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Resumo: Recentemente foram explicados alguns aspectos associados à formação de petróleo e à distribuição mundial de combustíveis fósseis. Entretanto, é ainda assunto para debate a fonte de energia associada a geração de petróleo. Neste trabalho é demonstrada a viabilidade energética de uma versão moderna da antiga teoria de radiação alfa para a origem do petróleo, tendo como base evidências acumuladas através dos anos. Esta antiga teoria é revisitada e examinada criticamente sob nova visão a fim de ser reformulada, usando-se dados interdisciplinares na maioria não existentes quando a antiga teoria da radiação alfa para a origem do petróleo foi sugerida, desenvolvida e por fim desacreditada. As idades geológicas aceitas para a formação da maior parte das reservas de petróleo conhecidas estão dentro de uma faixa de tempo que faz dos emissores de radiação alfa natural de meia vida longa uma fonte de energia viável pelo menos para parte da energia necessária à formação de hidrocarbonetos de petróleo.

Abstract. Some aspects of petroleum formation and the world distribution of fossil fuels deposits were recent clarified. However, the source of energy associated with petroleum genesis is still largely debatable. Evidence accumulated over the years allows to demonstrate the energetic feasibility of a modern version of the old alpha radiation theory of petroleum origin. This theory is revisited and examined critically under new light to be reformulated by taking advantage of relevant interdisciplinary data mostly not available when the old alpha radiation theory was suggested, developed and then discredited. The geological ages accepted for the formation of most of the known petroleum reserves are within a range that makes long-lived natural alpha emitters a feasible energy source for at least part of the energy necessary for the formation of petroleum hydrocarbon.

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Introduction

Qualitative and quantitative aspects of petroleum formation and world distribution of fossil fuels have been recently discussed by Tissot[1-3]. However, a full account of the energy necessary for the formation of petroleum hydrocarbons from organic matter consistent with the time elapsed for the chemical transformations to occur has proved to be elusive thus far. Thermal processes have been considered to be the sole energy source for the conversion of organic matter into petroleum[1-3,4-7]. However, the relative importance of the energy of alpha radiation as opposed to the classical idea of thermochemical conversion of organic matter into petroleum remains an open question. The objetive of the present work is to emphasize the feasibility that the long term natural radioactivity can be a strong candidate as one of the sources of energy associated with petroleum formation.

The overall significance of the application of relatively new concepts to the industry of oil exploration has been examined by a number of authors[1-3][8-11]. The present work however deals exclusively with the problem of petroleum origin as far as the source of energy associated with petroleum genesis is concerned. Arguments based on relatively modern data are presented to show that the energy involved in the chemical changes associated with petroleum origin can come partially from the natural alpha emitters embedded in the organic segments of marine sediments.

The Old Alpha Radiation Theory

Burton[12] reported in 1904 the presence of natural radioactivity in crude petroleum, and Joly[13] suggested in 1908 that the concentration of radium in the bottom of the ocean would depend on the supply of organic materials from above. The hypothesis that the energy from alpha particles emitted from naturally occurring radionuclides could play a role in petroleum origin was explicitly proposed by the first time in the late 1920s by Lind[14,15], as a follow up to observations that under the influence of alpha particles emitted by radon in a mixture of ethane, CH_3CH_3; propane, $CH_3CH_2CH_3$; or butane, $CH_3CH_2CH_2CH_3$, each condenses eliminating hydrogen, H_2, and methane CH_4 to give place to higher hydrocarbons.

Brooks[16] in 1931 discarded the idea that alpha particles could play a role in petroleum origin by stating several objections. Years later, Lind[17] himself rejected the idea that alpha energy could be connected with petroleum origin because he was unable to answer some of the objections raised by Brooks[16]. In 1940, part of the objections raised by Brooks[16] were overcome by the radioactive studies on the sedimentary rocks associated with petroleum made by Bell et al.[18].

In 1944, Sheppard[19] suggested that the conversion rate of organic material to petroleum, dM/dt, by alpha particle bombardment could be expressed by the following equation:

$$\frac{dM}{dt} = \frac{dM}{dN} \cdot \frac{dN}{dt} = \frac{dM}{dN} \text{ C.I.} \qquad (1)$$

where: dM/dN is the ratio of molecules converted to ion-pairs produced, and it is characteristic of each particular chemical reaction under consideration; dN/dt is the rate of ion-pairs formed by alpha particle bombardment; C is the relative concentration of organic material* (in grams per gram of sediment); and I is the total number of ion-pairs produced per second per alpha particle per gram of sediment.

Although Sheppard observed that the conversion efficiency would be higher if the radioactive materials were closely associated with the organic constituents of sediments[19] the calculation of conversion by primary radium (half-life 1.6×10^3 years), based upon Evan's data on radium concentration in sediments and marine organisms[20], resulted in the finding that only 10^{-8} grams of organic material would be converted by gram of sediment in 10^4 years[19]. Sheppard recognized promptly that this conversion rate was too low to be seriously considered in the problem of petroleum genesis, since the remaining activity of radium could not sustain the conversion of organic matter into petroleum longer than 10^4 years[19].

In 1948 Brooks discredited the idea of any connection between the energy of alpha particles and petroleum formation calling it ironically "the physicist's point of view" on petroleum genesis[21]. Evidence gathered between 1943 and 1952 by a group of investigators at M.I.T. made Whitehead to recognize that the amounts of petroleum found in sedimentary rocks were too large to be explained by chemicals effects of the alpha radioactivity of ^{238}U and ^{232}Th found in sedimentary rocks associated with petroleum[22].

New Light on an Old Idea

Data on the concentration of ^{238}U and ^{232}Th in plankton, organic sediments, and petroleum were not available in 1954 when Whitehead recognized the failure of the old alpha radiation theory. Relevant interdisciplinary data allow the development today of new ideas regarding alpha radiation and petroleum origin.

Data on the carbon, hydrogen and oxygen percentual composition of kerogen, asphalt, petroleum, and urano-organic substances are presented in Figure 1

* Only ions produced in organic material are effective to convert molecules.

to illustrate the similar pattern in these percentual compositions, which suggests a genetic association of these materials. As a matter of fact, kerogen is an organic constituent found in sedimentary materials which can be associated with petroleum formation according to the currently accepted ideas[1,25]. Petroleum geologists use two distinct terms for kerogen to designate types of organic matter deposits associated with sources of petroleum: humic varieties of organic matter are generally related to poor oil sources affected by dry-land conditions; while the sapropelic varieties are commonly related to subaqueous sediments which are deposited under conditions of isolation from land areas and are associated with rich oil sources[1,26].

Fischer and Arthur[8], relying on the hypothesis that the climate of the earth behaves cyclically, suggested that most of the petroleum of the world resulted from sapropelic episodes, occurred in the last 200 million years, which were favourable to the accumulation of petroleum source beds. These authors also mentioned that high phytoplanktic productivity, which migh have resulted in the formation of petroleum source beds, is associated with six sapropelic episodes (polytaxic) that occurred during Early-Jurassic, Late-Jurassic, Mid-Cretaceous, Late-Cretaceous, the Eocene and the Miocene[8].

Figure 2 shows the approximate percentual distribution of world crude oil in geological age. The data summarized in Figure 2 make conspicuous the disagreement existing in the open literature on the age distribution of the principal known oil reserves. However, one can observe that the six sapropelic episodes suggested by Fischer and Arthur[8], as associated with petroleum formation, are at least in qualitative agreement with the geological age span shown in Figure 2.

The uranium content of black shales, originally sapropel, is reported to be higher than the average uranium content of sedimentary rocks[29,30]. Degens et al.[31] reported a uranium content of about 40 ppm in sapropel found 100 meters deep in the Black Sea, deposited some 5000 years ago, and observed that most the uranium in these recent sediments seems to be bound to planktonic matter rather than to land-derived organic debris. More recently, Vassiliou[32] reported studies on the form of occurrence of uranium in deposits associated with organic matter and confirmed his earlier findings that the organic components of part of the uranium-bearing materials examined were genetically associated with petroleum[24].

The uranium content of some oil field brines has been reported to be 0.2 ppm by Pierce et al.[33], who observed also the presence of helium in accumulations of petroleum and natural gas. Nikanov[34] pointed out that examination of data on the distribution of helium concentrations in gas pools, gas-oil fields, gas-oil and oil pools from the Volga - Ural region, central Asia, and published works from the United States and Canada lead him to conclude that the relationship of helium to oil and to petroleum hydrocarbons has implications in the formation of these materials yet to be understood. As a matter of fact, helium can be expected to accumulate during the formation processes of petroleum and natural gas, even though in small amounts only, as a result of the alpha decayment of uranium and its alpha emitting daughters accumulated in the organic material in the depositional paleoenvironments of petroleum source beds.

Here it may be helpful to point out that most of the objections raised by Brooks[16,21] were becoming meaningless as data were being gathered along the time.

Alpha Energy Deposition in Sapropel

The lower and upper limits of the alpha energy available for deposition per disintegration of ^{238}U plus daughter products are 18.5 MeV and 43 MeV, respectively, with either total or no radon loss[35]. For the ^{232}Th series the lower and upper limits for the alpha energy available for deposition per disintegration of the parent atom are 15.1 MeV (with total thoron loss) and 36 MeV (with no thoron loss), respectively[35]. On the other hand, if there is excess activity in the organic segment of sediments of any daughter products in relation to either ^{238}U or ^{232}Th, due to direct accumulation of ^{226}Ra, ^{228}Ra or ^{224}Ra, the alpha energy limits presented above tend to be higher until the source of excess activity decays.

The subsequent estimates are made under the following restrictive assumptions: (i) the mean alpha energy available due to the disintegration of ^{238}U plus daughter products up to ^{226}Ra is totally deposited in the organic segment of sapropel; (ii) although the total alpha energy available for deposition per disintegration of ^{238}U daughter products lies between 18.5 and 43 MeV, each individual alpha particle emitted by ^{238}U and daughter products up to ^{226}Ra has energy below 5 MeV with a typical range in organic matter being less than 40μm[36]; and (iii) the contribution from radon plus daughters to the alpha energy available for deposition per disintegration of ^{238}U plus daughters will not be taken into account, because the atoms of radon and its daughter products can disintegrate far from the initial position of the ^{238}U parent atom.

The number, Z, of ion-pairs formed per year per gram of sapropel may be expressed as follows:

$$Z = 3.15\times10^{7} \left[\frac{\text{sec}}{\text{year}}\right] \frac{Y[\text{eV/sec.g sapropel}]}{T[\text{eV/ion-pair}]} \qquad (2)$$

where: $Y = 1.23\times10^{4}[\text{dis/sec.g } ^{238}U]\times1.85\times10^{7}[\text{eV/dis } ^{238}U]\times W[\text{ppm}]10^{-6}$
$= 2.28\times10^{5}\ W[\text{ppm}]$; T is the mean ionization energy for complex organic matter, which can be considered here as approximately 60 eV/ion-pair as compared with 56 eV/ion-pair adopted by Sheppard and Whitehead[37]; and W is the initial uranium concentration in the organic segment of sapropel.

Thus, assuming that the number of organic molecules per unit mass of sapropel is about $2.4\times10^{21}\ \frac{\text{organic molecules}}{\text{g sapropel}} = \left(\frac{6.02\times10^{23}\text{ molecules}}{250\text{ g/atom gram}}\right)$ one can state that the number, X, of years needed to convert the organic matter content of sapropel with W ppm uranium concentration into higher hydrocarbons of petroleum can be expressed as follows:

$$X = \frac{2.4\times10^{21}}{Z} = \frac{2.0\times10^{10}}{W[\text{ppm}]}\ \text{years} \qquad (3)$$

As, for example, if the reported 0.07% U_3O_8 assayed in a sample of sludge taken from a petroleum pit associated with a salt dome in Louisiana[38], can be considered as an indication that the uranium concentration in the initial organic matter is at least 600 ppm, then the geological time interval needed to produce petroleum would be, according to equation (3), of the order of 30 million years. Accordingly, the petroleum found in the reservoirs of such salt dome is reported to be associated with

Pliocene-Miocene (i.e., from 5 to 24 million years) lenticular sands[38].

Furthermore, it is interesting to mention here that Hyden[39] reported an average uranium content of 0.17% in ashes for 29 samples of crude oil from the western United States, Dickson et al.[40]. reported uranium concentrations in retort water from shale oil from Colorado and Utah up to 407 ppm, and Vassiliou[41] found from 1.0 to 3.5% uranium in ashes in 5 samples of uranium-organic matter associated with petroleum from La Bajada, New Mexico. The high radium content in waters of the Rift Valley that was tentatively associated by Nazor[42] with underground reservoirs of brines, oils and gases deserves to be further investigated. Fission track technique has been successfully applied to determine the uranium content of petroleum[43] and can now be used for systematic studies in petroleum from different deposits and ages.

Figure 3 shows a graph of equation (3) which is helpful to estimate the conversion time (from the cenozoic to the paleozoic) of organic matter into petroleum as a function of the uranium content of sapropel. A crude comparison between the information contained in Figures 2 and 3 suggests that most of the known world petroleum would have been formed from sapropel containing between 70 and 1000 ppm of uranium.

Of course, the contribution of the ^{232}Th series to the alpha energy available for deposition in the organic matter should have also been taken into account in the above calculations, since the time necessary for the conversion of organic matter into petroleum should be a function not only of the initial ^{238}U concentration in sapropel but also that of ^{232}Th. However, the orders of magnitude found above will not change significantly with the correction for the ^{232}Th contribution.

Concluding Remarks

The lack of data in the 1940s on the concentration of radionuclides of very long half-lives in marine organisms probably precluded Sheppard and Whitehead[37] from developing an acceptable alpha radiation theory of petroleum origin. Data now available are still meager, but are sufficient to show that at least part of the energy necessary to trigger the initial transformations of organic-rich sediments like sapropel into petroleum hydrocarbons can be provided by the alpha decay of ^{238}U and daughters products up to ^{226}Ra. To the best of my knowledge, data on the ^{232}Th content of sapropel are not yet available, but such data when available can easily be incorporated into the model now being suggested.

Additional research needed to test the model for petroleum origin suggested in the present paper should include the following studies: (i) the ^{238}U and ^{232}Th concentrations in sapropel, petroleum and associated liquid and gases; (ii) the microdistribution of natural alpha emitters with very long half-lives in the organic segment of sapropel, and the actual mechanisms triggered by the energy of alpha particles in the chemical transformations which occur in the organic matter segment of sapropel; (iii) determination of the fractions of radon and thoron escaping from the organic part of the sediments; (iv) the determination of the mean diameter of the organic constituents of sapropel; and (v) the relation between the age of petroleum and the ^{238}U and ^{232}Th concentrations in sapropel.

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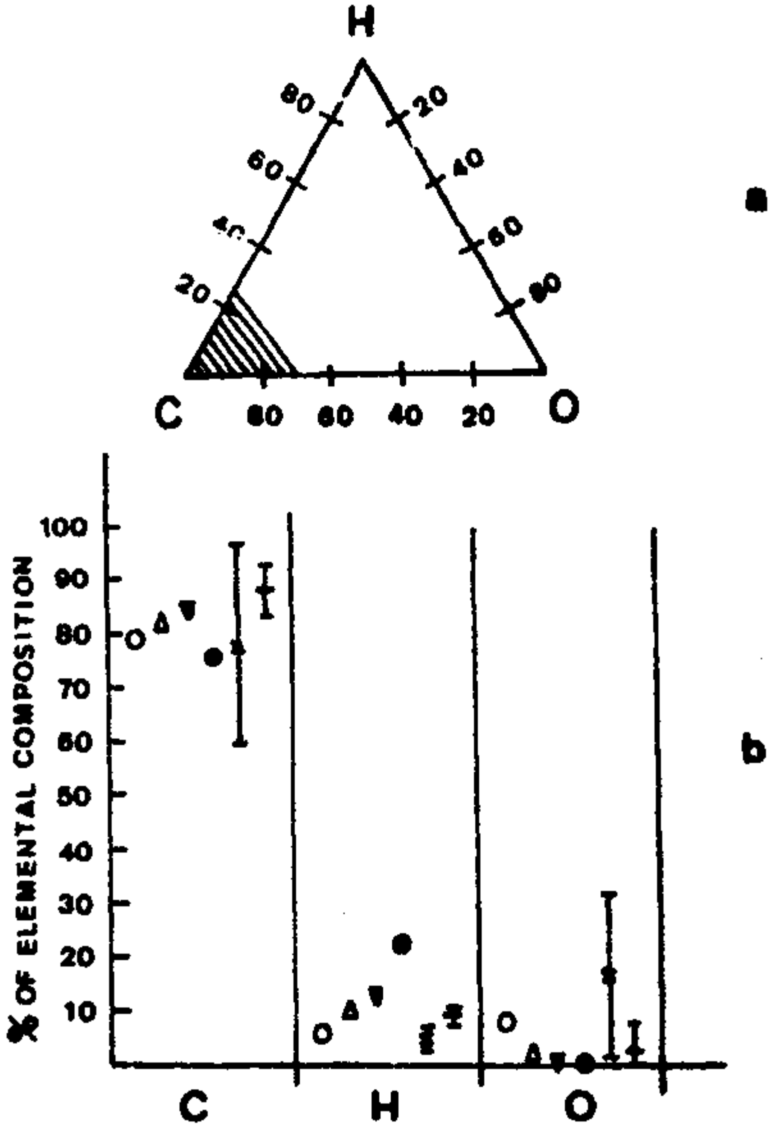

Figure 1. a) Kerogen, asphalt, petroleum, gas and urano-organic all fall within the smaller triangle in the lower left corner of the carbon-oxygen-hydrogen triangular diagram; b) Carbon, hydrogen and oxygen percentages in the total elemental compositions of the following substances: O kerogen Δ asphalt, ▼ petroleum, ● gas - from ref. 23; and ⌶ urano-organic (11 samples), ⌶ petroleum (7 samples) - from ref. 24.

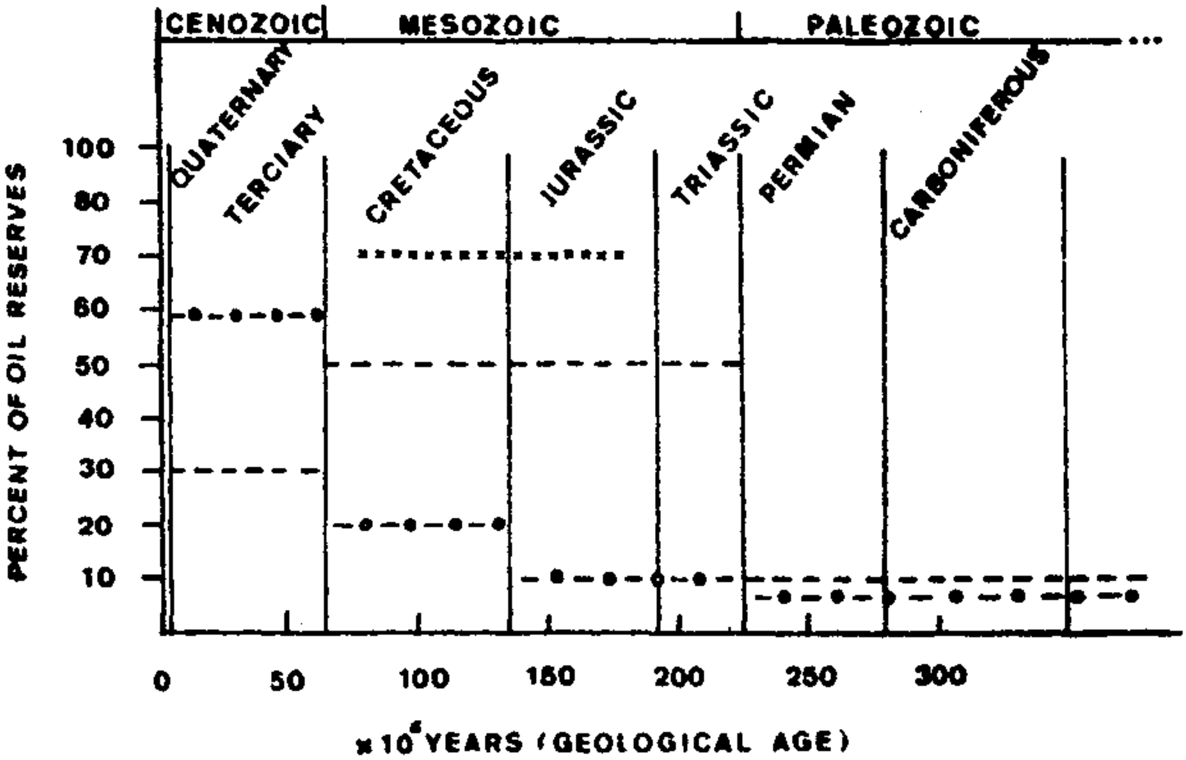

Figure 2. Approximate percentage distribution in geological of most known reserves of oil: – – ref. 27; O – O ref. 28; x x x ref. 2.

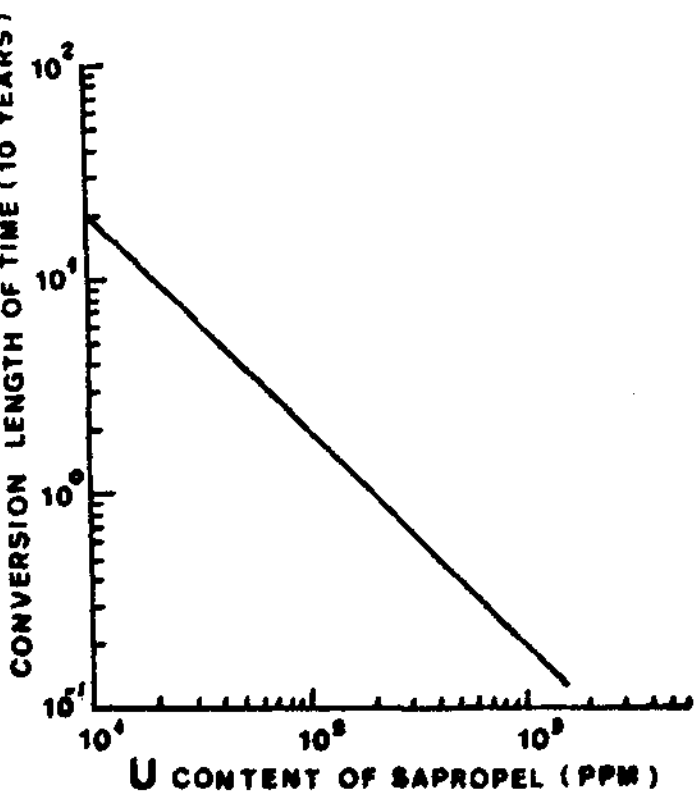

Figure 3. Graphical representation of equation (3) for 10 ppm < W < 0.2%.