
PAPER CHROMATOGRAM OF THE MEK SOLUBLE (U-MEK), AND MeOH SOLUBLE (U-MeOH) OXIDATION PRODUCTS, AND OF THE CORRESPONDING BLANKS (B-MEK, B-MeOH)



Abbreviations: A (acridine positive)
 Ab (ultraviolet absorbing)
 F (fluorescing)

FIGURE 9

TWO DIMENSIONAL PAPER CHROMATOGRAMS OF THE MEK SOLUBLE (U-MEK) AND MeOH SOLUBLE (U-MeOH) OXIDATION PRODUCTS AND OF THE CORRESPONDING BLANKS



(First Solvent: EAWS; Second Solvent: PFW).

Abbreviations as in Figure 9

FIGURE 10

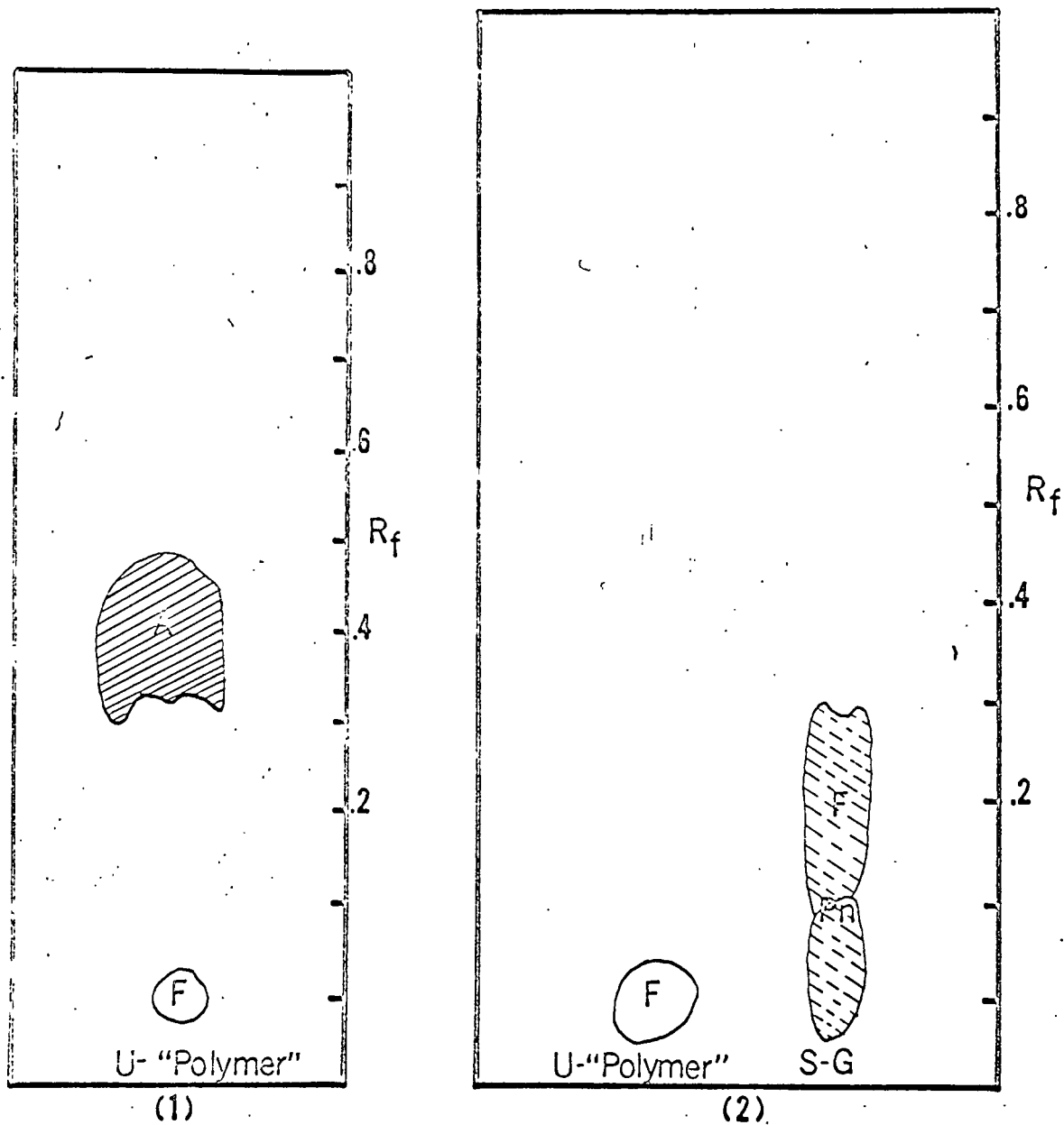
it should be mentioned that for some kerogens, from 34-46% of the carbon present could not be solubilized after treating for as long as 125 hours with alkaline permanganate (74).

It is possible that the so-called acid-insoluble "polymer", which was isolated from the meteorite material following its oxidation (see page 46) could represent the non-completely oxidized, initial breakdown products of the meteorite material. Paper chromatographic analysis of the "polymer" indicated that it was associated with an acridine positive component (R_f : 0.3-0.5), which did not absorb in the ultraviolet region; most of the material, however, remained at the origin in the slightly basic developing solvent, and displayed an orange-yellow fluorescence when exposed to ultraviolet light [Figure 11(1)]. This indicated that the material may be a relatively high molecular weight substance. The fluorescing material was tested with paranitraniline for the presence of aromatic hydroxy groups, but as shown in Figure 11(2) no reaction was observed.

The ultraviolet absorbing properties of the acid-insoluble "polymer" were examined in more detail, and Figure 12(2) shows the results. The spectrum was found to be essentially featureless with increasing absorption in the shorter wavelength region; a definite shoulder was present, however, at 280 $m\mu$, and this may indicate that aromatic structures are present.

Figure 12(1) shows the absorption spectrum of an artificial humic acid (synthesized from sugars), as taken from the literature (73); the spectrum is not significantly different from that of the acid-insoluble

PAPER CHROMATOGRAMS OF THE ACID INSOLUBLE "POLYMER" AND OF GALLIC
ACID (S-G) (EAW SOLVENT)



Abbreviations: A (acridine positive)
F (fluorescing)
Pn (paranitraniline positive)

FIGURE 11

- (1) ULTRAVIOLET ABSORPTION SPECTRUM OF HUMIC ACID SYNTHESIZED FROM SUGAR (73)
(2) ULTRAVIOLET ABSORPTION SPECTRUM OF THE ACID INSOLUBLE "POLYMER"

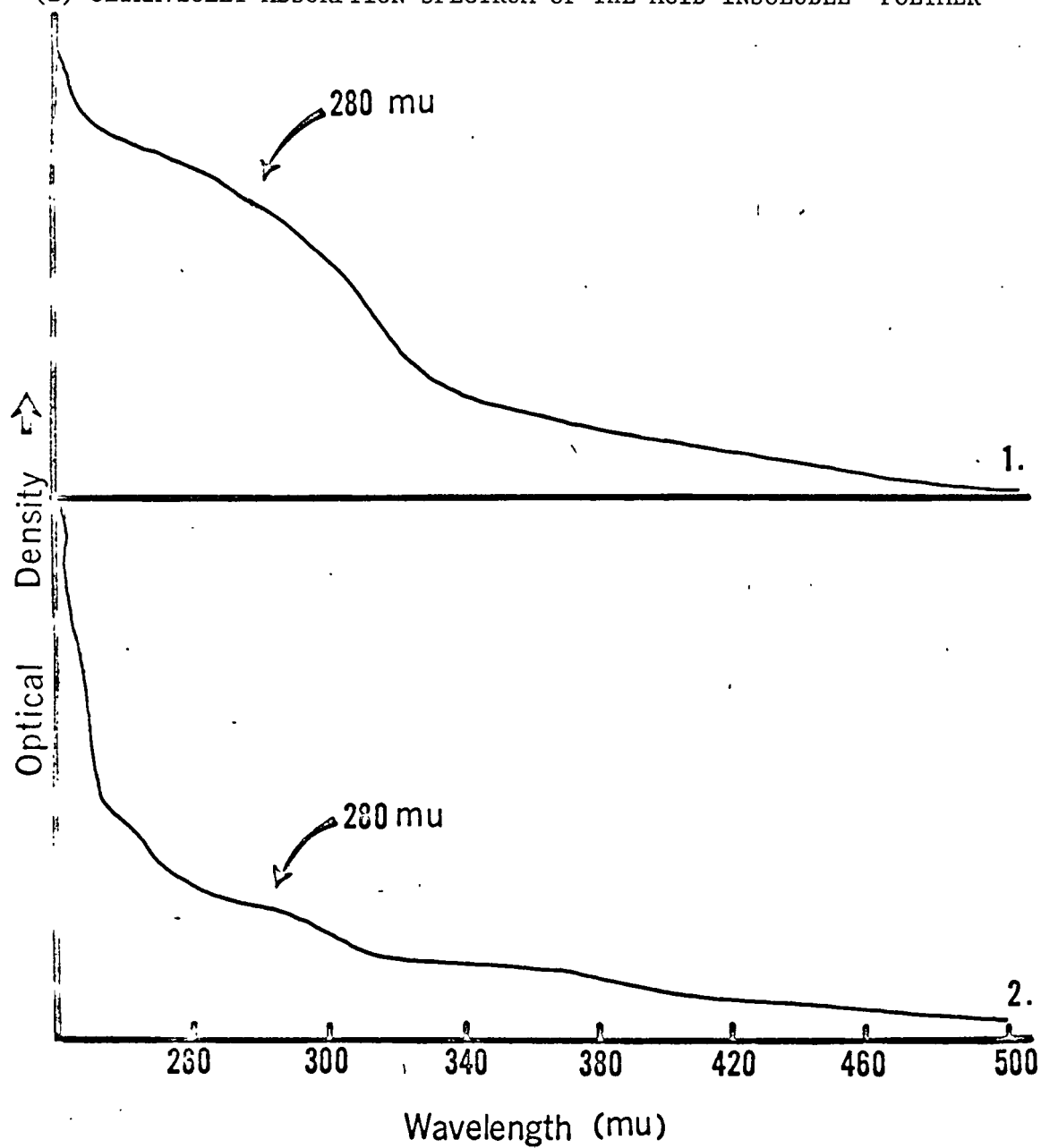


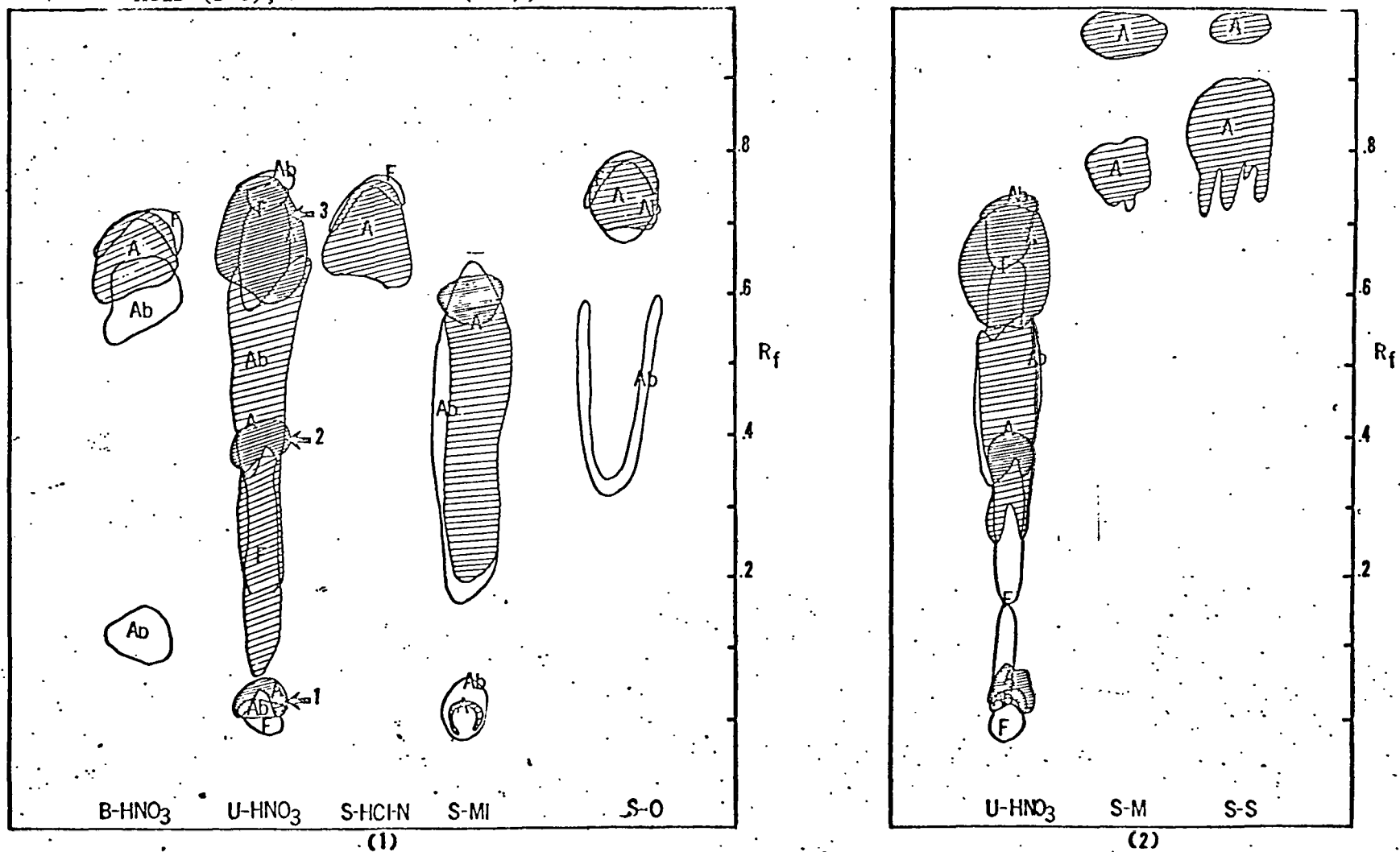
FIGURE 12

"polymer" [Figure 12(2)], and it appears that certain naturally occurring humic acids possess similar spectra, as Kumoda and Miyazato (89) have found that artificial humic acids obtained from glucose display an absorption spectrum similar to soil humic acids. This suggests another interesting analogy between the meteorite material and terrestrial kerogens, for humic acids are considered to be the initial breakdown products of kerogen upon oxidation (74).

b) Nitric Acid Oxidation Products: As indicated in Figure 13, the HNO_3 oxidation products (U- HNO_3) contained ultraviolet absorbing, fluorescing, and acridine positive components. Three distinct acridine positive regions were observed, which possessed the following respective R_f values in the EAWS developing solvent: 0.02-0.08 (1), 0.35-0.40 (2), and 0.58-0.78 (3). The region of highest R_f , designated as (3) also appeared in the corresponding blank sample (B- HNO_3) and it appears that this area contained residual inorganic acids arising from the procedural method; a standard made of hydrochloric and nitric acids (designated as S-HCl-N) showed an identical acridine positive region. The ultraviolet absorbing spot (R_f : 0.80-1.7) which appeared in the blank sample, but not in the unknown, was probably an artifact which arose in processing the blank run.

Because oxalic acid is generally one of the oxidation products of coal and kerogen, this compound was analyzed for in the oxidation products of the meteorite material. As shown in Figure 13(1), oxalic acid (S-O) has an R_f value which corresponded to region 3 of the unknown sample; even though it may be partially responsible for this acridine positive

PAPER CHROMATOGRAMS OF THE HNO_3 OXIDATION PRODUCTS (U- HNO_3), CORRESPONDING BLANK (B- HNO_3), A MIXTURE OF HYDROCHLORIC AND NITRIC ACIDS (S-HCl-N), MELLITIC ACID (S-Ml), OXALIC ACID (S-O), MALONIC ACID (S-M), AND SUCCINIC ACID (S-S) (EAWs SOLVENT)



Abbreviations as in Figure 9

FIGURE 13

region, the possible inorganic acids present in the oxidation mixture (as discussed above) prevents any definite conclusion to be made.

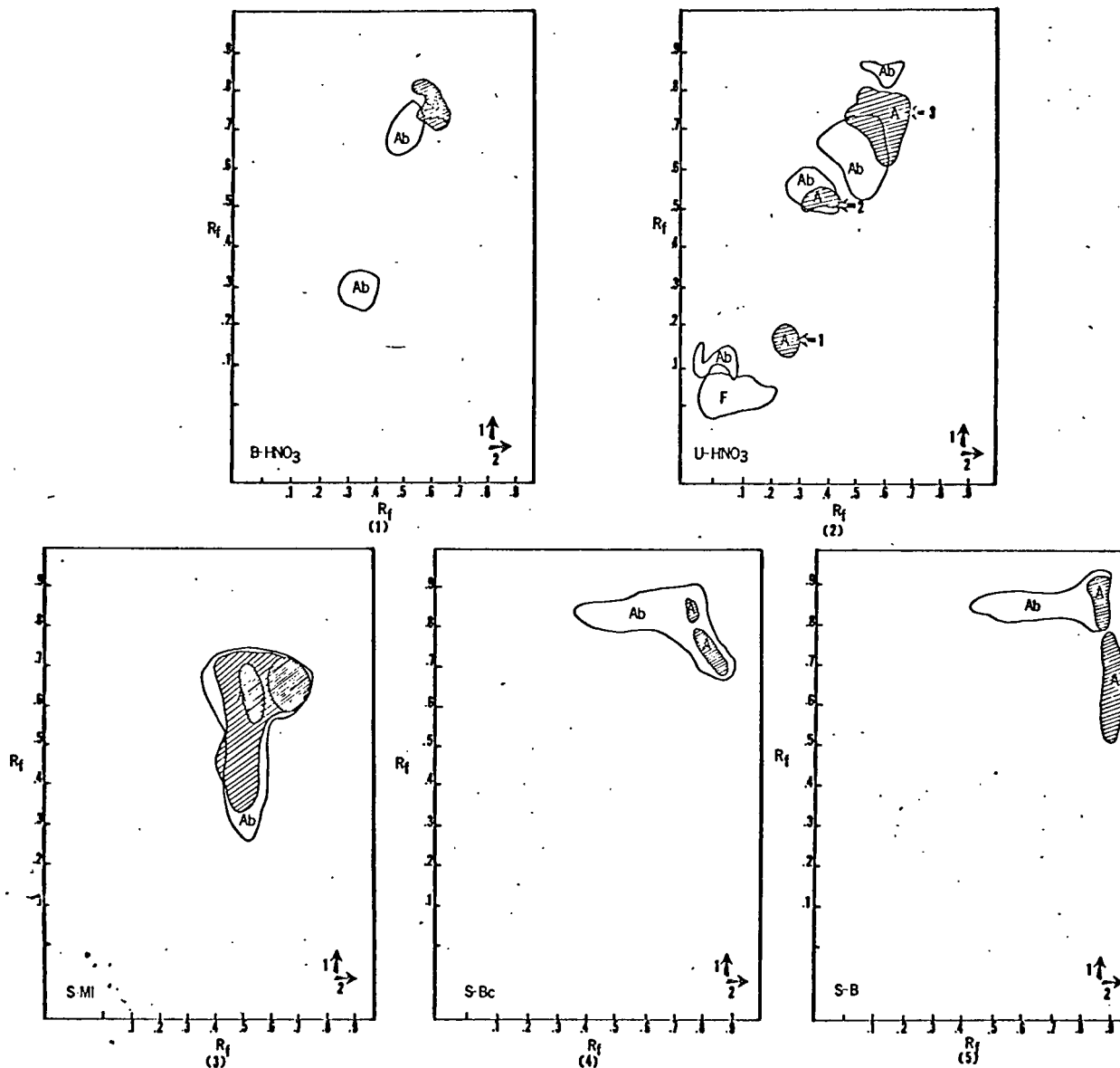
The non-acridine, ultraviolet absorbing region which appeared in the oxalic standard was apparently due to an impurity in the standard.

Neither malonic acid (S-M) nor succinic acid (S-S) appeared to be present in the oxidation products [Figure 13(2)]. This observation is in agreement with the previously discussed compositional data, for it appears that dibasic acids higher than oxalic are characteristic oxidation products of less aromatic carbonaceous substances, such as the non-coaly kerogens (84,90).

The production of benzenecarboxylic acids upon oxidation has been used as an indication of ring condensation in coal; specifically, it has been found that the yields of mellitic acid from coals increases with rank (75,76). Figure 14 shows the results of two dimensional chromatography of the nitric acid oxidation products, the corresponding blank, and of the following standard acids: mellitic acid (S-Ml); 1,2,4,5 benzenecarboxylic acid (S-Bc); 1,2,3 tribenzenecarboxylic acid (S-B). The data indicated that there were no detectable amounts of 1,2,3 tribenzenecarboxylic acid and 1,2,4,5 benzenecarboxylic acid. In addition, the gross similarity between mellitic acid and the unknown (U-HNO_3) that was apparent in Figure 13(1) was not as evident by the two dimensional technique. A more definitive method would be necessary, however, before the presence or absence of these acids can be ascertained.

Figure 15 shows the results of an attempt to determine if the acridine positive regions of Figure 13(1) designated as (1), (2), (3), were

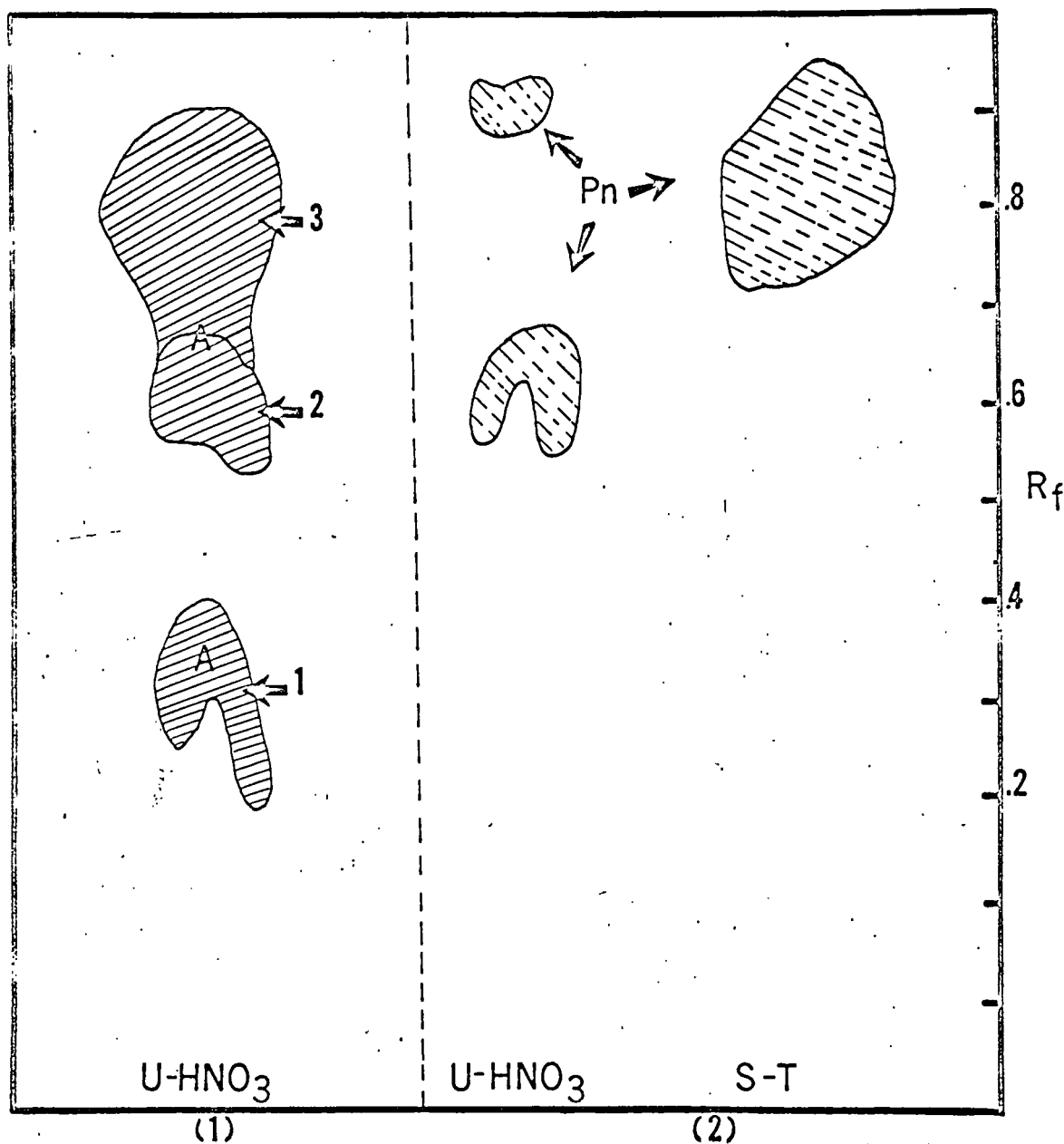
TWO DIMENSIONAL PAPER CHROMATOGRAMS OF THE HNO_3 OXIDATION PRODUCTS (U- HNO_3), CORRESPONDING BLANK (B- HNO_3), MELLITIC ACID (S-Ml), 1,2,4,5 BENZENECARBOXYLIC ACID (S-Bc), AND 1,2,3 BENZENETRICARBOXYLIC ACID (S-B) (FIRST SOLVENT: EAWS: SECOND SOLVENT: PFW)



Abbreviations as in Figure 9.

FIGURE 14

PAPER CHROMATOGRAMS OF THE HNO_3 OXIDATION PRODUCTS (U- HNO_3), AND OF 2,4,6 TRIHYDROXY BENZOIC ACID (S-T) (EAWs SOLVENT)



Abbreviations: A (acridine positive)
Pn (paranitraniline positive)

FIGURE 15

also paranitraniline positive. Chromatogram 15(1) was sprayed with acridine and chromatogram 15(2) with paranitraniline. It was observed that region (1) consisted of an acridine positive material which was not sensitive to the paranitraniline, and thus did not contain hydroxy aromatic acids. If such acids were present in this region, they should be more sensitive to the paranitraniline reagent than to the acridine reagent (it was found that as little as 0.4 μg of 2,4,6 trihydroxybenzoic acid could be detected by the paranitraniline reagent, while the acridine could only detect 3-4 μg of this acid.)

Region (2) was found to be paranitraniline positive, and a small part of region (3) was apparently sensitive to the reagent. This suggests that (2) may be due to the presence of an aromatic hydroxy acid, and that (3) contains a similar substance. There is the possibility, however, that these may be artifacts since the procedural blank was unfortunately not also tested with the reagent.

The result of infrared analysis of the nitric acid oxidation products is given in Figure 16. The spectrum was characterized by definite maxima occurring at 3.2-3.4 μ , 7.9-8.1 μ , and 9.2-9.8 μ , respectively. The 3.2-3.4 μ band is characteristic of the C-H stretch of aromatic compounds, and the 7.9-8.1 band is observed for C-O linkages such as those occurring in phenols, esters, and ethers. The intense band at 9.2-9.8 μ may indicate the presence of ethers, and/or aromatic rings (singly or condensed). Residual silicate minerals may however also contribute to this band, since it is displayed by Si-O linkages.

INFRARED ABSORPTION SPECTRUM OF THE HNO_3 OXIDATION PRODUCTS (UNKNOWN) DISSOLVED IN CARBON DISULFIDE

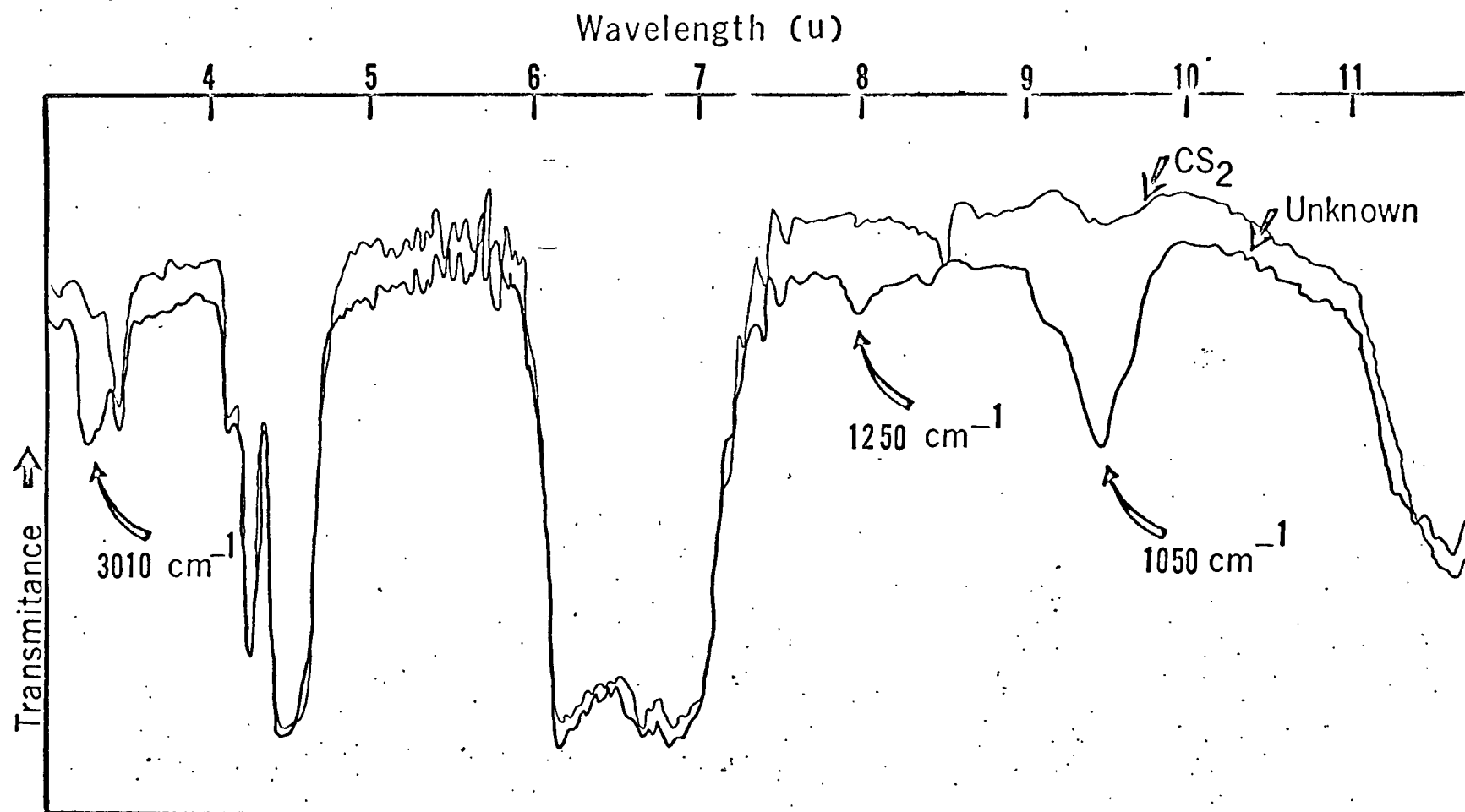


FIGURE 16

The C-H stretch of carboxylic acids which occurs at $3.8-3.9\mu$ was not observed in the present case, and the carbon disulfide bands prevented determination of the possibility of aliphatic structures. The acids detected by paper chromatography thus were not observed by infrared analysis, which suggests that these substances were not sufficiently soluble in the carbon disulfide to allow their detection. The use of a more polar solvent may provide more information in this regard, despite the difficulties which may be encountered due to the absorption of many of such solvents in the same region of the spectrum where the carboxylic acids absorb.

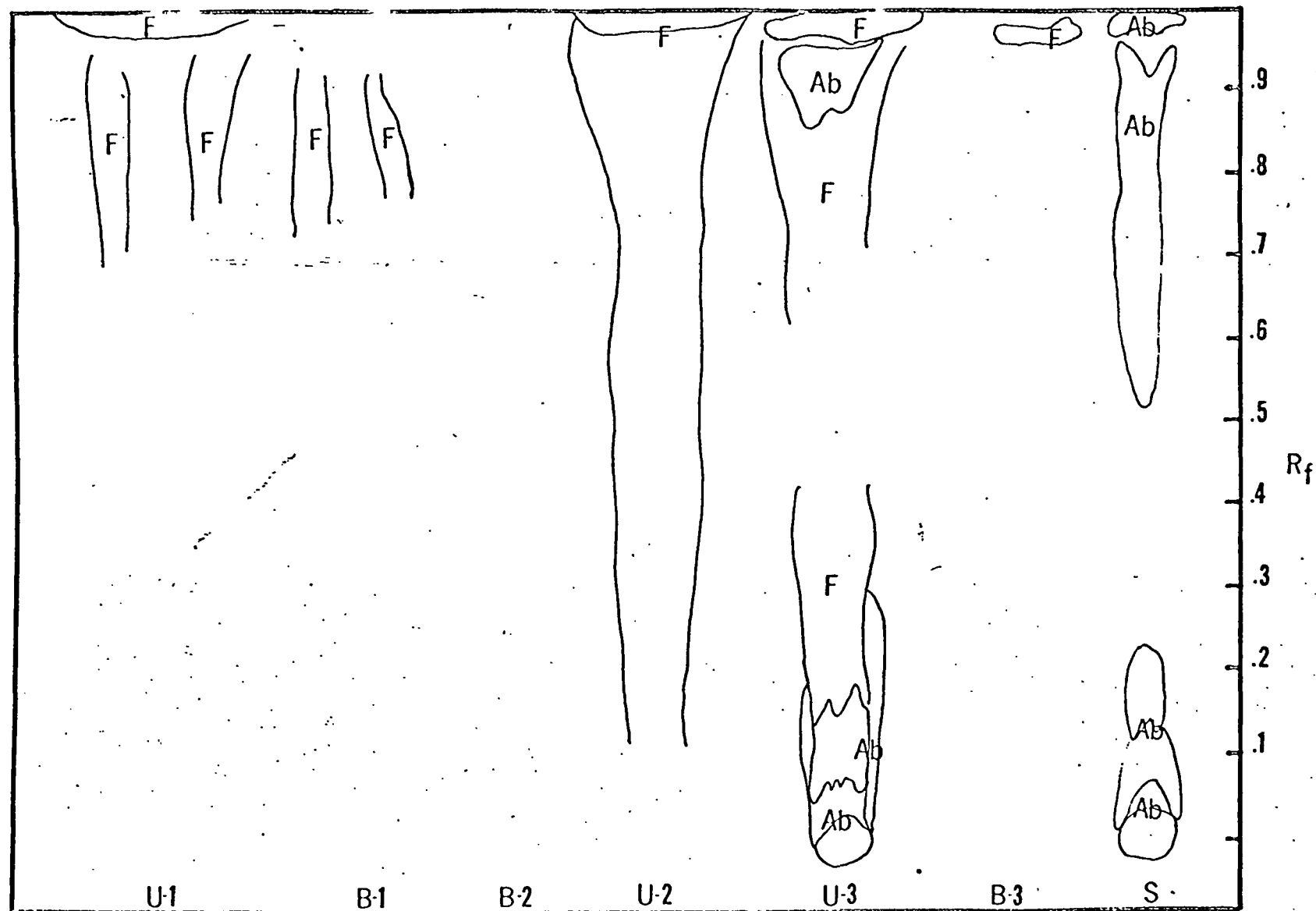
The Nujol technique and KBr disc method were both tried in the present analysis, but without success due to the resinous nature of the oxidation sample. This difficulty may be eliminated however if the soluble oxidation products are separated from the resinous material prior to analysis.

4. Analysis for Aromatic Hydroxy Compounds. Paper chromatographic analysis indicated that the first, second, and third ether extracts of the meteorite (designated as U-1, U-2, and U-3, respectively) contained no paranitraniline positive compounds (Figure 17). The third ether extract did contain several ultraviolet absorbing compounds, but this was probably due to inorganic material, as a standard (S) showed similar absorbing areas (this standard contained some of the major inorganic substances present in the Orgueil). Using a different solvent (BAW), Figure 18(1) shows that the third ether extract contained a substance exhibiting a green coloration when sprayed with paranitraniline

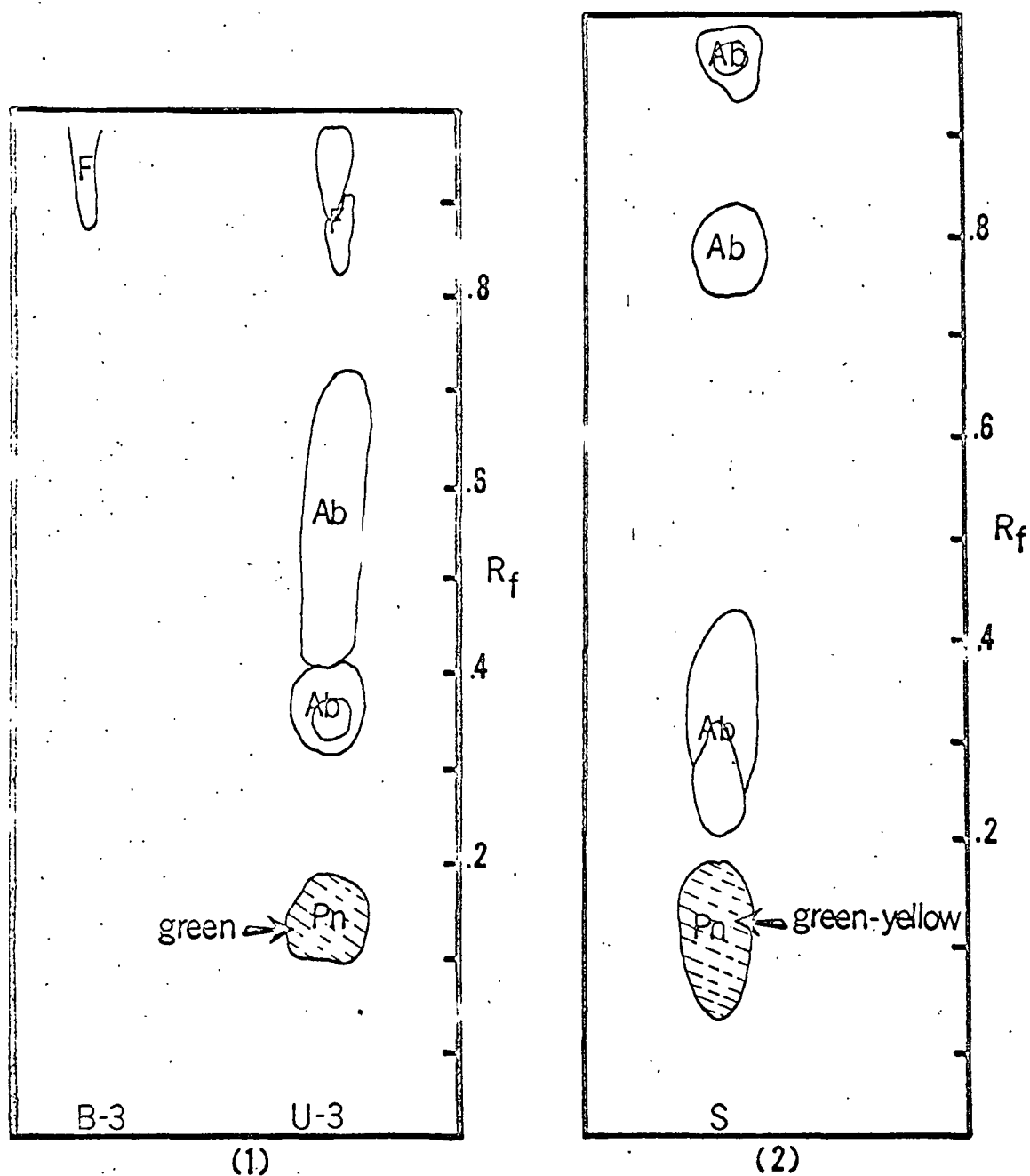
FIGURE 17

PAPER CHROMATOGRAM OF THE FIRST (U-1), SECOND (U-2), AND THIRD (U-3)
ETHER EXTRACTS OF THE ORGUEIL METEORITE, CORRESPONDING PROCEDURAL
BLANKS (B-1, B-2, B-3), AND INORGANIC STANDARD (S) (BzAW SOLVENT)

Abbreviations: Ab (ultraviolet absorbing)
F (fluorescing)
Pn (paranitraniline positive)



PAPER CHROMATOGRAMS OF THE THIRD ETHER EXTRACT OF THE ORGUEIL METEORITE (U-3),
CORRESPONDING PROCEDURAL BLANK (B-3), AND INORGANIC STANDARD (S) (BAW SOLVENT)



Abbreviations as in Figure 17.

FIGURE 18

(R_f : 0.10-0.19). This material is apparently inorganic, however, as the synthetic standard also contained a similar substance as shown in Figure 18(2).

As pointed out in the Introduction, Kaplan et al. (6) have reported the presence of diazonium sensitive compounds in hydrochloric acid hydrolysates of several meteorites, including the Orgueil, and have indicated that they were aromatic hydroxy compounds or perhaps amines. They, as well as Nagy et al. (29) were unable, however, to detect hydroxy organic compounds when more non-polar solvents were used to extract the meteorites. The results of the present study, using ether as the extraction solvent, thus appear to be in agreement with those of the above mentioned investigators. In addition, however, the sensitivity to the paranitraniline reagent, which was observed in the present study for the inorganic materials, may indicate that many of the diazonium sensitive compounds which were detected by Kaplan and coworkers in acid hydrolysates were due to inorganic salts. The work of Steelink et al. (42), as discussed in the Introduction, provides special evidence that this may be true, as they have studied the chromatographic and spectral similarities between phenols and certain inorganic salts.

5. Origin of the Non-Extractable Carbonaceous Material. Although much more definitive data will be necessary before the precise chemical structure of the non-extractable carbonaceous material can be ascertained, the similarities which have been presented between the meteorite material and carbonaceous substances of biogenic origin such as coal and kerogen, suggest that the bulk of the carbon in the Orgueil is

present in the form of a condensed aromatic structure associated with polar oxygenated functional groups. Regarding the origin of this material, it appears that on the basis of the data obtained in this and other studies, three possibilities present themselves:

(i) That the meteorite material, though apparently similar in compositional and other aspects to terrestrial substances of biogenic origin, originated via a non-biogenic process.

(ii) That the meteorite material originated from terrestrial biogenic materials.

(iii) That the meteorite material originated from extraterrestrial biogenic materials.

Although the third of the above possibilities is conceivable, this author considers on the basis of evidence presently available that either of the first two possibilities is the more probable explanation for the origin of the meteorite material.

The theory of Urey (91) can be invoked if the material is considered to originate from terrestrial biogenic substances. Based on various lines of evidence, Urey has proposed that some or perhaps most of the stony meteorites (including the Orgueil and related carbonaceous chondrites) come from the moon. He suggests that the moon became contaminated with terrestrial material during its escape from or capture by the earth and that any biological material in these meteorites may ultimately be of terrestrial origin.

The work of Dayhoff and co-workers (92) perhaps provides the best evidence for a non-biogenic origin for the meteorite material. These

workers have made calculations representative of thermodynamic equilibrium processes under many conditions of temperature, pressure, and elemental composition. From this they theoretically determined the relative abundances of organic compounds which would be present in prebiological atmospheres. It was found that abundant aromatic and polynuclear aromatic structures could be formed within a definite carbon, hydrogen, and oxygen compositional region which they designated as the "asphalt" region.

It can be shown that the compositional data obtained in the present study placed the meteorite material well in the carbon-rich area of the asphalt region, indicating that such material could have originated abiogenically under conditions of thermodynamic equilibrium. Studier et al. (93) have suggested that the extractable meteoritic organics may have originated from the primeval solar nebula under conditions approximating thermodynamic equilibrium.

Finally, it should be mentioned that such an origin would be compatible with the apparent absence of amino acids and hydroxy aromatic compounds as indicated in the present study, since these type substances were calculated by Dayhoff and coworkers to be present in only minor amounts relative to the more highly condensed aromatic structures.

III.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSION

ANALYSIS FOR AMINO ACIDS. Types I, II, and III carbonaceous chondritic meteorites were analyzed for their amino acid content employing methods similar to those used to isolate amino acids from terrestrial sediments. An automatic ion-exchange chromatographic technique indicated that only one of these meteorite samples, the Murray, contained ninhydrin positive compounds identified as common protein amino acids. The Mokoia and Lancé meteorites contained no detectable amounts of these type acids. The trace amounts of amino acids found in the Orgueil were not above those present in the procedural blank, and are considered to have arisen from contamination acquired during the analysis.

The amount of amino acids found in the Murray was much higher than that found in the procedural blanks, and thus did not arise from contamination during analysis. Available data indicated, however, that the amino acids found were not indigenous to the meteorite sample, but originated from terrestrial contamination acquired since its fall. This contamination most probably arose over the years from handling of the sample (though apparently slight) and from remnants of once-living microbial organisms which had been deposited in the meteorite.

Finally, from the results of the present study, other meteorite studies (38,41) and contamination studies (45,46,47,69), it appears that there is yet no conclusive experimental evidence for the indigenous presence of amino acids in carbonaceous chondrites.

ANALYSIS OF THE NON-EXTRACTABLE CARBONACEOUS MATERIAL.

1. Analysis of the Non-Extractable Material and Its Degradation Products

The bulk of the carbonaceous material in the Orgueil meteorite was analyzed by physical and chemical methods.

Elemental analysis indicated that the major elements present in the substance were carbon, hydrogen, oxygen, nitrogen, and sulfur. The sulfur content was found to be relatively high and this undoubtedly was due, at least in part, to inorganic or elemental sulfur; to what extent organic sulfur may be present was not determined. On the basis of x-ray diffraction and compositional data, the non-extractable material was considered to be similar to terrestrial carbonaceous materials such as lignitic coals and coaly type kerogens. This suggests that it is a macromolecule having a condensed aromatic structure associated to some extent with polar oxygenated functional groups. Future work is necessary however before such a structural picture can be unequivocally established.

Paper chromatographic analysis of the oxidative degradation products of the meteorite material suggested the presence of soluble ultraviolet absorbing, fluorescing, and acridine positive (suggesting the presence of acidic groups) compounds. The exact identity of the compounds present could not be ascertained because of the complex nature of the mixture. Infrared analysis, however, suggested that aromatic, hydroxy aromatic, ester, and ether compounds may be present. An acid insoluble substance was isolated from the oxidized meteorite material by extraction with

alkali. Paper chromatographic and spectral properties of this substance suggested that it may be of relatively high molecular weight, and may represent the non-completely oxidized, initial breakdown products of the meteoritic carbon.

A more detailed study employing more definitive methods of analysis is needed before the true chemical nature of these degradation products can be elucidated.

2. Analysis for Aromatic Hydroxy Compounds in the Soluble Meteorite Organics

Soluble aromatic hydroxy compounds were searched for in ether extracts of the Orgueil meteorite, employing methods which have been used to extract phenolic substances from terrestrial sediments. Sensitive paper chromatographic methods failed to detect any such compounds in the meteorite sample.

3. Origin of the Non-Extractable Carbonaceous Material

Three possible origins for the non-extractable carbonaceous material were considered. These were that it originated: (1) via non-biogenic processes, (2) from terrestrial biogenic materials, or (3) from extraterrestrial biogenic materials. (1) or (2) was considered to be the most probable origin for the material on the basis of data presently available.

IV.

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