

## **Where does coal & petroleum come from?**

I got to thinking about fossils when we went to a place near Dhar where a lot of marine fossils have been found. That area is more famous for the dinosaur eggs that have been found in one of the sites, but these dinosaurs were not marine. The marine fossils are amazing because this place is hundreds of kilometres from any sea right now. But I was told that this area was under the sea twice in the past, and so you get marine fossils from two different ages. So that means that the solid land that we were standing on formed the continental shelf long, long ago.

It is wonderful to think that the face of the earth has changed so much, and what is even more amazing is the role that living creatures have had in forging the present earth. I have known about fossils since I was a kid, but I got to know of other mega features which show the signature of life only recently when I read that the chalk cliffs in a place called Dover were formed by the deposition of the skeletons of marine organisms over hundreds of years. These layers formed the sediment in the sea-bed which then turned rock-like over the millions of years since they were under the pressure of still more layers continuously being laid down above them. Other processes inside the surface of the earth then brought these rocks to the surface. Then you think of the marble rocks in Jabalpur, it is known that marble is formed when chalk (or limestone) is pushed down to still deeper layers inside the earth where they are subjected to not just high pressures, but also high temperatures. Hence, limestone is the parent sedimentary rock which is changed into marble which is a metamorphic rock. Similarly, another kind of sedimentary rock – shale – is turned into the metamorphic rock – slate.

### **Coal and Petroleum**

Then, of course, there is coal and petroleum which are also generally believed to have been formed from material which was ultimately of organic origin, that is, made during life processes. In this article, I would like to talk about the origin (or proposed origins) of coal and petroleum. Let us start with where the major deposits of coal and petroleum are found. It is hypothesised that coal was formed in areas where large amounts of organic matter (well, dead bodies of both animals and plants; but mainly plants according to some people) was buried under the soil on land while petroleum was formed under the sea. Of course, we know of oil-fields off the coast of Mumbai, but what about all the oil-wells in the Arabian peninsula – they are on solid land, right? The theory is that these areas were under the sea when the oil deposits were formed and then the continuous movement of the tectonic plates, and the consequent pushing up of some areas above the ground and subduction of some other areas below the neighbouring plates, have turned things topsy-turvy and hence some petroleum deposits are found in areas which are on dry land right now (and the Arabian peninsula is very, very dry!).

The origin of coal from the transformation of huge deposits of organic matter under the earth does not seem to be the subject of much debate. One of the reasons for this is the large number of fossils which are found in the coal-beds – some of these being fine impressions of leaves and other fragile materials. It is proposed that these organisms got buried and were covered immediately by soil so that they were not exposed to air and the various scavengers that quickly decompose any organic matter and lead to the recycling of nutrients in the living world. Left out in the open, the various bacteria and fungi would have consumed the material, but since they were buried, they just underwent other changes, mainly dehydration, so that coal consists of mostly carbon.

### **How was petroleum formed?**

But what about petroleum? No fossils have been found in petroleum and the first theory about the origin of petroleum was given by Mendeleev. Yes, this is the same Mendeleev who gave us the periodic table. He did a lot of work all over the field of Chemistry and the inorganic theory for the origin of petroleum was one of his contributions. According to Mendeleev, and some others who followed him, the petroleum on earth was formed deep beneath the surface of the earth when simple hydrocarbons (compounds made of carbon and hydrogen) joined together to form the more

complex and longer chain hydrocarbons which are found in petroleum. The simple hydrocarbons were proposed to have formed when the water percolating down into the deeper layers reacted in the presence of iron (or other metallic) carbides to give acetylene or methane. This reaction was known to occur in the laboratory and the origin of petroleum seemed to have been settled. However, the problem was that no one could show that iron carbides were to be found at the depths proposed.

This inorganic theory of the origin of petroleum fell out of favour when various other facts came to light and other theories were proposed. For one, it was discovered that plankton had tiny droplets of oil inside their single-celled bodies (plankton are single-celled organisms that make up nearly 95% of the life-forms in the oceans). The presence of the oil was explained on two counts – one, its formation was explained by the relation between the carbon chains in the fatty acids and the common fractions found in these oils, and two, the plankton were thought to benefit from the presence of oil because this would increase their buoyancy and make it easier for them to float on the surface. This was necessary because photosynthesis is not possible a few metres from the surface of the ocean because the sunlight does not penetrate very deep into the water.

Thus, it has been hypothesised that when the plankton die, they get deposited at the bottom of the ocean and the oil in them undergoes various transformations to give us the petroleum that we are busy extracting and burning up. Some people have suggested that this process may happen in as little as a million years – in geological terms, a million years is over in the blink of an eye. So when people tell you that the known deposits of petroleum will all be finished in the next fifty years at the rate at which it is being used up, you can relax knowing that if human beings can last for another million years, we will have some more freshly formed petroleum that can be used!! This time period for the formation of petroleum is supported by the discovery of oil in some rocks (sediments) that date back to just the Pliocene.

What are the other factors which lend support to this theory for the origin of petroleum? For one thing, some compounds which are found in living systems have been found unaltered in petroleum. This includes not just some hydrocarbons, but also compounds called porphyrins. Now, this is very interesting because porphyrins contain nitrogen and are very easily decomposed in the presence of oxygen, hence we can conclude that even petroleum was formed under reducing conditions. The other interesting property of these compounds is that they decompose when exposed to higher temperatures also. So it looks like the formation of petroleum was also a low-temperature (comparatively, these compounds are destroyed at temperatures above ~ 200 °C) process, at least for those sources that contain porphyrins.

Does this look like all the problems concerning the source of petroleum have been resolved? Not quite. Almost as old as the inorganic theory for the origin of petroleum was this theory that proposed an extra-terrestrial origin for the petroleum reserves on the earth. Does this sound far-fetched? Sokoloff had proposed that the primordial nebular matter that was condensed to form the earth and other planets contained this oil and various geological processes on the earth have caused all the oil to be forced into the rocks in the mantle. This was in 1890, but this theory was revived in another form when two discoveries came to light – one was the presence of methane in the atmospheres of not just other planets, but also their satellites. It is known that methane is mainly formed by inorganic reactions, that is, reactions in which the starting materials are inorganic. So if the methane is present in the solar system, on earth, the local conditions of favourable temperatures and pressures might have led to the methane polymerising to give rise to the higher chain hydrocarbons found in petroleum. The other discovery was that meteorites could also be carbonaceous. The earliest meteorites known and studied were metallic, in fact, it is even thought that humans used the iron found in the meteorites before learning to extract it from its ores. Then in the 1960's, meteorites that contained organic matter (not just graphite) were discovered and Sokoloff's theory got a second lease of life.

The basic bone of contention between these two theories is the ultimate source of the carbon compounds in petroleum. Either the starting material was methane or acetylene which were formed by inorganic processes, or was found on the primordial earth as a result of the materials from which it was formed and these polymerised under the conditions to be found in the earth's mantle to give

us petroleum. Or the source of organic carbon is photosynthesis wherein carbon dioxide was converted into glucose in the first place, and then other, more complex, compounds are formed in various life processes. These compounds are further transformed into petroleum or oil (various fractions) either within the living system itself or once again in the earth's mantle when these are decomposed in anaerobic conditions. The jury is still out about what actually happened, what do you think?

### **Where is petroleum to be found?**

I had mentioned earlier that coal is found in areas where sedimentary geological formations are to be seen. This, plus the fact that fossils have been found amongst the coal seems to indicate the coal was formed the same way that sedimentary rocks are formed, the difference being that the starting materials were organic in this case.

But the story seemed to be more complicated for petroleum because it seemed to be found in places which were clearly not of sedimentary origin. For example, sometimes petroleum is to be found in rocks of igneous origin. Some of it was also found in rocks which were not of marine origin. These anomalies could only be explained if the oil (being a liquid) had seeped from the place of its origin in marine sedimentary rocks to nearby igneous rocks or rocks of other non-marine origins. This was confirmed when analyses of the composition of oil found in these anomalous areas were compared with the oils found nearby and were found to be the same. Hence, not only is petroleum formed under the sea (generally in areas which formed the continental shelf) due to the deposition of successive layers of unicellular organisms and their subsequent transformation, it is also generally found only in areas where it is surrounded by non-permeable rocks. That is, once the petroleum is formed, it seeps through the surrounding rocks till it gets trapped on all sides by material that will not allow its farther passage. The petroleum may thus end up under considerable pressure. This is the reason why the crude oil oozes out (or even gushes out) when wells are first dug to tap a reservoir. But even after this stops, plenty of oil can be recovered from these areas, this is done by pumping water and natural gas through one tube causing the oil to be forced out of another tube. Water is also used because oil being less dense will be forced to the upper layers.

### **Will we really run out of coal and petroleum in the near future?**

The answer to this question really depends on whom you ask. Companies which are in the business of extracting coal and petroleum would like us to think that there is plenty more lying around, and that it just needs more sophisticated methods to detect these fields and appropriate technology for their extraction. In some ways, these claims seem to be justified. For example, when petroleum was first extracted, then an oil-well was given up on when the oil stopped gushing out. Now, we would pump in water and natural gas and squeeze out some more from the same place. Who know what new techniques will appear in the future?

At the same time, we need to consider the economics of these processes (I am not even considering the environmental costs of extracting and burning coal and petroleum, that is a topic for an entirely different article (**NOTE FOR MADHAV: but I will not be writing this article!!**)). As the deposits are found in more and more inaccessible places and new improved methods are required to be used for extracting the same, at some point it would become economically non-viable to use these sources. The exact point where this happens does not depend on coal and petroleum as such, but rather, it depends on what alternative sources are being developed in the meantime, how much we continue to subsidise the search for coal and petroleum, and finally how energy-intensive our society wants to be.

### **Box: The Age of the Earth and Various Rocks:**

If I were to go into the long tale of how different time-periods in the past are associated with different rocks, that would make for another article, but here I shall try and give you a brief outline. Firstly, the different rocks / geological strata were identified first, and they were mostly named after

the places where they were first observed and recorded. For example, Devon is a place in UK after which the Devonian period is named. Later on, it was realised that these strata always occur in definite sequences, and various techniques were used to date them. Fossils found embedded in one layer will belong to that particular age in most cases. Sometimes, deeper layers are exposed due to erosion and we might find fossils millions of years old scattered on the present surface, but newer fossils will not be found in deeper and older layers (general rule of thumb, the deeper the layer, the older it will be). All the time scales given below have been rounded off to give a broad idea of what we are talking about.

Let us look at how time has been divided since the earth was formed approximately 4.5 billion years ago (billion is 1,000,000,000 and million is 1,000,000 in this usage, while the British billion is 1,000,000,000,000). A huge stretch from 4.5 billion years ago till 500 million years ago is called the Precambrian. This is further divided into the Hadean, the Archean and the Proterozoic. Life in the form of the versatile bacteria is supposed to have arisen 3.5 billion years ago. They had the earth all to themselves till the appearance of eukaryotic cells which are to be found today existing as single cells like the bacteria or organised into multicellular forms – plants, animals and fungi. Some formations in rocks found in Australia dated to the Archean (upto 2.5 billion years ago) are said to be the fossils of the first multicellular living organisms. But the true variety of almost all the animal phyla seen today seem to make an appearance all of a sudden in the Cambrian which dates to a period 500 million years ago.

Then we have periods called the Ordovician, Silurian, Devonian, Carboniferous and Permian (between 500 to 300 million years ago). The coal beds were mostly laid down in the Carboniferous era, as is indicated by the name. This was the period when the oxygen content of the atmosphere was the highest ever known. A broader classification called the Paleozoic era contains the Cambrian to the Permian periods. This is followed by the Mesozoic era which is divided into three periods – the Triassic, the Jurassic and the Cretaceous (from 200 to 100 million years ago). We all know from the movie that the dinosaurs roamed the Jurassic period.

Now we come to the latest era which is the Cenozoic which has two periods Paleogene (60 million years ago) and Neogene (20 million years ago). The Pliocene belongs to this last period. Recently geologists were debating that the time-period since the appearance of modern human beings should be called the Anthropocene since we have impacted the earth so drastically! How long do you think this would be?

Of course, all this talk about billion and million years will not make much sense, I find it difficult to imagine life just a hundred years ago! But there is a simple activity which can put these huge time-scales into perspective. Take a length of twine 9 metres long. If this were to depict the entire period since the formation of the earth 4.5 billion years ago, where do you think the important markers will fall? Starting from one end, mark off a point two metres down – this will be where bacteria first made an appearance 3.5 billion years ago. Then? The proliferation of multicellular animal life happens in the Cambrian which is a mere 0.5 billion years ago which would be 6 metres from the first mark (a mere metre from the other end of the twine). The dinosaurs would be found 50 to 60 cm from this point, but between the markers for the Cambrian and the dinosaurs, you can put down the marker for the time when coal was formed – where do you think this will come?

And where do human beings make an appearance? Generous estimates think that something that could be called human has been around for seven million years, but others think it is just 2 million years; while our species *Homo sapiens* dates back to just about half a million years – we are pretty close to the edge, right?! **(Please check these dates, I have found lots of different dates for human origins.)**

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### **Box: Plankton:**

Biologists like to give names to all sorts of coarse or fine differences to be seen around. Take, for example, how they view the variety of organisms to be found in the sea (or ocean). First, they sort them out into categories they call planktic, nektic and benthic. These are the terms used to describe all living things that float about in the sea at different depths under the mercy of various waves and

currents (planktic); the ones that can propel themselves along (nekctic), and the ones living at the bottom are benthic. Now this is obviously a very broad classification. The planktic organisms are commonly called plankton. They are further classified using different criteria – on their size, on their source of energy, etc. Plankton range from the microscopic to the tiny larvae of various animals. And they may be photosynthetic (in which case, they will be found fairly close to the surface because they need light), others might eat these photosynthetic plankton, still others would subsist on the dead remains of both of the above, and these would be found at different depths since they could eat the detritus as it slowly sinks down to the bottom of the sea or ocean.

The abundance of plankton depends on the availability of various nutrients in the water, especially iron. Surprisingly, it is found that seas next to particularly arid and unproductive areas have an abundance of plankton. For example, this is true for the Atlantic Ocean off the west coast of Africa where winds blow the sand from the Sahara into the sea providing the necessary mineral nutrients. Once the plankton die, they sink to the bottom since the organic matter they are made up of is slightly denser than the surrounding water. Over long periods of time, this seems to have given us all the petroleum that we are using today.

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### **Box: Fractions and Porphyrins in Petroleum:**

What can we learn from the various compounds that are found in petroleum about its possible origin? Petroleum is a mixture of a variety of carbon compounds. Carbon is a versatile element which forms compounds by linking itself commonly with hydrogen, oxygen, nitrogen and sulphur among others. But more importantly, the carbon atom links itself to other carbon atoms in any numbers in straight or branched chains, and even forms closed rings.

In petroleum, these various compounds are separated by a process by called fractional distillation. In this process, the compounds having similar boiling points are separated into 'fractions', the heavier compounds having the higher boiling points. Petroleum from different sources will give slightly different fractions, and on this basis, the origin of petroleum can usually be identified.

In living systems, carbon is initially trapped by the process of photosynthesis to give glucose. This is then used not just to provide energy for various activities in the cell, but also is the starting material for many of the compounds synthesized. This often limits the variation in the number of carbon atoms, the kind of branches that are seen and placement of multiple bonds within the carbon chain.

The fractions commonly found in petroleum are seen to reflect the carbon chains (number of carbon atoms and branching also) found in living organisms, especially the plankton. Not only that, some compounds like porphyrins have also been found in petroleum which are closely related to compounds like chlorophyll.

Caption for the illustration: The compound on the left is a porphyrin found in petroleum which is very similar to chlorophyll whose structure is given on the right.

