

# ON THE ORIGIN OF PETROLEUM INSIDE FRESHWATER CARBONATE CONCRETIONS OF MIOCENE AGE†‡

*by*

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## INTRODUCTION

Most crude oil reservoirs occur in sediments which were deposited under shallow marine or brackish water conditions. In the past, this relationship was interpreted to mean that either marine organisms or an oceanic environment or perhaps both factors are essential for the formation of hydrocarbons. As more geological details on the distribution pattern of petroleum in time and space were gathered, it became evident that even sediments deposited in isolated freshwater basins such as the Green River Formation were capable of producing hydrocarbons. Thus the environment in terms of fresh water versus salt water (marine) was no longer regarded as the crucial factor in controlling the generation of hydrocarbons and the final formation of crude oil.

The scarcity of economically important petroleum reservoirs associated with freshwater sediments was partly attributed to the fact that as a result of continental weathering and denudation, freshwater sediments have less chance of survival than their time-equivalent marine pendants. Consequently the ratio of the total volume of recent freshwater deposits to the volume of marine sediments progressively decreases with time up to a certain point.

In addition to erosional processes, the structural set-up and tectonic history of marine and continental basins can differ considerably. The difference has often been used to account for the apparent ease with which petroleum is generated from a rock suite of marine origin and the general lack of crude oil formation in continental sediments. The higher percentage of clays in

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sediments of marine facies as compared to those deposited in freshwater environments is a third criterion which is used to explain the greater abundance of petroleum in marine sediments.

The various sedimentological, petrographical, and tectonic factors that control the distribution of crude oil are now relatively well understood, but there still remains a geochemical "Petroleum problem". The crux of the problem has to do with the unsettled question as to how hydrocarbons and the associated organic compounds in petroleum deposits are ultimately generated. The second part of this problem, which is not necessarily of secondary importance, has to do with the migration and accumulative phenomena that can finally lead to the formation of economically important petroleum deposits.

Various theories have been advanced bearing on this twofold problem. After Smith (1952, 1954) for the first time isolated  $C^{14}$  active hydrocarbons from recent sediments, several outstanding papers appeared on the distribution of hydrocarbons in present day sediments: Hunt and Jamieson (1956); Judson and Murray (1956); Stevens *et al.* (1957); Meinschein (1957, 1959, 1961); Meinschein and Kenny (1957); Evans *et al.* (1957); Erdman *et al.* (1958, 1958b); Erdman (1961); Veber and Turkeltaub (1958); Sokolov (1959); Emery and Hoggan (1958); Bray and Evans (1961); Hunt (1962); and Dunton and Hunt (1962).

On the basis of the presence and similarity of hydrocarbons in the  $C_{15}$  to  $C_{30}$  range found in plant and animal materials, recent sediments, and petroleum, some writers concluded that all have the same origin and are biogenic in nature. Inasmuch as petroleum is made up of about 50 per cent of light hydrocarbon fraction in the  $C_3$  to  $C_{14}$  range, all of which are not present in recent sediments, Veber and Turkeltaub (1958), Sokolov (1959), Hunt (1962), and Dunton and Hunt (1962) pointed out that there have to be other sources besides living matter from which hydrocarbons are ultimately derived. The idea of a diagenetic maturation process is supported by the absence of low-molecular-weight hydrocarbons in the near-surface recent sediments and their relatively high abundance in ancient rocks: Erdman (1961). Traces of benzene, toluene, and the xylenes as found by Emery and Hoggan (1958) in off-shore sediments of California may suggest that the production of low-molecular-weight aromatic hydrocarbons starts at an early diagenetic stage.

From the present state of knowledge, it seems reasonable to assume that hydrocarbons in petroleum and ancient sediments are a product of both biogenesis and slow inorganic maturation. The lipid and, perhaps, the protein fractions are regarded as the most suitable organic sources that during diagenesis can be converted to hydrocarbons: Erdman (1961); Hanson (1959); Breger (1960).

The manner in which the finely disseminated hydrocarbons in sediments become concentrated is of great importance and constitutes the second part of the "Petroleum problem". In this connection, the suggestion made by Bak-

(1959, 1960) on the solubilizing effect of formation waters, which would enhance considerably the solubility of hydrocarbons, is noteworthy. Inasmuch as the solubility of hydrocarbons is a function of the salt concentration of formation waters, and that brines saturated with inorganic salts will eventually expel a great number of organic molecules (including even polar ones, such as some phenols), an organic phase has to develop. Degens *et al.* (1962a, 1963) concluded that formation waters have to have brine properties before oil droplet formation is initiated.

The mechanism by which this post-depositional increase in salinity can be accomplished has been presented in detail by von Engelhardt (1961). According to his studies, upon subsidence of a basin and compaction of the strata, clay minerals will release saline waters to the overlying sediments. Consequently, shales retain interstitial waters poor in electrolytes. On the other hand, ions will be filtered off when formation waters, in obeying the laws of migration, have to pass from a rock such as a sandstone through overlying clay strata.

Experimental work by the writers (research in progress) on the resistivity of naturally occurring waters, squeezed from clays at different overburden pressures, supports von Engelhardt's statements. On increasing the pressure from 1000 to 15,000 psi, the resistivity of the waters released increased by 16 to 30 per cent; upon changing the overburden pressure from 15,000 to 50,000 psi, the resistivity increased by about 70 per cent. In other words more electrolytes are released from the clay strata at the initial stages of compaction.

The solubility of hydrocarbons generally decreases with increasing molecular weight. On assuming that hydrocarbons will be flushed from the sediments upon compaction only in quantities which are soluble in the formation waters at a given pressure and temperature, the extractable hydrocarbon fraction will be small in comparison to the amounts left in the sediment: Chilingar (1961). The odd-carbon preference in *n*-paraffins at carbon numbers greater than 21 (Meinschein, 1962), as displayed in recent and ancient sediments should, therefore, have no effect on the hydrocarbon spectrum of crude oils, which actually does not exhibit odd- over an even-carbon preference: Bray and Evans (1961).

The principal objective of the present investigation was to collect some data which may help to understand the puzzling occurrence of petroleum inside freshwater concretions of Miocene age. Inasmuch as these petroliferous nodules are found in widely scattered localities throughout Nevada, Utah and California, and do not show any obvious connection with any known petroleum reservoir, they may offer some insight into the general "Petroleum problem".

Besides petroleum, silicified organisms which exhibit minute morphological and structural details are located in the center portion of some of the concretions. A study on the mechanism of silification, as well as of the formation of the carbonate nodules themselves, is also important, because it may show that some relationship exists between carbonatization, silicification, and the occurrence of petroleum.

DESCRIPTION AND LOCATION OF PETROLIFEROUS  
NODULES AND RESULTS OF PREVIOUS STUDY

The petroliferous nodules described here were collected from the Calico Mountains in San Bernardino County, California. They are embedded in freshwater lake sediments of Miocene age. One can distinguish between two types of fossil- and petroleum-bearing nodules: the pale-whitish ones which are restricted to the older deposits, and the bluish-grey ones which appear higher in the section.

Degens *et al.* (1962b) investigated the origin of these nodules by using various geochemical tools, which included X-ray diffraction analysis, stable isotope work of the carbonate phase in terms of  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  ratios, wet chemical analysis, spectroscopical trace-element determinations, and infrared analysis of the extractable hydrocarbon fraction.

The wide variation that exists in the total concentration of boron, strontium, barium, and magnesium and, on the other hand, their relationship to the oxygen isotope distribution of carbonates, was interpreted as a result of short term environmental fluctuations from normal fresh waters to highly saline brines and *vice versa*. The systematic internal  $\delta O^{18}$  variations from about  $-8$  to  $0$  (relative to the Chicago Belemnite Standard, Craig (1957)), as observed by moving from the center to the rim of a nodule, and, conversely the light value of  $-12$  per mil in carbonates of the host sediment suggested that the surrounding strata were deposited under normal freshwater conditions, whereas the concretions gradually developed as the evaporation started and the salinity increased. The light  $\delta C^{13}$  values of the calcites, in the range of  $-8$  to  $-14$ , indicated that isotope exchange between atmospheric carbon dioxide and the bicarbonate phase along the water-air interface was incomplete (non-equilibrium), probably a result of a rapid water turnover.

The data available at the time the forementioned environmental studies were accomplished (Degens *et al.*, 1962b), did not allow any conclusive statements bearing on the origin of petroleum inside the nodules. The authors believe that the new information gathered in the meantime and the results of their former study have some significance for the "Petroleum problem" in hand.

## RESULTS

*Petrography*

Figure 1 shows a typical cross-section of a nipple-shaped carbonate concretion. The lower half of the nodule pictured consists of flat-lying layers (or slightly convex upward) which are oriented parallel to the bedding plane of the surrounding strata. The horizontal bands do not continue into the host rock strata and they are petrographically distinctly different. Whereas the percentages of clastic materials in the host rock are of the order of 10 to 80 per cent, the amount of clastics in the nodules rarely exceeds 5 per cent.

Thin-section studies reveal that the lower portions of the concretions are predominantly made up of micro-crystalline calcite and the banding is caused by interlayering of clay particles. In the case of the pale-whitish concretions from the older deposits, films of  $\text{SiO}_2$  layers are often present instead of clays, and produce a similar stratification pattern.

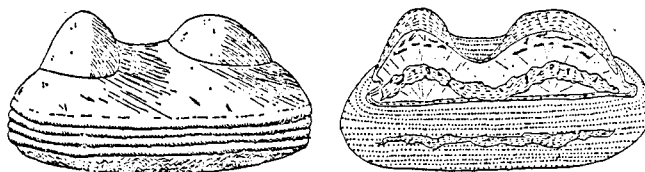


FIGURE 1.—Cross-section through nipple-shaped freshwater concretion of Miocene age. Fan-shaped primary calcites (broken lines); fan-shaped co-existing primary calcites, quartz and micro-crystalline calcite (radiating lines and light dots); horizontally layered carbonates and silica (dotted lines); petroleum (solid black areas).

The upper portion of the nodules exhibits dome-like structures. In general, a nodule has only one dome; however, occasionally, about one in fifty cases, two or more domes may be developed. In many cases the nodules are not nipple-shaped but are simply dome-shaped. For demonstration (Fig. 1) a nodule having two domes was selected. The degree of bending in the top layer varies from one specimen to the other. Some nodules display a pronounced dome structure, whereas others are just slightly curved at the top. At the rim of the contact zone of the upper to the lower portion of the nipple-shaped concretion, the uppermost layers of the basal section are sometimes sharply bent upward, and gradually thin out.

Calcite is the most dominant material in the dome-shaped portion of the nodule. The size of the individual calcite crystals ranges between 0.2 and 2 mm. Most characteristic is the anisotropic fabric pattern, and the large calcite crystals are oriented in a fan-shaped fashion (convex upward arrangement). This "fan-shaped" feature is most beautifully developed in the top section of the domes (Fig. 1, light dashed lines). The area, indicated by the light stipple and radiating lines, is a mixture of micro-crystalline and "fan-shaped" calcite, and the former type is the more dominant phase. Besides the larger calcite crystals, thin layers of secondary quartz display a convex upward arrangement in some of the pale-whitish nodules.

In summary, calcite is the principal mineral phase throughout the nodules, and accounts for about 90 to 95 per cent of the total rock. Quartz of the chalcedonic type is abundant in the older pale-whitish nodules (1 to 5 per cent), but occurs only in traces in the younger bluish-grey ones. Illites are the predominant clays; and with the other clastic compounds are essentially restricted to the lower half of the concretions. Barytes, celestine and gypsum are also found in small concentrations.

TABLE 1.—DISTRIBUTION OF AMINO ACIDS  
(in parts per million)

		Freshwater Concentration (total)			Soil†		MnO <sub>2</sub> Nodule† (free)
		1	2	3	(free)	(combined)	
Basic	Arginine	—	trace	—	—	trace	—
	Ornithine	0.17	0.25	0.13	—	—	0.06
	Lysine	0.14	0.28	0.11	0.08	145	0.16
	Histidine	0.09	0.15	trace	trace	11	—
Acidic	Aspartic acid	0.20	0.32	0.19	0.28	3	0.40
	Glutamic acid	0.44	0.70	0.39	0.29	7	0.39
Neutral	Glycine	0.91	1.18	1.26	0.24	141	0.59
	$\alpha$ -alanine	0.43	0.50	0.48	0.11	260	0.20
	$\beta$ -alanine	—	—	—	—	50	—
	Serine	0.64	0.67	0.57	trace	59	0.80
	Proline	—	—	—	—	202	—
	Valine	0.11	0.18	0.13	0.19	176	0.10
	Threonine	0.07	0.12	0.07	—	51	0.89
Aromatic	Leucines	0.32	0.50	0.42	trace	357	0.21
	Tyrosine	trace	trace	trace	—	5	0.01
	Phenylalanine	0.19	0.28	0.16	trace	145	0.11
Sulfur	Cystine	—	—	—	—	trace	—
	Methionine	—	—	—	—	—	—
	Total (ppm)	3.71	5.13	3.91	1.19	1612	3.92
	Total organic carbon (%)	0.40%	0.80%	0.41%	1.12%		not determined

† For comparison.

Mineral size and fabric change consistently from the bottom to the top of the nodules. The fan-shaped arrangement of the calcites is the most characteristic feature of the dome area.

Petroleum rarely occurs by itself in the banded layers of the lower half of the concretion. Its presence seems to be exclusively governed by geological micro-structures (domes) developed inside the nodules.

#### *Geochemistry*

The total organic matter of three representative nodules from the pale-whitish type (analysis 1, Table 1), and bluish-grey type (analyses 2 and 3, Table 1), ranges from 0.5 to 1.0 per cent. Most of the organic matter is extractable by a benzene-methanol-acetone mixture (70:15:15). Upon acid hydrolysis, small amounts of amino acids are released to the hydrolysis liquors (Table 1). Carbohydrates and amino-sugars are not present.

Some of the hydrocarbons of sample 3 (Table 1) have been studied in detail. The data on the yield of hydrocarbons in the  $C_1$  to  $C_8$  range are presented in Table 2. It is noteworthy that combined butanes and pentanes account for more than two-thirds of the total hydrocarbon fraction of the  $C_1$  to  $C_8$  range.

TABLE 2.—HYDROCARBON YIELD FROM A MIOCENE FRESHWATER CONCRETION

Hydrocarbon	ppm
Methane and Ethane	0.26
Propane	0.48
Isobutane	0.71
<i>n</i> -butane	0.74
Unidentified butanes	0.02
Pentane isomers	1.44
<i>n</i> -pentane	0.48
Hexane isomers	0.98
<i>n</i> -hexane	0.42
Heptane isomers	0.44
<i>n</i> -heptane	0.11
<i>n</i> -octane	present†
Octane isomers	0.15
Total hydrocarbons $C_1$ to $C_8$ range	6.23

† Total concentration cannot be determined (interference).

The infrared analysis of the extractable heavy hydrocarbon fraction reveals the presence of a complex mixture of compounds. The ratio of alkanes to cycloalkanes is about 4:1. Results on the total amounts of high-molecular-weight hydrocarbons, O-N-S compounds, and the benzene-methanol-acetone

extractable fraction are presented in Table 3. The ratio of aliphatic to aromatic hydrocarbons is roughly 1:2. One-fourth of the organic matter present in the nodule is of the organic solvent extractable type. The remainder of the organic matter is acid-insoluble and kerogenous in Nature.

#### *Palaeontology*

The organisms found inside the nodules from Calico Mountains include the following:

- (1) Turbellaria, or flat worms of three families; and also many strings of eggs (some showing embryos)
- (2) Mollusca
- (3) Anostraca, or fairy shrimps, in various stages of growth. Multitudes of their coprolites, and even the eggs in the ovarium
- (4) Ostracoda, from Calico Mountains and from Lenwood Hill
- (5) Copepoda, from Lane Mountains
- (6) Acarina, water mites and their eggs (several species)
- (7) Arachnida, water spiders (several species)
- (8) Scorpionida (claw of a scorpion)
- (9) Chelonethida, pseudo-scorpion (several claws)
- (10) Myriapoda, a centipede
- (11) Collembolan, springtails
- (12) Odonata, dragon flies and damsel flies
- (13) Ephemera, May flies with clusters of eggs
- (14) Plecoptera, stone fly nymph
- (15) Corrodentia, young bark louse
- (16) Isoptera, five species of termite wings and a soldier head
- (17) Thysanoptera, both sub-orders of thrips (several species)
- (18) Chermodea, jumping plant lice (adults and wings)
- (19) Aphidodea, aphids
- (20) Homoptera, several species of leaf hoppers
- (21) Hemiptera, several families of bugs
- (22) Orthoptera, fragment of one grass hopper
- (23) Coleoptera, several families of beetles, including larvae and adults
- (24) Lepidoptera, crystallized aquatic moths
- (25) Hymenoptera, a crystallized Braconid parasite, an ant, and impression of a wasp
- (26) Diptera, several families of midges and flies (including eggs, larvae, pupae, and adults)
- (27) Pisces, two fish skeletons
- (28) Aves, crystallized feathers and feather impressions.
- (29) Mammalia, crystallized hairs of mammals.

Several Heleid midges caught half-way out of their pupa cases, a pair of bugs and a pair of flat worms in copula, strings of eggs showing embryos in various stages of development, and fairy shrimps with eggs in the brood pouch, all testify to the sudden death and quick preservation in many cases.



As far as the plant kingdom is concerned, the following plant materials have been discovered inside the nodules from Calico Mountains:

- (1) Diatoms of several types
- (2) Algae of many kinds
- (3) Mosses of several types (stems and leaflets)
- (4) Pond weeds, sometimes entire plants
- (5) Seeds of higher plants and an impression of a leaf.

## INTERPRETATION OF RESULTS AND DISCUSSION

### *Origin of Nodules*

The anisotropic fabrics in general and the fan-like arrangement of the calcites around the entrapped organisms in particular serve as an indication for the syngenetic or, at most, early diagenetic origin of the nipple-shaped nodules. The decrease in elastic materials in moving from the bottom to the top of a nodule further suggests that the nodules formed at a time when the deposition of elastic constituents was at a low point and close to being discontinued, and evaporates such as sulfates and borates started to precipitate. Systematic internal variations in  $O^{18}/O^{16}$  ratios and trace elements are in support of the inferences drawn from the petrographical data: Degens *et al.* (1962).

The kind of stratification in the way of horizontal bedding, and the presence of detrital clay particles in interlayered positions can be used as evidence that the lake beds were still covered with water, when deposition and precipitation of the bottom half of the nodule took place. The upper half of the nodule displaying the dome-shaped structure, however, was formed at a time when the free water phase on top of the lake beds was gone, but still sufficient moisture was left in the deposits.

The removal of the water cover is certainly the diastrophic event that caused sudden death for all the multitudes of benthonic and planctonic life forms that inhabited the lake. Organic materials ranging from algae to various types of insects and larvae apparently served as crystallization centers for the calcites by supplying ammonia to the reacting system and causing the precipitation of carbonates. Inasmuch as the ammonia escape has an upward trend, a massive shield of calcite, displaying the convex upward arrangement of the individual crystals was able to develop.

Some of the fossil material is silicified and exhibits detailed morphological and structural features, Pierce (1961). There are two conceivable sources for the silica, one of which is inorganic in origin and the other is organic in nature. As shown by Iler (1955), Krauskopf (1956), Okamoto (1957), and Siever (1957), silica can be present in natural waters in two possible forms: (1) Molecular-dispersed, and (2) Colloidal. Silica dissolves in water, forming a true ionic solution ( $H_4SiO_4$ ) up to a certain concentration (120 to 140 ppm, 25° C). Above this concentration silica tends to polymerize.

Most of the exogenic solutions (oceans, rivers, ground waters, lakes) have silica content values below 100 mg/l. Most of the silica in these waters will therefore, be in the molecular-dispersed stage. The least stable form of silica (amorphous silica) shows the greatest solubility, and (as is expected on physico-chemical grounds) the most stable form (quartz) the least. For quartz at ordinary temperatures the solubility in near-neutral solutions is about 6–8 ppm, whereas amorphous silica has a solubility of about 120–150 ppm: Siever (1957). Theoretically, quartz should crystallize from a solution supersaturated with respect to quartz, but fails to do so in any humanly reasonable time, apparently because of the extreme slowness of the reaction (kinetics). Hence, silica can be carried in surface waters at concentrations far in excess of the solubility of quartz, cristobalite or tridymite.

Although colloidal silica is rarely present in surface waters, precipitation of amorphous silica is widespread in Nature. This is largely brought about by the action of certain organisms such as sponges, radiolaria, or diatoms which are capable of extracting silica from an environment undersaturated with respect to amorphous silica. The only other way to increase the silica content of surface waters is by contributions from thermal springs, or by evaporation of large volumes of water.

The lake sediments under investigation frequently contain relics of diatoms, particularly in the older deposits. It is known that the skeleton of any silica-secreting organism is rather metastable and tends to dissolve very rapidly. Silica, diagenetically mobilized, migrates in the molecular-dispersed stage in the direction of a concentration gradient to reprecipitate as quartz and accumulate at points of least solubility: Bramlette (1946). This reorganization may occur shortly after deposition.

The occurrence of interlayers of volcanic tuff in the Miocene lake beds could mean that silica, by way of thermal springs, was simultaneously introduced into the lake. Upon evaporation, the level of silica could have been raised to such a degree that the precipitation of opaline silica was initiated. The perfect preservation of some insects and other organisms may be due to the fact that they became embedded in amorphous silica, which on evaporation of water precipitated out of the lake environment. It is noteworthy that on the older nodules contain silicified organisms and banded chert layers.

Today, most of the silica in the nodules is in the form of micro-crystalline quartz, rather than opal. Thin sections show that carbonatization generally preceded silicification. Calcites are often metasomatically replaced by silica, although occasionally a reverse order of events is evident. The reorganization of silica from the amorphous to the crystalline phase, therefore, proceeded during the early stages of diagenesis. As a function of the degree of dissolution and precipitation of secondary silica and calcite, and their effect on the original fabric, the pore space may increase or decrease in size.

One can conclude that the nodules were formed at a time when the continental lakes gradually evaporated. This "catastrophic event" caused sudden

death for the benthonic and planctonic organisms inhabiting the lake. Periodic volcanic activity also could have caused sudden death of organisms. The original fabric of the nodules as syngenetically fixed became slightly modified during the early stages of diagenesis as a result of recrystallization phenomena.

#### *Origin of Petroleum*

The expectation of finding larger quantities of preserved biochemical constituents inside the nodules or petrified insects proved to be wrong. Amino sugars, such as glucosamine or galactosamine, which constitute one of the principal biochemical building blocks of arthropods, are not present at all. With respect to proteinaceous matter, only traces of amino acids are left. For comparison the amino acid spectrum of a nearby desert soil of recent age, and a present-day concretion from the Atlantic Ocean floor is shown here (Table 1). The soil contains about 500 times as much amino acids as the Miocene concretions, and only the contents of their free compounds are of comparable magnitude. The analysis of amino acids, adsorbed to a manganese nodule on the other hand, is identical in amount and type with those amino compounds which occur in the freshwater nodules. The data suggest that the proteinaceous materials have been nearly completely eliminated from the nodules during diagenesis, leaving behind only traces of amino acids, very likely in an adsorbed state. The complete destruction of the biochemical record was accomplished early in the history of the nodule, but not necessarily at the time of deposition, as is indicated by the perfect preservation of impressions or moulds of organisms.

Liquid petroleum and bitumens account for about one-fourth of the organic matter in the nodule; the rest is kerogen. The hydrocarbon spectrum is of considerable interest, because the gas and gasoline fraction in the  $C_1$  to  $C_8$  range constitutes only about 2 per cent of the total hydrocarbon cut, high-molecular-weight aromatics, alkanes and cycloalkanes in the  $C_{15}$  to  $C_{30}$  range are the dominant hydrocarbon fraction (Table 3). The presence of small amounts of gasolines in the  $C_9$  to  $C_{14}$  range is conceivable.

TABLE 3.—HIGH-MOLECULAR-WEIGHT HYDROCARBON YIELD  
FROM A MIOCENE FRESHWATER CONCRETION

Compound	ppm
Paraffins and naphthenes ( $C_{15}$ - $C_{10}$ range)	103
Aromatic hydrocarbons	191
Total hydrocarbons	294
O-N-S compounds	250
Total soluble fraction	1044
Organic carbon	4100

Isoprenoids, steroids, and related cyclic constituents of the lipid fraction are the most likely sources of the arenes. Some of the low-molecular-weight

aromatic hydrocarbons may, in addition, be generated from aromatic amino compounds such as phenylalanine or tyrosine. Erdman (1959, 1961), Hansson (1959), Breger (1960), and Meinschein (1962) proposed simple exothermic reactions by which some of the forementioned constituents are converted to aromatic hydrocarbons.

For our studies, the findings of Meinschein (1959, 1962), and Meinschein and Kenny (1957) on the distribution of isoprenoids and arenes in modern soils and marine sediments, are of particular interest, because isoprenoids may account for the aromatic hydrocarbons in our freshwater petroleum. Isoprenoid-containing wax esters, common in soils, are rarely found in aquatic sediments deposited in a reducing environment. Conversely, aromatic hydrocarbons are abundant in aquatic deposits, but they are low or missing in continental soils.

With regard to the aliphatic hydrocarbons, the distribution pattern in soils, and marine and freshwater sediments is not greatly different. Hydrocarbons in the  $C_{15}$  to  $C_{30}$  range are actually omnipresent in all soils and basins and sediments. Their concentration may range from a few ppm to a couple of hundred ppm: Smith (1954); Stevens *et al.* (1956); Bray and Evans (1961). Values above 100 ppm, however, are rare. The gas and gasoline fraction in the  $C_3$  to  $C_{14}$  range, which constitutes about 50 per cent of most crude oils, is missing from recent deposits: Veber and Turkeltaub (1958); Sokolov (1959); Dunton and Hunt (1962); Hunt (1962).

Taking these facts and data into consideration, the hydrocarbon spectrum of the petroleum inside the nodules is similar to that of hydrocarbons present in recent aquatic deposits. In both cases, the content of high-molecular-weight aromatics, paraffins and naphthenes, is high, whereas the content of the gas and gasoline fraction in the  $C_3$ - $C_{14}$  range is low, if present at all. One may point out that the traces of gases and gasoline hydrocarbons found in the Miocene nodules are of the same magnitude and type as found in non-productive ancient sediments of comparable lithology: Hunt (1962). The relatively high abundance of the combined pentanes and butanes may be due to a possible decarboxylation and deamination of a great number of amino acids (Erdman, 1961), by which processes these types of hydrocarbons would be preferentially generated.

The high-molecular-weight hydrocarbons present in recent sediments and soils are believed to be of biogenic origin: Meinschein (1962). On the other hand, the low-molecular-weight compounds found in ancient sediments and crude oils are undoubtedly a product of slow inorganic maturation processes. Inasmuch as the hydrocarbons inside the Miocene freshwater concretions resemble to a surprising degree those obtained from recent sediments, but conversely are distinctly different in type or distribution pattern from crude oils found in marine or terrestrial deposits, a biogenic origin of the hydrocarbons studied seems to be very likely. This relationship further suggests that the petroleum was generated and introduced into the concretions early in the history of the nodules and their surrounding strata, before an inorganic

maturation process could produce the low-molecular-weight hydrocarbon species. The geochemical data in connection with the regional distribution of petroliferous nodules across Utah, Nevada and California, suggest that an infiltration of hydrocarbons from nearby ancient petroleum reservoirs is unlikely. A syngenetic incorporation of bituminous substances during deposition can be dismissed for various reasons, Degens *et al.* (1962b).

Thus, the possible explanations for the occurrence of liquid petroleum and solid bitumens inside the nodules include the following:

- (1) *In situ* generation of hydrocarbons by micro-organisms living on the entrapped organic matter; and
- (2) Introduction of petroleum into the void space from the surrounding strata.

The first explanation, however, would mean that all the entrapped organic matter must have been nearly totally converted to hydrocarbons, because in some cases the space formerly occupied by organic debris is now almost completely filled with petroleum. Even spaces developed by dissolution of calcite, silica or water-soluble evaporites contain liquid hydrocarbons. The first hypothesis, therefore, is very unlikely because of various biological and geochemical grounds.

In view of the data and mechanisms presented by von Engelhardt (1961), Baker (1959, 1960) and Degens *et al.* (1963), the second alternative, according to which petroleum was introduced from outside into the empty space of the nodules, seems most reasonable. As a function of capillary or intergranular forces operating during compaction (von Engelhardt, 1961; Chilingar, 1961) and evaporation, the salinity of subterranean waters will increase considerably. The solubility of hydrocarbons is enhanced in the presence of higher quantities of electrolytes (Baker, 1960); however, brines saturated with certain inorganic salts will eventually release their hydrocarbons. In the case of an emulsion transfer, salts will act as a de-emulsifying agent. In both circumstances, an organic or oil phase will instantaneously develop as soon as the solubility product of NaCl is exceeded.<sup>1</sup>

According to Brod (personal communication), bituminous substances either in a dissolved state or more likely as an emulsion migrating in sub-capillary pores together with water are released in the form of petroleum only at the time of their transition from a semi-bonded into a free state. This is accomplished during the transition from sub-capillary into capillary and super-capillary pores. The process of molecular migration is accompanied by a series of complex physical-chemical transformations of mobile substances during their migration in a semi-bound state in sub-capillary pores of argillaceous, marly and clayey-silty rocks which have started to compact. In other words, the keynote of Brod's hypothesis is the effect of pore space on the release of hydrocarbons. Vassoevich and Veber (personal communication) outlined the reactions that converted organic matter into bitumens during lithification and low-grade metamorphism of a clayey-silty rock suite.

<sup>1</sup> The high-molecular-weight *n*-paraffins extracted from the nodules display no odd carbon preference.

## CONCLUSIONS

The history of formation of the Miocene freshwater nodules and the origin of petroleum inside these nodules can be summarized as follows:

- (1) The depositional environment of the freshwater lake sediments characterized by short-term fluctuations from normal fresh water (low salinity) to highly saline brines and vice versa.
- (2) The formation of some of the carbonate nodules embedded in the lake strata started upon evaporation at intermediate salinities at a time the lake beds were still covered with water. Dead organisms possibly acted as nuclei for the formation of nodules.
- (3) In the later stages of evaporation, the water cover disappeared and evaporites developed. Suddenly death visited all aquatic life in the lake (catastrophic event).
- (4) Dead organisms spread out over the dry lake beds served as crystallization centers for the calcites. The dome-like micro-structures in the upper half of the nodule developed (convex upward arrangement of calcite crystals).
- (5) Most of the silica, deposited as an amorphous phase, reorganized itself shortly after deposition and possibly re-precipitated as microcrystalline quartz. Primary calcites were occasionally metasomatically replaced by silica and secondary calcites developed.
- (6) Dissolution and precipitation of calcite and silica changed the original fabric of the nodule by disintegration or cementation.
- (7) Finely disseminated hydrocarbons in the lake beds were taken up by interstitial waters in amounts soluble at a given temperature and salinity content of the waters.
- (8) As a function of capillary and intergranular forces operating during evaporation, the water movement in the strata had principally an upward direction. The salinity gradually increased up to a point, where hydrocarbons and other organic constituents were expelled, thereby producing an organic phase. This step most likely occurred during the transition from sub-capillary into capillary and super-capillary pores.
- (9) Dome-shaped micro-structures served as petroleum traps where fair amounts of crude oil could accumulate, giving rise to the present occurrence of oil inside the nodules.
- (10) Petrographical, palaeontological, and geochemical data indicate that petroleum, as found in the nodules, is probably biogenic in origin and was collected by means of interstitial waters in the early stages of diagenesis from the surrounding freshwater lake beds.

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