Introduction to Atmospheric Science
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Lecture-09
The Earth system -- Carbon in the oceans Earth's crust

Okay so, we will continue the discussion on the earth system. As you may recall we are looking at the carbon cycle, right.

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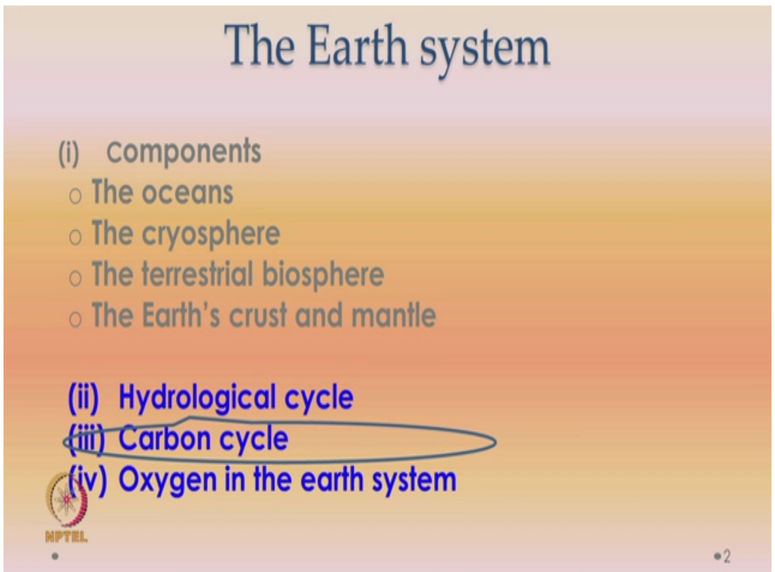

So, we started with the the earth system, the components, the oceans cryosphere, terrestrial biosphere, the Earth's crust and climate we completed that. And we looked at the hydrological cycle. I would not say in fair detail but at least more than just an introduction. Now, we are looking at carbon cycle and the last part will be the oxygen in the Earth's system.

In today's class, we will complete the carbon cycle as well as the oxygen in the Earth's system with which we will complete this chapter 2. That is the Earth System and so the next class will move on to atmospheric thermodynamics, okay where we get back to chalk and talk, okay.

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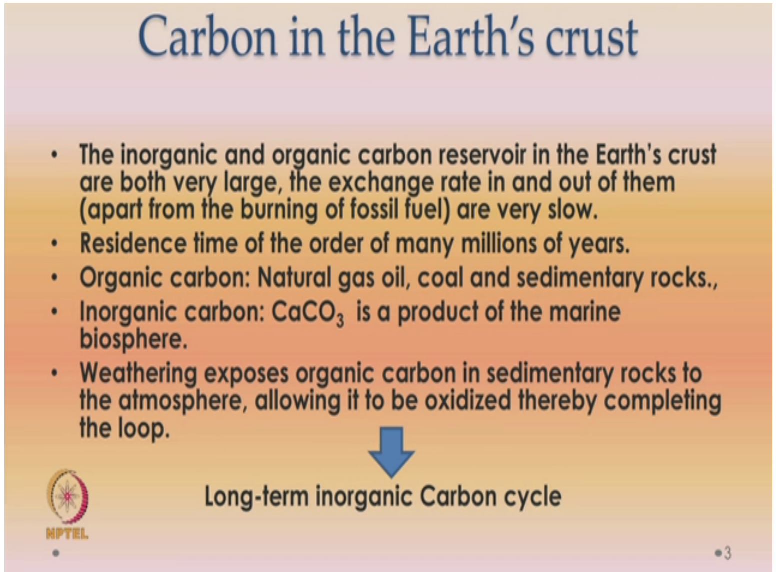

Carbon in the Earth's crust; You have got carbon both from inorganic and organic sources. So, the inorganic and organic carbon reservoir they are very, very large, ok. I already gave you an estimate what does the estimate in one of the previous tables. Can you say so many kilograms per meter square or something? It is very huge, right okay. So, for example, the organic carbon sedimentary rocks is 20,000 kilograms per meter cube right.

And then, you all also have inorganic carbon in the sedimentary rocks which is like 80000 kilogram per meter squared, lot of carbon, okay so and the, look at the residence time. The residence time is basically organic carbon is 2 into 10 to the power of 8 years and the inorganic carbon is about 10 to the power of 8 years. So, it is the processes are very slow. The processes are very slow so the residence time is the order of millions of years it is not in not even 10 to the 10 to the 6; it is 10 to the 8 100 of, millions of, years.

So, what are the sources of this organic carbon and the inorganic carbon? The organic carbon, natural gas, oil, coal and sedimentary rocks, okay as far as the inorganic carbon is concerned basically you have limestone or calcium carbonate which is a product of the marine biosphere, okay. Weathering is an action or activity which exposes organic carbon in sedimentary rocks to the atmosphere allowing it to be oxidized; okay thereby it completes the loop.

So this we have already seen to some extent, in the earlier class. So, this is called the long term inorganic carbon cycle. Calcium carbonate beside reliable carbonic acid and then silicon dioxide all these reactions we saw in the last class, okay. So, this weathering and organic carbon in the sedimentary rocks, oxidation and this is basically a part of the long term inorganic carbon cycle.

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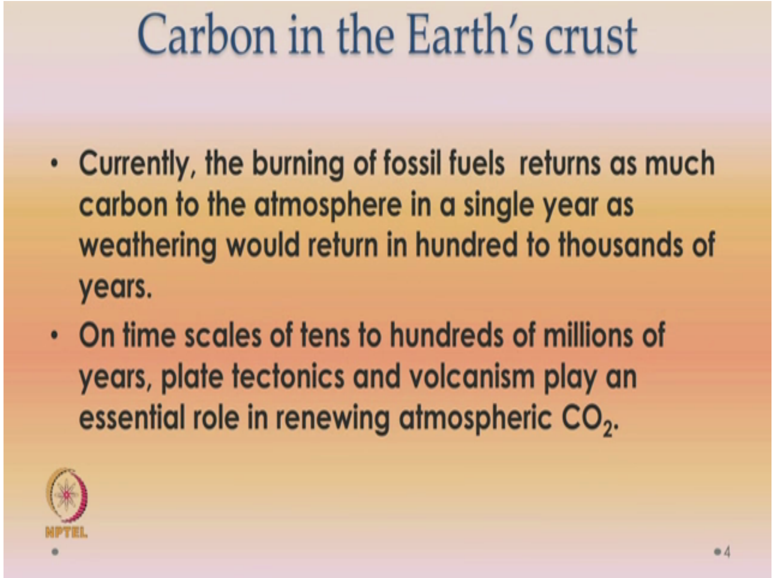

The problem now is currently the burning of fossil fuels returns as much carbon to the atmosphere in a single year as weathering would return in 1000s of years. That this way there is a rapid increase of carbon dioxide as confirmed by the Mauna Loa experiments from the late 50s, all right. So, on timescales of tens to 100 of, millions of, years plate tectonics and volcanism also play a role in ruining the atmospheric carbon dioxide because atmospheric carbon dioxide can and carbon dioxide can just come from below the Earth's mantle.

And through this volcanic eruption can be directly sent out into the atmosphere. So, there are several ways where this carbon dioxide or carbon reaches the atmosphere. One is through the burning of the fossil fuels and long-term occasionally it can be through the volcanic eruptions. This can also be through the weathering and okay, right. Then it comes to the ocean and this thing and so on, okay, okay. So, if you want you can take it down.

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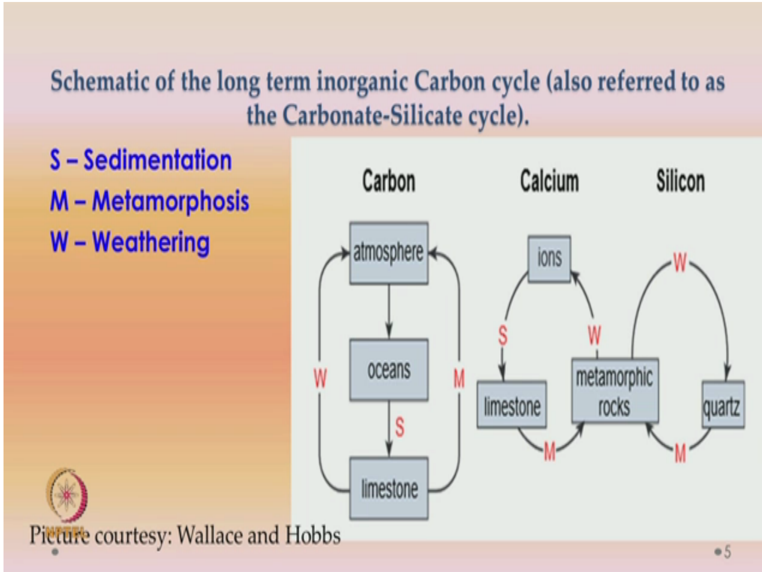

Anyway I will give this presentation. If you take it on you can understand this better. It is called the carbonate silicate cycle, okay. The terminology is S means sedimentation, M means metamorphosis or change and W is the weathering, okay. So, the three elements involved at the carbon, calcium and silicon. So, it is also called the carbonate silicate cycle. So, this is basically from a brief survey of atmosphere by Professor Wallace and Hobbs.

So that is a very famous book the Wallace and Hobbs, okay. Let us look at this in a little more detail. Let us look at the carbon. So, you can look at in the atmosphere, carbon in the oceans and carbon in the limestone. So, from the atmosphere, you can have the carbon getting into the ocean. We saw the route through which this happens and then, from the oceans there can be sedimentation and then this can go to the bottom Earth's crust or mantle where limestone is formed, okay.

This is a way of drawing the atmospheric carbon dioxide and keeping it as a reserve in the form of limestone which can mitigate increases in carbon dioxide in the atmosphere to a certain extent, okay. But uncontrolled release of carbon dioxide into the atmosphere is very difficult because this process is slow or fast? Slow, there is a natural pace associated with this process. You start pumping more you pump you burn more fuel and release carbon dioxide all of a sudden for something it is used in millions of years in 100, in 10s of years.

You start releasing so much carbon dioxide it cannot handle. So, the atmospheric carbon dioxide will increase is it, okay? So, atmosphere arrow mark ocean, sedimentation, limestone, from limestone, weathering can take place weathering can take place because of the action of ocean waves and this thing and all that and then again it can be so we can recycle it back to the atmosphere which is the left side of this.

Or you can also have metamorphosis and then which can recycle it back to the atmosphere. Next, go to the calcium cycle. Calcium, we say, we saw that Ca^{2+} ions are available. So, the Ca^{2+} ions can combine with carbon dioxide, carbonic acid and through sedimentation it will form limestone, right. It will form limestone, okay and this Ca^{2+} is coming from no it cannot it can come from weathering of calcium carbonate. The reverse reaction that is one and the skeletons and the skeletons and shells calcium, okay it comes from calcium silicate also.

So, the various sources of calcium so calcium 2 + will react to the high carbonic acid which you have already seen in the earlier class. So, this can form limestone. This limestone can again change into metamorphic rocks and this metamorphic rocks can undergo weathering and the reverse reaction will take place which will again release calcium ions into this cycle. So, this ocean so, this, this cycle keeps going. This is called the calcium cycle.

So, this metamorphic rocks, there is one more activity where you have got calcium carbonate + silicon dioxide results in calcium silicate + CO_2 + $2CO_2$ which we combined all these reactions then we wrote up some equations in the last class, chemical reactions, right. So, you can have silicon or silicon also enters the picture. So, from it from quartz what is quartz? Chemical form calcium, what? Silicon dioxide, quartz is silicon dioxide.

So, the silicon dioxide can metamorphose. Metamorphosis can take place in metamorphic rocks and then some weathering you can also take place then you can again form quartz and all this. So, this is basically called the long term inorganic carbon cycle, okay. The long term inorganic carbon cycle, also referred to as the carbonate silicate cycle, is it okay, fine.

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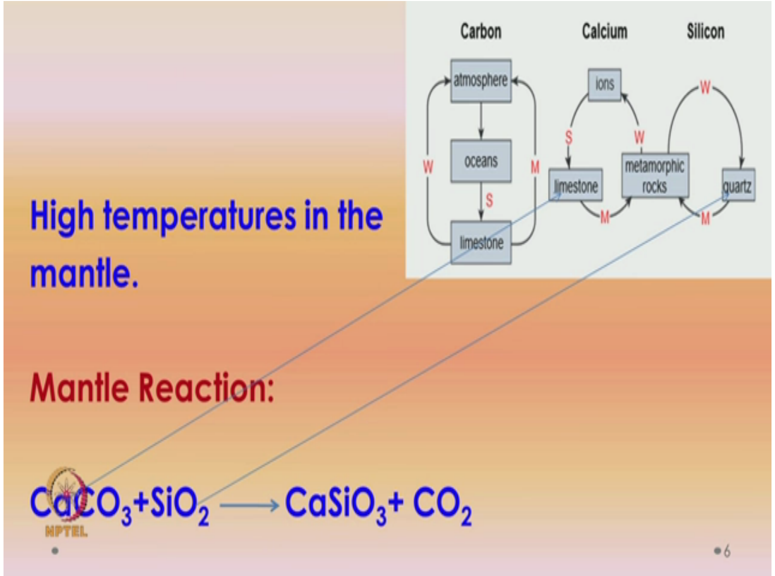

Now, let us look at this in detail. So inside the, now, we are looking at the carbon cycle in the Earth's crust, right. So, the mantle, the temperatures are very high. What is the range of temperatures in the mantle? 900 to 4,000 degrees centigrade +, okay it is of order of a few 1000 degrees centigrade. High temperatures are there, are present in the mantle. So, it leads to what is called the mantle reaction. Please take down this mantle reaction.

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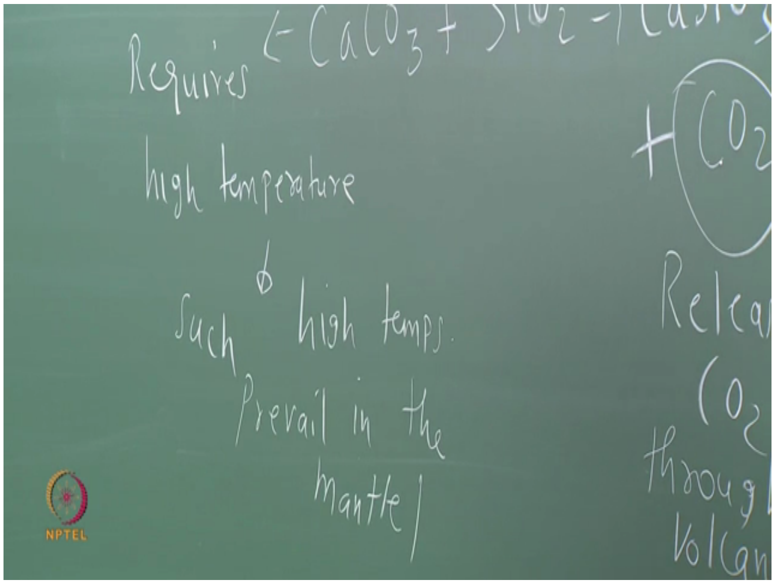

So, calcium carbonate + SiO_2 + Co_2 what is the big deal with this? It does not store up; it actually releases, okay. It stores what you are saying is partially correct. It is making the carbon dioxide, how is it released? So, correct. What he is saying is if the stores the CO_2, but what is the vent for it? Volcanic eruption, okay.

Release of CO_2 through volcanic eruption so, immediately the proponents of people who are against its climate change theory and all that will say no anyway through volcanic eruptions carbon dioxide is being released. How can you say that fossil fuels are responsible for all this? People have done calculations and shown. Volcanic eruptions are not occurring every Monday or Tuesday, right, right.

But every minute, every second, there is, some so many Jets, now how many Jets are flying over the globe. How many long distance Jets are flying? I mean how many Jets are flying in India, how many are flying from Chennai airport, from Bombay airport? Carbon dioxide is continuously increasing. Clear, all right because of this burning of the fossil fuel, okay. So, this is basically a very important this thing.

So, calcium carbonate + limestone + say what gives calcium silicate, this CO_2, the production of CO_2 storing it up, storing up of CO_2 within the mantle and then whenever there is a volcanic eruption large quantity of CO_2 is released. So, there is a possibility that carbon can be transferred. Carbon from deep inside the mantle can be transferred directly to the atmosphere. God has given some route for that also. It is not forbidden. There is an, erosion then there is an ad it has to cross the ocean, right but there is a direct route, okay that is through volcanic eruption.

Please remember this, okay. However, high temperatures are required for this reaction to take place which reaction? Calcium carbonate + silicon dioxide results in calcium silicate, how many of you are civil engineers here? Calcium silicate has other uses. We use it in engineering where is it used? Cement, so, calcium silicate but this is very difficult. This is a very bad way of trying to get somewhere where you have to go deep into the ocean and my dazzling cement in the land, right.

So, calcium silicate has lot of uses in civil engineering also, right. So, this reaction requires high temperature. Such high temperatures prevailed in the mantle, all right. So, the last portion in this chapter is oxygen in the Earth's system, okay. Do we have internet on this laptop? No. the last part is oxygen in the Earth's system. The earth is very unique. It is a very, the earth is a very habitable planet, largely because of the presence of oxygen and also the presence of water, okay.

So, 72 % is water and also because of the presence of oxygen. There is also ocean layer, ozone layer. We already discussed what is ozone layer and all this in one of the earlier classes. And what happens if is ozone layer is there is a hole in the ozone layer and all that. Actually many of you will be surprised to know that the atmospheric oxygen accounts for only a very small amount of the free oxygen available in the earth system.

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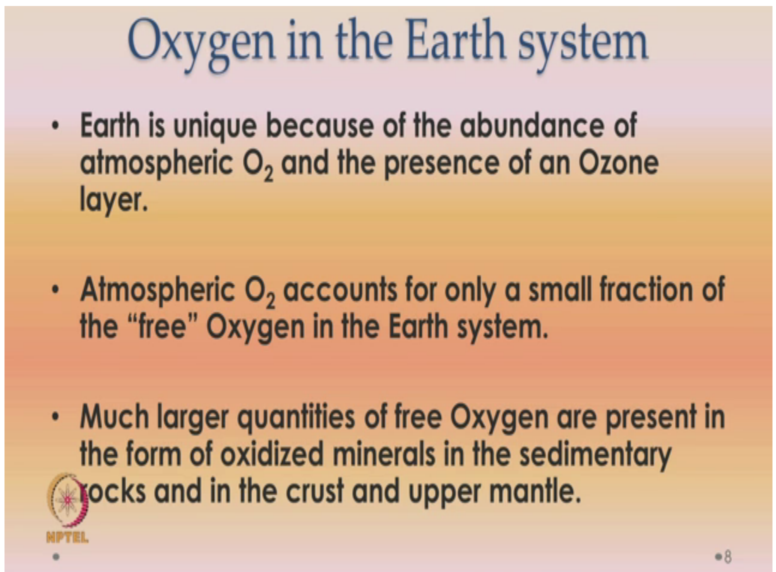

Many of you do cannot believe that there is lot of oxygen stored up deep inside in various other forms, okay. The atmospheric oxygen is only a fraction of the total free oxygen in the Earth's system and also if you look at the evolution of the earth, there is not this much amount of oxygen was not present originally in the earth. So, there is an oxidation which has which is taking place which has resulted in the availability of more oxygen to support more life, right.

So, actually originally if you look at Big Bang Theory and all this and all those things in the evolution of oxygen, in the evolution of the earth, you can see that initially it was largely devoid of oxygen, okay. So, oxygen reservoir oxygen concentration has built up over so many or so much of time. Now we will see from where this oxygen has come and so on. We work out some problems so that there is more clarity on this.

Much larger quantities of free oxygen are present in the form of oxidized minerals largely Fe2 O3, Fe3 O4 and so on, okay oxides of iron. So, much larger quantities of free oxygen are present in the form of oxidized minerals in the sedimentary rocks. Where are these sedimentary rocks, in the sedimentary rocks as well as in the Earth's crust and in the mantle? The Earth's crust in the mantle as well as sedimentary rocks from the earth, you get lot of this oxygen present in the form of oxidized minerals, okay.

That means oxygen is hiding into the hiding in all this minerals. But for their current level of oxidation, they must some lower form of this oxide must have oxidized in the presence of oxygen to, are you getting the point? Fe2O3 + 02 balance that if gives you results in Fe3O4 and there is an abundance of Fe3 O4 you actually we say that the oxygen is present in the Fe3O4.

If you are able to get if you do this redox reaction, if you are able to look at the reaction in the opposite direction then, it will lead to so from Fe3O4 it can go back to Fe2O3 and we can get back the oxygen. So, we will have to see whether so this is one way of getting oxygen in the Earth's system. What is the traditional, what is the theory over your geography teacher what has she taught you, photosynthesis okay.

So, the geography teacher is she he or she is not wrong. We are all; we always believe that photosynthesis is the source of right, source off, it is a source of oxygen, correct. But it is not fully correct okay because if you look at the current oxidation level of the earth, I prove before the end of the class will prove through problems that photosynthesis is insufficient to explain for this to explain or account for so the current oxidation of the earth. So, we have to see some other mechanism which has resulted in this oxygen, okay.

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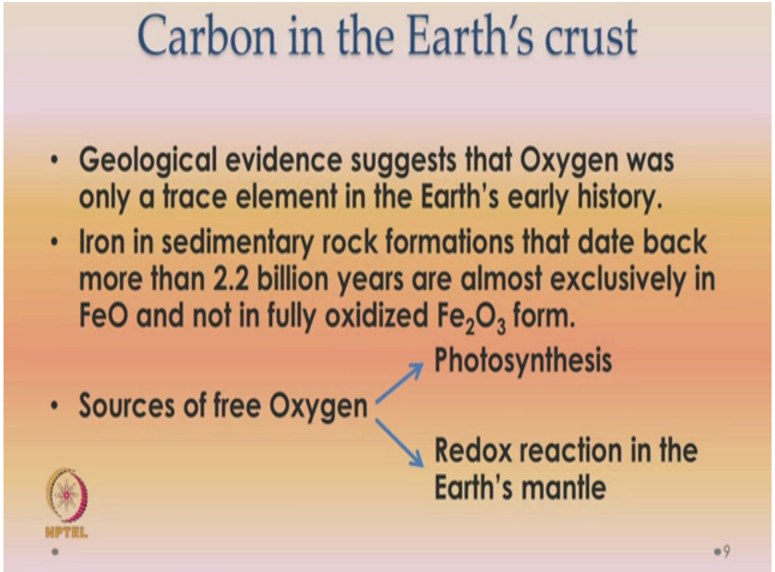

Please keep this in mind. Geological evidence suggests that oxygen was only a trace element so geologists have confirmed, okay using various analysis models and marrying mathematical models with measurements and all this. And then we are tracing it back, okay back if you go back in time. So, geological evidence confirms that oxygen was only a trace element in the, that is early history.

Iron, the iron which is present in sedimentary rock formations that date back you can do dating right you can do dating and find out what is the age. Suppose, those sedimentary rocks which are more than 2.2 billion years it is seen that they are almost exclusively having Fe2, FeO which is ferrous oxide, is it some. There are so many, right? It is a lower form of FeO, are not in its fully oxidized Fe2 O3 form, okay. Now, with that in mind, let us look at the sources of free oxygen.

The sources of free oxygen and basically photosynthesis but photosynthesis reaction we always we already looked at, right. So, there is an uptake of carbon dioxide, right. There is an uptake of carbon dioxide, water and then radiation is absorbed in 0.43 micrometer and 0.66 micrometer which are essentially blue and orange light, okay. Energy is growing in. So, it is not taking that. The plants are taking food in the form of energy, okay. The E is equal to H2 is there with that E is equal to H2 know, they make that have what is that H2CO, the food the glucose, right.

Now let us look so the sources of free oxygen are photosynthesis and redox reaction in the Earth's mantle. Now, you have to copy down this equation.

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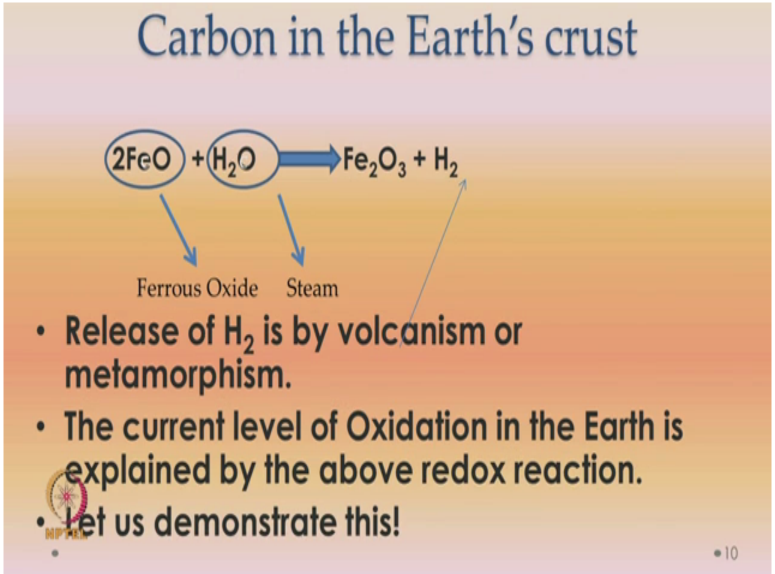

The ferrous oxide + H2O results in Fe2 O3 + H2 let us write this FeO, is it? Is it not, it getting balanced? 2O + one O, three okay – 2Fe, Fe it is 2h2. So it is alright. That is balanced. So, this water is actually steam. This is ferric oxide is it is it okay it is Fe3O4 also is it. So, iron is so much of trouble, okay. And this release of H2 is by volcanism or metamorphism. Volcanism is directly it can send H2 into the atmosphere or H2 can combine with they say CaCO3 all those reactions which you have already seen.

And so, this is the redox reaction which is taking place in the Earth's, Earth's crust. So, the current level of oxidation, so the thesis is the hypothesis is the current level of oxidation in the earth is explained only by the by the above Redox reaction. In the absence of this redox reaction if this redox reaction were not to take place we are not present. Then, you would have conjectured or you would have asserted or you would have averted that photosynthesis is responsible photosynthesis is responsible.

And you can fully account for the oxygen oxidation of the current level of the, the current oxidation level of the Earth system, okay. Let us demonstrate this we will solve three problems in today's class at the end of the three problems will prove that the reader, redox reaction is responsible for this that brings us to the end of this chapter and we are all set to start our new chapter on thermodynamics from tomorrow. You know this can also be released know, okay. So, yes please take down this table.

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Mass of O_2 required to raise oxidation of Earth

Reservoir	Mass in kg/m^2
Atmospheric O_2	2.353
Crust Fe^{3+}	>100
Crust CO_3	~100
Crust (other)	>100
Mantle Fe^{3+}	>100

The mass of O2 required to raise the oxidation of the earth. So, this is a table where there are 5 entries right, all right. Column one gives the reservoir and column two gives the mass in kilograms per meter squared. Please take down this table because I am going to work out some problems based on this and based on the table which I press which you have taken down in an earlier class.

Atmospheric oxygen 2.353 kilogram per meter square, crust Fe3 + greater than 100, crust CO3 100, Crust others greater than 100. Please note the difference between crust and mantle is deep inside and mantle Fe3 + is greater than 100, okay. It is all in kilogram per meter square. These are all some estimates based on some scientific reasoning with some arguments and some measurements and matching of the models with the measurements, okay.

It could be three 2.351 or 354, I mean the point is it is around 2. something. It is not 23. or .23 all done, okay. Shall we proceed?

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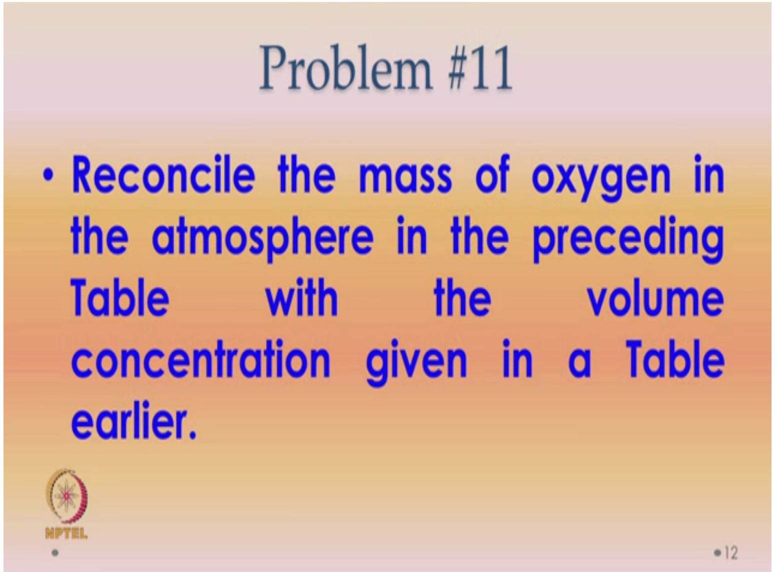

Problem number 11: problem number eleven. Please take this problem down. Reconcile the mass of oxygen in the atmosphere in the preceding table with the volume concentration given in a table earlier. So, quiz questions will also be like this. So, I do not have the table if you say I have no answer to that so open notes exam. So, you need to have all the tables whatever, okay. Copy down, okay. Reconcile the mass of oxygen in the atmosphere in the preceding table with the volume concentration given in a table earlier, okay. Now, let us go to please go to the earlier table.

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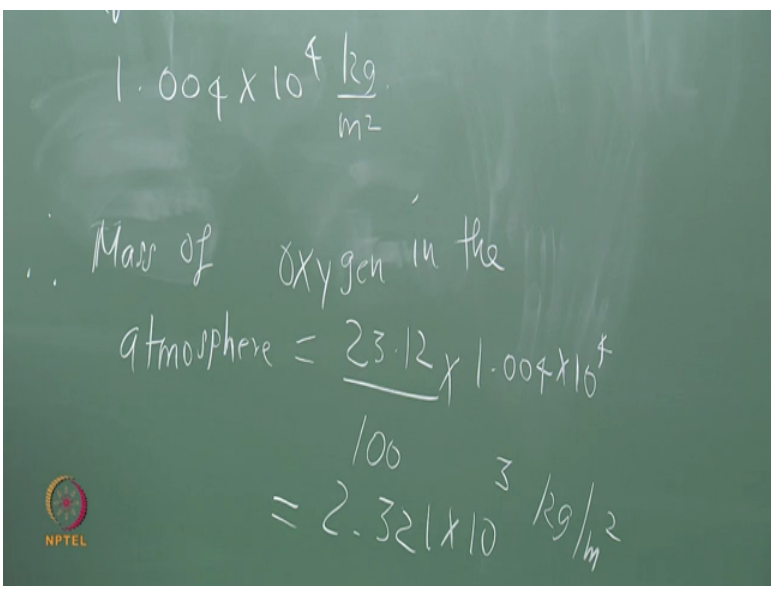

What is the volume concentration of O2? 20 point okay. This is from our earlier table, right? What is the mass concentration? Step 20.9 into 32 by molecular weight of air, wait molecular weight of air. What is the molecular weight of air is 20. Shall we say it is already calculated, okay? 20.9 please tell me how much is this coming? 23.12, what is the mass of the air itself? 5 point 100 into 10 the power of 18 but that came from some mass density know, 1.04 into 10 to the power of 4, correct?

We calculated this value. What is the problem? Reconcile, therefore mass of oxygen in the atmosphere, correct. So, you have to say 1.004 into10 to the power of 4, out of that 23 points on whatever %age what is this 23.1% is oxygen therefore 0.23 into 1.004 will be oxygen right, okay. Therefore, mass of oxygen it must be close to the value given in the table. Otherwise we are in trouble. I hope to get it.

What is that? What is it given in the table. That is 2.3 to something into 10 to the power you always say kilogram per meter square we do not say kilogram per meter cube area, all right. So, it says 2.35 so we can say within limits it is reconciled. So, the reconcile is a term used in Accountancy, right. You all debit you all credit it they are not matching that means you are not reconciled. That becomes an accountant headache.

So, now we will say reconciled. That means it is agreeing with the, what is reconciled? The entry in this table and the entry in the previous table are reconciled; they are not contradicting each other, this table. So, it will be into 10 to the power of -3. That is mass into 10 to the power of -3 kilogram per meter square is 2.35, okay. Just please make the change I am not able to. So, mass into 10 to the power of -3, we can call it as gram per meter square know.

How do you need to more trouble okay so my mass into 10 to the power of -3 kilogram per meter square is 2.35, is it okay, done.

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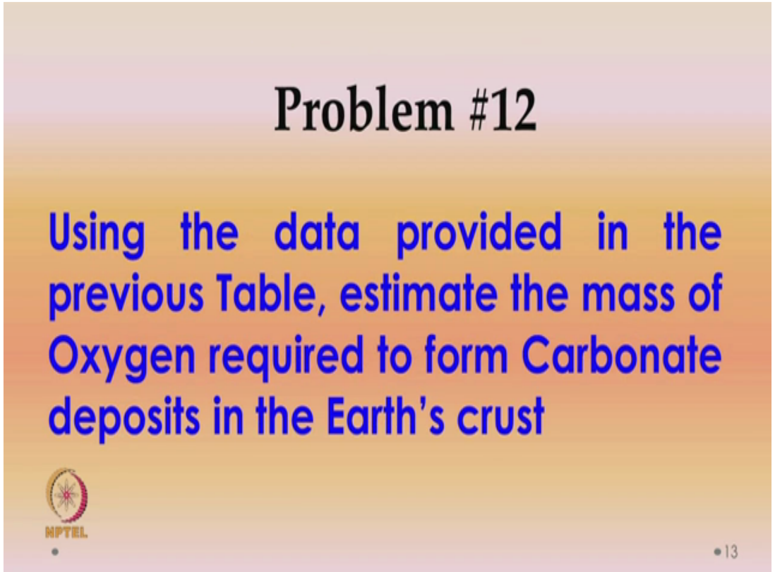

Problem number 12: Please take down the problem. Using the data provided in the previous table estimate the mass of oxygen required to form the carbonate deposits in the Earth's crust. What is the total amount of carbonate deposit? 80,000 kilograms per meter square, correct? In the previous table; 80,000 kilogram per meter square correct.

That is the last entry, that that is okay. It is correct, what I am saying is correct. So, if we, if that is the 80,000, what is that? Correct. Inorganic carbon in sedimentary rock, okay is 80,000 kilo gram per meter square. That is a data given to you. How much of oxygen is required for getting this value of 80,000 kilo gram per meter square, okay. That is a question.

Now, you have to just write some equations and next question will be how much of oxygen is released by photosynthesis? How will you work it out? That is problem 13. How much oxygen is released during photosynthesis then, some plants are there. Then, they decayed they die and all that and finally what is the proxy for that? The photosynthesis activity, the final proxy of all this is the organic carbon, which is 20,000 finally.

Everything is dead than going now. The organic carbon is 20,000 kilogram per meter square. That 20,000 kilogram per meter square if you find out the amount of oxygen which has been used. That is a proxy for the amount which is released during photosynthesis. Now, you will not be able to reconcile that that means the photosynthesis cannot fully explain what is there in the inorganic. So, therefore that FeO + whatever it is H2O gives it Fe2 O3. That the, H2 that redox reaction which is basically coming because of steam is acting with all that.

And that is responsible for fully accounting for the current oxidation. That is what we are trying to drive at. So, systematically solve problem 12 and problem 13, okay. So, problem 12 cannot be done straight away. So, you have to write some get back to your chemistry, okay.

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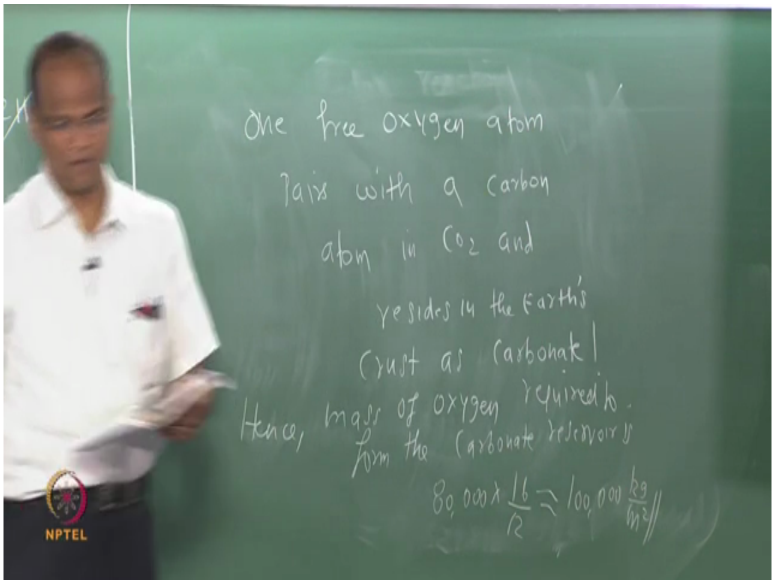

So, solved? I am getting more. Let us write the, I think you are all getting struck by me. So, CO2, this is balanced? Correct, okay. So, this carbon dioxide + calcium 2 ions are reacting with the high carbonic acid, right. And it results in calcium carbonate + this thing. Then, no wait. Now, add 1 and 2. What do you get? O2 - CaCO3 is it? We are using the sedimentary rocks, right. Yes, we have said that. We have said only sedimentary rocks, right.

Carbonate deposits, we are not, but the combination of calcium carbon empowerment is so high compared to other things. That is predominant. That is the leading order now. Other things are not you can do an analysis and your geochemist and you geochemist can give you the data on that, okay. Now, what is happening? 1 free oxygen atom is combining with 1 see the calcium, okay.

1 free oxygen atom is combining with 1 carbon atom and it becomes calcium carbonate, okay. The carbon in this is about 80,000 kilogram per meter square. Therefore, the amount of oxygen required will be 80,000 into 16 by 12. Is the funda clear? Yes, now, we are going to the root? What is the carbon? The carbon, that is 80,000 kilogram per meter square, okay. So, I hope this logic is clear. So, I will write it clearly.

1 free oxygen so, one free oxygen atom pairs with a carbon atom in CO2 and resides in the Earth's crust as carbonate. So, this is the funda. Hence, how much is a correct 100,000, is it 100,000, okay approximately, okay. We are through with this okay. I just wrote some reactions and final which simple this thing is this is 16. Do not worry about 2 - is only the charge, it is a single atom. This is 16, this is 12. So, this somehow it is 80,000.

80,000 when it combines it will be 16 divided by 12. So, the oxygen required is 100,000. Let us go to the problem, fine. Some people are still copying.

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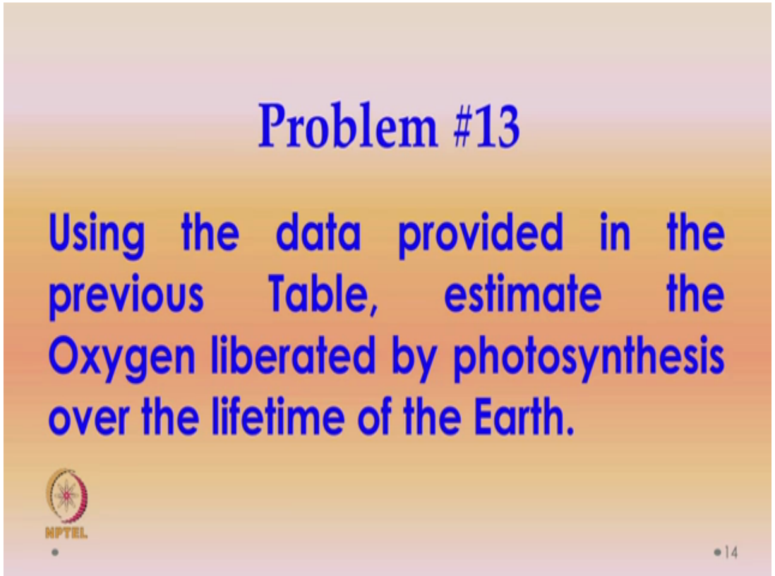

Problem 13: Using the data provided in the previous table, estimate the oxygen, liberated by photosynthesis over the lifetime of the earth. So, look at the organic carbon in the sedimentary rocks is 20,000 kilogram per meter square, okay. So, for that you will have to look at the equation CO2 + H2O gives food + O2 oxygen find out what is a combination between, look at that equation.

And then, the burial of 1 carbon atom releases 1 oxygen molecule, correct. CO2 + H2 give food + O2. So, one carbon atom leads to 1 oxygen molecule. Therefore, 20,000 kilogram per meter square of carbon will release 20,000 kilogram per meter square into 32 divided by 12. That will be 50,000 kilogram per meter square.

But from the carbonate this thing, it is 100,000 kilogram per meter square. But here from photosynthesis only 50,000 kilogram per meter square. So, for the 50,000 we have to account for something which is coming from the redox reaction which is the where some oxygen is coming because of the Reda, redox reaction which is actually because Fe2 O3 + steam which is also produced because of the high temperature.

There is some O in that water and then there is some O in the Fe2 O. If you want all this so there is additionally O in that redox reaction which is taking place deep inside the mantle. And all of the O cannot be attributed just to the photosynthesis reaction. That is the bottom line. Is that clear, ok? Complete the problem.

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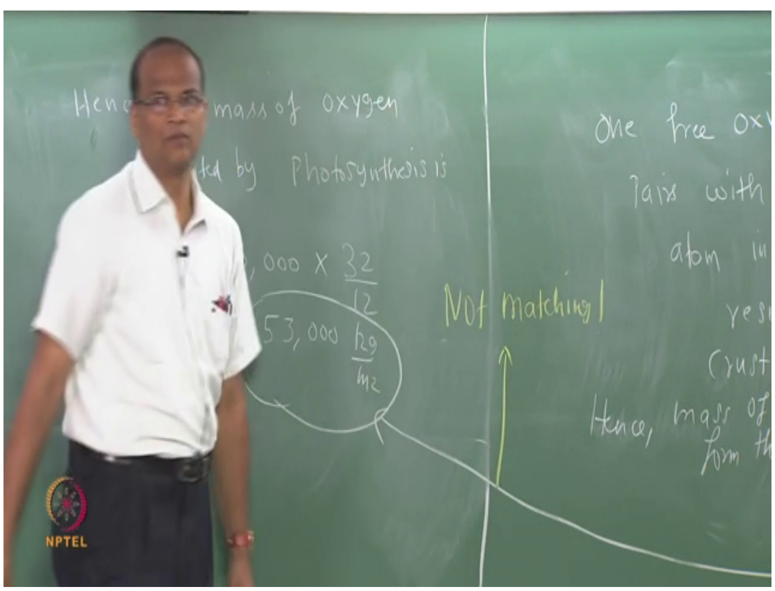

Mass of oxygen, what was that; in the mass of organic carbon, Photosynthesis reaction in the burial of each carbon atom 1 O2 molecule is released. Since, into so what we learn from the problem 12 and 13 is they are not matching. So, an additional mechanism is required to explain the oxidation of the earth. That is to the redox reaction which we already saw. If this reaction were not to be there then, we will not be able to reconcile.

So, one way of doing I could have re reoriented it the whole classes today's class I could have taught like this. From the table given workout problem 12 drop and workout problem 13 and see that the inorganic 100,000 from photosynthesis 50,000 how could I account for the remaining 53,000 kilogram per meter square that 53,000 kilogram per meter square should have come from somewhere. It is coming from the Earth's crust and mantle because of this reaction. This is another way of teaching today's class, all right okay.

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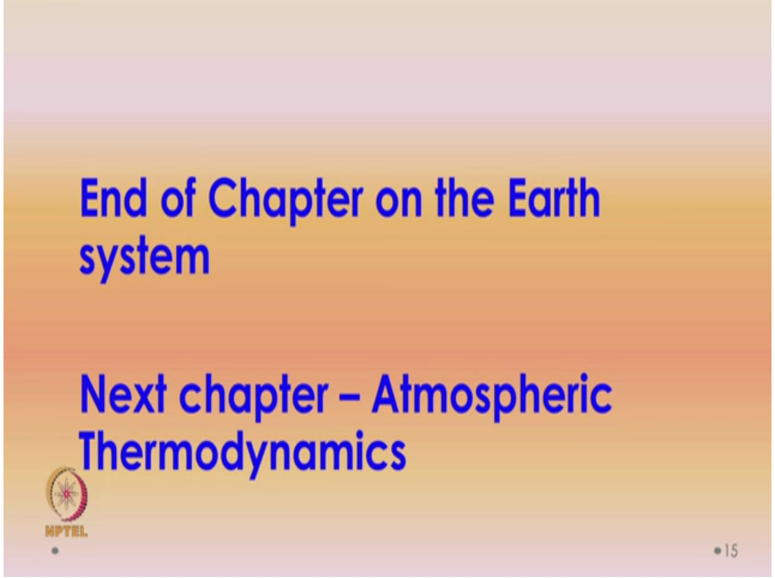

End of the story so it is the end of the chapter on the earth system you have come. We have little time available to us I think. We have got a bird's eye view or a helicopter view of the various subsystems. The next chapter will be atmospheric thermodynamics. We will start with some basic definitions and then ideal gas equation. Dalton's law of partial pressures and all that will start working out problems from tomorrow. Any doubts?