

CHEMICAL FOSSILS: TRENDS IN ORGANIC GEOCHEMISTRY†

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ABSTRACT

It is now clearly recognized that many organic compounds which were the complex biochemical products of ancient organisms have survived in geological sediments for relatively long periods, often with little or no transformation of their basic skeleton. Other constituents, however, may be altered severely under these conditions and retain little which indicates their original structure. All these chemical fossils are, of course, far more numerous than their morphological counterparts, due to the multifarious chemical processes which occur in the subsurface environment. In recent years, application of modern analytical techniques has led to a greater knowledge of the discrete molecules, especially those related to the porphyrins, which can be isolated from oil and sediments, and has thrown much light on diagenetic processes including the rate and mechanisms of several geochemical reactions. Such knowledge has, in turn, been applied to the elucidation of the more difficult problem of the origins of diverse geopolymers. The processes outlined above and the conclusions which can be drawn from the results obtained are comprehensively reviewed.

INTRODUCTION

The chemistry of our environment has been shaped by two related but chemically very different elements: silicon, which dominates inorganic chemistry, and carbon, upon which organic chemistry rests.

The chemistry of silicon is determined by its affinity to oxygen, by the great multiplicity of structural arrangements of the Si—O—Si group and by generally rapid reactions that result in an approach to thermodynamic equilibrium within a short time. Carbon, though far less abundant, has been vital to the evolution of life. Its chemistry is dominated by the ease of formation and by the great stability of the covalent carbon to carbon bond, by the extreme multiplicity of isomeric and homologous compounds and by generally slow reactions which favour the preservation of metastable compounds, since thermodynamic equilibrium may not be reached even within time spans equivalent to the age of the earth¹.

The existence of organic compounds within the lithosphere has long been recognized because of their unusual properties, such as the inflammability

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of coal and the semiliquid or liquid nature and low density of earthwax, petroleum and asphalt. Man has long been curious about the origin of these materials. On occasion, early speculations approached the truth in a colourful way; thus, the Triassic Tyrolian oil shales, which are rich in vertebrate fossils as well as in chlorophyll and haemin derivatives, were thought to have resulted from an impregnation of the local rock with the blood of a slain dragon².

Only recently, in the early part of this century, did geological observation finally establish that sediments with high organic content are also often rich in macro- and micro-fossils; therefore, a genetic relationship between ancient life and organic compounds in sediments was implied³. Because of this correlation, sedimentary organic compounds came to be looked upon as *fossil chemicals*, as materials which had been formed by organisms living in the remote past, but were altered in the subsurface environment in an unpredictable manner and beyond recognition.

These views changed when the scientific tools of structural and analytical organic chemistry were applied to the earth sciences: Treibs' isolation of pigments related to chlorophyll and haemin marks the origin of *organic geochemistry*⁴⁻⁸. Treibs immediately recognized the important geological consequences of his findings. The carbon skeleton of complex biochemical products of ancient organisms had survived geologically long time spans; only the less stable peripheral groups had been altered by the chemical conditions of the subsurface environment, in a manner that was rationally explainable. Therefore, the fossil porphyrins of ancient sediments and of petroleum are *chemical fossils*; just as the more commonly known morphological fossils, they represent surviving evidence of ancient life processes that had achieved an increased structural order on the macroscopic and on the molecular level and in inorganic as well as in organic structures.

Since Treibs' discovery many types of chemical fossils have been discovered and most of the important building blocks of biochemistry are now recognized in the fossil record.

ORGANIC GEOCHEMISTRY AND PALEONTOLOGY

Organic geochemistry and especially the study of chemical fossils have much in common with the much older science of paleontology. Some comments on the growth and trends in that field may help us to assess the present status and future direction of organic geochemistry.

In paleontology, as in most natural sciences, early efforts were devoted largely to the gathering and cataloguing of specimens. Fossils were grouped with other 'strange materials in the mineral kingdom' such as crystals and stone axes (*Figure 1*) and their proper classification was frustrated by the lack of scientific information in the life sciences. Gradually, it became evident that fossils represented remains of ancient life; however, early taxonomic attempts remained unsuccessful, especially if they were influenced by contemporary religion. A classical example is the interpretation by J. J. Scheuchzer (1672-1733) of a fossil salamander as a human skeleton that had been preserved as a witness of the biblical flood ('homo diluvii testis') (*Figure 2*). We are not surprised that the much younger field of organic

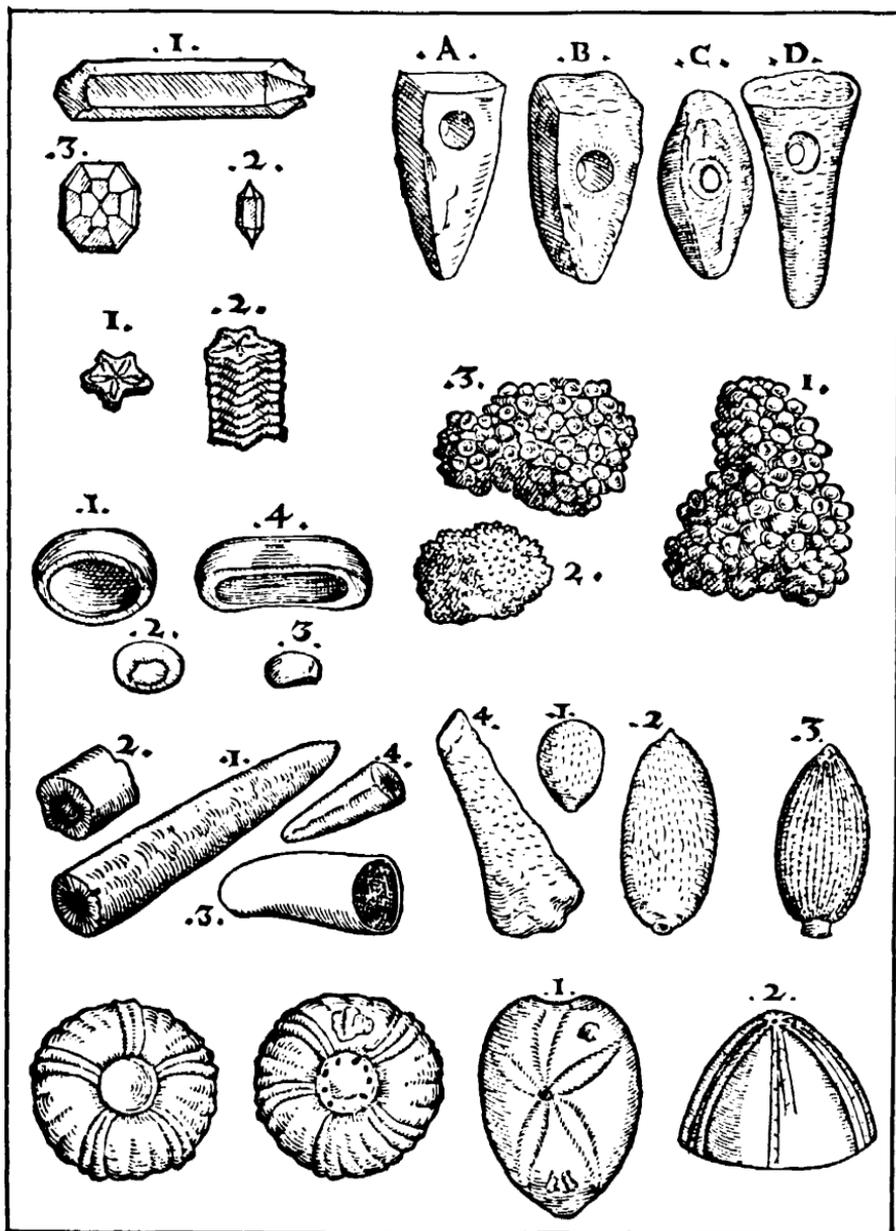


Figure 1. Fossilia, from Conrad Gessner, *De rerum fossilium...* (1565), in: Kuhn-Schnyder⁹. In early paleontology, fossils were grouped with other strange materials in the mineral kingdom such as crystals, stone axes and oolites. Similarly, in organic geochemistry, the distinction between chemical fossils and artifacts has not always been sharp.

geochemistry still experiences occasional difficulties in the classification and interpretation of chemical fossils.

Eventually, the interaction of paleontology with biology, with structural and historical geology and with geochemistry and geophysics, led to an understanding of the origin of fossil species and of the accumulation, preservation and transformation of fossils in sediments. Few paleontologists would now collect fossils merely for the joy of adding another specimen to a collection. After a history extending over several centuries, paleontology has become a mature science which interacts with other natural sciences, and it has found important practical applications.

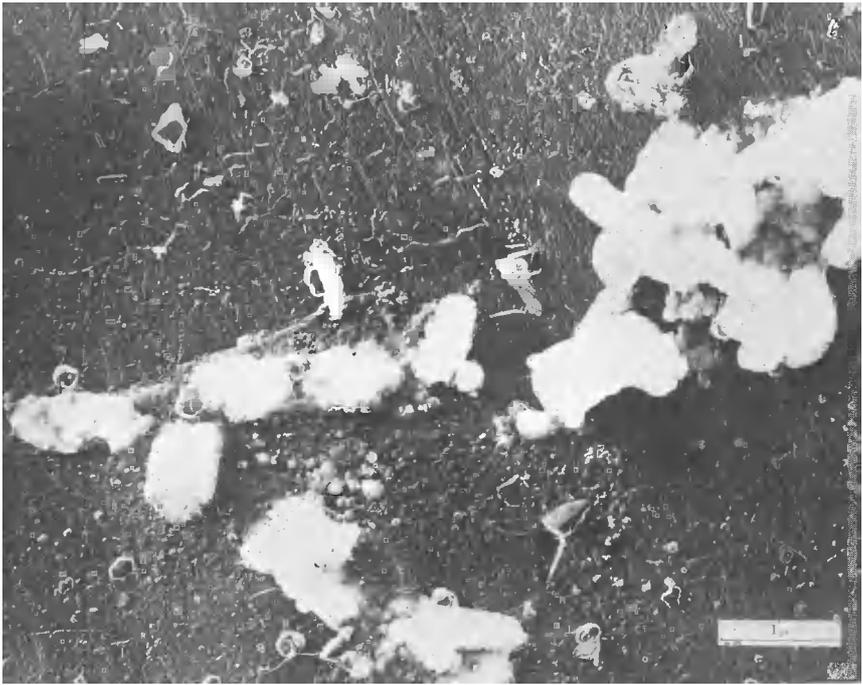


Figure 3. Fossil bacteria from the Gunflint Chert, middle Precambrian, 2 billion years old. Electron microscopy has extended the fossil time record into a past that was once thought barren of life. Chemical fossils may be equally valid evidence of early life on earth. From: Barghoorn¹⁰.

These are some of the applications of paleontology:

Fossils present evidence of the appearance and of the evolution of life on earth (*Figure 3*). Fossil assemblages reflect the existence of ancient faunal and floral communities (*Figure 4*). Fossils serve for the correlation between strata, often over great horizontal and vertical distances (*Figure 5*). Fossils are indicators of postdepositional chemical and physical changes in the sediments (*Figure 6*).

Paleobiochemistry deals with chemical fossils, the molecular remains of ancient life, and can serve science in similar ways; yet, the potential of

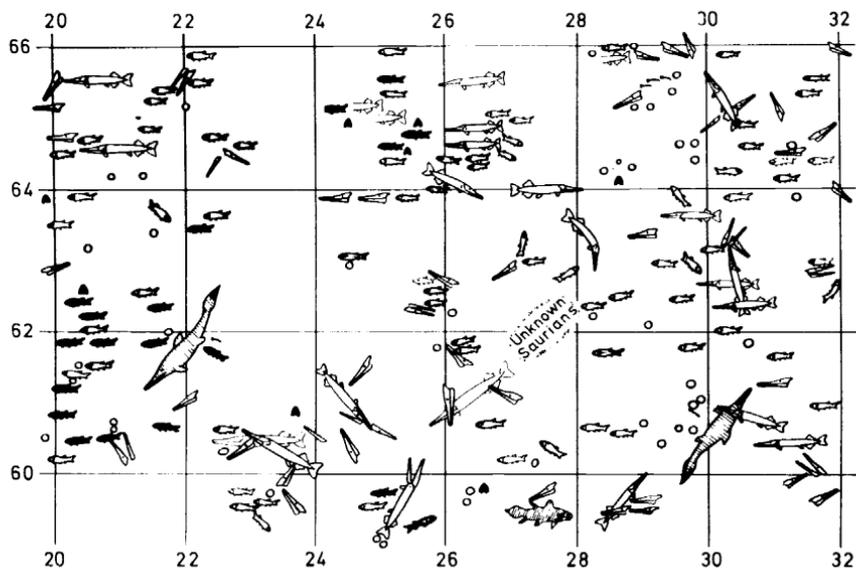


Figure 4. Assemblage of fossil vertebrates in the Triassic oil shale of San Giorgio, Switzerland. The study of fossil floral and faunal assemblages recreates ancient ecosystems. From Kuhn-Schnyder⁹.

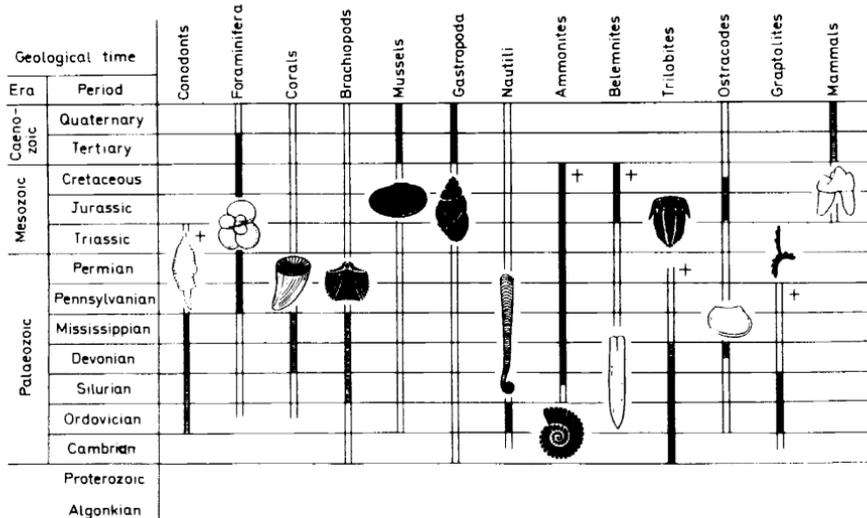


Figure 5. Fossils suited for stratigraphic correlation—one of the best known applications of paleontology. From Kuhn-Schnyder⁹.

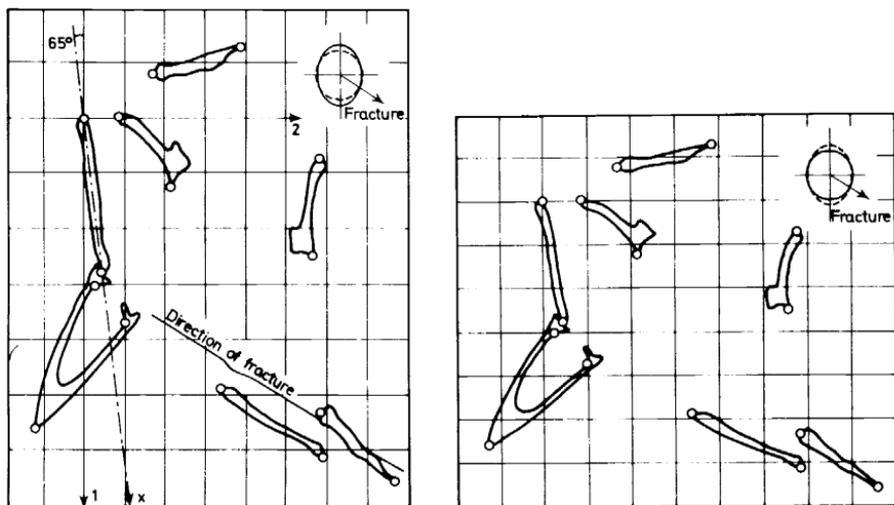


Figure 6. Tectonic deformation of fossil vertebrates bones (left) and graphic reconstruction of the original dimensions (right). This permits the determination of extent and direction of tectonic stress. From Kuhn-Schyder⁹.

chemical paleontology is greater. Chemical compounds are far more sensitive to the physical and chemical conditions in the subsurface than morphological fossils. Also, in terms of numbers, chemical fossils are far more abundant than their better known morphological analogues. More than 90 000 species of fossil animals are known at present⁹; but the almost limitless possibility of structural variation in organic chemistry and the complexity of the processes in the subsurface has produced in a single Triassic sediment more than 2×10^6 distinct derivatives of chlorophyll *a* alone¹¹. Each of these compounds reflects some of the unique conditions which existed in that sediment at the time of deposition, during diagenesis and during the more recent uplifting and weathering of the consolidated rock.

The great diversity of the fossil chemical record suggests a great scientific potential and a fruitful interaction between organic geochemistry and geology. What, then, is the present state of chemical paleontology; how much use has been made of the information encoded into the structure of chemical fossils; how much research potential remains and in which directions should we turn our attention?

An examination of the published geochemical literature suggests a situation not unlike that in early paleontology when the exploration of the fossil record was more urgent and less difficult than the understanding of the forces that had shaped the fossils. This is understandable. The organic chemistry of ancient sediments is far more complex than that of living organisms. Therefore, the isolation and identification of pure fossil chemicals is one of the most challenging tasks for the natural products chemist; also, it provides the most stringent test of the capability of analytical equipment such as high resolution gas chromatography and mass spectrometry. The progress in the application of these tools to certain areas of organic geochemistry is well

documented by recent reviews¹². Yet, I believe that the potential which organic geochemistry holds for furthering our understanding of natural processes has been poorly utilized. I am not alone in this judgement; Maxwell *et al.*¹³ remarked that 'organic geochemistry is in its infancy but that its *raison d'être* is already evident.'

The history of paleontology suggests to me that the potential in organic geochemistry lies less in the purely analytical area than in the assimilation of existing data and in the acquisition of new *selected* data, which are needed for the understanding of the chemical processes in the subsurface environment. This implies that we need to turn our attention from the isolation of chemical fossils *per se* to an understanding of their preservation and transformation in the context of the physical and chemical conditions in their surroundings. From a study of a small number of selected sediments (e.g. the Green River oil shale) we should proceed to a much wider spectrum of samples, differing in their depositional environment, their age and their post-depositional history.

Organic chemists have been reluctant to interpret fossil chemicals in terms of the processes which have shaped them. Indeed, Scheuchzer's 'homo diluvii testis' illustrates the hazard of premature speculation. Yet, hypotheses are necessary for the growth of science, and their content approaches certainty with each successful test. I am convinced that the fossil chemical record contains ample material for testing geochemical hypotheses.

PROBLEMS IN ORGANIC GEOCHEMISTRY

Organic geochemistry is concerned with the composition, formation, transformation and eventual destruction of organic compounds in the earth's crust. Within this area, many of the most basic questions remain unanswered. To take one example, even in petroleum geochemistry which has seen much activity and ample support, we are ignorant of the quantitative importance of geochemical reactions and of their rates and mechanisms. The study of chemical fossils can contribute materially to the solution of the open questions which are discussed in this review.

GEOCHEMICAL TRANSFORMATIONS—EXTENT

Reference has already been made to the changes in our views on the origin of sedimentary organic compounds. Earlier, these were considered as the random transformation products of biological source materials. Treibs' work⁴⁻⁸ and much of the succeeding effort in this field have revealed identifiable structures of biological origin in ancient geological specimens. In many instances, seemingly unaltered biochemicals have been isolated, even from Precambrian sediments. Examples are the straight-chain, iso, anteiso and isoprenoid hydrocarbons and the corresponding fatty acids, the amino acids and certain carbohydrates. In other chemical fossils, the biochemical architecture remains recognizable, but peripheral groups have been altered, polar substituents have been reduced or eliminated and the overall size of the molecules may have been changed.

The abundance and the obvious importance of these chemical fossils have suggested to some that the fossil organic matter consists largely, if not

exclusively, of biochemicals that have been preserved without or with minimal postdepositional change. This led to a complete reversal in the theories of the origin of petroleum: crude oil initially thought to be an unexplainable product of postdepositional randomization now was considered fully explained as an accumulation product of biologically derived hydrocarbons.

Present knowledge no longer justifies this extreme view. Research on the constitution of crude oil and of oil shales has revealed severely altered biochemicals and numerous structures which occur neither in living organisms nor in recent sediments. Among these are the light hydrocarbons, the substituted benzenes and the many substituted multiring aromatic and hetero-compounds of petroleum. Also, crude oil and sediments contain polymers (asphaltenes, kerogen) of a type not found in living organisms. There seems to be fairly general agreement now that the fossil organic matter is a mixture of biochemicals, surviving with little or no modification, together with compounds that have been altered severely, with or without retention of a recognizable nucleus of their original biochemical architecture. Although it is agreed that unaltered and heavily transformed organic compounds occur simultaneously in ancient sediments, agreement on the extent and importance of postdepositional chemical transformation has not been reached.

In fact, this is one of the principal areas of disagreement among petroleum geochemists. The relative predominance in crude oil of steranes, triterpanes and phytol-derived isoprenoid hydrocarbons and acids make a strong point for the survival of relatively unmodified biochemicals. On the other hand, the overwhelming complexity of the remaining petroleum constituents, the existence of a vast array of chlorophyll derivatives and the nature of the polymeric fraction, which remains largely in the source rocks, make an equally strong point for extensive chemical modification during the process of petroleum formation.

The gradual and at least partial transformation of biochemicals in the subsurface does not represent an irreversible trend. This further complicates the assessment of the relative importance of subsurface chemical reactions. Buried sediments or deep oil deposits may again be exposed to recent bacterial populations when uplifting and erosion bring the strata within reach of meteoric waters. Bacterial activity at that late stage leads to deep changes in crude oil composition¹⁴. In terms of the overall material balance, this leads to a loss of organic matter through conversion to carbon dioxide. However, new biochemical metabolites may be formed and introduced into the oil, the formation waters and the sediments. These compounds, which include hydrocarbons and acids, may be entirely different from the metabolites which are formed during the early diagenetic history, when oil as a substrate for bacterial growth is not yet present. Possibly, this could serve as a basis for recognizing the extent of bacterial reworking at a late diagenetic stage.

It is evident that knowledge of the extent of the subsurface modification of biochemicals is a key to the understanding of organic geochemistry. If crude oil were entirely an aggregate of unchanged biochemicals, we would understand its origin through studies of the source materials and of the

accumulation processes. If subsurface chemistry plays a dominant role in its origin we need the much more difficult understanding of the rates and mechanisms of the contributing reactions.

The study of the degree and rate of conversion of selected biochemicals into chemical fossils as a function of age and depth of burial of a sediment offers a substantial contribution to the resolution of these questions. Pioneering work on the formation and transformation of petroleum at depth has been done by Louis and Tissot¹⁵, Philippi¹⁶, Poulet and Roucaché¹⁷, Tissot *et al.*,^{18, 19} and Albrecht and Ourisson²⁰. These authors have demonstrated that consistent geochemical results can be obtained from studies in a geological basin of sediments exposed to a different time-temperature history. Straight-chain, branched-chain and some cyclic hydrocarbons have been used in this work for correlation and for the assessment of the 'maturity' of the source rocks and oils. Studies of this kind, extended to varied biochemical structures, should be well suited to defining the changing ratios between biochemical precursors and chemical fossils as a function of depth, age and thermal history.

The questions raised here have far more than academic interest. It is important for crude oil exploration to know whether oil forms in young sediments through accumulation of biochemical products, or at depth as a result of chemical processes. The same knowledge is important for the understanding of the environmental effect of spilled crude oil and oil products. A purely biochemical product would be far less severe in its environmental effect than an oil that has been formed at depth by random processes capable of generating compounds which are foreign and toxic to living organisms.

GEOCHEMICAL TRANSFORMATIONS: RATES AND MECHANISMS

The biochemical products which contribute to the sedimentary organic matter in recent sediments are thermodynamically unstable. During diagenesis, the least stable and the most reactive components or their substituents are gradually eliminated. This process leads with increasing age and depth of burial to a gradual stabilization, not necessarily of each individual compound but of the sedimentary organic matter as a whole. In terms of structures, the transformation of open chains to saturated rings and finally to aromatic networks is favoured; hydrogen becomes available for inter- or intra-molecular reduction processes. The approach to thermodynamic equilibrium is very slow; therefore, unstable compounds may survive, at least at moderate temperatures, for time spans equivalent to the age of the earth.

Much of our knowledge of sedimentary organic reactions has been deduced from the study of the *in situ* conversion products of sensitive organic compounds, especially of pigments²¹. Typical reactions involve the elimination of oxygen functions, primarily in sterically unfavourable positions, decarboxylations, hydrogenations and dehydrogenations, isomerizations, polymerizations and cleavage reactions. As a rule the ordered building pattern of the biochemical structures is gradually randomized. Inherently, such reactions are irreversible, since it is unlikely that an abiotic reverse

reaction would have the specificity needed to recreate the ordered structure that was produced by enzymatic reactions. Metastable reaction intermediates, though unstable relative to graphite and hydrogen, may persist and participate in reversible equilibrium reactions, predominantly, in acid-base, in redox, and possibly in esterification reactions.

In spite of this limited knowledge of the general reaction trends we are virtually ignorant of the reaction mechanisms and reaction rates. How can this situation be changed?

In organic chemistry and in biochemistry two approaches are used to study reactions. One involves repetitive sampling of a reacting mixture and a sufficiently complete chemical analysis that permits reconstruction of the processes. The other uses model experiments with the incorporation of tracers into complex mixtures or simplified experimental systems.

Both approaches have a limited scope in organic geochemistry. The sufficiently complete analysis of geological specimens for the most important reaction components may be beyond the state of the art. Tracer experiments may succeed in documenting the complexity of the reaction pathways but only at an early stage of sedimentary history. The limitations of simplified laboratory experiments are even greater. In nature, the transformation of organic compounds can proceed over many different reaction paths. Their relative contribution may depend on the presence of other compounds, including unstable reaction intermediates, and on the physical conditions in the environment, especially on the temperature and redox potential. It is not likely that two identical source materials will produce the same conversion products, unless all details of the diagenetic history correspond. It is similarly unlikely that laboratory model experiments can duplicate the diagenetic history of a sediment sufficiently well to permit a realistic interpretation of the products in terms of geochemical reactions. This is not to deny the value of model experiments under 'simulated earth conditions' (e.g. Eisma and Jurg²²) in providing valuable but noncomprehensive information on *possible* reaction pathways.

A compromise between the complete analysis of a sediment and model experiments is possible and promising. Chemical fossils are derived from biochemical precursors that are formed in relatively small numbers by specific biochemical reactions. These biochemicals react to the stresses in the subsurface with a modification of their sensitive structural features. Therefore, the chemical fossils bear an imprint of the chemical conditions and of some of the possible processes that affect the organic matter in their surroundings. This, and the immense complexity of some extended series of chemical fossils, such as the porphyrins, provides an almost unlimited wealth of natural tracers. The analysis, not necessarily of the entire sedimentary organic matter, but of selected chemical fossils derived from known precursors and isolated from sediments of increasing diagenetic age should provide much insight into the sequence, mechanisms and rates of diagenetic reactions.

POLYMERS IN ORGANIC GEOCHEMISTRY

Organic polymers are abundant in organisms, in sea water and in recent and ancient sediments. Quantitatively, they far outclass those lower molecu-

lar weight compounds which are relatively well known because of their simple analytical chemistry. Yet, as Eglinton pointed out²³, for the recent environment, a far greater information content is encoded into biopolymers than into lower molecular weight structures. In a modified sense this is true for the geopolymers as well: they carry far more information about the source material and the postdepositional environment than the lower molecular weight fraction.

In terms of their origin and composition, the geopolymers span a wide range. Generic names (fulvic and humic acid, resins, asphaltenes, kerogen, etc.) are used because of the lack of a more accurate chemical description. However, these names do not imply a specific structure or structural or genetic homogeneity within each class. Fleeting transitions may exist between these different types of geopolymers and between their different molecular weight fractions (e.g. resins, asphaltenes and kerogen in the case of crude oil and its source rocks). Therefore, many of the structural features of the high polymers, except for the high degree of crosslinking, may be mirrored in the structures of the intermediate weight polymers. These are much more readily accessible for analytical and structural determination.

In their structural analysis of kerogen, Burlingame *et al.*, noted the gradual transition from loosely bound peripheral groups to a heavily crosslinked internal structure²⁴; similar subunits may be represented in both.

An interesting aspect of the sequential chemical changes during the transformation of the geopolymers lies in the transition from well-ordered polymers over randomized geochemical structures to a crystallographically well-ordered structure which approaches the composition of graphite. This transition reflects the three principal types of process which form and transform the geopolymers; ordered structures are produced initially by enzymatic processes, metabolic energy supplied by organisms is the driving force. Late in the diagenetic history, order returns and results in thermodynamic stabilization. The higher degree of disorder at an intermediate diagenetic age represents the breakdown of the ordered biochemical building pattern during the initial phases of the approach to thermodynamic equilibrium.

The greatest structural disorder at this intermediate diagenetic age coincides with the phase of greatest geochemical activity; here petroleum originates (though there is an active hydrocarbon chemistry above and below this level). The work of Philippi^{16, 25}, Tissot^{18, 19} and Albrecht²⁰ suggests that this stage correlates roughly with a depth of 1000–3000 metres; however, deposition rate and geothermal gradient are more important controlling factors than depth alone. At that intermediate stage in the life history of fossil organic compounds, the geopolymers show the greatest structural dependence on their depositional, postdepositional and recent geological history. In other words, maximum geochemical information content is encoded into their structures at that time.

Thus, the geopolymers span a wide structural and size range and are in dynamic transition from an ordered biochemical to an ordered crystallographic state through a labile intermediate phase. These dynamic processes within the kerogen matrix are intimately involved also with the formation and transformation of the lower molecular weight fraction of petroleum and ancient sediments. The progressive aromatization of the kerogen network

liberates hydrogen for intra- and inter-molecular reactions. Therefore, the aromatization of kerogen is indirectly the driving force for the lowering of the redox potential and for the reduction and reductive elimination of functional groups which occur during diagenesis. The increasing crosslinking of the kerogen matrix at this intermediate diagenetic stage also facilitates the fragmentation of peripheral groups; hydrogenation of these radicals follows, though some may be involved in secondary reactions such as dimerizations and substitutions. The overall result is the regeneration of some of the biogenic structures—not in their original composition, but after modification of functional groups and after fragmentation at random positions. It is quite likely that these processes can explain the increased randomization, the higher aromaticity and the higher degree of substitution in the sedimentary hydrocarbons, compared to their biochemical precursors. In that sense, the dynamic chemistry of the kerogen may hold the key to the formation of petroleum.

Geopolymers may also be involved in the physical process of oil migration. Polymers of moderate crosslinking can accommodate liquids by occlusion within their structural network. Typical examples are the swelling of rubber and of polystyrene in organic solvents and of some polar polymers, such as polyacrylamide, in water. Similarly, a 'young' kerogen with limited polymerization and crosslinking is capable of retaining hydrocarbons in its relatively loose network structure. Since young sediments contain a small amount of hydrocarbons relative to the total organic matter²⁵, the entire hydrocarbon content may be physically retained in this manner. With increasing diagenesis the hydrocarbon content and the crosslinking increase simultaneously. Therefore, the kerogen may become saturated with hydrocarbons; further hydrocarbon production and crosslinking will lead to the expulsion of the least strongly sorbed hydrocarbon fraction from the kerogen matrix. Liquid oil should appear at this moment; it could then be moved by physical processes, such as flushing or gravitational separation.

Though hypothetical, this view of the origin of petroleum is not in disagreement with known geochemical facts and does not require the operation of unknown forces. It has several attractive features. It offers a mechanism for the release of hydrocarbons from source rocks (primary migration) that depends only on the progressive chemical changes in the organic matter in deeply buried sediments; compaction and subsidence enter only indirectly, since they provide the proper temperature history for the diagenesis of the organic matter in the sediments. Movement of the hydrocarbons as a continuous or discontinuous bulk phase through the source rock is not required. The release of hydrocarbons from larger surfaces contiguous to migration paths may be followed by redistribution and equilibration of the hydrocarbons within the kerogen of the sediment.

Crude oil and the oil retained in source rocks differ in composition to a degree, principally in the higher aromatic content of the source rock hydrocarbons. This may reflect the preferred retention of aromatic hydrocarbons in the aromatic kerogen matrix.

Commercially important oil deposits are formed only after a certain 'maturity' of the source rock has been reached¹⁶, even though hydrocarbons of petroleum composition are present at a somewhat earlier stage. This may

be accounted for by the requirement of a minimal time-temperature history before oil can be released from the source rock.

Liquid petroleum is not generally associated with oil shales, even though their hydrocarbon content resembles petroleum. This could result from a high sorptive capacity, associated with the high organic content of the oil shales, and from an insufficient degree of crosslinking of the oil shale kerogen, due to insufficient thermal exposure or a highly paraffinic nature.

These hypotheses have obvious practical implications: sorption measurements should provide an indication of the relative saturation of the kerogen with petroleum hydrocarbons. They would be a measure of the 'maturity' of a source rock and suggest whether the sediments could have been capable of releasing hydrocarbons into a migration path.

This discussion suggests a deep involvement of the polymeric organic matter in the transformation of biochemical products in subsurface sediments. I believe that the mode of transformation of the lower molecular weight organic components of sediments, including petroleum, can be understood only through an understanding of the sedimentary polymers and of their gradual transformation. In view of the complexity and variability in the composition of the geopolymers, the analytical task appears forbidding. However, a complete structural analysis may not be necessary for an understanding of the role of 'kerogen' in organic geochemistry.

Conventional analytical techniques deal more easily with the lower to intermediate than with the higher molecular weight range of the geopolymers. Because of the implied similarity in structural features and reactive properties throughout the entire range of geopolymers, structural studies on one may reflect on the composition of the other. This approach has been used in the investigation of fossil chlorophyll conversion products^{26,27}. There, gel permeation chromatography and mass spectrometry showed the existence of complex homologous series of pigments extending from the molecular weight of chlorophyll into the very high molecular weight range. These pigments are thought to be the result of and to reflect the diagenetic processes in the sedimentary polymer. It will be interesting to search for other highly modified biochemicals of similar molecular weights and to study their structural dependence on the diagenetic history of the sediments.

Another promising approach to the structural analysis of geopolymers involves stepwise degradation by chemical or physical means. Cautious oxidation of kerogen with chromic acid under increasingly severe conditions has demonstrated the existence of straight chains and branched peripheral chains surrounding a more heavily crosslinked nucleus²⁴. This work should be extended from Green River kerogen, where it was first applied, to other sediments and to other chemical degradation techniques. Flash pyrolysis of thin kerogen films in the high vacuum of a mass spectrometer minimizes secondary reactions amongst the structural units which are released from the polymer²⁸.

Geopolymers may be surprisingly labile; the analysis of breakdown products from mild thermal or chemical degradation may give insight into both the polymer structure and its environmental chemistry. Thus, crude oil asphaltene are photosensitive and some higher molecular weight porphyrins are known to be dissociated not only by mild chemicals but even on chroma-

tographic adsorbents²⁹. In the mass spectrometer probe,²⁷ partial pyrolysis of higher molecular weight fossil porphyrins proceeds already at 155°C. Asphalt³⁰ and ancient sediments³¹ that have been quantitatively extracted with low boiling solvents yield additional extracts upon refluxing with higher boiling solvents of similar polarity. This may reflect, at least in part, incipient thermal fragmentation of the most labile peripheral groups of the polymer. It may be fruitful to re-examine and to reinterpret the results of stepwise extractions of ancient sediments with solvents of increasing boiling point²⁴, in the light of partial degradation of the kerogen, rather than exclusively as reflecting physical occlusion. The low temperature breakdown of the sedimentary polymers may resemble closely the regeneration of randomized chemical fossils under actual geological conditions at moderate environmental temperatures.

Other, conventional techniques of polymer analysis may be applied to the study of the composition of the sedimentary organic matter. Progress in this area is less a matter of new analytical developments than of the application of existing techniques and of an understanding of the importance of the problems.

THE SIGNIFICANCE OF CHEMICAL FOSSILS: FOSSIL PORPHYRINS

The preceding pages summarize the reasons for my belief that organic geochemistry is still in its infancy. In spite of rather extensive knowledge of the occurrence of chemical fossils—though limited to smaller molecules and few geological specimens—we remain uncertain of the extent, the rates and the mechanisms of geochemical reactions and of the composition and role of the sedimentary polymers. Only a small number of investigators have attempted to view the transformation of the sedimentary organic matter as the result of the thermal and chemical history of the sediments.

If we are to understand organic geochemistry in more than a qualitative, descriptive sense, we need research in these areas. A substantial contribution can come from the study of the preservation and transformation of chemical fossils.

I wish to demonstrate some of the research potential inherent in just one class of chemical fossils: the tetrapyrrole pigments. These are the conversion products of one principal biochemical precursor, chlorophyll *a*, and possibly of some related minor pigments. These fossil pigments bear the imprint of the environmental conditions and represent a record of the chemical subsurface environment and of the diagenetic history of their mother rock. From a few biological precursors, a vast number of chemical fossils is produced; we have estimated that more than 2×10^6 chemically distinct tetrapyrrole pigments are present in a single Triassic oil shale. This reflects the complexity of the diagenetic processes; it is diagnostically valuable because of the uniqueness and the multiplicity of the '*in situ* markers' which the porphyrins can provide.

Table 1 lists some of the known structural features of fossil tetrapyrrole pigments and suggests the interpretation of analytical measurements in terms of diagenetic processes.

Table 1. Porphyrins, structural features and geochemical significance*

Structural features	Analytical ratios	Possible geochemical interpretation
Vinyl-groups	$\frac{\text{total DPEP} + \text{MEP-pigments}}{\text{vinyl pigments}}$	Early stages in reduction.
Carbonyl-group	$\frac{\text{total DPEP} + \text{MEP-pigments}}{\text{carbonyl pigments}}$	Early to intermediate stages of reduction
—COOH Group	Bases/Acids	Thermal (+ 'bacterial'?) decarboxylation, late reduction(?)
Metal-chelation (V, Ni)	Free pigments/Chelates	Availability of metal (?), thermal diagenesis
Metal-chelation (V, Ni) Dihydroporphyrins	V/Ni Porphyrin/Chlorin	Rate versus equilibrium Stabilization through aromatization, later reduction as redox potential decreases.
Isocyclic C ₅ ring	DPEP type/MEP type	Early differences due to plant or animal predominance, later due to ring opening.
Benzoporphyrins	Alkyl/benzo-substitution	Cyclization, aromatization, probably intermediate to late diagenesis.
Low MW envelope (390–560 in free pigments)	DPEP/DPEP ± n14 MEP/MEP ± n14	Ratio decreasing from infinity, evidence of 'classical' conversion, later of diagenetic scrambling.
High MW envelope	Extent; pigment type-distribution; sum high/low MW pigments.	Severe diagenesis, polymerization processes; later decrease due to pyrolytic depolymerization.
MW envelope of Me-chelates	Extent in free pigments relative to complexes	Stabilization of a 'fossil' envelope in stable complexes, diagenetic trends.
Dimers	Dimer/monomer at same MW	Formation of aromatic sheets and crosslinking.

* From Blumer¹¹.

In chlorophyll some of the pyrrole nuclei are substituted by vinyl groups; these are converted to ethyl groups during diagenesis. In some cases, devinylation appears to take place. Similarly, the carbonyl groups of chlorophyll are reduced geochemically; but the partial survival in Tertiary sediments of some pigments containing carbonyl groups suggests a slower reduction than that of the vinyl groups, and possibly another reaction mechanism. These reductions must proceed simultaneously with other hydrogenations in the remainder of the sedimentary organic matter. A study of the gradual hydrogenation of the porphyrins should therefore provide insight into the reductive processes in the subsurface and into the interaction between hydrogen donors and hydrogen acceptors during diagenesis.

The tetrapyrroles of living organisms and of recent sediments are esters or free acids; in ancient sediments and in petroleum, carboxyl-free pigments predominate. Different reactions, e.g. enzymatic or thermal decarboxylation or exhaustive reduction, may be responsible for this conversion. Presumably these reactions represent increasingly severe transformation; therefore, a study of the gradual diagenetic conversion of esters and acids into basic

pigments should give insight into the environmental conditions that will bring about these reactions in the subsurface.

Chlorophyll and haemin are magnesium and iron chelates; the fossil porphyrins are either metal-free or chelated with nickel or vanadium. It has been suggested that the chelation with nickel proceeds more rapidly, though eventually the vanadium chelates are more stable. In this area we see opportunities for studies of interaction between trace elements and the organic matrix of the sediments.

Chlorophyll is a dihydroporphyrin; its fossil equivalents occur largely as fully aromatic systems. The presence of chlorins (dihydroporphyrins) in some ancient sediments has been suggested to be the result of a secondary reduction of porphyrins at low redox potentials during late diagenesis. Measurements of the chlorin to porphyrin ratio in sediments of increasing age could reflect the stabilization of the organic matter through aromatization and the reappearance of partially hydrogenated aromatic rings at a late stage, as a result of intermolecular disproportionations.

The saturated isocyclic carbon ring of chlorophyll and of its early degradation products is absent in haemin and in most ancient porphyrins. Postdepositional ring opening may increase the predominance of 'haemin-type' pigments; this would represent a slight stabilization of the aromatic structure. Thus, the ratio between pigments containing and lacking this isocyclic ring may reflect the relative contribution of plant and animal matter to a young sediment, while in an older one it could be indicative of postdepositional reactions.

In some fossil porphyrins one or more of the pyrrole rings are fused to benzene rings. This structural feature is absent in the pigments of living organisms and it is thought to have arisen through the ring closure of alkyl groups, followed by dehydrogenation. Again, this would represent a stabilization of the porphyrin which liberates hydrogen for other inter- and intra-molecular reductions. Measurements of the rate of appearance of benzoporphyrins during diagenesis are of obvious geochemical importance.

Present data suggest a gradual conversion in the subsurface of the tetrapyrroles to pigments that span a far wider molecular weight range than their biochemical precursors. Almost certainly, many different reaction types and mechanisms are involved in this far reaching conversion. A detailed study of this gradual transformation is one of the most challenging geochemical research topics which I can envisage. It is likely that the interaction between low and high molecular weight geochemicals plays a considerable role in this process; conversely, its study should provide information on a wide range of compounds and their reactions.

It has been suggested that the chelated tetrapyrroles are stabilized relative to their metal-free equivalents. This implies that the chelates may lag behind in the degree of their diagenetic transformation. An analysis of the composition of chelated and free pigments in the same specimen might reveal in addition to the present, a 'frozen' record of an earlier diagenetic stage and give insights into the compositional history of a sediment.

Dimeric porphyrins have been isolated from a Triassic oil shale²⁷. They are thought to be late diagenetic transformation products, whose formation reflects the production of large aromatic sheets through the fusion of aromatic

subunits. Again, studies of the rate and mode of formation of these pigments promise insight into geochemical processes that may affect a much wider range of the sedimentary organic matter than the porphyrins.

These examples give just some suggestions of the potential inherent in the study of chemical fossils. The fossil tetrapyrroles cover an immense structural and molecular weight range and only a minute fraction of all existing components have been isolated. There is little reason to doubt that other chemical fossils exist as similarly complex, extended homologous series. They may simply have escaped our attention which had been directed to younger, diagenetically immature, sediments and to compounds in a limited structural and molecular weight range. In combination, fossil porphyrins and other chemical fossils, present an unmatched opportunity for the understanding of organic geochemistry.

CONCLUSIONS

The study of chemical fossils is an important segment of organic geochemistry. It offers great challenge for the analytical chemist, the natural products chemist and the geochemist. Yet, this should not leave the impression that we are dealing just with one of the many intellectually stimulating but practically unimportant research areas. Organic geochemistry has contributed materially to better methods for the exploration and production of fossil fuels through the understanding of their mode of occurrence and formation and through the development of better analytical tools. Organic geochemistry is also critically important to the understanding of many pressing environmental problems. For instance, the severe effect of spilled fossil fuels is directly related to their composition and therefore to the diagenetic processes which have produced them within the earth. Our understanding of the chemistry of fossil fuels and of the changes which they undergo during diagenesis is directly applicable also to the understanding of their biological and chemical degradation in the environment. The analytical techniques which have been—and continue to be—developed for the analysis of chemical fossils are directly applicable to their determination after accidental spillage into the present day environment, and to their distinction from the recent, biochemical, hydrocarbon background. It is to be regretted that so little of our knowledge on the formation, composition, transformation, degradation and analysis of fossil fuels has been considered and applied to studies of their environmental effect. I believe that much of the present 'controversy' about the persistence and effect of oil pollution would be resolved if intelligent use were made of this geochemical background knowledge.

Organic geochemistry is a difficult but a challenging field. In spite of the complexity of fossil chemistry there is much opportunity for the application of simple analytical techniques; in fact, many of the problems in porphyrin chemistry which I discussed can be attacked through a combination of visible absorption spectroscopy with column, thin layer and gel permeation chromatography. A similar potential for simple analytical work exists in environmental geochemistry. There is probably no other area of chemistry which has been influenced so little by the analytical development of the last

decades. It is saddening to observe that hydrocarbon analyses in fisheries products are still based on the human sense of smell and taste, and that decisions which affect public health are based on these 'analyses'.

The organic geochemist who feels the emotional or economic need to justify his science to society may proudly point to the existing record and to the still much greater potential which his area holds for the understanding of important processes in the past and in the present environment.

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REFERENCES

- ¹ M. Blumer, In *Equilibrium Concepts in Natural Water Systems* (R. F. Gould, ed.) Advances in Chemistry Series, No. 67, pp. 312. American Chemical Society, Washington, D.C. (1967).
- ² G. Hradil, *Veröffentlichungen des Museums Ferdinandeum* **26/29**, 25 (1949).
- ³ E. Blumer, *Neujahrsblatt der Naturforschenden Gesellschaft in Zuerich* **122**, 1 (1920).
- ⁴ A. Treibs, *Annalen der Chemie* **509**, 103 (1934).
- ⁵ A. Treibs, *Annalen der Chemie* **510**, 42 (1934).
- ⁶ A. Treibs, *Annalen der Chemie* **517**, 172 (1935).
- ⁷ A. Treibs, *Annalen der Chemie* **520**, 144 (1935).
- ⁸ A. Treibs, *Angewandte Chemie* **49**, 682 (1936).
- ⁹ E. Kuhn-Schnyder, In *Die Evolution der Organismen* (G. Heberer and G. Fischer, eds.) Vol. 1, p. 238 Stuttgart (1967).
- ¹⁰ E. S. Barghoorn, *Scientific American* **224**, 30 (1971).
- ¹¹ M. Blumer, *An. Brasil. Acad. Cienc.* (in press), (1972).
- ¹² G. Eglinton and M. T. J. Murphy, *Organic Geochemistry*, Springer Verlag, New York (1969).
- ¹³ J. R. Maxwell, C. T. Pillinger and G. Eglinton, *Quart. Rev.* **25**, 571 (1971).
- ¹⁴ C. R. Evans, M. A. Rogers and N. J. L. Bailey, *Chem. Geol.* **8**, 147 (1971).
- ¹⁵ M. C. Louis and B. P. Tissot, Seventh World Petroleum Congress, Mexico, **2**, 47 (1967).
- ¹⁶ G. T. Philippi, In *Advances in Organic Geochemistry* (P. A. Schenk and I. Havenaar, eds), p. 25 Pergamon Press, Oxford (1969).
- ¹⁷ M. Poulet and J. Roucaché, *Revue de L'Institut Français du Pétrole* **25**, 127 (1970).
- ¹⁸ B. Tissot, *Revue de l'Institut Français du Pétrole* **24**, 470 (1969).
- ¹⁹ B. Tissot, J. L. Oudin and R. Pelet, *Critères d'Origine et d'Evolution des Pétales, Application a l'Etude Geochimique des Bassins Sedimentaires*. Institut Français du Pétrole, Ref. 19539, (1971).
- ²⁰ P. Albrecht and G. Ourisson, *Angewandte Chemie* **10**, 209 (1971).
- ²¹ M. Blumer, *Science* **149**, 722 (1965).
- ²² E. Eisma and J. W. Jurg, In *Organic Geochemistry* (G. Eglinton and M. T. J. Murphy, eds), p. 676, Springer Verlag (1969).
- ²³ G. Eglinton, In *Organic Geochemistry* (G. Eglinton and M. T. J. Murphy, eds) p. 20. Springer Verlag (1969).
- ²⁴ A. L. Burlingame, P. A. Haug, H. K. Schnoes and B. R. Simoncit, In *Advances in Organic Geochemistry*, (P. A. Schenk and I. Havenaar, eds.) p. 85. Pergamon Press, Oxford (1969).
- ²⁵ G. T. Philippi, *Geochimica et Cosmochimica Acta* **29**, 1021 (1965).
- ²⁶ M. Blumer and W. D. Snyder, *Chemical Geology* **2**, 35 (1967).
- ²⁷ M. Blumer and M. Rudrum, *Journal of the Institute of Petroleum* **56**, 99 (1970).
- ²⁸ J. J. Schmidt-Collarus, and C. H. Prien, *An. Brasil. Acad. Cienc.* (in press), (1972).
- ²⁹ M. Sugihara, J. F. Branthaver, G. Y. Wu and C. Weatherbee, In *Symposium on Hetero-compounds in Petroleum—Known and Unknown*, p. C5. Division of Petroleum Chemistry, American Chemical Society, Houston Meeting, February 22-27, 1970.
- ³⁰ G. Zebger, Thesis on: *Abtrennung und Identifizierung von Porphyrin-Farbstoffen aus 'Asphalt-enen' eines Südamerikanischen Rohöls*. Braunschweig (1967).
- ³¹ D. K. Vitorovic, *An. Brasil. Acad. Cienc.* (in press), (1972).