"MER D'HUILE" ON PANTHALASSA: AN ADDITIONAL CONJECTURE FOR THE BIRTH OF GIANT MACROMOLECULES ON THE YOUNG EARTH.

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Introduction: During the first ~ 500 Ma of the post-lunar Hadean period, the Earth-Moon system suffered a massive early bombardment. In particular, the accretion of about 5×10^{24}g of cometary hydrous-carbonaceous micrometeorites formed the air and the early ocean (Panthalassa). Moreover, a very efficient prebiotic chemistry was effective during this cataclysmic period, because this was the only time in the ocean's history when the concentrations of reactants were so high as to form very concentrated prebiotic "soups" (see ref. 1 for further details). This led to the synthesis of the giant macromolecules of precellular life, i.e., proteins and nucleic acids. But this prevalent view hits the stumbling block of transforming a bunch of small molecules inherited from cosmic chemistry into magnificently ordered macromolecules involving billions of atoms!

Conflicting conjectures: Therefore, only conflicting conjectures have been proposed, as yet, to tackle this major mystery, such as: – panspermia; – the world of catalytic minerals (clays and sulfides); – the world of "coercervats"; – the world of enzymes (proteins), which can speed up reactions rates by factors of about 10^6–10^{11} (with this high value a reaction that should last 0.1 s with an enzyme would require 3.2 centuries without it); – biological self-organization, inspired from the observation of ants colonies; – intelligent design, etc.

These conjectures have two common features: (i) they underappreciated initial conditions in Hadean times; (ii) with the exception of panspermia and intelligent design, they all require a long lasting rather quiet layer of water highly concentrated in reactants. In this case, a huge diversity of *parallel and/or congruent* chemical reactions could be triggered, as to build the world of giant macromolecules. We outline below a new conjuncture that both uses an improved vision of Hadean times, and equips Panthalassa with a diversity of long lasting, quiet and reactive layers that were spreading at all depths.

Micrometeorites are also petroleum "source rocks": We just consider the total mass of Hadean hydrous-carbonaceous micrometeorites, which survived unmelted upon atmospheric entry and got deposited on the ocean floor (about 5×10^{23} g). Upon further burial in sediments they behaved as "source rock" of petroleum. Indeed, in his classical paper ("Fundamental conditions for economic hydrocarbon accumulation"), Rondeel [2] defines petroleum "source rocks" as: *"mostly fine clays with more than 0.5% kerogen*". Therefore, micrometeorites are also petroleum source rocks because they are made of about 50% of clays (mostly smectites) and they contain about 2-2.5% of kerogen.

We thus argued [3] that in the fraction of unmelted micrometeorites that get buried on the sea floor as to reach the "oil window" (at depths of 1-6 km), kerogen was cracked under the effect of heat and pressure (catagenesis) and transformed into petroleum ("oil"), thus following the ordinary fate of terrestrial source rocks. A fraction did leak to the surface, where it formed long-lasting gigantic black tides (BTs). Indeed there were neither "bugs" nor oxygen around as to digest and/or burn this oil, respectively.

This might have generated oily viscous prebiotic soups. Indeed, petroleum is first the richest source of organics available to date, as it might probably contain over 100,000 organic molecules with molecular weight (m/z) of up to 10,000 [4]. But it also floats on water.

A giant collector of dust and small rocks in contact with a "dirty" haze: Therefore, rocky materials "raining" from the sky were piling up on the floating BTs when they were sufficiently thick. They included: – a minor component of ordinary volcanic fall-out; – meteorites and micrometeorites; – "smoke" particles generated during the kind of diffuse micrometeoritic volcanism gently "erupting" from the thermosphere, and which was induced by the volatilization and/or melting of micrometeorites upon atmospheric entry.

These components thus aggregated in kinds of oily-dusty mantles on BTs, which were in contact with a dirty haze made of sulfuric acids aerosols and reactive organic molecules synthesized in the atmosphere by many processes (in particular those effective in the wake of shooting stars and in their "persistent" trails where a glow discharge chemistry is active). This rich mixture of ingredients should have assisted the synthesis of the giant macromolecules.

However, one should know better about the complex interactions between the surface of Panthalassa, oil, strong winds and giant impacts to identify the most favorable zones of Panthalassa for this synthesis. We present experimental observations that clearly establish the role of oil in damping breaking waves. We next rely on a model developed by one of us [5] to give some hints about the huge diversity of potential zones of prebiotic chemistry on Panthalassa, starting with the most superficial ones, looking like a "*mer d'huile*" (i.e., defined as "sea as smooth as a millpond").

Experimental observations of *mer d'huile*: Benjamin Franklin greatly contributed to this abstract when he wrote a remarkable paper, entitled "On the stilling of waves by means of oil" [6]. He quoted in particular the following key observations: – The water, which had been in great agitation before, was instantly calmed, upon pouring in only a very small quantity of oil, and that to so great a distance round the boat as seems a little incredible; – When seals are devouring a very oily fish, which they always do under water, the waves above are observed to be remarkably smooth, and by this mark the fishermen know where to look for them!

These observations about the calming effect of oil on water waves, leading to the formation of *mer d'huile*, have been confirmed many times. But the interpretation of this phenomenon by Franklin, at a time when variable surface tension was unknown, has been invalidated since (7). Anyway, these observations were relevant to small oily surfaces. They cannot be extended to the unexplored situation where the whole top surface of Panthalassa was an oily-dusty "skin".

The making of *mer d'huile*: Today, breaking waves play an important role in both climate and the development of marine life. We first focus on wind waves created in the deep open ocean, as to form the ~ 100 m long swell, which can propagate over ≥ 1000 km. When the swell sweeps the surface, the water molecules describe approximately a vertical circle. For molecules initially on the surface its diameter is roughly scaled by the height of the waves. But for molecules initially below the surface, the circle diameter decreases exponentially with the initial depth of the molecules. Therefore, at depths ≥ 50 m, water molecules are no longer affected by waves. For the very long waves of tsunami, the effect is felt all the way down to the ocean floor.

We considered the effects of spreading on Panthalassa a global oil thickness, Δ, varying from 0.3 mm (i.e., corresponding to the present day world reserves of biotic Jurassic oil) to 1 cm and 1 m. These thicknesses correspond to an efficiency of oil production from micrometeoritic kerogen delivered during the first ~ 200 Ma of the post-lunar period (i.e., a global thickness, Δ_0~ 60m), of about 5×10^{-6}, 2×10^{-4} and 2×10^{-2}, respectively.

The rigidification of the deep open ocean is already observed at Δ~ 0.3 mm. However the precise role of oil in the damping of waves still is an open problem. For such small thicknesses, the key parameter is the surface elasticity and the surface viscosity has in practice a negligible effect, at least on damping of ripples. The main effect of oil is on the processes by which energy is continually fed into the system from the wind [8]. Oil somehow reduces the surface roughness, thus decreasing the drag of the wind and reducing the probability of a given wave breaking. In case of breaking, the kinetic energy given to the mass of water thrown off the top of the wave during the breaking event is reduced.

Wave breaking on the open sea in deep water is thus strongly affected by the wind acting on individual wave crests. At high wind speeds the damping effect can vanish in the background noise of wind-generated waves and at higher wind speed the oil disappears from the sea surface because it is washed down by breaking waves. When the wind has calmed down, the coverage of the sea by surface-active material, such as oil, increases because these substances are being transported to the sea surface by turbulence and rising air bubbles generated by breaking waves.

No study has been reported yet, about the effects of either a worldwide coverage of oil on Panthalassa or an oil thickness, Δ~ 1 m. We just have the intuition that the effects of viscosity dominate in both cases, thus strongly damping any wave system, except during giant impacts of 10 km-sized bodies that definitively triggered giant waves of tsunami type. With such a thick oil coating, Panthalassa would have been probably looking as a gigantic brownish Darwinian quiet pond with a *mer d'huile*. One could even wonder about the effects of this dark oil global coverage on the Earth's albedo, and consequently on Hadean weather.

A slow descend of BTs in Panthalassa for a recycling of its abiotic petroleum "skin": In open seas, BTs first float on water because their densities, which range from about 0.83 to 0.92 g/cc, are larger than that of sea water (about 1.03 g/cc). This triggers their functioning as surface chemical reactors. However, some BTs soon start a slow submersion, when they are ballasted by a mass of "rocky" freight representing about 10-20% of their mass, thus behaving as kinds of giant BT-submarines. They slowly reach the zone of great quietness where their dusty mantles stop being redistributed by strong surface winds and their associated breaking waves. As their "ballasts" were continuously loaded with new rocky material collected by Panthalassa, they further slowly sank with a terminus on the ocean floor. There, they could be recycled either as various oil fractions at shallow depths in the sediments or as new petroleum in the Hadean oil windows, etc.

The survival of BT-submarines during the massive early bombardment: This kind of armada of BT-submarines certainly triggered a huge network of diverse chemical chain reactions at all depths in Panthalassa. This multiple sources of chemical reactions, which could only be triggered during the massive early bombardment, certainly assisted the synthesis of the giant molecules.

But, one should better understand how they were affected by both the higher tides produced when the young Moon was closer to the Earth and the giant impactors of this massive bombardment. In this kind of Hadean naval battle impacts could shorten the lifetimes of both BTs and oil windows. They also induced a reprocessing of BTs leading possibly to new families of nanomaterials, including carbon nanotubes. Indeed, it has been proposed [9] that *gas phase hydrocarbons pyrolysis might be a solution to mass producing carbon nanotubes*!

Such nanotubes show striking affinities with giant macromolecules of comparable diameters. For example, proteins have already been observed to self-assemble into helicoidal structures only on nanotubes showing a distribution of diameters. In this case, a given protein selects the best diameter to guide its helicoidal growth [10]. In another experiment, fragments of DNA quickly got adsorbed inside carbon nanotubes with the right diameters.

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