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Dismissal of the Claims of a Biological Connection for Natural Petroleum.

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1. Introduction.

With recognition that the laws of thermodynamics prohibit spontaneous evolution of liquid hydrocarbons in the regime of temperature and pressure characteristic of the crust of the Earth, one should not expect there to exist legitimate scientific evidence that might suggest that such could occur. Indeed, and correctly, there exists no such evidence.

Nonetheless, and surprisingly, there continue to be often promulgated diverse claims purporting to constitute "evidence" that natural petroleum somehow evolves (miraculously) from biological matter. In this short article, such claims are briefly subjected to scientific scrutiny, demonstrated to be without merit, and dismissed.

The claims which purport to argue for some connection between natural petroleum and biological matter fall into roughly two classes: the "look-like/come-from" claims; and the "similar(recondite)-properties/come-from" claims.

The "look-like/come-from" claims apply a line of unreason exactly as designated: Such argue that, because certain molecules found in natural petroleum "look like" certain other molecules found in biological systems, then the former must "come-from" the latter. Such notion is, of course, equivalent to asserting that elephant tusks evolve because those animals must eat piano keys. In some instances, the "look-like/come-from" claims assert that certain molecules found in natural petroleum actually *are* biological molecules, and evolve only in biological systems. These molecules have often been given the spurious name "biomarkers."

The scientific correction must be stated unequivocally: There have *never* been observed any specifically biological molecules in natural petroleum, except as contaminants. Petroleum is an excellent solvent for carbon compounds; and, in the sedimentary strata from which petroleum is often produced, natural petroleum takes into solution much carbon material, including biological detritus. However, such contaminants are unrelated to the petroleum solvent.

The claims about "biomarkers" have been thoroughly discredited by observations of those molecules in the interiors of ancient, abiotic meteorites, and also in many cases by laboratory synthesis under imposed conditions mimicking the natural environment. In the discussion below, the claims put forth about porphyrin and isoprenoid molecules are addressed particularly, because many "look-like/come-from" claims have been put forth for those compounds.

The "similar(recondite)-properties/come-from" claims involve diverse, odd phenomena with which persons not working directly in a scientific profession would be unfamiliar. These include the "odd-even abundance imbalance" claims, the "carbon isotope" claims, and the "optical-activity" claims. The first, the "odd-even abundance imbalance" claims, are demonstrated to be utterly unrelated to any biological property. The second, "carbon isotope" claims, are shown to depend upon measurement of an obscure property of carbon fluids which cannot reliably be considered a measure of The third, the "optical-activity" claims, deserve particular note; origin. for the observations of optical activity in natural petroleum have been trumpeted loudly for years as a "proof" of some "biological origin" of petroleum. Those claims have been thoroughly discredited decades ago by observation of optical activity in the petroleum material extracted from the interiors of carbonaceous meteorites. More significantly, recent analysis, which has resolved the previously-outstanding problem of the genesis of optical activity in abiotic fluids, has established that the phenomenon of optical activity is an inevitable thermodynamic consequence of the phase stability of multicomponent fluids at high pressures. Thereby, the observation of optical activity in natural petroleum is entirely consistent with the results of the thermodynamic analysis of the stability of the hydrogen-carbon [H-C] system, which establish that hydrocarbon molecules heavier than methane, and particularly liquid hydrocarbons, evolve spontaneously only at high pressures, comparable to those necessary for diamond formation.

There are two subjects which are particularly relevant for destroying the diverse, spurious claims concerning a putative connection of petroleum and biological matter: the investigations of the carbon material from carbonaceous meteorites; and the reaction products of the Fischer-Tropsch process. Because of their importance, a brief discussion of both is in order.

1.1 The carbonaceous meteorites.

The carbonaceous meteorites, including particularly the carbonaceous chondrites, are meteorites whose chemical composition includes carbon in quantities ranging from a few tenths of a percent to approximately six percent, by mass.¹⁻⁵ The age of the carbonaceous meteorites is typically 3-4.5 billion years; and their origins clearly abiotic. The mineral structures in these rocks establish that the carbonaceous meteorites have existed at very low temperatures, much below the freezing point of water, effectively since the time of their original formation. Such thermal history of the carbonaceous meteorites eliminates any probability that there ever existed on them life, or biological matter.⁶ The evidence obtained from scientific investigations of the carbon material in carbonaceous meteorites has destroyed many claims which assert a biological connection between natural petroleum and biological matter.

Significantly, much of the carbon material of the carbonaceous meteorites consists of hydrocarbons, as both solids and in liquid form.^{1, 5, 7, 8} However, the petroleum material contained in carbonaceous meteorites cannot be considered to be the origin of the natural petroleum found in the near-surface crust of the Earth. The heating which inevitably accompanied the impact process during the accretion of meteorites into the Earth at the time of its formation would almost certainly have caused decomposition of most of their contained hydrocarbon molecules. The carbonaceous meteorites provided the Earth with its carbon (albeit much of it delivered in the form of hydrocarbons) but not its hydrocarbons or natural petroleum. (The processes by which hydrocarbons evolve from the native materials of the Earth are described, and demonstrated, in the following article.)

1.2 The Fischer-Tropsch process.

The Fischer-Tropsch process is the best-known industrial technique for the synthesis of hydrocarbons, and has been used for more than seventy-five years. The Fischer-Tropsch process reacts carbon monoxide and hydrogen at synthesis conditions of approximately 150 bar and 700 K, in the presence of ThO₂, MgO, Al₂O₃, MnO, clays, and the catalysts Ni, Co, and Fe. The reactions are as follow:

When a Ni-Co catalyst is used, the Fischer-Tropsch synthesis proceeds according to the reaction:

$$n \operatorname{CO} + 2n \operatorname{H}_2 \xrightarrow{} n \operatorname{H}_2 \operatorname{O} + \operatorname{C}_n \operatorname{H}_{2n}$$

When a Fe catalyst is used, the Fischer-Tropsch synthesis proceeds according to the reaction:

$$2nCO + nH_2 \xrightarrow{(Fe)} nCO_2 + C_nH_{2n}$$

The yield of the Fischer-Tropsch process is approximately 200 g of hydrocarbons from 1 m^3 of CO and H₂ mixture. During World War II, the production of liquid fuels by the Fischer-Tropsch process was used extensively in Germany; approximately 600,000 t of synthetic gasoline were synthesized in 1943.

The reaction products of the Fischer-Tropsch process are only metastable in the thermodynamic conditions of their synthesis; at pressures of approximately only 150 bar and 700 K, the destruction of liquid hydrocarbons is inevitable. During the industrial

Fischer-Tropsch process, the reaction products are promptly cooled and moved to conditions of lower pressure. The natural environment does not mimic the highly-controlled, and highly-regulated, industrial, Fischer-Tropsch process. The Fischer-Tropsch process cannot be considered for the generation of natural petroleum.

2. The specious "biomarker" claims: The irrelevancy of the presence in petroleum of porphyrins, - and similarly of isoprenoids, pristane, phytane, clorins, terpines, cholestane, etc.

One may read, in almost every textbook published in the English language purporting to deal with the subject of petroleum geology, diverse claims made that the presence of certain molecules found in natural petroleum constitute "evidence," or even "proof," that the petroleum evolved from biological matter. Such molecules, claimed as evidence of a biological connection, include such as porphyrins, isoprenoids, pristane, phytane, cholestane, terpines, and clorins. Closer investigations have proven such claims to be groundless. Pristane and phytane are simply branched alkanes of the isoprenoid class. Cholestane, $C_{27}H_{48}$, is a true, highly-reduced hydrocarbon, but is not to be confused with the oxidized, biotic, molecule cholesterol. Cholestane and cholesterol have similar geometric structures, and share similar carbon skeletons; there the similarity ends. Cholestane is a constituent of natural petroleum; cholesterol is not. Significantly, the Fischer-Tropsch synthesis produces isoprenoids, including phytane and pristine.

Material of truly biogenic origin, such as fossil spores or pollen, is indeed often observed in petroleum, - and too often mislabeled as "biomarkers," supposedly indicating a connection between the natural petroleum and biological material. Careful investigation has established that such material has been leached into solution by the crude oil from buried organic matter in the (typically sedimentary) reservoir rocks from which the oil has been taken.^{9, 10}

Contrarily, the indisputably biological material, such as spores and pollen, found in petroleum can be considered as "abiomarkers" of petroleum origin. For examples, crude oil found in reservoir rocks of the Permian age always contain not only spores and pollen of the Permian age but also spores and pollen of older ages, such as, for example, the Carboniferous, Devonian and Precambrian in petroleum investigated in Tatarstan, Russia. In the same region and in other portions of the Volga-Urals geological province, crude oils in the Carbonaceous sediments are characterized with concentrations of spores of Carbonaceous-through-Precambrian ages, and crudes in the Devonian sandstones with spores of Devonian-through-Precambrian ages.^{9, 11}

The types of porphyrins, isoprenoids, terpines, and clorins found in natural petroleum have been observed in material extracted from the interiors of no fewer than fifty-four meteorites, including amphoteric meteorites (Chainpur, Ngavi, Semarkona), bronze chondrites (Charis, Ghubara, Kulp, Tieschitz), carbonaceous chondrites of all

four petrological classes (Alais, Bali, Bells, Cold Bockeveld, Eracot, Felix, Groznaia, Haripura, Ivuna, Kaba, Kainsaz, Karoonda, Lance, Mighei, Mokoia, Murchison, Murrey, Orgueil, Ornans, Pseudo, Renazzo, Santa Cruz, St.Capraix, Staroye Boriskino, Tonk, Vigarano, Warrenton), enstatite meteorites (Abee, Hvittis, Indarkh), hypersthene chondrites (Bishunpur, Bruderheim, Gallingebirge, Holbrook, Homestead, Krymka), iron meteorites (Arus (Yardymli), Burgavli, Canyon Diabolo, Odessa, Toluca), aubrite meteorites (Norton County), and ureilite meteorites (Dyalpur, Goalpara, Novo Urei).^{9, 12, 13}

The observations of such molecules in meteorites thoroughly discredited the claims that their presence in natural petroleum might somehow constitute evidence of a biological connection. Because especially strenuous (and especially erroneous) claims are often made particularly about the porphyrins observed in natural petroleum, those molecules will be discussed in modest detail.

Porphyrins comprise a class of molecules designated cyclic ionopheres, a special class of polydentate ligands for metals. Porphyrins are heavy, approximately planar, chelating molecules, found in both biotic and abiotic systems. Several porphyrin molecules are of special biological significance: vitamin B_{12} ; chlorophyll, the porphyrin which is the agent of the photosynthesis process in plants; and the heme molecule, the porphyrin component of the protein hemoglobin which is responsible for the transport of oxygen in mammalian blood. As an example of the high molecular weight of porphyrins, hemoglobin has the empirical chemical formula, $[C_{738}H_{1166}O_{208}N_{203}S_2Fe]_4$. Neither vitamin B_{12} , nor chlorophyll, nor heme (nor hemoglobin), nor *any* biotic porphyrin has ever been observed as a component of natural petroleum.

The porphyrin molecules found in natural petroleum possess different side-groups than do those of chlorophyll or heme. The central chelated metal element in chlorophyll is always magnesium; in heme, it is iron. In porphyrin molecules found in natural petroleum, the central chelated metal element is typically vanadium or nickel.

As stated, porphyrin molecules evolve both biologically and abiologically. During the 1960's and 1970's, porphyrin molecules, which are the same as those found in terrestrial natural petroleum, were observed in the hydrocarbon fluids extracted from the interiors of carbonaceous meteorites.

The observations of petroleum-type porphyrins in the hydrocarbon fluids extracted from the interiors of carbonaceous meteorites destroyed, *a fortiori*, the claims that such molecules constitute "evidence" for a connection of petroleum with biological matter. Additionally, after the observations of porphyrins in carbonaceous meteorites, those petroleum-type porphyrins were synthesized abiologically in the laboratory under chemical and thermodynamic conditions specially set to mimic the abiotic conditions in meteorites.^{8, 14}

The "porphyrin evidence" claims were destroyed by the investigations of carbonaceous meteorites approximately thirty years ago, and are well known throughout the community of scientists working in the field of petroleum. Every compound

designated as a "biomarker," and not otherwise identified as a contaminant, has been either observed in the fluids extracted from the interiors of meteorites, or synthesized in laboratories under conditions comparable to the crust of the Earth, - or both.

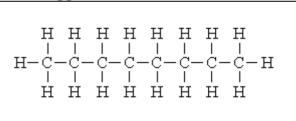
Such scientific facts, and the general knowledge of same, not withstanding, every textbook published in the English language purportedly dealing with the subject of petroleum geology, including the ones cited above, continues to repeat the old discredited claims that the presence of (abiotic) porphyrins in natural petroleum provide evidence for its origin from biological matter.¹⁵⁻¹⁷ Such assertions, thirty years after having been demonstrated scientifically insupportable, must be acknowledged to be intellectual fraud, pure and simple.

3. The "odd-even" abundance claims, - involving the small imbalance of the relative abundances of linear hydrocarbon molecules containing an odd number of carbon atoms, compared to homologous ones containing an even number.

The claims concerning the imbalance of linear molecules containing odd and even numbers, respectively, of carbon atoms is another of the genre of "the constituents of natural petroleum 'have the same properties as' the constituents of biological systems, in such-or-so a way, and therefore petroleum must have evolved from biological matter."

No intelligent teenage student at, for examples, a Russian, German, Dutch, or Swiss gymnasium, would accept such reasoning. Nonetheless, such claims are commonly put forth in English-language textbooks purporting to deal with petroleum geology. Such claims are herewith shown to be without merit and insupportable.

Natural petroleum is a mixture of hydrocarbon molecules of several classes. The most common class of molecules in petroleum is that of the normal alkanes, or n-alkanes, which have the chemical formula C_nH_{2n+2} and a chain-like structure (as noted

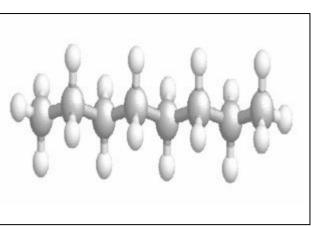


in the first article). For example, n-octane, Fig. 1 Symbolic C_8H_{18} , has the structure shown schematically representation of a molecule in Fig. 1. Correctly, the carbon atoms do not of normal octane, n-C₈H₁₈.

lie exactly along a straight line; a picture of n-octane which more accurately represents its geometric properties is shown in Fig. 2, where $n-C_8H_{18}$ is drawn as a "stick-&-ball" model. Nonetheless, in both figures, the linear chain-like aspect of the n-alkane molecule is shown clearly.

Similarly as for cyclohexane as described in the first article, the hydrocarbon $n-C_8H_{18}$ is geometrically related to one or more biological molecules by substitution of some of the hydrogen atoms by OH radicals. Specifically, if one of the hydrogen atoms on each carbon atom in $n-C_8H_{18}$ were replaced by an OH radical, the resulting molecule, $n-C_8H_{18}O_8$, would be a carbohydrate, as shown in Fig. 3, a simple sugar related to fructose (and whose chemical potential is approximately 2,500 cal *lower* than that of n-octane).

In a distribution of linear hydrocarbon molecules which comprise natural petroleum, the chain-like n-alkanes manifest a slight imbalance of abundances which favors molecules possessing an odd number of carbon atoms, as compared to those with an even number. Similarly, a distribution of linear biological molecules, such as the chain-like carbohydrates, manifests also a



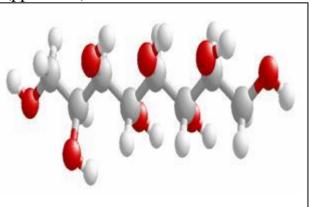
similar slight imbalance of molecules Fig. 2 Stick-&-ball possessing an odd number of carbon atoms, representation of a molecule again as compared to those with an even of normal octane, n-C₈H₁₈. number. From this modest, and somewhat arcane, similarity of odd-to-even abundances, assertions have been made that hydrocarbons evolve from biological matter. Of course, the second law of thermodynamics prohibits such, which fact should obviate any such assertion.

Simple investigation of hydrocarbons generated from abiotic matter manifest also such odd-to-even imbalance of molecular abundances for the linear molecules. The reaction products of the Fischer-Tropsch process manifest the same odd-to-even abundance imbalances of linear molecules as do both natural petroleum, as well as biological molecules.

A specific example of the inevitable genesis of hydrocarbon molecules which manifest such odd-to-even abundance imbalances of linear molecules was demonstrated by Zemanian, Streett, and Zollweg more than fifteen years ago. Zemanian *et al.* demonstrated the genesis of heavy and liquid hydrocarbons at high pressures and temperatures from a mixture of methane and propane. Particularly, Zemanian *et al.* measured the relative abundances of the linear chain hydrocarbon molecules. Their observations, of the imbalance of abundances, and slight excess, of chain molecules with odd numbers of carbon atoms are quoted here (pp. 63-64):¹⁸

"These results are also notable when one considers the even-to-odd carbon number ratio of petroleum.

One of the arguments for a biological origin of petroleum has been that these fluids generally show a small marked prevalence of odd numbered hydrocarbons. It is also well known that living organisms



produce primarily odd numbered Fig. 3 The simple carbon [or carbohydrate] chains. carbohydrate, $n-C_8H_{18}O_8$.

Abiological processes have been presumed to produce even and odd numbered hydrocarbons in roughly equal concentrations. The results of this work demonstrate that presumption to be false. Both biological and abiological hydrocarbon chemistries favor reactions involving two carbons over single carbon reactions [leading to preferred reactants of odd-numbered chain molecules]."

It deserves note that the "odd-even abundance-imbalance" claim, as "evidence"[sic] of a biological origin of hydrocarbon molecules, was rejected by competent physicists and statistical mechanicians, almost immediately when it was introduced. The odd-even abundance imbalance is simply a result of the directional property of the covalent bond together with the geometry of linear molecules.

4. The phenomenon of optical activity in natural petroleum: Evidence of an abiotic, high-pressure genesis.

Perhaps for reason of its historical provenance in fermented wine, the phenomenon of optical activity in fluids was for some time believed to have some intrinsic connection with biological processes or materials.^{20, 21} Such error persisted until the phenomenon of optical activity was observed in material extracted from the interiors of meteorites; some of which material had been believed previously to be uniquely of biotic origin.

From the interiors of carbonaceous meteorites have been extracted the common amino-acid molecules alanine, aspartic acid, glutamic acid, glycine, leusine, proline, serine, threonine, as well as the unusual ones α -aminoisobutyric acid, isovaline, pseudoleucine.²²⁻²⁴ At one time, all had been considered to be solely of biotic origin. The ages of the carbonaceous meteorites were determined to be 3-4.5 billion years, and their origins clearly abiotic. Therefore, those amino acids had to be recognized as compounds of both biological and abiological genesis. Furthermore, solutions of amino acid molecules from carbonaceous meteorites were observed to manifest optical activity. Thus was thoroughly discredited the notion that the phenomenon of optical activity in fluids (particularly those of carbon compounds) might have any intrinsic connection with biotic matter. Significantly, the optical activity observed in the amino acids extracted from carbonaceous meteorites has not the characteristics of such of common biotic origin, with only one enantiomer present; instead, it manifests the characteristics observed in natural petroleum, with unbalanced, so-called scalemic, abundances of chiral molecules.²⁵

The optical activity commonly observed in natural petroleum has been for years speciously claimed as "proof" of some connection with biological detritus, - albeit one requiring both a willing disregard of the considerable differences between the optical activity observed in natural petroleum and that in materials of truly biotic origin, such as wine, as well as desuetude of the dictates of the laws of thermodynamics.

Optical activity is observed in minerals such as quartz or Iceland spar, as well as in oil, and among biological molecules. The optical activity observed in petroleum is more characteristic of the same in abiotic minerals, such as naturally occurring quartz, which are polycrystalline minerals, with a scalemic distribution of domains of left- and right-rotational properties. The chiral molecules in petroleum manifest scalemic distributions, and significantly lack the homochiral distribution which characterize biotic optically active matter. The optical activity in natural petroleum is characterized by either a right (positive, or dextrorotary) or left (negative, or levorotary) rotation of the plane of polarization. By contrast, in biological material left (levorotary) rotation dominates.

The observation of optical activity in hydrocarbon material extracted from the interiors of carbonaceous meteorites, and typical of such in natural petroleum, discredited those claims.^{2, 26} Nonetheless, the scientific conundrum as to why the hydrocarbons manifest optical activity, in both carbonaceous meteorites and terrestrial crude oil remained unresolved until recently.

The chiral molecules in natural petroleum originate from three distinct sources: contamination by biological detritus in the near-surface strata from which the oil has been taken; the biological alteration and degradation of the original oil by microbes which consume and metabolize oil; and the chiral hydrocarbon molecules which are intrinsic to the petroleum and generated with it. Only the last concerns the origin of petroleum.

The genesis of the scalemic distribution of chiral molecules of natural petroleum has recently been shown to be a direct consequence of the chiral geometry of the system particles acting according to the laws of classical thermodynamics. The resolution of the problem of the origin of the scalemic distributions of chiral molecules in natural petroleum has been shown to be an inevitable consequence of their high-pressure genesis.¹⁹ Thus, the phenomenon of optical activity in natural petroleum, contrary to supporting any assertion of a biological connection, strongly confirms the high-pressure genesis of natural petroleum, and thereby the modern Russian-Ukrainian theory of deep, abiotic petroleum origins.

5. The carbon isotope ratios, and their inadequacy as indicators of origin.

The claims made concerning the carbon isotope ratios, and specifically such as purport to identify the origin of the material, particularly the hydrocarbons, are especially recondite and outside the experience of most persons not knowledgeable in the physics of hydrogen-carbon [H-C] systems. Furthermore, the claims concerning the carbon isotope ratios most often involve methane, the only hydrocarbon which is thermodynamically stable in the regime of temperatures and pressures of the Earth's crust, and the only one which spontaneously evolves there.

The carbon nucleus has two stable isotopes, ${}^{12}C$ and ${}^{13}C$. The overwhelmingly most abundance stable isotope of carbon is ${}^{12}C$, which possesses six protons and six

neutrons; ¹³C possesses an extra neutron. (There is another, unstable isotope, ¹⁴C, which possesses two extra neutrons; ¹⁴C results from a high-energy reaction of the nitrogen nucleus, ¹⁴N, with a high-energy cosmic ray particle. The isotope ¹⁴C is not involved in the claims about the isotope ratios of carbon.) The carbon isotope ratio, designated δ^{13} C, is simply the ratio of the abundance of carbon isotopes ¹³C/¹²C, normalized to the standard of the marine carbonate named Pee Dee Belemnite. The values of the measured δ^{13} C ratio is expressed as a percentage (compared to the standard).

During the 1950's, increasingly numerous measurements of the carbon isotope ratios of hydrocarbon gases were taken, particularly of methane; and too often assertions were made that such ratios could unambiguously determine the origin of the hydrocarbons. The validity of such assertions were tested, independently by Colombo, Gazzarini, and Gonfiantini in Italy and by Galimov in Russia. Both sets of workers established that the carbon isotope ratios cannot be used reliably to determine the origin of the carbon compound tested.

Colombo, Gazzarini, and Gonfiantini demonstrated conclusively, by a simple experiment the results of which admitted no ambiguity, that the carbon isotope ratios of methane change continuously along its transport path, becoming progressively lighter with distance traveled. Colombo et al. took a sample of natural gas and passed it through a column of crushed rock, chosen to resemble as closely as possible the terrestrial environment.²⁷ Their results were definitive: The greater the distance of rock through which the sample of methane passes, the lighter becomes its carbon isotope ratio.

The reason for the result observed by Colombo *et al.* is straightforward: there is a slight preference for the heavier isotope of carbon to react chemically with the rock through which the gas passes. Therefore, the greater the transit distance through the rock, the lighter becomes the carbon isotope ratio, as the heavier is preferentially removed by chemical reaction along the transport path. This result is not surprising; contrarily, such is entirely consistent with the fundamental requirements of quantum mechanics and kinetic theory.

Pertinent to the matter of any claim that a light carbon isotope ratio might be indicative of a biological origin, the results demonstrated by Colombo *et al.* establish that such a claim is insupportable. Methane which might have originated from carbon material from the remains of a carbonaceous meteorite in the mantle of the Earth, and possessing initially a heavy carbon isotope ratio, could easily have that ratio diminished, along the path of its transit into the crust of the Earth, to a value comparable to common biological material.

Galimov demonstrated that the carbon isotope ratio of methane can become progressively heavier while at rest in a reservoir in the crust of the Earth, through the action of methane-consuming microbes.²⁸ The city of Moscow stores methane in water-wet reservoirs on the outskirts of that city, into which natural gas is injected

throughout the year. During summers, the quantity of methane in the reservoirs increases because of less use (primarily by heating), and during winters the quantity is drawn down. By calibrating the reservoir volumes and the distance from the injection facilities, the residency time of the methane in the reservoir is determined. Galimov established that the longer the methane remains in the reservoir, the heavier becomes its carbon isotope ratio.

The reason for the result observed by Galimov is also straightforward: In the water of the reservoir, there live microbes of the common, methane-metabolizing type. There is a slight preference for the lighter isotope of carbon to enter the microbe cell and to be metabolized. The longer the methane remains in the reservoir, the more of it is consumed by the methane-metabolizing microbes, with the molecules possessing lighter isotope being consumed more. Therefore, the longer its residency time in the reservoir, the heavier becomes the carbon isotope ratio, as the lighter is preferentially removed by methane-metabolizing microbes. This result is entirely consistent with the fundamental requirements of kinetic theory.

Furthermore, the carbon isotope ratios in hydrocarbon systems are also strongly influenced by the temperature of reaction. For hydrocarbons produced by the Fischer-Tropsch process, the δ^{13} C varies from -65% at 127 C to -20% at 177 C.^{29, 30} No material parameter, the measurement of which varies by almost 70% with a variation of temperature of only approximately 10%, can be used as a reliable determinant of any property of that material.

The $\delta^{13}C$ carbon isotope ratio cannot be considered to determine reliably the origin of a sample of methane, - or any other compound.

6. Conclusion.

The claims which have traditionally been put forward to argue a connection between natural petroleum and biological matter have been subjected to scientific scrutiny and have been established to be baseless. The outcome of such scrutiny comes hardly as a surprise, given recognition of the constraints of thermodynamics upon the genesis of hydrocarbons.

If liquid hydrocarbons might evolve from biological detritus in the thermodynamic regime of the crust of the Earth, we could all expect to go to bed at night in our dotage, with white hair (or, at least, whatever might remain of same), a spreading waistline, and all the undesirable decrepitude of age, and to awake in the morning, clear eyed, with our hair returned of the color of our youth, with a slim waistline, a strong, flexible body, and with our sexual vigor restored. Alas, such is not to be. The merciless laws of thermodynamics do not accommodate folklore fables. Natural petroleum has no connection with biological matter.

However, recognition of such fact leaves unanswered the conundrums which eluded the scientific community for more than a century: How does natural petroleum evolve ? And from where does natural petroleum come ?

The theoretical resolution of these questions had to await development of the most modern techniques of quantum statistical mechanics. The experimental demonstration of the required equipment has been only recently available. The following article substantially answers these questions.

- 1 M. H. Studier, R. Hayatsu and E. Anders, "Organic compounds in carbonaceous chondrites", *Science*, 1965, **149**, 1455-1459.
- 2 B. Nagy, *Carbonaceous Meteorites*, Elsevier, Amsterdam, 1975.
- G. P. Vdovykin, Carbonaceous Matter of Meteorites (Organic Compounds, Diamonds, Graphite), Nauka Press, Moscow, 1976.
- B. Mason, "The carbonaceous chondrites", *Space Science Review*, 1963, **1**, 621-640.
- 5 C. A. Ponnamperuma, "The carbonaceous meteorites", in *Carbonaceous Meteorites*, ed. B. Nagy, Elsevier, Amsterdam, 1975, 747.
- J. D. Bernal, "Significance of carbonaceous meteorites in theories on the origin of life", *Nature*, 1961, **190**, 129-131.
- E. Gelphi and J. Oro, "Organic compounds in meteorites IV. Gas chromatographic mass spectrometric studies of isoprenoids and other isomeric alkanes in carbonaceous chordrites", *Geochim. Cosmochim. Acta*, 1970, **34**, 981-994.
- G. W. Hodgson and B. L. Baker, "Evidence for porphyrins in the Orgueil meteorite", *Nature*, 1964, **202**, 125-131.
- 9 V. A. Krayushkin, *The Abiotic, Mantle Origin of Petroleum*, Naukova Dumka, Kiev, 1984.
- 10 V. B. Porfir'yev, "Inorganic origin of petroleum", American Association of Petroleum Geologists Bulletin, 1974, **58**, 3-33.
- P. N. Kropotkin, Y. I. Pikovskii, B. M. Valyaev, K. B. Serebrovskaya, A. P. Rudenko, A. L. Lapidus, E. B. Chekaliuk and G. N. Dolenko, Journal of D. I. Mendeleev, All-Union Chem. Soc., Moscow, 1986.
- 12 M. H. Studier, R. Hayatsu and E. Anders, "Origin of organic matter in the early solar system: I. Hydrocarbons", *Geochim. Cosmochim. Acta*, 1968, **32**, 151-173.
- 13 G. P. Vdovykin, *Meteorites*, Nauka, Moscow, 1968.
- 14 G. W. Hodgson and B. L. Baker, "Porphyrin abiogenesis from pyrole and formaldehyde under simulated geochemical conditions", *Nature*, 1967, **216**, 29-32.
- 15 F. K. North, *Petroleum Geology*, Allen & Unwin, Boston, 1985.
- 16 B. Tissot and D. H. Welte, *Petroleum Formation and Occurrence*, Springer, Berlin, 1981.
- 17 R. C. Selley, *Elements of Petroleum Geology*, W. H. Freeman, New York, 1995.
- 18 T. S. Zemanian, Chemical Kinetics and Equilibria of Hydrocarbon Mixtures at Advanced Temperatures and Pressures, Cornell, Ithaca, 1985.
- 19 J. F. Kenney and U. K. Deiters, "The evolution of multicomponent systems at high pressures: IV. The genesis of optical activity in high-density, abiotic fluids", *Phys. Chem. Chem. Phys.*, 2000, **2**, 3163-3174.

- 20 L. Pasteur, "Sur la dissymétrie moleculaire", C.R. Hebd. Séanc, 1848, 26, 535.
- 21 L. Pasteur, "Sur la dissymétrie moleculaire", in *Leçons de chimie professées en 1860 par M. M. Pasteur, Cahours, Wurtz, Berthelot, Sante-claire Deville, Barral, et Dumas, Paris 1861*, Hachette, Paris, 1886.
- 22 M. H. Engel and B. Nagy, "Distribution and enantiomeric composition of amino acids in the Murchison meteorite", *Nature*, 1982, **296**, 837-840.
- 23 M. H. Engel, S. A. Macko and J. A. Silfer, "Carbon isotope composition of individual amino acids in the Murchison meteorite", *Nature*, 1990, **348**, 47-49.
- 24 M. H. Engel and S. A. Macko, "Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite", *Nature*, 1997, **389**, 265-268.
- 25 S. Pizzarello and J. R. Cronin, "Non-racemic amino acids in the Murray and Murchison meteorites", *Geochim. Cosmochim. Acta*, 2000, **64**, 329-338.
- B. Nagy, "Optical Activity in the Orgueil meteorite", *Science*, 1965, **150**, 1846.
- 27 U. Colombo, F. Gazzarini and R. Gonfiantini, "Die Variationen in der chemischen und isotopen Zusammensetzung von Erdgas aus Suditalien", Leipzig, 1967, vol. Vortrag ASTI-67.
- 28 E. M. Galimov, Isotope Zusammensetzung des Kohlenstoffe aus Gassen der Erdrinde, Leipzig, 1967.
- 29 V. A. Krayushkin, "Origins, patterns, dimensions, and distributions of the world petroleum potential", *Georesursy*, 2000, **3**, 14-18.
- 30 P. Szatmari, "Petroleum formation by Fischer-Tropsch synthesis in plate tectonics", Bull. A.A.P.G., 1989, 73, 989-996.

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