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Analysis for Sulfur Compounds in Lipid Extracts from the Orgueil Meteorite

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Abstract

Solvent extracts of the Orgueil carbonaceous meteorite were investigated by thin-layer chromatography, ultraviolet, infrared, and mass spectrometry, and by ultramicro elemental analysis for sulfur. Long chain thiols were absent but trace amounts of open-chain sulfides and some heterocyclic compounds containing sulfur appear to be present in the meteorite lipid fraction. The conditions for the formation of the sulfur compounds are in agreement with the generally accepted concepts regarding the environment of the meteorite parent body(ies). The meteorite lipid fraction appears to differ in part from petroleum.

Introduction

NINETEEN STONES from a total of approximately one thousand authentic meteorites are known to contain organic matter, and are therefore classified as carbonaceous. The organic substances in these meteorites may amount to as much as 7% by weight, although only a small fraction of this material is soluble in common solvents. The remainder of the material appears to be a type of random polymer, perhaps similar to kerogen in sedimentary rocks or tarry products from abiological syntheses (1,2).

In addition to organic matter, carbonaceous meteorites contain clay-type minerals and also water up to 20% by weight (3). Boato's determination of the deuterium/hydrogen ratios of the bound water distilled out of the stones at elevated temperatures indicated that part of the water present in the Orgueil meteorite had significantly higher values than the known deuterium/hydrogen ratios of terrestrial waters (4). The presence of minerals known to be formed at low temperatures in Orgueil is generally accepted to indicate that the meteorite has been subjected only to low temperatures from the time it was on the parent body until it reached the earth. During its passage through the earth's atmosphere, the interior of the stone remained relatively cool even though the stone's outer fused crust, only a few millimeters thick, was formed by high temperatures. The presence of gypsum in Orgueil indicates that the temperature in the interior of the various stones was less than 90C, assuming that this mineral can set an upper temperature limit for the stone. Mineralogical studies of stony meteorites have suggested that the parent body of the meteorites contained water; mineral phase equilibria studies have pointed to a reducing and somewhat alkaline environment (5). The age of the mineral matter in these stones has been determined to be 4.6 billion years (6).

Urey recently suggested that the carbonaceous meteorites might have come from the moon, and that in early geological times the moon could have been contaminated by terrestrial biological matter (7). According to this theory, the organic material present in the carbonaceous meteorites may represent a remnant of early terrestrial life.

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The lipid fraction of the extractable organic matter in the Orgueil meteorite represents only a very small part of the total organic matter, but the variety of compound classes identified to date in such extractable material is remarkable. Berthelot, in 1868, identified branched and/or *n*-alkane type hydrocarbons in the Orgueil meteorite, which had fallen only four years earlier (8). Nagy, Meinschein and Hennessy confirmed the presence of *n*-alkanes and also found other saturated and cyclic hydrocarbons in a distillation experiment conducted nearly 91 years later (9). In this study, mass spectroscopy in conjunction with ultraviolet and infrared absorption analyses identified steranes, saturated steroid nuclei, and several classes of aromatic compounds, including naphthalenes, acenaphthalenes, acenaphthylenes, and larger fused ring systems (10). Briggs and Mamikunian (11) reported the presence of several aromatic acids, including some hydroxy and acetoxy derivatives.

Nagy and Bitz isolated a series of fatty acids ranging from C_{14} to C_{28} (12). This work has been confirmed by Hayatsu (13). A small levo rotation has been obtained in three laboratories on the Soxhlet extracts of three Orgueil meteorites using benzene/methanol (6:4, v/v) with 2.8% KOH added in the flask for simultaneous saponification (14). The optical rotation work has yet to be confirmed by other invesigators; Hayatsu (13) has carried out a variation of the procedure of Nagy et al. without detecting any optical rotation in the extract.

In addition to the lipids, Hodgson and Baker (16) have reported the presence of a pigment indistinguishable from vanadyl-porphyrin in the organic extract from the meteorite. No chlorins indicative of recent matter were detected, which points to ancient rather than recent organic material, if an analogy can be drawn between the meteorite and terrestrial sedimentary rocks (16). Hayatsu detected pyrimidines and purines, although his work has yet to be duplicated by other laboratories (15).

Amino acids in varying amounts have been reported by several investigators (17–19). The significance of these results again must await more accurate and reproducible analyses, but, Hamilton has already shown that the percentages of the free amino acids were comparable to those from a single fingerprint (20). This finding tends to emphasize the fact that the interior of the Orgueil stones was relatively uncontaminated. In this connection, Oro has recently submitted values for free fatty acids from fingerprints (22).

Both hydrocarbons and elemental sulfur have been identified in the Orgueil meteorite by earlier investigators (9,10,14,21). If both were present under conditions favorable for reaction, organic sulfur compounds would be expected products which would be extracted in the lipid fraction. Alkanes, free sulfur, and a variety of sulfur compounds are present in crude oil although their origin in petroleum is not firmly established. The American Petroleum Institute Research Project 48 has systematically identified at least 40 short open-chain thiols, 30 short open-chain sulfides, and an equal number of cyclic sulfur compounds in petroleum distillates (23–28).

The occurrence of these compounds in the Orgueil meteorite could conceivably indicate a history similar to that for the formation of petroleum on earth (29), whereas their absence might point to a dissimilar environment particularly in regard to the sedimentation-erosion cycle (30,31). The presence of hydrocarbons, sulfur, and possibly organic sulfur compounds in the meteorite must also be evaluated in terms of the generally accepted environment of the Orgueil meteorite derived from mineralogical data, that is a low temperature, aqueous, alkaline, and slightly reducing conditions on the parent body (5, 32,33).

Materials

The following reagents were used:

Octadecane, 1-octadecene, 1-octadecanethiol, Matheson, Coleman and Bell Company.

Sulfur flowers, Baker and Adamson Company; dissolved in hexane to give a 1 mg/ml solution.

Di-n-octadecyl trisulfide, obtained through the courtesy of N. Nicolaides of the University of Oregon Medical School.

Rhodamine 6G, Allied Chemical Corporation; 1 ml aqueous stock solution (1 mg/ml) diluted with 100 ml water to give a 0.001% solution.

Hexane, chloroform, carbon tetrachloride, methanol (spectro quality) Matheson, Coleman and Bell; freshly distilled before use in 300 mm columns packed with Raschig rings.

Ether, absolute anhydrous, Mallinckrodt Chemical Company; freshly distilled before use.

Acetic acid, glacial, Baker and Adamson; distilled before use.

Silica Gel, Plain, Research Specialties Company, Richmond, California.

Magnesium silicate, synthetic; ratio of magnesium oxide to silica, 2:5; moisture, 12%; Allegheny Industrial Chemical Corporation, Butler, New Jersey.

Sodium sulfide, Baker and Adamson Company; crystal, 0.23 mg/ml of water.

N, N-dimethyl-p-phenylenediamine, Matheson, Coleman and Bell Company; 0.03 g in 10 ml water. To this solution 20 ml concentrated sulfuric acid was added, and then diluted to 100 ml with water.

Ferric ammonium sulfate, Mallinckrodt; crystal, 12.5 g in 2.5 ml concentrated sulfuric acid diluted to 100 ml with water.

Zinc acetate, sodium acetate, and sodium chloride, Baker and Adamson Company; 6.0 g zinc acetate, 1.0 g sodium acetate, 5.1 mg sodium chloride, diluted to 100 ml with water.

Experimental

The organic matter extracted from the Orgueil meteorite was first examined by thin-layer chromatography (TLC), and subsequently the main components were isolated by preparative TLC. These major fractions were subjected to infrared and ultraviolet spectroscopic analysis, ultramicroanalysis for sulfur, and mass spectrometry.

Extraction of Stones

Samples of the Orgueil meteorite used in this investigation were obtained from the Montauban Museum and the Museum National d'Histoire Naturelle, Paris, France. The samples were transferred with solvent-cleaned forceps or spatulas into glassware cleaned with a mixture of hot sulfuric and nitric acids (85:15, v/v). The lipid fraction was extracted from the meteorite samples ground in an acid-cleaned mortar. The extractions were carried out with chloroform at room temperature on a mechanical shaker. The Paris stone was also extracted with tetrahydrofuran after the initial chloroform fraction was removed. The extracts were evaporated under nitrogen (water pumped and filtered through a Matheson Molecular Sieve gas purifier). The samples were redissolved in hexane, carbon tetrachloride or methanol for spectroscopic analyses and TLC.

The ultraviolet and fluorescence spectra were obtained with a DK-2A Beckman spectrophotometer. In the fluorescence measurements, samples placed in quartz cells were excited with 365 mμ radiation only. The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer using 1.0 mm cavity NaCl cells and NaCl optics.

Thin-Layer Chromatography

After the thin layers were examined to detect the composition of the extracts, preparative TLC was used to isolate the major components from elemental sulfur. The TLC technique for determining sulfur and sulfur compounds in lipid fractions has been described recently in this journal (21), and a previous TLC of the saponified material from the Orgueil meteorite has also been published (14).

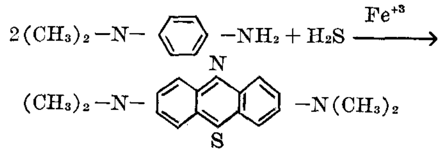
In this investigation a mixture of Silica Gel, Plain, and 10% (by weight) magnesium silicate adsorbent required thorough washing before it was acceptable for preparative chromatography. After sieving the magnesium silicate through a 200-mesh screen, the adsorbent was washed in a fritted glass funnel with the following solvents in order to remove impurities: *n*-hexane, *n*-hexane-acetic acid, (99:1, v/v), carbon tetrachloride, and methanol. The clean adsorbent was then dried and activated for 24 hr at 150C before storing it in glass stoppered flasks until plates were prepared. Each batch of adsorbent was first checked for purity by washing 5 g of adsorbent with 50 ml of hexane and then hexane-ether-acetic acid (70:30:1, v/v/v), the same solvents used later to remove the meteorite components from the adsorbent. After concentration of the solvents, the residual eluent was examined for impurities by ultraviolet, fluorescence, and infrared spectroscopy.

Immediately before the plates were spotted with the sample, they were prewashed by ascending development in chloroform to remove any contaminations picked up after preparation of thin layers. Samples were applied to the adsorbent with a microliter syringe immediately after the plates were removed from the prewashing chambers. The spotting technique has been described previously (21).

Samples dissolved in carbon tetrachloride or hexane were spotted on the adsorbent in 100 μg quantities. The chloroform extract of 6.2935 g of the Montauban stone yielded 9.7 mg of material including elemental sulfur. This was dissolved in carbon tetrachloride and applied in 100 μg amounts on ten thin-layer plates. On two additional plates, 150 μg of extract was spotted in each application to account for the 9.7 mg of original organic matter plus sulfur isolated from the meteorite. The plates were developed with hexane by ascending chromatography in glass chambers lined on all sides with Whatman No. 1 filter paper to ensure that the chambers were saturated with solvent vapor. One chromatogram was visualized with Rhodamine 6G to locate the three major components: hydrocarbons, sulfur, and the polar component. The lower half of the chromatogram was protected with a glass plate during the spraying operation in the preparative procedure. The fluorescent indicator under ultraviolet light helped to locate the exact area of the hydrocarbons on the preparative plates. The polar material exhibited natural fluorescence under ultraviolet radiation. The hydrocarbon and polar fractions were scraped separately from the plates using a razor blade. Hexane was used to elute the hydrocarbons from the adsorbent, but this solvent did not remove Rhodamine 6G. The polar material remaining at the origin, however, required hexane-ether-acetic acid (70:30:1, v/v/v) as eluting solvent. Since Rhodamine 6G would also be removed from the adsorbent with this mixture and interfere in subsequent analyses, it was necessary to protect this sample component from the dye during the spraying operation. The fluorescence of the material located its position on the thin layers. After evaporation of the solvents under nitrogen, the individual components were subjected to spectral analyses. Isolated components were then divided for the elemental sulfur test and mass spectroscopy, both performed by independent laboratories.

Ultramicroanalysis for Sulfur

Because of the small amount of meteorite extracts available for the analysis, the Schwarzkopf Analytical Laboratory, Woodside, New York (34), refined its usual microanalytical method to detect the trace quantities of sulfur. The colorimetric method employed for the sulfur trace analysis is based on the Lauth synthesis of methylene blue formed when N, N-dimethyl-p-phenylenediamine reacts with hydrogen sulfide in the presence of ferric ion. The reaction is:



(35–38). The method involves the reaction of the sample with metallic potassium to form the sulfide, generation of the hydrogen sulfide with acid, and distillation of the released gas into zinc acetate forming zinc sulfide. Upon acidification, the liberated hydrogen sulfide reacts with N, N-dimethyl-p-phenylenediamine hydrochloride in the presence of Fe^{+3} to form methylene blue, which is then measured colorimetrically at 670 mμ. The colorimetric method developed for the meteorite analyses followed Beer's law from 0.15 to 10 μg of sulfur.

Mass Spectroscopy

An Orgueil meteorite stone, 2.4615 g, obtained from the Musée National d'Histoire Naturelle, Paris, France, was finely ground and extracted on a mechanical shaker for 16 hr with 35 ml of chloroform, followed by similar extraction with tetrahydrofuran for 20 hr. Both extracts were evaporated to dryness under a stream of nitrogen. The thin-layer procedure and the preparative chromatographic method described above were used, except that Silica Gel G was the adsorbent in this part of the investigation.

The area just below elemental sulfur on the thin layers was the region where open chain sulfides and thiols were found under identical conditions in control experiments. This region and the hydrocarbon fraction were scraped from the plates and eluted from the adsorbent with hexane.

Mass spectrometric analyses were performed by Bendoraitis (39) at the Socony-Mobil Research Laboratories, Paulsboro, New Jersey, using a Consolidated Engineering Co. Model 21-103 spectrometer, equipped with a heated inlet system. Because of the small quantities of the samples, it was necessary to increase the normal operating sensitivity and to modify the sample introduction system. An approximate 300-fold increase of normal sensitivity was obtained by reduc-

TABLE I

Percentage of Organic Matter Extracted from the Orgueil *Meteorite at Room Temperature* (Based on Total Organic Matter 6.9%)

Weight of meteorite, g	Solvent	Volume ml	Time hr	Weight of extract[a] mg	Extract[a] %
2.4615 Paris	Chloroform	35	16	35.2	20.6
	Tetrahydrofuran	35	20	16.4	9.5
6.2935 Montauban	Chloroform	50	8	9.7	2.8

[a] These weights include variable amounts of elemental sulfur.

ing the sample reservoir from 4 to 0.75 liters, increasing the ionization current from 25 to 75–100 microamperes, and operating the ion current amplifier at a maximum gain. The sample tube itself was placed in an acid-washed ampoule provided with magnetic break-off tip, evacuated, sealed directly to the spectrometer inlet system, and maintained at 300C.

The chloroform extract of the Paris stone yielded 35 mg of residue, some of which was known to be elemental sulfur. The subsequent tetrahydrofuran extraction produced 5.34 mg of hexane-soluble material. It was evident that the qualitative composition of the material was the same from a preliminary thin-layer chromatogram of both extracts. Both extracts were combined in order to obtain larger fractions for the preparative thin-layer chromatographic procedure used to isolate fractions for mass spectroscopy.

From the six thin-layer chromatograms, used for the separation of approximately 2.8 mg of extract, 40 μg of hydrocarbons were recovered after elution from the adsorbent. This hydrocarbon fraction appeared as a colorless oil. The weight of the fraction, possibly sulfides and thiols, eluted from the thin-layer region just below elemental sulfur amounted to 140 μg when finally freed from the adsorbent. This fraction had a dry powdery appearance and may possibly have contained some adsorbent.

Test for Hydrogen Sulfide Evolution

The test for hydrogen sulfide is based on the Lauth synthesis of methylene blue described above. The method was first standardized with known amounts of hydrogen sulfide. Varying amounts of a sodium sulfide stock solution were diluted to release 1, 5, 10, 100 μg of hydrogen sulfide when two drops of concentrated HCl were added. The released gas was forced, by heating, into the zinc buffer solution (1.2 ml). The delivery tube was submerged below the level of the liquid in the receiver at 0C. When the receiver was removed, 0.42 ml of N, N-dimethyl-p-phenylenediamine and 0.145 ml of Fe^{+3} were added immediately to the solution.

All samples and controls, in acid-cleaned vials, were heated in a sand bath for 30 min at 100, 150, 200, 250, and 300C. As control samples, 23 and 25 mg of elemental sulfur were heated under similar conditions. A second control of 3.8 mg of elemental sulfur, representing 2%, was added to 178 mg of Pembina crude oil (Alberta, Canada) before heating.

TABLE II

Ultramicroanalysis of Orgueil Meteorite Extracts for Sulfur

Sample	Weight, μg	Sulfur, μg	Absorbance @ 670 mμ	Sulfur, %
Reagent blank	0.0	0.0	0.050	0.0
Procedure blank for hydrocarbons	9.91	0.0	0.055	0.0
Procedure blank for fluorescent fraction	30.37	0.0	0.055	0.0
Hydrocarbon fraction	50.15	0.80	0.196	1.60
Fluorescent fraction	100.7	5.62	0.52	5.58
	150.02	8.30	0.800	5.53

The organic matter from the meteorites was tested for evolution of H_2S. Duplicate samples were obtained from 1.8045 g of the Paris meteorite and 1.0822 g from the Montauban stone. Both meteorite samples were extracted with $CHCl_3$ on a mechanical shaker for 8 hr.

Results

The results of the various extraction procedures are summarized in Table I. The quantity of elemental sulfur removed by chloroform varied in the different extractions. The subsequent preparative TLC effectively separated the hydrocarbon, sulfur, and polar components from one another making subsequent analytical work on the individual components possible. From the chloroform extract of the Montauban stone, 285 μg of polar material was recovered.

Infrared and Ultraviolet Spectra

The hydrocarbon fraction, which was a colorless oil, showed only those infrared absorption bands characteristic of alkanes; this was in agreement with the R_f values obtained from TLC and the ultraviolet and mass spectral data.

The polar, yellowish-brown solid material remaining at the origin on the thin layers exhibited a pronounced ultraviolet absorption band below 350 mμ. Shoulders appeared in the region of 310 mμ, 285 mμ, and 278 mμ. Upon dilution, the spectrum of this polar extract also displayed small absorption peaks between 245 mμ and 255 mμ. The fluorescence spectral peak of this fraction appeared between 445 mμ and 455 mμ when excited with 365 mμ radiation. The same fluorescence spectrum was observed in the original chloroform extract of the meteorite befor TLC. The infrared spectrum of this fluorescent material showed the typical methyl and methylene absorptions at 3.42 μ and 3.52 μ, and carbonyl absorptions from 5.7 μ to 5.9 μ, characteristic of esters and acids.

Subsequent TLC of this polar extract in a hexane-ether-acetic acid system (70:30:1, v/v/v) indicated at least three fluorescent and two nonfluorescent components. It was difficult to identify the components in the mixture from the available spectral information. The ultraviolet spectrum, however, did resemble the spectra of 2,2′-dicarboxydiphenyl disulfide, 2-mercaptobenzoic acid, diphenyl sulfoxide or β-phenylmercaptohydrocinnamic acid (40). These data were supported by the infrared spectrum of an acid carbonyl and by the ultramicro elemental analysis which detected sulfur in this fraction. The substance responsible for the blue fluorescence of this fraction requires further chemical fractionation of the polar component.

Organic Sulfur Content

The results of the microanalysis for sulfur on the two fractions recovered from the preparative thin layer are summarized in Table II. The meteorite hydrocarbon fraction contained 1.6% sulfur, whereas the polar fluorescent fraction contained 5.6%. On this basis, small amounts of sulfides were thought to be present in the hydrocarbon fraction; mass spectrometric results indicated that thiols were apparently not present. The fluorescent fraction containing a greater percentage of sulfur may have included heterocyclic compounds. This conclusion is in agreement with Biemann's recent mass spectrometric results on the Murray meteorite (41). In contrast to the meteorite samples, the procedure blanks contained no sulfur, indicating that the sulfur was not introduced during analysis. The adsorbent used for the preparative TLC was a mixture of silica gel and 10% magnesium silicate, rather than the more commonly used Silica Gel G which contains gypsum, a sulfate.

Mass Spectrometric Data

Meteorite fractions extracted from the Paris stone and isolated by TLC were examined by mass spectrometry for the presence of sulfur compounds, especially thiols. 1-Octadecanethiol served as a reference standard. Figure 1 shows the mass spectra of the open chain thiol and the comparable meteorite fraction. This fraction migrated behind elemental sulfur in the region of thiols on the thin-layer chromatograms.

The spectrum of octadecanethiol showed a prominent parent ion peak at m/e = 286, and also ions at m/e = 288 and 290. Since the octadecanethiol was not pure, these latter parent ions were attributed to 5–10% of octadecylchloride, perhaps a synthetic intermediate. The TLC of this thiol compound also revealed an impurity. Major ion peaks also appeared at m/e = 252, 224, and 210 with this standard thiol. The mass spectrum was characteristic of straight chain alkanes with low peaks at high m/e and a definite buildup of fragment ions at lower m/e (39).

The mass spectrum of the meteorite fraction in the position of thiols is much more complex, but showed the same low peak ions at higher m/e and a characteristic buildup of fragment ion intensities at lower m/e values. The more complex spectrum at lower m/e suggested the presence of cyclic compounds as well as open chains in the sample. No ion peak was observed for m/e 286 or 252. Perhaps more significant is the lack of any prominent parent ion pattern characteristic of long chain thiols at higher m/e. Fragment ions at m/e 95 and 78 were more intense for this extract than for the long chain thiols. Both samples showed peaks at m/e 48 and 64 attributable to sulfur dioxide, which appeared to have originated from traces of sulfuric acid remaining on the glassware cleaned with sulfuric-nitric acid mixture rather than from any organic sulfur compound in the meteorite sample. The spectrum also indicated the presence of cycloalkanes and some monocyclic aromatic compounds in addition to the paraffin-type compounds.

The hydrocarbon fraction isolated from thin-layer chromatograms of the Orgueil extract from the Paris Museum had a mass spectrum indicative of alkanes along with some cyclic and aromatic hydrocarbons.

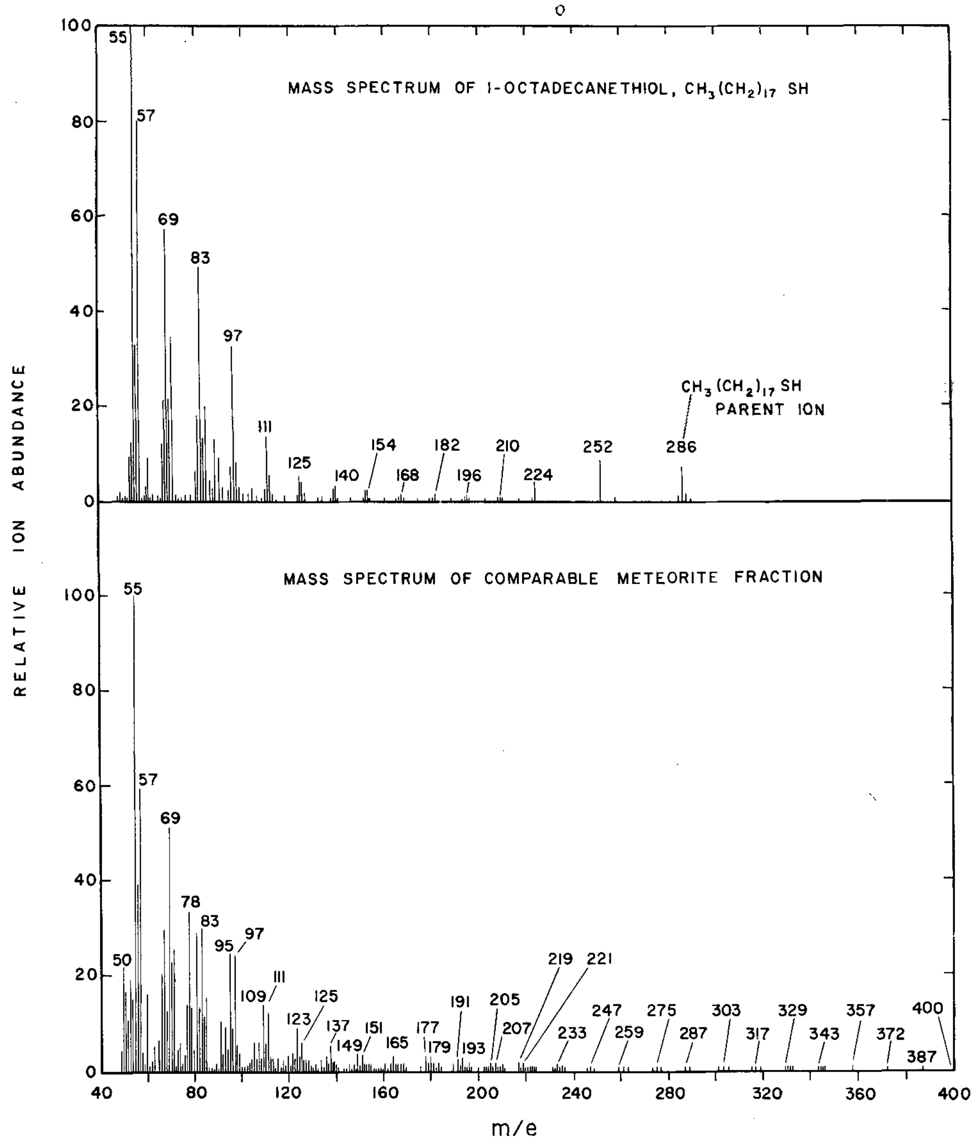


FIGURE 1

These compounds have been reported by Ryhage and other investigators (42,43).

Ryhage (42) examined by mass spectrometry both the hydrocarbon and polar fractions previously isolated by preparative TLC from the Montauban stone. The combination of thin-layer with gas chromatography and mass spectrometry identified *n*-alkanes from C_{13} to C_{26} and several other hydrocarbons, probably cycloalkanes. The gas chromatography on the more polar component was not performed under optimum conditions; consequently, only fatty acids and two phthalic acid derivatives were identified. A peak at m/e = 348 was suggestive of a steroid.

The mass spectra of the meteorite fractions were themselves not conclusive, but indicated that long chain thiols, if present, were in low concentration. This information was in agreement with the results of TLC and elemental analysis. Long chain sulfides could not be detected because their cracking pattern is similar to that of hydrocarbons.

H_2S Evolution

If sulfur is present in petroleum, H_2S is a reaction product when the oil is heated (44,45). The evolution of hydrogen sulfide upon heating served as an additional test for the evaluation of the similarities and dissimilarities between the Orgueil extracts and petroleum.

As little as 5 μg of hydrogen sulfide produced methylene blue; in the reaction of hydrogen sulfide with N, N-dimethyl-p-phenylenediamine. Even 1 μg gave a definite green color to the solution. Reagent blanks were yellow for this test. Elemental sulfur heated to temperatures less than 200C gave no color to the reagents, but a faint tint of green was obtained after heating sulfur to 250–300C. Elemental sulfur standing overnight in the zinc acetate buffer at room temperature did not impart any color to the solution.

The results of the experiments with the Pembina petroleum and the Orgueil meteorite are summarized in Table III. The crude oil, with 2% sulfur added, gave negative results at 100C, but showed the evolution of hydrogen sulfide at 150C. A pale green solution was obtained, which may not be caused by hydrogen sulfide but rather by interference from elemental sulfur, since the sulfur control gave the same reaction at this temperature. Duplicate experiments performed with the sulfur control and the meteorite extract confirmed these results.

Discussion

The information obtained from the combination of TLC, infrared, ultraviolet, and mass spectroscopy must be correlated with available information on the origin of the organic substances in carbonaceous meteorites and the nature of the parent body. The preparative chromatographic procedure effectively separated the hydrocarbon fraction from the polar fluorescent material, and both of these from elemental sulfur. Analysis for elemental sulfur indicated small amounts of sulfur compounds in these fractions.

The ultraviolet absorption bands of elemental sulfur at 260 mμ and 280 mμ were not observed in the polar fraction even though the quantity of sulfur present was sufficient to show the characteristic sulfur absorption. It is likely, therefore, that the sulfur in the hydrocarbon and polar organic fractions represents hetero atoms in the organic molecules rather than elemental sulfur which was not separated in the chromatography.

TABLE III
Evolution of Hydrogen Sulfide Test

Sample	Temperature, C	Color
Blank	100	Yellow
Hydrogen sulfide		
1 μg	100	Blue-green
5 μg	100	Blue
10 μg	100	Blue
100 μg	100	Blue
Sulfur		
25 μg	100	Yellow
	150	Yellow
	200	Trace green
	250	Green
	300	Green
Pembina crude oil + 2% sulfur		
	100	Yellow
	150	Blue
Orgueil meteorite		
	100	Yellow
	150	Yellow
	200	Trace green
	250	Green
	300	Green

Traces of open chain sulfides were probably present in the hydrocarbon fraction. The more polar material, known to be a mixture of at least five components, probably contained heterocyclic compounds. This conclusion is not surprising in view of the presence of free sulfur in Orgueil. Biemann recently detected substituted thiophenes but no open chain thiols or sulfides in the Murray meteorite (41).

The *n*-alkanes from C_{13} to C_{26}, and probably cyclic hydrocarbons, were identified in the hydrocarbon fraction from the Montauban stone by mass spectroscopy in work reported earlier by Nagy et al. (9) and more recently by Oro (43). The results of the analysis of the more polar component, while incomplete, are nevertheless consistent with previous findings of traces of fatty acids in the Orgueil meteorite (12). The significance of the phthalic acid derivatives is not known and may represent a contaminant introduced into the extract after the preparative chromatography.

From the abundance of hydrocarbons and free sulfur in Orgueil, a chemical reaction at moderate temperatures would be expected to form thiols and sulfides in the organic matter. The mass spectroscopic study of Bendoraitis showed *only* traces of sulfur compounds. It would appear that favorable conditions for the formation of these sulfur compounds did not exist on the parent body.

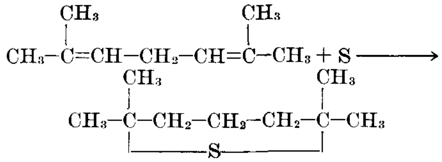
It is well known that sulfur compounds of some complexity are formed when paraffins are heated with elemental sulfur (46). Sulfides and thiols are the expected products and their absence would indicate temperatures less than 200C on the parent body. Underlying this hypothesis is the assumption that the extraction of the meteorite with chloroform removed the thiols and sulfides. Hennessy suggested that if these compounds were present as mercaptides, an acid extraction would be necessary to remove them from the meteorite (47). Considering the nature of the hydrocarbons and the amount of sulfur present, this is a reasonable possibility.

Nagy et al. (5) and Anders et al. (32), from the phase equilibria diagrams of Garrels (48), suggested that a low-temperature, aqueous environment existed on the meteorite parent body. These studies were based on the examination of the mineralogy of Orgueil and other carbonaceous chondrites. This conclusion is again supported by the conditions necessary for the synthesis of sulfides and thiols. Briefly, if thiols were once formed with elemental sulfur present, moderate oxidation conditions would favor the formation of disulfides. If alkenes reacted with elemental sulfur, thiols would have formed. Farmer has described such a reaction with *n*-alkenes at 140C under conditions favoring a free radical mechanism (50).

Urey has proposed hydrogen sulfide as a means of introducing sulfur into the carbonaceous meteorites (51). Hydrogen sulfide reacts readily with olefins at moderate temperatures to give thiols using catalysts such as dry clay, metallic sulfides or sulfur (49). Both the catalyst and temperature requirements for such a reaction were probably available on the parent body. Vaughan and Rust have determined that the reaction of hydrogen sulfide with olefins under ultraviolet light proceeded slowly in the gas phase but rapidly in the liquid phase (52). If condensation of primordial matter occurred on the parent body, a liquid phase possibly existed where such a reaction could have easily proceeded. If ultraviolet radiation is not available for the reaction of hydrogen sulfide and olefins, temperatures in excess of 200C are necessary, a rather unlikely condition for the parent body considering mineralogical data.

Recently Knight (53) reported the insertion of a sulfur atom in a carbon-hydrogen bond of *n*-alkanes. Thiols were the primary products when short chain hydrocarbons reacted with carbonyl sulfide in a photolysis reaction at 25C using 229–255 mμ radiation.

Under certain conditions cyclic compounds are synthesized when dienes react with sulfur in a free radical reaction (54):



$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_3 + S \longrightarrow$$

$$CH_3-\underset{\lfloor\text{———}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_2-CH_2-\underset{\text{———}\rfloor}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \quad (\text{bridged by } S)$$

Any di- or polysulfides formed in this reaction decomposed at temperatures greater than 140C to hydrogen sulfide, thiol and monosulfides. Such a reaction could produce thiophenes or heterocyclic sulfur compounds on the Orgueil parent body. A similar reaction may account for the thiophene-type compounds Biemann found in the Murray meteorite (41).

A comparison of the organic matter in Orgueil with petroleum reveals several similarities. Both contain hydrocarbons and free sulfur. The American Petroleum Institute (API) Research Project 48 identified a variety of short open chain thiols, sulfides, saturated cyclic and thiophene compounds in petroleum. Most authorities suggest a biogenic origin for petroleum and consider thiols and sulfides products of altered biogenic materials (29,31). Could carbonaceous matter in meteorites have undergone a similar history?

The API Project 48 has only examined petroleum distillate fractions of low boiling ranges for sulfur compounds because of the analytical problems involved. Precise information on longer open chain thiols in petroleum must await further analytical work. However, the absence of these compounds in Orgueil does suggest that the meteorite organic matter had in part a history different from that of petroleum. Although water existed on the meteorite parent body (3), other conditions for petroleum formation, such as bacterial action, pressure, or temperature, were perhaps not present.

The temperature at which the hydrogen sulfide evolution occurs when crude oil and sulfur are heated is generally considered as the upper temperature limit for the formation of petroleum (44,45,55). When sulfur was added to Pembina crude oil, hydrogen sulfide evolved at 150C. On the contrary, in the Orgueil extracts hydrogen sulfide was not detected at this temperature. It cannot be ascertained whether the meteorite extract actually generated hydrogen sulfide in a similar reaction at 200C or 250C because of interference of elemental sulfur. However, such a reaction for hydrocarbons and elemental sulfur could proceed at even lower temperatures over a long period of time. Again, the organic matter in the Orgueil meteorite appears to be different from that of petroleum.

Conclusions

The absence of open chain thiols and the presence of trace amounts of sulfides in the chloroform extractable matter from the Orgueil meteorite support the concept of a low temperature environment on the parent body. Furthermore, the presence of hydrocarbons and elemental sulfur in the meteorite suggests these possibilities: the accumulation of free sulfur without hydrocarbons available for chemical reaction; unfavorable conditions for such a reaction; or a subsequent desulfurization to produce the observed amounts of elemental sulfur and hydrocarbons. The presence of thiols and sulfides in petroleum and the upper temperature limit of petroleum points to a different history from the organic matter in the Orgueil meteorite.

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