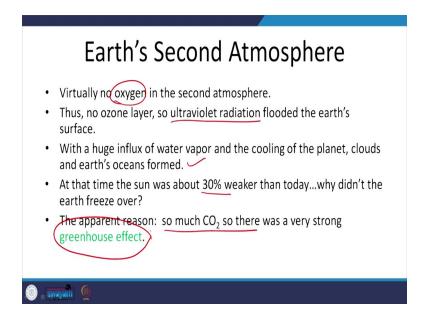
Introduction to Atmosphere and Space Science Prof. M. V. Sunil Krishna Department of Physics Indian Institute of Technology, Roorkee

Lecture – 04 Earth's Second Atmosphere and rise of Oxygen

Hello dear students. So far, we have been discussing about the evolution of first atmosphere. We started from the beginning that is the time when the earth formed or the planetary system or the solar system came into existence; then we looked at different cycles or different steps in which the primordial atmosphere transformed into giving a secondary atmosphere. And we were looking at the processes in which the secondary atmosphere was transforming to give you the present-day chemical composition of the atmosphere.

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So, just to have a recap, so we were discussing something about the Earth's Second Atmosphere where still there was no hint of any oxygen. There is no hint of any direct oxygen in the system and it means that, there was no ozone; that means, the earth was continuously receiving large amounts of ultraviolet radiation from the sun that is at ultraviolet radiation flooded the earth's surface.

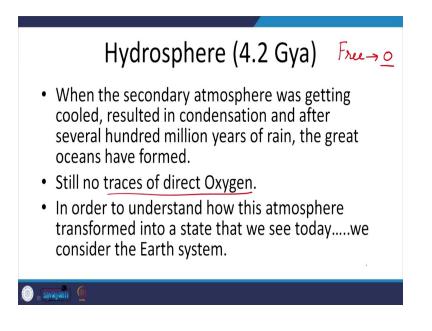
So, there was no mechanism to prevent the ultraviolet radiation from reaching the surface of the earth. And with the huge influx of water vapor the cooling of the planet or clouds and

earth surface formed. They have resulted from the huge influx of water vapor. And at that time, it was assumed that nearly 3 or 3.5 billion years ago, the sun was weaker; it was not as bright as it is today, it was weaker by nearly 30 percent than what is today.

And it the obvious question that arises is that; if the sun was were weaker at that time, the earth should have frozen, the planet should have frozen. Because there was a lot of water vapor and there was a lot of liquid water in terms of great oceans; so, earth must have frozen leaving you a frozen planet, which did not apparently happen.

The reason is that, there was large amounts of CO2 which was existing; because of the volcanic eruptions which left enhanced or serious amounts of greenhouse effect. That means, the heat that was trying to get away from the planet was retained in the planet, in the atmosphere of the planet by CO2 which traps the infrared radiation; thereby keeping an average temperature which is which should be larger than in the absence of the sun.

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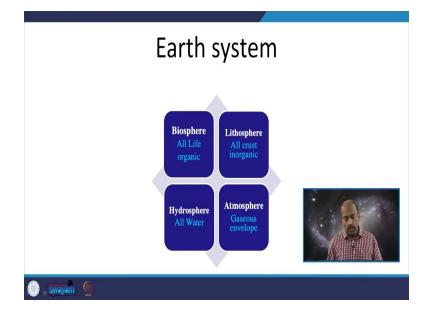


Then we are now looking at the different processes which led to the formation of free oxygen. Now our objective is to identify the processes which left free oxygen in the atmosphere. So, the discussion; so right now, the point is that, majority of the atmosphere is water vapor right now, because of the volcanic eruptions and there are some sulfur compounds and majority is anyway water vapor.

Now we have to look at the processes which will transform this water vapor into oxygen and leave a nitrogen to a very large percentages in the atmosphere, right. So, we will start the discussion from the hydrosphere. So, when the secondary atmosphere was getting cooled, it resulted in condensation and after several hundred million years of rain which lasted and the great oceans have formed, we have seen this.

And still even after the formation of water, there are no direct traces of oxygen; oxygen was still not to be found directly So, in order to understand how this atmosphere, the secondary atmosphere resulted or transformed into a state that we see today, we consider the earth as a complete system not just the atmosphere.

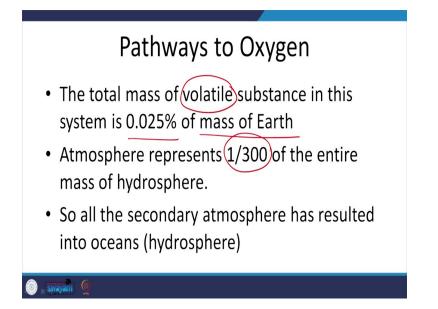
We complete the earth as a complete system or we complete we take into account other aspects of the earth which may have influenced the formation of atmosphere; or which may have influenced the transformation of secondary atmosphere into an atmosphere that we see today.



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So, the earth system is composed of the biosphere which is all organic life, carbon based. Lithosphere all the crust which is inorganic in nature; hydrosphere is all the water and the atmosphere which is the gaseous envelope that we see. So, we have already seen atmosphere does not way not to any percentage any reasonable percentage of the entire mass of the earth or mass of the hydrosphere, right. Now, we should look at the path of pathways which led to the formation of oxygen, free oxygen.

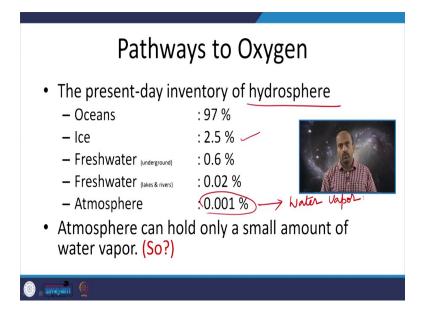
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So, the total mass of volatile substances in this system that we have seen in the earth system is nearly 0.025 percent of the mass of the earth itself; that means, it is a very very small number to be considered, but still. So, mass of earth is a very large number of course, it is a huge number; and the mass of volatile substances, what comes into volatile substances? Gases, liquid will come into the volatile substances.

So, it is to be always remembered that 0.025 percent is the mass of all the volatile substances in the mass of the earth. And atmosphere represents nearly, of this atmosphere represents nearly 1 by 300th of the entire mass of hydrosphere. So, all the secondary atmosphere has resulted in to oceans. So, these oceans were come were result were giving you this percentage of mass of the earth, ok.

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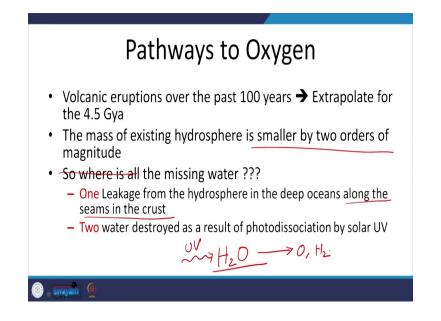


And if you consider it was only the water that is dominant that is to be seen on the planet; but at the same time which is a very very small number in comparison to the mass of the earth. So, this, so oxygen has to be extracted or oxygen cannot come from anywhere else; it has to come only from the hydrosphere, there is the only way.

So, if you want to understand how oxygen has come into the atmosphere; we have to see, how the ocean or how the hydrosphere transformed itself to give away oxygen. So, if you look at the present way invent, present day inventory of the hydrosphere today; oceans nearly compose 97 percent, ice at the caps let us say 2.5 percent, fresh water in the undergrounds and lake and rivers will compose nearly 0.62 percent, and the atmosphere is nearly 0.01 percent.

So, this is the water vapor that exists in the atmosphere. So, this is today's composition of the hydrosphere. So; that means, that atmosphere has a very small capability of retaining water vapor. So, it cannot be thought that the water vapor that is existing in the atmosphere must have given away the oxygen, ok. So, where does the oxygen come from?

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So, if you look at the volcanic eruptions that happened over the past 100 years. Let us say over you take a indicative number of the volcanic eruptions, the number of volcanic eruptions that happened over the past 100 years and you extrapolate this number over the period of entire the age of earth; then this many number of volcanic eruptions must have left, so much amount of water vapor and so much amount of Sulphur dioxide things like that.

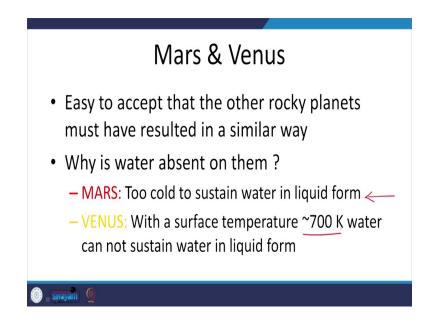
Now, if you convert this water vapor into let us say oceans or rivers or any other hydrosphere, hydrosphere system what you will realize is that; the mass of existing hydrosphere is smaller by nearly two orders of magnitude. So, two orders of magnitude is a huge difference that is to be formed. So, the although volcanic eruptions are the only reasons for the water vapor to exist in the atmosphere; the volcanic eruptions have been able to throw water vapor into the atmosphere, this water vapor upon cooling only resulted in the formation of oceans.

If it is the case, then all the volcanic eruptions releasing water is not matching the amount of water that is to be found today. And how much is missing? The missing factor is nearly two orders of magnitude, smaller or is missing from the original number.

So, where does this all the missing water go? One theory is that, this missing water must have gone or must have leaked into the solid earth or the crust of the earth by leaking along the seams of the crust which is just a theory. The second theory is that water the molecule H2O must have been dissociated by solar ultraviolet radiation. So, ultraviolet radiation can dissociate H2O giving you oxygen and hydrogen which is just a theory.

Now, there are this there are different means or methods by which we can substantiate these theories or we can rule out these theories, let us see.

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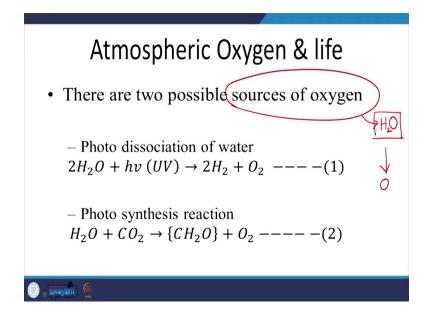
Now just for an example; if so far the all the processes we have discussed are for the earth of course and we realize that these processes are more or less true and there is nothing which is specific for the earth in these theories. Any planet which have formed lot of the agglomeration of solid rocky substances, must have gone through the same physical processes in which or by which the earth has gone, right.

There, so there is no distinction; I mean if you bring in Mars or Venus, they must have also gone through the same physical processes. So, if it is the case; then why is it that you do not find water on Mars or Venus? There must have been volcanic eruptions on Mars and Venus, there must have been water vapor which was thrown away from the volcanoes and which must have condensed. So, why is it that these the neighboring rocky planets do not have water?

So, one idea is that, Mars is far away from the sun, so it receives less amount of solar radiation and; obviously, it is very cold. So, Mars must have not sustained the water in liquid form. So, it is now known that the water does exist on Mars in form of ice.

And Venus is very close to the sun, so it receives a maximum amount of radiation and the surface temperatures are very large so; that means, that Venus may not be able to sustain water in liquid form and then there are other things which will come into picture, ok.

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Now, continuing with the theory with the two theories of the escape of water vapor; the first atmospheric oxygen may have resulted from these two physical processes 1 and 2. So, there are two possible sources of oxygen. So, these sources of oxygen you always remember; these sources of oxygen are only to be out of the water vapor.

So, we have seen that in the secondary atmosphere, it was mainly the water vapor which was existing nothing else. And if you want to consider the evolution of oxygen, it is only the water vapor which must have resulted into the formation of oxygen. So, if it is the case; then let us look at these two processes. So, the first process is the photo dissociation of water.

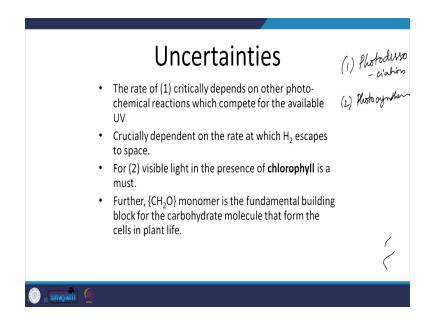
So, water vapor or water molecule getting acted by an ultraviolet photon, dissociates to form hydrogen and oxygen. This is one method in which oxygen was released. Now you see free oxygen being released out of a chemical reaction, ok. Then the second process could have been photosynthesis reaction in which H2O combines with a carbon dioxide molecule leaving you an organic compound plus oxygen, ok.

Now there are it is obvious that these two processes are just two theories nothing else. So, one theory thought; one theory was based on the idea that photo dissociation of water

molecule is the main source by which oxygen was brought into the atmosphere. And another theory was based on the idea that photodissociation was the process by which oxygen was brought into the atmosphere.

Now, these two theories of course, may not be true completely and they may be true in different times; they may have been true in different instances of the history of earth, ok. Let us see, I mean let us see how these two theories are meaningful.

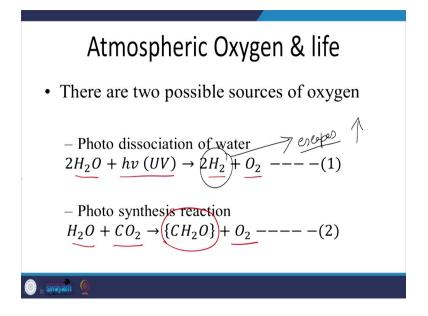
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So, the reaction rate of let us say if you consider the photodissociation reaction. So, the reaction 1 is the photodissociation and reaction 2, for reference reaction 2 is the photo synthesis. So, the reaction rate of one critically depends on other chemical reactions which compete for the available ultraviolet; that means, it is not only the water vapor or water molecule which is trying to get hold, get the ultraviolet photon for it is dissociation.

There are other physical processes, another chemical processes which are trying to complete; that means, there are other molecules in the atmosphere, there are other atoms in the atmosphere which can also get excited or dissociated by the action of ultraviolet radiation. So, eventually the rate at which this chemical reaction will proceed will only depend on the availability of ultraviolet; more ultraviolet is captured by the water molecule more amount of oxygen will be released.

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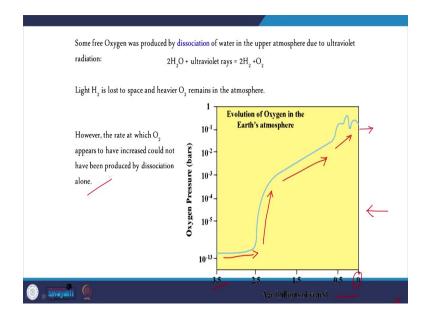


Now, the second thing is that, in this reaction there is hydrogen which is released in this reaction. So, what are the, hydrogen is a very light molecule and it generally escapes the atmosphere; it reaches the topmost parts of the atmosphere and it generally escapes. Now, so; that means, that it is leaving the system and oxygen is being heavier will be in the system. So, that is one thing which will decide the rate of this reaction, right. And for 2, for photosynthesis reaction the visible light in the presence of chlorophyll is a must; that means, you require an organic compound to be present for the reaction 2 happen.

And so, if you have to understand this reaction; if this reaction cannot proceed as if there is no organic compound. So, this reaction cannot proceed if there is no organic compound, the availability of chlorophyll. So, chlorophyll is essentially life. So, further the monomer that is released in this second reaction is the fundamental building block of for the carbohydrate molecule that form the cells in plant life.

That means, there are two, I mean there are this chlorophyll is required and the organic compound that is released is a fundamental building block in the lifecycle.

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So, it is now believed that some free oxygen was produced by the dissociation of water vapor, by the dissociation of water in the upper atmosphere due to ultraviolet radiation. So, it must have. So, it is not there is no way that, the process 2 can begin the formation of oxygen; because there is no life.

There was there was no life in the beginning, there was no chlorophyll that was existing in the beginning and there was no organic compound to begin with; it was rocks, dust and water vapor that was the only chemical composition in the beginning. So, there was no life; it was no organic compound, it was only H2O and SO2 and it was a lot of rock and dust, ok.

So, now you cannot imagine this reaction to happen; because there is no chlorophyll. So, this reaction may not have started to begin with. So, it is only the photo dissociation which must have started the building up of oxygen, right if it is the case. So, this is what we have seen already. So, this leaves oxygen right and what happens is? So, light H 2 which was produced in this reaction was lost to space and heavier O2 remain in the atmosphere, right.

So, now, I am ruling out the second process from the picture saying that since there was no life in the on the earth this reaction cannot proceed and as a result the oxygen must have resulted only from the physical process or the chemical process; number one which is the photo dissociation it is accepted.

It is accepted to the fact to the idea that, in the beginning in the very beginning it was only the high water vapor water molecules in the upper atmosphere or in the high altitudes; were dissociated by ultraviolet giving you free oxygen molecules. The same reaction also resulted in the formation of hydrogen molecules which were lost to the space, ok.

But, the rate at which O2 appears to have increased over the past 3 or let us say 4 billion years, could not have been only due to photo dissociation; that means, that let us say if you look at this figure, what you have on the x axis is the age. So, 0 is the present day and then you have the past up to 3.5 billion years.

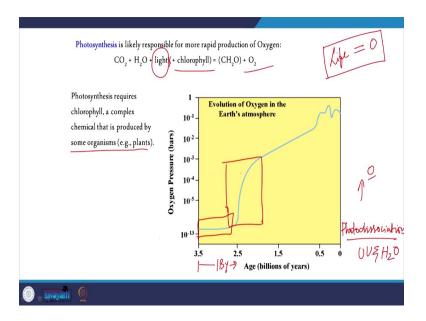
So, from the fossils or from the rocks it may be possible for estimating for the it may be possible to estimate the amount of oxygen in the atmosphere at different points in the past, at different ages in the past. So, out of those experimental results what has been, this is kind of an accepted figure; that means, the oxygen was very slowly rising over the past 1 billion years from 3.5 billion years.

Then it the rise was very steep and it was kind of steep; then it reaches a kind of a saturation here, ok. Now, what you see here, the rise of oxygen was very very slow in the beginning and after that it was very steep; I mean it was at an exponential rate almost, right.

What I mean to say by this figure is that, the rise of oxygen or the production of oxygen in the atmosphere could not have been only due to photo dissociation to be able to account this rate. Because in the beginning itself I have already told that, it is very crucial that ultraviolet is supplied in abundance for the photo dissociation to happen; only then it can be very fast reaction, otherwise it is a very small reaction, right very slow reaction sorry.

So; however, the rate at which the O2 appears to have increased could not have been produced by dissociation alone. So, you cannot just keep dissociation as a source of oxygen. So, there must be something else.

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So, it is now believed that photosynthesis is likely responsible for the rapid production of oxygen; that means, this increase let us say, this increase must have been due to the photo dissociation not photo sorry, must have been due to photosynthesis not due to photo dissociation. So, photosynthesis requires chlorophyll and it requires light, you see light, it is not ultra violet, it is light; light as in the visible spectrum that you get.

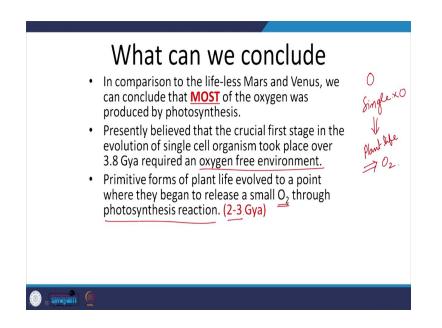
So, visible spectrum is always in abundance, it is not absorbed anywhere in the atmosphere we have already seen that; it reaches almost the surface of the earth, because no molecule or atom has the energy excitation levels in the suitable for the visible spectrum. So, visible radiation penetrates the entire volume or the height of the atmosphere in bridges so; that means, that visible radiation may have been responsible for the formation of oxygen at a very high or very steep rates.

So, photosynthesis requires of course chlorophyll, a complex chemical compound that is produced by some organism. So, it requires I mean. So, now, you see that life and oxygen these two are interconnected. Now you have the beginning of the oxygen was formed; I mean there was some oxygen which was formed or the let us say 1 billion years.

For 1 billion years it was mainly the photo dissociation; for 1 billion years I mean you have to, for 1 billion years it was mainly the photo dissociation which have at least left out a trace of oxygen; otherwise there was no oxygen, there was no free oxygen in the system. So, photo dissociation due to ultraviolet and H2O resulted in the formation of, some amount of oxygen of course; it was very small of course.

But then the photosynthesis picked up; the it picked up to certain to such an extent that, the rate was very very high. I mean it picked up such an extent that it the rate was almost exponentially increasing. So, what can we conclude?

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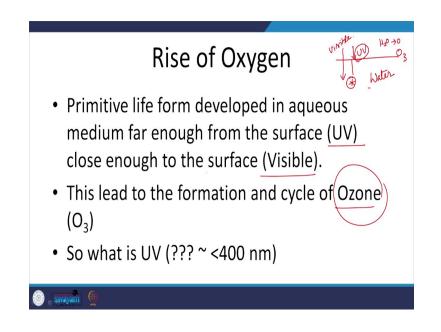


So, in comparison to lifeless Mars and Venus, we can conclude that most of the oxygen was produced by photosynthesis. Presently it is believed that the crucial first stage in the evolution of single cell far, single cell organisms took place over 3.8 billion years ago; which and which absolutely required an oxygen free environment, it does not require oxygen to be able to grow or to be able to sustain, to be able to live, ok.

So, this single cell organism evolved to a point that it required an oxygen free environment, ok. And primitive forms of plant life evolved to a point where they began to release small amount of oxygen through photosynthesis reaction. So, after the initial release of oxygen by photo dissociation; single cell organisms evolved on the planet which does not require oxygen.

Then primitive forms of plants; primitive form of plant life evolved which released oxygen and this happened over the past to 2 to 3 billion years. So, now you just go back here. So, here, so 3.8 billion years. So, this is the single cell organism period. So, this time and here somewhere here the plant life evolved, ok.

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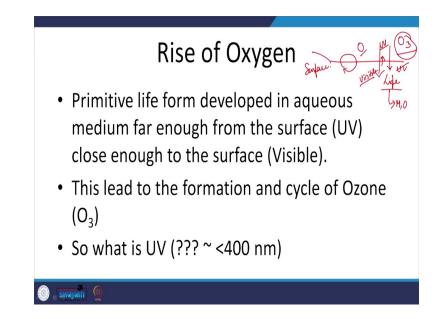
Then the rise of oxygen; so primitive life form developed in aqueous medium far enough from the surface and close enough; sorry far enough from the surface, so that UV can penetrate and close enough to the surface such that visible radiation is accessible. So, that is the reason that we know it for a fact that life originated in the ocean or in the water.

So, now primitive forms of plants, primitive life form evolved in the water; because water provided is shielding for the incoming ultraviolet radiation and it also provided access to the visible radiation. So, this height at which this evolution took place is very crucial; it is believed that, it was an optimal height where the ultraviolet could not reach and also where the visible is accessible. So, that photo dissociation reaction must always be maintained to release oxygen into the system, ok.

And this led to the formation of cycle of ozone; I mean this eventually led the, see ultra violet was doing it is part by breaking H2O of course, and releasing oxygen. And photosynthesis was also doing it is part by providing by the formation of, was doing its part by forming the life or organic compound, the monomer, the main basis for the life and also producing the oxygen because; that means, that the.

Now, the ozone cycle comes into existence. It is a very interesting and very important process to understand how ozone was responsible in a way for the formation of oxygen or for the formation of life itself. Now you have to understand why the water; I mean ultraviolet of course, the reason is if there is no ozone. If there is let us say if there is; now there is a it is a very tricky thing here.

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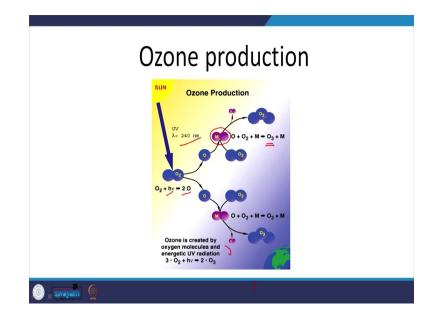
Now, let us say I am saying life. So, this is the ocean surface let us say. Now I am saying that a life existed below the surface of the ocean such that, it is protected by the ultraviolet; ultraviolet does not reach and at it is accessible for the visible radiation, right. Now, in the beginning I always say that there was no ozone. So, when there is no ozone ultraviolet reaches and ultraviolet is hazardous for the life.

So, life cannot exist if there is ultraviolet radiation. So, life comes out of the ocean, ultraviolet will kill it that is it. So, as long as there is no ozone, the life form will not venture into the surface. So, this is the surface let us say, this is a very crucial thing. So, as long as there is no ozone, life will not venture out and onto the surface; and by being below the surface of the ocean it is accessing visible, it is producing the monomer and it is also producing the oxygen. Meanwhile outside ultraviolet is still doing its job by breaking the water molecule or water vapor molecule and still providing oxygen, ok.

Now, somewhere this balance must have been gone out of the place. Let us say, somewhere I mean life venturing onto the surface is the only way that it can produce enormous amounts of

low oxygen come with having complete access to the visible radiance. Somewhere so; that means, that somewhere something must have happened which have resulted in the formation of ozone. So, there must have been some cycle which has resulted in the formation of ozone. Let us see what it is.

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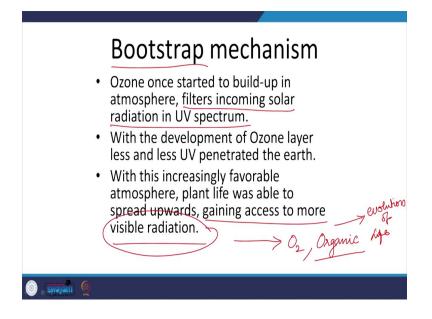


And if you look at the ozone production, the process by which ozone is produced. You require ultraviolet radiation in less than 250 240 nanometers. So, 240 nanometers is a very energetic radiation, ok. Now, what happens is if you have ozone oxygen; this 240 or less than 240 nanometer radiation is able to break or dissociate oxygen molecule into free oxygen atoms.

Now these free oxygen atoms in term in the presence of a third body which does not participate in the reaction; this third body does not actively participate in the reaction rather it just serves as a platform for this chemical reaction to happen. We know this very well in the chemical reaction, ok.

So, what happens this oxygen atom in term in the presence of a third body and in the presence of an oxygen molecule results in the formation of an ozone molecule, ok. Now, thus ozone is created by oxygen molecules and energetic ultraviolet radiation, ok.

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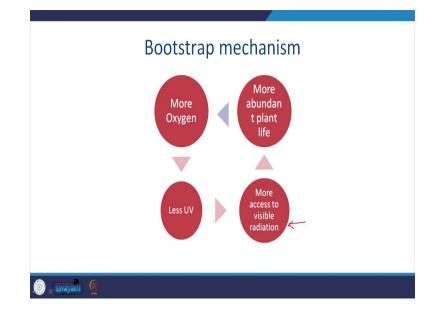
For understanding this we always talk about this bootstrap mechanism which has resulted in the formation of ozone layer. Now ozone once started to build up; once ozone started to build up in the atmosphere by the action of ultraviolet radiation on the water molecules, it started filtering the incoming solar radiation in the ultraviolet spectrum, ok.

So, with the development of ozone layer; so periodically as the ozone started to build up as the number of molecules, number of molecules of ozone started increasing with the development of ozone layer; less and less amount of oxygen sorry, less and less amounts of ultraviolet radiation started penetrating in the atmosphere and reach the earth, so with the increasingly favorable atmosphere.

So, now as the ozone layer started building up as the concentration or the of ozone molecules increased in the ozone layer, less it started filtering out the ultraviolet radiation; that means, less and less amounts of ultraviolet radiation was able to reach the surface. Why surface important to us? Surface is the ocean surface and below the ocean surface there is life which is trying to venture out onto the surface onto the rocky surface, so that it can release more amounts of oxygen.

So, with the increasingly favorable conditions; that means, with the decreasing Ultraviolet radiation which was reaching the surface, the plant life was able to spread upwards and gaining more access to visible radiation, is the main thing. So, the more amount of visible radiation that it gets, more amounts of oxygen it releases and more amounts of organic

chemical compounds or complex organic chemical compounds it will be able to form; which will eventually lead to the evolution of life, this is a very crucial process.

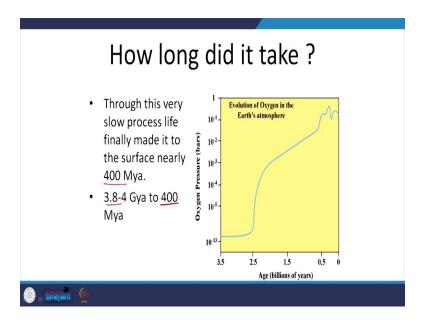


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So, this bootstrap is a very important part in the history of the atmosphere. That is what is this bootstrap? The bootstrap less is more oxygen less; let us say more access to visible radiation will give you more abundant plant life; more abundant plant life will produce more oxygen and more oxygen is produced it will be broken by the ultraviolet creating oxygen creating ozone.

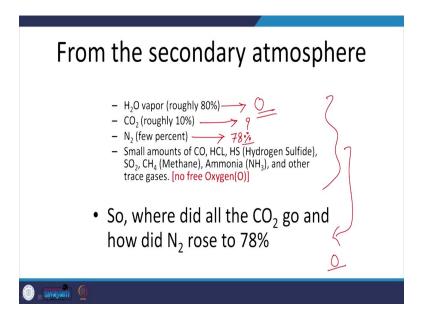
More is the amount of ozone less is the amount of ultraviolet radiation reaches that the surface and less is the ultraviolet more access to visible radiation. So, this bootstrap continued for several millions of years and it resulted in the formation of large amount of oxygen.

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So, through this very slow process life finally, made it to the surface nearly 400 million years ago; it is not very distant in the past, it is just 400 million years ago when the life started making it to the surface. And so, this is the entire process; how long did it take? So, from 3 point million years ago to nearly 400 sorry 4; 3.8 billion years ago, it started the dissociation and the photosynthesis and they lasted for almost 3.7 billion years and it is only in the 4 last 400 million years this life ventured onto the surface.

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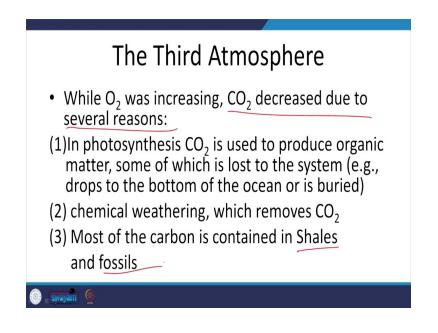


Now, just to recap from the secondary atmosphere it is mainly the water vapor, CO2 and N2 a very small percentages and other chemical compounds other molecules; but there was no still oxygen, so this is a secondary atmosphere. And from here at least we know understand how oxygen has resulted. Now we should understand this. So, this large amount of water vapor has resulted in the formation of oxygen that is what we know now; this resulted in the formation of oxygen, right.

And now, we have to understand where it is this all this CO2 go, right. And nitrogen which is now, which was a very few percentages very small percentage in the secondary atmosphere has increased to nearly 78 percent of the atmosphere.

Now, so now, we understand how the water vapor gave away oxygen, right through this discussion. Now we will try to see where did all this CO2 go and how to come nitrogen which was a very small chemical constituent in the secondary atmosphere, became the most dominant constituent in the present-day atmosphere.

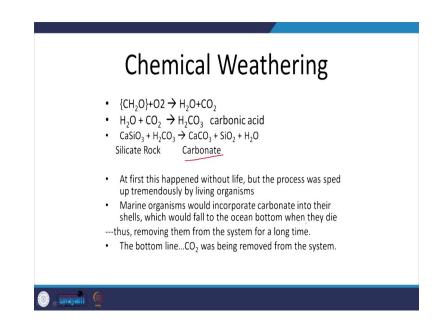
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So, the third atmosphere; then we talk about the third atmosphere. So, while the O2 was increasing by the photosynthesis and photo dissociation reaction, CO2 decreased due to several reasons I mean there were there are several theories which were proposed to understand the loss of CO2 in the atmosphere.

So, one is photosynthesis, CO2 is used to produce the organic matter right; when the photosynthesis reaction CO2 is consumed. And so, some of which is lost to the system and so, it eventually drops to the bottom of the ocean and it gets buried, right.

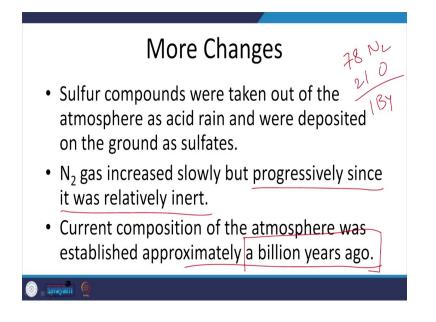
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Chemical weathering must have removed the CO2 and most of the carbon is contained in the Shales and fossils. So, CO2 must have lost, must have been lost in this form. The chemical weathering is the monomer interacting with the O2 giving you H2O plus CO2. So, it eventually leads to the formation of carbonates.

So, at first in the beginning it happened without life, but the process was sped up tremendously by the evolution of life by the living organisms. The marine organisms would incorporate carbonate into their shells, which would fall into the oceans bottom when they die. And thus, they remove a large amount of carbon dioxide from the atmosphere into the ocean. So, they did eventually deposit it at the bottom of the ocean. So, bottom line is that CO2 was being removed from the system effectively.

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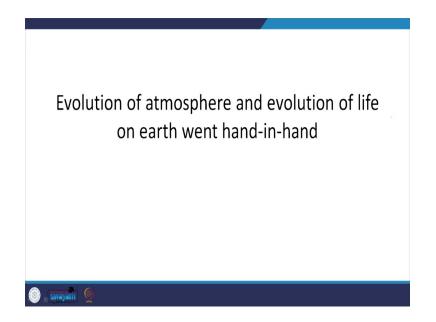


And sulfur compounds which are also the basic chemical compounds which were released in the volcanic eruptions were taken out of the atmosphere as acid rains and were deposited on the ground as sulfates. The nitrogen gas increases slowly but progressively since it was relatively inert.

So, nitrogen it is not, no theory will tell you that nitrogen increased; nitrogen was there, I mean it was eventually it is a conservative quantity; it was present in the very small proportion in comparison to water vapor and CO2. Water vapor gave away the oxygen, hydrogen was lost mainly and nitrogen which was there by small numbers that time remained as it is, it did not participate in the chemical reactions. And as a result, it progressively, it relatively I mean its number is increased appears to have been increased when you change the reference with which you see, ok.

And the current composition of the atmosphere was established approximately a billion years ago. So, 4.5 or 4.5 billion years ago does not really matter. So, what matters to us is 78 percent oxygen 78 percent nitrogen and 21 percent oxygen were established nearly 1 billion year ago.

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So, one thing what we can say is that the evolution of atmosphere and the evolution of life on the earth went hand in hand. So, these two processes are dependent on each other. So, one created the other and the other created helped creating the first one. So, both of them were parallel with each other. So, this is where I stopped today.

So, now we have seen how the atmosphere has formed out of the volcanic eruptions, right. Now in the tomorrows lecture, we will try to understand the atmosphere of the earth, a few basic details about the atmosphere of the earth and how the atmosphere of the earth compares itself to the atmosphere of other planets in our solar system, ok.

Thank you.