

Bioelectricity
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Lecture – 38

Welcome back to the lecture series on bioelectricity. So, today we were on the thirty eight lecture. So, we are finished with the animal bioelectricity we have talked about the plant bioelectricity, and in the plant bioelectricity, we have talked about the venus fly trap, and touch me not plant we have talked about in depth about photosynthesis, and electron transport, and how light harvesting pigments are used by nature to transmit signals, and thereby you know synthesizing molecules for their survival, then we talked about the dye sensitized solar cells, and pretty much now we have a clear over view about several life forms which are involved in transforming energies, and in that process generating electricity.

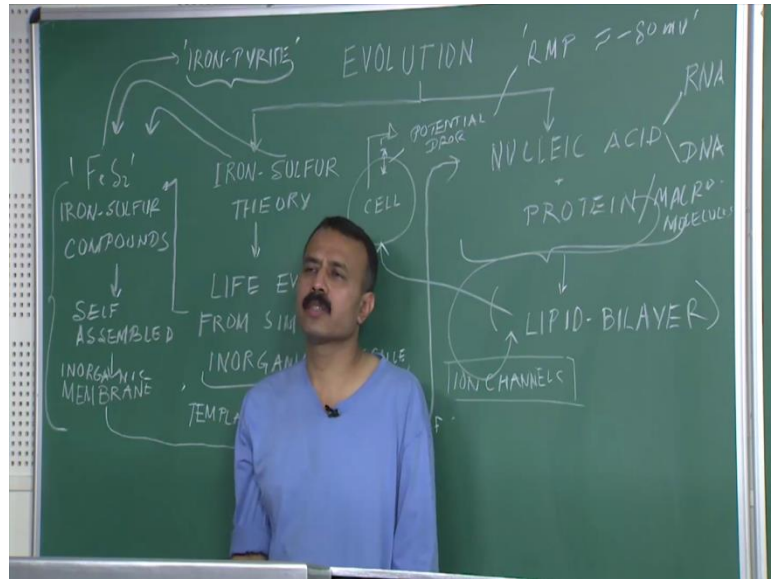
So, now this last three lectures thirty eight thirty nine, and fortieth one, we will be talking about some unconventional systems which are not really well explored in terms from the biological perspective. So, as of now we have all talked about some living systems where we see whether it is a plant whether it is an animal whether it is an insect. So, now will be talking about a specific kind of ancient molecules which has evolved over the period of time, and has some very interesting role in information transfer or in terms of you know energy transduction as well as they have a significant role in the whole evolutionary process to start off with.

So, those who have just even a very minimalistic idea about biology knows that we it is being believed that you know the life has evolved from the genetic materials or from the proteins. So, this is where it all started some form of genetic material either they translate those genetic material into proteins or vice versa, there are proteins something some unknown chemical reaction took place which led to the genesis of what we call about life, if there are this is not the only theory about life evolution of life there are other theories. So, if you have to broadly classify these theories.

So, there is one theory which is called the inorganic evolution of life which essentially believes that the present day life forms what we see has evolved over billions of years from very, very simple elemental or you know very simple compounds somewhere or

other these simple compounds may have self assembled by some unknown reaction which we are at least have not deciphered yet, and they form what we call the modernly membrane, and in that whole process those self assembled molecule acted as a template for series of chemical reactions, which led to the evolution of organic molecules, and one such theory which exist whenever you listed evolution is called iron sulfur theory.

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So, if I had to broadly classify the evolutionary theories which are currently kind of debated upon, then you will see one is the nucleic acid followed by, and proteins of course, we do not know this evolution that who can from what, and within the nucleic acid we talk about ribonucleic acid, and deoxyribose nucleic acid this is one theory the other theory is iron sulfur theory. So, this is the theory which believes life evolved from simple inorganic molecules, and as a net fact.

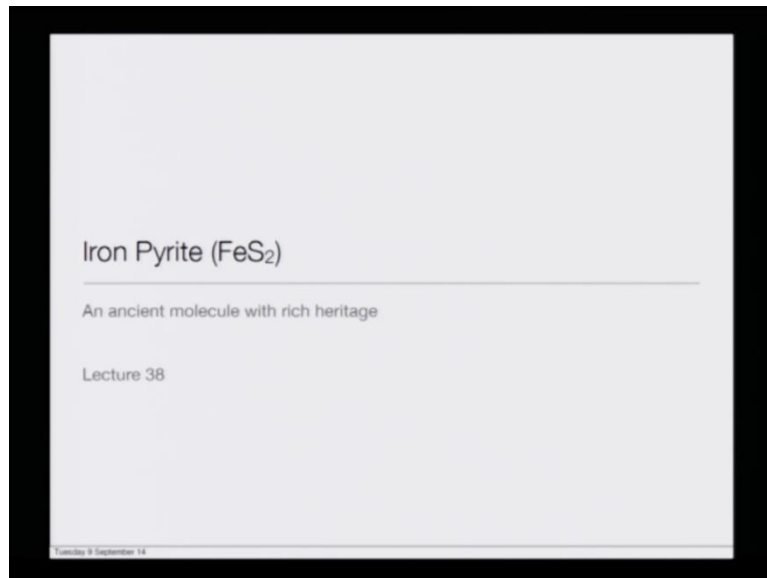
The whole idea is very simple what it claims is a some very specific inorganic molecules very early in the evolution which can sits of iron, and sulfur which acted as a with self assembled these iron sulfur compounds compounds self assembled, and form something what we call as membrane like structure or you can call it an inorganic membrane where as if you look at the other side you will see here we talked about the membranes which are in very initial classes I have taught you about lipid bilayer. So, these inorganic membranes acted as it is belief it is again these are all believed acted as template for synthesis of nucleic acid proteins and all these kind of different molecules.

So, this is what essentially these two different theories kind of proposed. So, there are lot of varying fractions between these theories, and no one can say with hundred percent certainty that which one is right or which one is wrong, because we cannot really go back four billion years back in time to figure out what is true? What is right? what the reason why I picked it up this topic its totally different perspective. So, if you look at it when I started this course I told you that we are talking about the moment of current across the lipid membrane. So, there are lipid bilayers on those lipid bilayers you have these proteins which are embedded which are called the ion channels.

And there are several other proteins which are involved in it, and it is a potential difference across this lipid membrane in a cell which ensures that there is a flow of current in, and out depending on what kind of ions we are talking about this is the cell, and and this is the lipid membrane, and there is a potential drop across the membrane, and what we called as r m p resting membrane potential which is approximately minus eighty milli volt depending on the cell type of course, now by this time you guys are well worse with it. So, now if this is the case, then we will be interested to know about if assumptions.

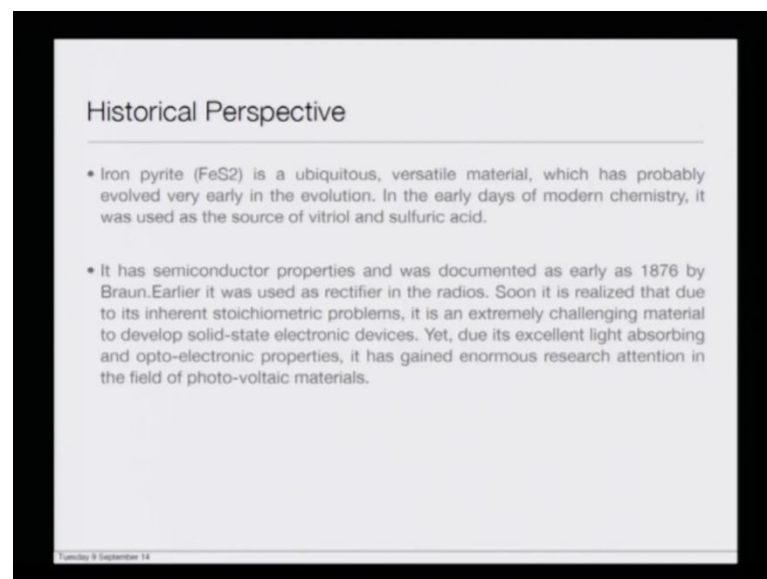
So, there is an assumption. So, if we assume that these inorganic molecules leads to the formation of you know nucleic acid proteins, and other macro molecules which includes lipids, and carbohydrates, then it may be a good idea to understand what are the electrical properties of these kind of inorganic molecules if they are the once which are involved information of these kind of lipid bilayer, and what we call as modern day cell. So, one of the molecule which has kind of a remain in the center stage of the iron sulfur theory is f e s two which is also commonly called as iron disulfide, because there are two sulfur or iron pyrite. So, today's class you see the slide to start off with the slide.

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So, today's class will be on iron pyrite, and ancient molecule with rich heritage. So, what I will essentially do I will expose you to the iron pyrite, and I will end a class with what are the possibilities where we are adding. So, again I am not going to get into the device development or anything in this section, because this is not really meant for it, but I will just give you a glimpse of what really we know about it.

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So, historical perspective of iron pyrite, if you look at it, it is a ubiquitous molecule iron pyrite is available all over the place specially, if you are walking by the road, and there is a drain you know.

So, if you just you know go little like you know if you spoke likely underneath while there is backup oxygen you will see there is iron pyrite present there. So, it is a ubiquitous molecule it is a versatile material which is probably evolved very, very early in the evolution very early. So, what we assume is when probably these molecules are evolved this was at least four to six billions of years a condition when earth was in a very very hostile, and buoyant in the early days of modern chemistry it was used as the source of vitriol, and sulfuric acid this was used to manufacture sulfuric acid, and vitriol. So, this is overall the about the material.

What is very interesting to know that it has a very amazing semiconductor property, and it is one of the very potential material for photovoltaic as many fact, if you look at the development of semiconductors in last hundred fifty years the most land mark is nineteen forties, and fifties when barden britain, and shaklee discovered the crystalline silica, but story of semiconductor is way before that it was during the time of michele faraday there are lot of sulfites which were being suspected, and there were showing, because it is faraday who observe that there is a non-linear property current, and voltage he observed, and he really could not explain it that why there is a nonlinearity, because there is no word call semiconductor.

It was about insulator or resistors that is it either sorry insulators or conductors there was nothing called semiconductor in between there after it was bose who worked on galena crystals likewise and. So, forth, but it was known as early as eighteen seventy six if you could see braun it has semiconductor properties, and documented as early as nineteen seventy six earlier very early in the development of semiconductor, and this is I am talking about much before crystalline silicon was even on the scene it was used in the rectifier circuits in the radials, but the problem there is a problem with this. So, when it was realized that was inherent stoichiometric problem what does that mean?

It means that whenever we write something like this FeS_2 our assumption is that there is one molecule of iron, and two molecules of sulfur, but in real life that does not happen its always two minus x, and this x could be anything of course, it cannot be

greater than a tube, but it could be anything it could be point five it could be point one it could be point two likewise, and this is the problem of these kind of molecules there is always a defect it is never stoichiometrically a balanced one, but that leads to a problem since very soon it was realized that there is a stoichiometric problems. So, it was extremely challenging material to develop solid state electronic devices, yet this is the most important part yet due to its excellent light absorbing and opto-electronic properties it has gained enormous research attention in the field of photovoltaic materials though this material is defective yet, and we will come later in the lecture that it has some absolutely amazing opto-electronic property.

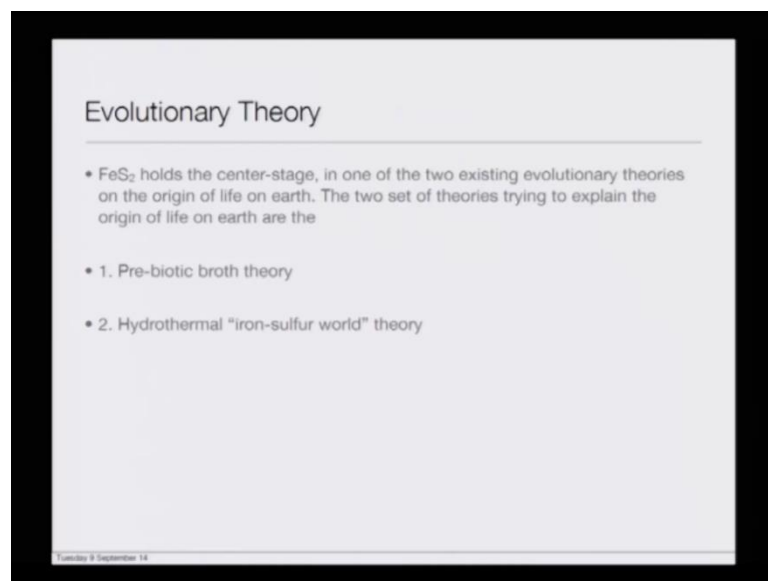
So, an ancient molecule which probably evolved some four to six billion years ago as the ability to absorb sun light, and transform it into some kind of electrical currents. So, in the history of the molecules these will be very, very first molecule which we should consider as evolution of photovoltaic or p n molecules which has the ability to you know translate light to electricity and very interesting part if you see this spectrum where it absorbs this molecules can absorb the spectrum very far red lights. So, it means on your left hand side if you have $u v$ which is starting from two hundred nano meter, and it is going all the way to seven hundred nano meter or. So, you will see the maximum absorption is on towards the right which is red far red likewise. So, if we could develop solar cell out of such materials which are biologically evolved over period of billions of years chemically evolved this could harness low light situations it is not dependent on two hundred or three hundred or four hundred nano meter more on the left side of the spectrum.

So, this interesting property is the reason why there always remain an interest to develop devices out of it, and specially in the modern day when you realize that crystalline silicon is reaching its limit we are unable to minimize the cost. So, we need it a cost effective system which could harness maximum amount of solar energy, because there is a solar energy which has when involved in the evolution of life form, and most likely where the way solar energy must have worked is what you have understood in photosynthesis. So, the sun light is falling on a light trapping molecule, and from the light trapping molecule it leads to some form of you know electron hopping, and leading to eventually leading to the evolution of energy rich molecules, and in that process evolving oxygen, and transforming carbon dioxide into biomass.

So, one common feature or one common thing what you can see about our evolution is some of the molecules have played a critical role. So, one of them if one of them is chlorophyll, then definitely in the same comes f e s two they all have one commonality if you look at the evolution they all should have ability to cross talk with the solar energy, because it is the solar system which is responsible for evolving life they all our life dependent systems, and this is very, very important for us to understand that, because sun light is ample in nature. So, if you could harvest sunlight that the same way plants have evolved.

So, successfully they could harvest the sunlight, and you know they could make lot of energy rich molecules same way, if you could harvest the sunlight using these kinds of molecules you can generate sufficient amount of power which could you know sustain our energy requirements across the global.

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So, coming to the next slide moving on evolutionary theory. So, as I was telling you f e s two holds the center stage in one of the two existing evolutionary theories on the origin of life on earth the two set of theories trying to explain origin of life on earth is the pre-biotic broth theory which is essentially your nucleic acid, and protein r n a, and d n a starting point of life.

This is one the second one is the hydrothermal iron sulfur world theory, and those of you who are keen to understand more about this you can refer to of course, I will be giving

you in your hand out seminal work which is done by scientist called (()) has done significant work on iron sulfur hypothesis as a man fat is one of the pioneer who proposed the origin of life in the iron sulfur rich environment. So, having said this let us look at it what are the arguments in favor of iron sulfur evolution of life. So, if you look at evolution. So, so according to the hydrothermal origin. So, I will come to why it is called the hydrothermal origin of life f e s two might have evolved in the pre-archaeon era in an extremely harsh anoxic sulfur rich environment by spontaneous reaction of f e s, and h two s having said this, let me tell this is the condition where possibly this whole iron sulfur world was evolving out here. This is the world where there was no oxygen there was absolutely no oxygen there was no way that there could be any u v protection. So, that mass fair is getting form, and temperature was very high there is all over the place there where sufficient amount of hydrogen sulfide in a very harsh, and in a very, very you can say where for us even to stimulate or even to imagine how the life would have been is really tough.

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FeS₂ Evolution

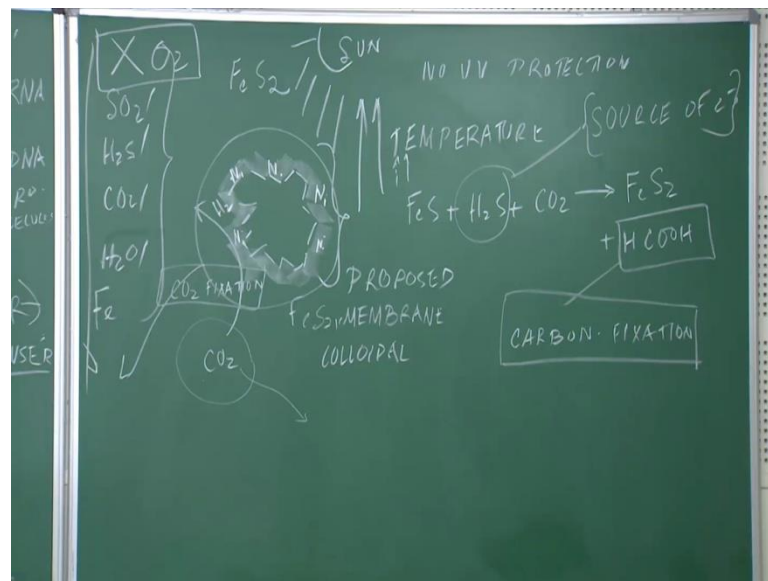
- According to the hydrothermal origin of life, FeS₂ might have evolved in the pre-archaeon era, in an extremely harsh, anoxic, sulfur rich environment, by the spontaneous reaction of FeS and H₂S
- $\text{FeS} + \text{H}_2\text{S (Aqueous)} \rightarrow \text{FeS}_2 + \text{H}_2$ (Delta G° = -41 kJ/mole) Eq 1
- The hydrogen evolved during the formation of FeS₂ is used to drive the CO₂ fixation reaction by a coupled reaction taking place across a proposed **semi-permeable iron-sulfur colloidal membrane** containing Ni as a catalyst
- $\text{CO}_2 \text{ (Aqueous)} + \text{H}_2 \rightarrow \text{HCOOH (Aqueous)}$ (Delta G° = +30 kJ/mole) Eq 2
- Adding Eq 1 + Eq 2:
 $\text{FeS} + \text{H}_2\text{S (Aqueous)} + \text{CO}_2 \text{ (Aqueous)} \rightarrow \text{FeS}_2 + \text{HCOOH (Aqueous)}$ (Delta G° = -11.7 kJ/mole)

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So, under those conditions possibly in the harsh anoxic sulfur rich environment by the spontaneous reaction of f e s, and h two s possibly it leads to reaction where we are having f e s two, and h two got evolved, and of course this reaction is thermodynamically feasible.

Because it has minus forty one kilo joule per mole, but the hydrogen evolved during the formation of FeS_2 is used to derive the carbon dioxide fixation reaction by coupled reaction taking place across a proposed semi-permeable iron sulfur colloidal membrane. So, coming back I highlighted this part to you the self assembled inorganic membrane, now what this inorganic membrane is doing out here or at least what is being proposed it is doing out there.

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So, imagine somewhere or other it is self assemble, and forming something called a you knows a FeS_2 membrane on these membrane, when the FeS_2 is getting formed. So, it has in a site, I am just putting in a site somewhere or other just imagining this kind of thing has found and.

In that process there is evolution of H_2 is H_2 the existing CO_2 , and this is environment which is filled with you know sulfur dioxide H_2S CO_2 of course, there was water iron likewise. So, very harsh environment a very high temperature, and no UV protection. So, there is enormous amount of UV which was reaching the substrate, then this what is really known how it has happened if at all it has happened CO_2 , and H_2 this is how CO_2 started getting fixed where exactly what you have seen in photosynthesis where CO_2 is getting fixed same thing was possibly happening in where CO_2 fixation reaction was taking place on top of the iron pyrite membrane.

coming back to the slide if you look at it the hydrogen evolved during the formation of FeS_2 is used to drive CO_2 fixation reaction by a coupled reaction taking place across a proposed semi-permeable iron sulfur colloidal membrane. So, this is that proposed iron sulfur colloidal membrane, and it is mainly that these membrane has lot of nickel these kind of ions which are present there which were catalyzing this reaction containing nickel as a catalyst if you see the slide you will see this. So, it was the series of nickel ions or may be few other ions which are you really do not know which one which all were present there. So, those ions which are present there if you look at the slide now containing nickel as a catalyst.

So, what essentially happen is the at $\text{CO}_2 + \text{H}_2$ you are getting first carbon fixed molecule HCOOH , but for that reaction ΔG was thirty kilo joule per mole. So, now, if you add these reaction one, and $2\text{FeS} + \text{H}_2\text{S} + \text{CO}_2$ you're getting. So, now, you have $\text{FeS} + \text{H}_2\text{S} + \text{CO}_2$ this is what is happening you're getting $\text{FeS}_2 + \text{HCOOH}$. So, this is your carbon fixation. So, this is how possibly again this is all possibly this is how possibly this evolution of the first membrane has happened as a matter of fact if you try to correlate this with the lipid bilayer membrane which is on this side the board if you look at them, then you realize all the lipid bilayer membranes have lot of iron sulfur clusters, and there are lot of iron sulfur proteins.

So, it has been argued by the proponent of these queries that possibly those iron sulfur clusters in the in those proteins has evolved from that proposed FeS_2 colloidal membrane what is true what has happened nobody can tell with certainty, but this is one of the possibilities, and next at the as we are looking, and mind it as I am repeatedly telling you this is the situation where there was no oxygen absolutely divide of oxygen, then arrow of evolution was moving in a totally different in one direction such a process is a sulfide as the major source of electrons. So, it was your H_2S which was the major source of electron now earth was cooling down.

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Arrow of Evolution & Evolution of Oxygen

- Such a process used sulfide as the major source of electrons. What exactly is the nature of the catalyst, catalyzing the formation of FeS₂ from FeS in the "iron-sulfur world" is not precisely clear. It is believed that during Achaean era, several primitive microbial life forms evolved using FeS₂ as the direct source of energy and even this day some of those microbes survived the test of changing time.
- As the earth was cooling down, the raw materials of nature like H₂S was getting depleted and this forces nature to search for newer abundant raw material to fix CO₂. Nature slowly evolved to use a more efficient work-station where H₂O can be used as the prime source of electrons to provide the necessary energy to drive the fixation of CO₂, thereby replacing the equivalent H₂S source.

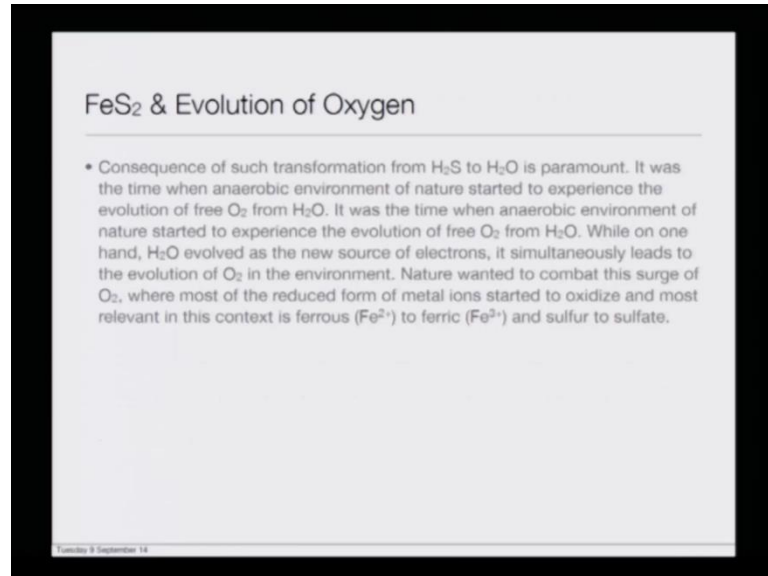
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So, this is the situation when this temperatures were now falling as time was passing by temperatures were falling down what exactly is the nature of catalyst catalyzing the formation of FeS₂ from FeS iron sulfur world is not precisely clear it is believed that during achaeon era several primitive microbial life forms evolved using FeS₂ as a direct source of energy, and even this day some of these microbes survived the test of changing time. So, what is important here to highlight is FeS₂ has been used as a source of energy by a series of microbes, and probably they have evolved in the pre-achaeon era or soon during that time, but as the earth was cooling down things were started changing the raw material like H₂S was getting depleted.

So, now we there is a depletion of this H₂S as we are evolving out there, and nature needed another molecule as a donor of electron, because it is our whole evolution if you look at it the evolution of molecules will be accepting, and donating electrons. So, who will be the next electron donor. So, the only other molecule which was present there in abundance was water, and now carbon dioxide fixation. So, forces the nature to search for newer abundant material to fix carbon dioxide nature slowly evolved to use more efficient work station, where H₂O can be used as a prime source of electron to provide necessary energy to drive the fixation of carbon dioxide thereby replacing H₂S now if you replace, and this way reaction H₂O.

So, what will be evolving is here you are sulfur was evolving, now what will be evolving will be oxygen.

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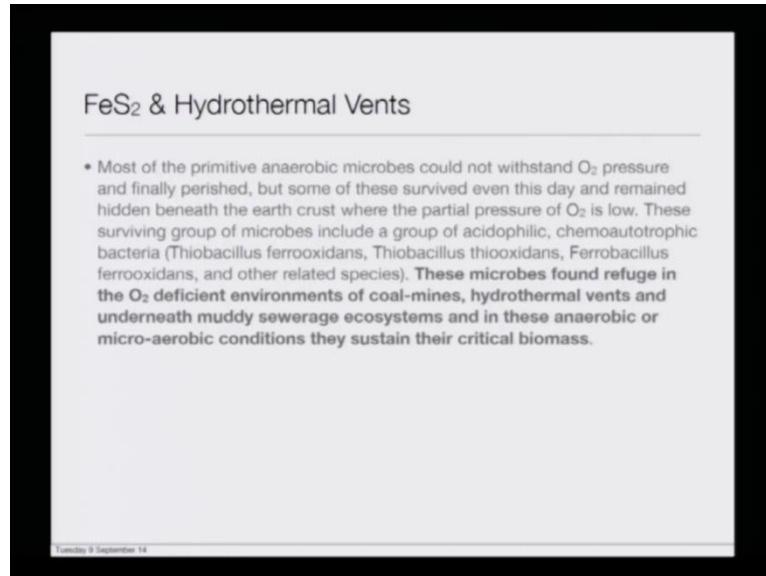


So, move on to the next slide f e s two, and the evolution of oxygen consequence of such transformation from hydrogen sulfide to water is paramount it was the time when anaerobic environment. So, this was all anaerobic environment of nature started to experience the evolution of free oxygen from water. So, now the situation from anaerobic is moving towards aerobic environment it was the time when anaerobic environment of the nature started to experience the evolution of free oxygen from water while on one hand water evolved as a new source of electron it simultaneously leads to the evolution of oxygen in the environment nature wanted to combat the surge of oxygen where most of the reduced form of metal ions started to oxidize most relevant.

In this context is most of the f e two plus, which were present which is present in iron disulfide they can f e three plus. So, they all gone oxidized, and that process giving away the electron, and the second thing happen is sulfur started forming sulfates. So, all the inorganic sulfurs going towards. So, this was the major transformation which was taking place, and slowly, and slowly as this reaction was progressing environment was there was a stip or there was a slow rise of oxygen in the environment. So, oxygen pressure was now increasing as this reaction was prolonging on the floor of earth most of the

primitive anaerobic microbes could not withstand the oxygen pressure, and finally, perished

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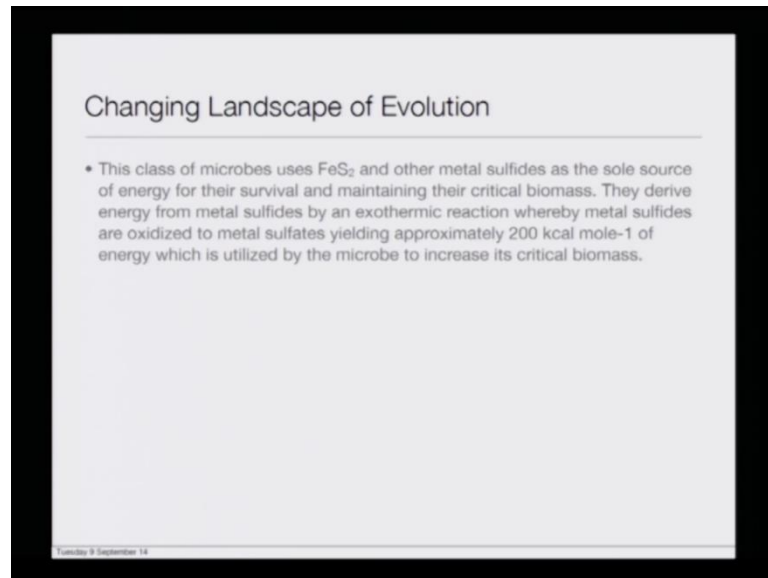


So, all those microbes which evolved in this pre-archean era or the archaean era started perishing, because they were not in a position to withstand the oxygen partial pressure, because they are not used to with appear they were all develop under this kind of situation oxygen pressure was totally allegiant to them, but the evolution of now oxygen taking the center stage into this, and all the iron are now getting oxidize, and sulfurs are getting oxidized it was a totally new world which was about to evolve, and what essentially happen most of the primitive anaerobic microbes could not withstand oxy[gen]- oxygen pressure, and finally, perished, but some of these survived even this day, and remain hidden the beneath the earth crust, where the partial pressure of oxygen is low these surviving group of microbes include a group of acidophilic chemoautotrophic bacteria thiobacillus ferrooxidans thiobacillus thiooxidans ferrobacillus ferrooxidans, and other related species.

These microbes found refuge in the oxygen deficient environment of coal mines hydrothermal vents, and that is the word what I was trying to tell you why it is called the hydrothermal hydrothermal origin of life, I was kind of try to mention you the iron sulfur ah theory is called as the hydrothermal origin of life, because these life forms now survive in the hydrothermal vents underneath the muddy sewerage ecosystem that is why

I told you if you walk by the street on there is a drain on the other side if you just go will under the depth tightly under the mud where this is lack of oxygen you will see iron sulfur or iron pyrite present out there, and there will be bacteria which will eat up on those iron pyrite bacteria coming to in these anaerobic, and micro aerobic conditions they sustain their critical biomass.

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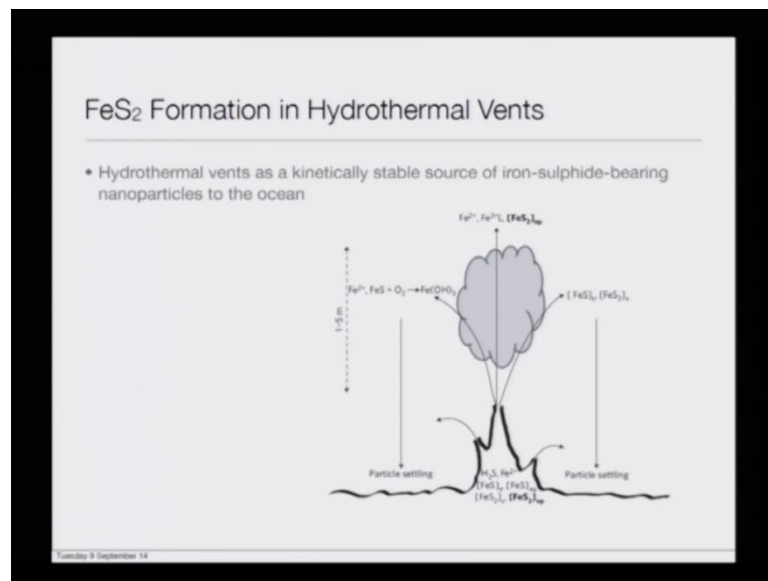


So, this is what we really know about the story of iron pyrite the molecule which is evolved as I was telling you a molecule which is evolved, and which is a very rich heritage at some I mean it is one of the most amazing molecules, and as I will closing in inching towards the end of this lecture you will realize what are the applications of it which has intimately involved in the evolution. Of course, if you are a supporter or if you are convinced with the iron sulfur theory of evolution, but the irrespective of that whether you like iron sulfur theory whether you are a proponent of nucleic like you know pre-biotic broke theory whatever whatever one thing cannot be taken away from the chemistry of it is iron sulfur iron pyrite is an very ancient molecule.

And it has absolutely amazing properties iron sulfur clusters are pretty much lubricators in the life forms all over the life forms iron sulfur cluster are very integral part of the lipid bilayer these pieces of information's cannot be taken away from it one more thing, which cannot be taken away from iron sulfur is its amazing potential what I was trying to tell you out here out here it has absolutely amazing potential to absorb sunlight just like

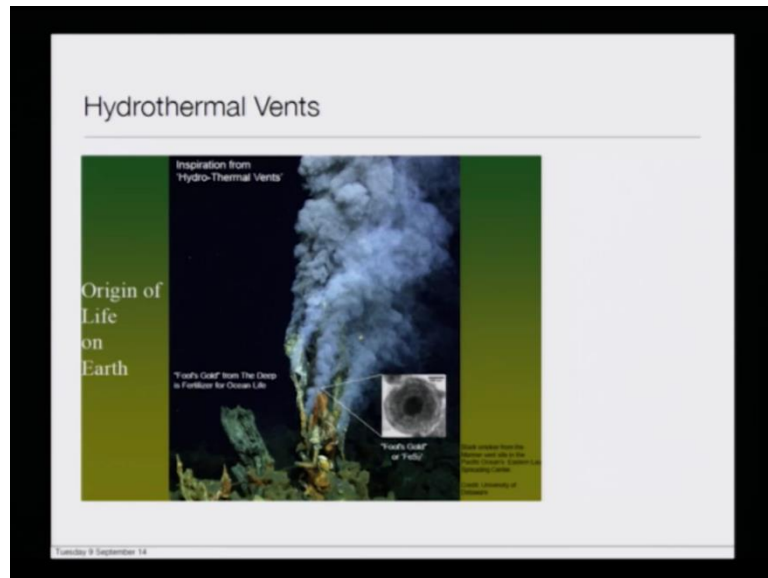
the chlorophyll have of course, not good as chlorophyll, but definitely is closed to that now coming back to the slides. So, the there is a changing landscape of evolution the class of microbes uses f e s two, and other metal sulfides has a sole source of energy for their survival and maintaining their critical biomass they derived energy from metal sulfides by an exothermic reaction, where by metal sulfides are oxidized to metal oxy sulfates yielding approximately two hundred kilo calorie per mole of energy which is utilized by microbes to increase their critical biomass.

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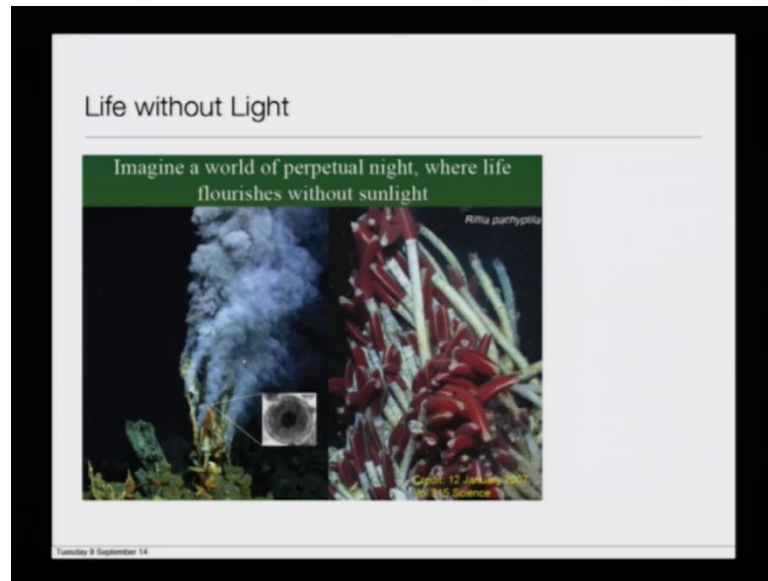
So, as the landscape was changing these microbes got lost into oblivion, but that where they are currently where f e s two is more prominent f e s two formation in hydrothermal vent. So, if you look on the floor of earth if this is the earth. So, if you looking at the floor of earth if you go down the sea pretty much at the base of it where this you know molten magma, and all those gases are coming out from the core of the earth it is out there you are having this hydrothermal vents if you look at this slide, and I will show the real picture of hydrothermal vents where there is kinetically stable source of iron sulfide bearing nano particles in the ocean.

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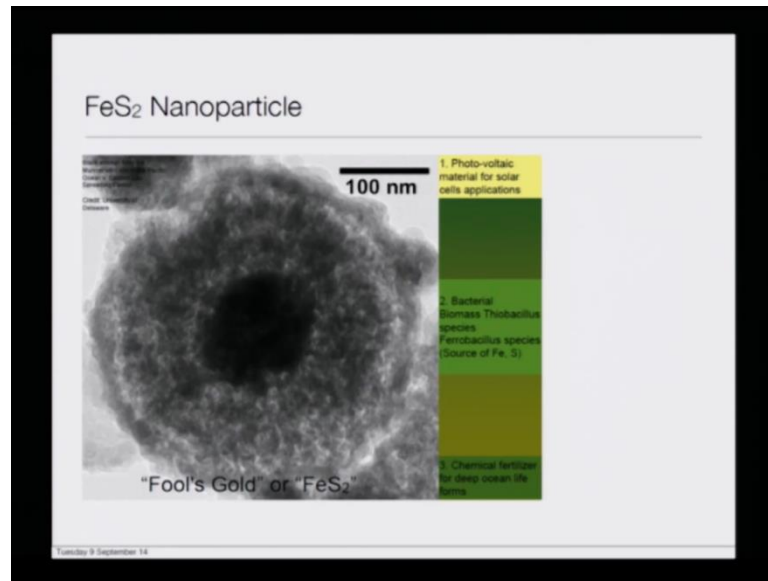
So, this is where a series of iron pyrite nano particle are getting de form continuously from, because earth's core is iron core. So, there is no depth of iron or the floor of earth, and this is the real picture of hydrothermal vent, and iron pyrite is also called fool's gold, and this is fertilizer this is considered as a fertilizer in the ocean which helps in you know helping the life form to survive deep inside the sea, where there is no light there is no oxygen. So, situation even more worst. So, now, there is no oxygen in the situation in these hydrothermal vents. So, it is pretty much similar situation like this, what you see here iron water $c o_{2} h_{2} s s o_{2}$, and there is no sunlight like you know sunlight cannot penetrates out there, and these are called black smokers from the merinal vent site or the pacific oceans.

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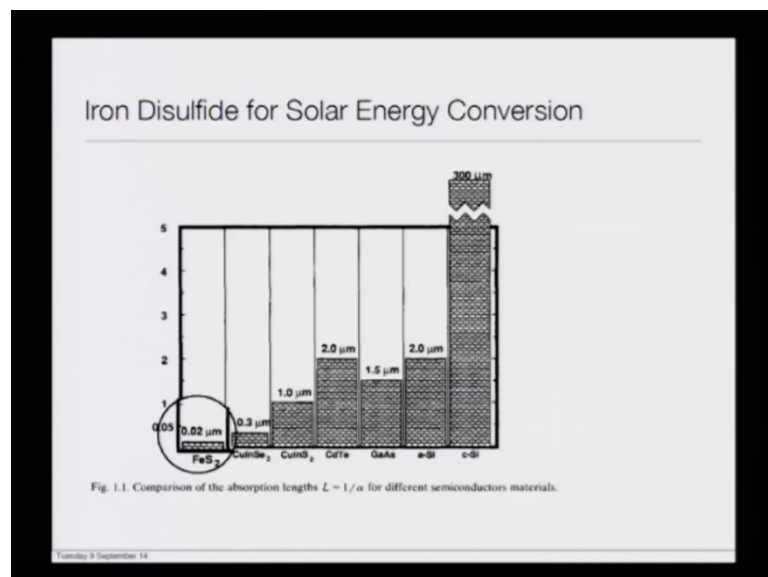
This is picture from the pacific ocean, and then set what you see is f e s two nano particle which is present there, and life without light imagine a world or perpetual night where life flourishes without sunlight, and these are the life pumps what you see no rectia accu are some of the life forms which has evolved deep inside the sea which utilizes all these inorganic molecules you know to derive energy for its survival. So, what essentially means at these molecules are there, because of the oxygen iomin they cannot survive I mean you they cannot remaining they gets oxidized, but once they found neat they need survive, and if you see this particle they look like this this is a typical f e s two particles this also called fool's gold, because it it act as a shiny you know gold like lustier.

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So, it is used for the photovoltaic material in solar cell application bacterial biomass, and it is used as a chemical fertilizer in the ocean life forms. Now if you look at the solar energy conversion ability of f e s two, this is a comparison of saying if we assume in this graph equal amount of say for example, you want to produce say x unit of energy x unit of conversion you wanted to see how much relative material you will be needing.

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So, if you look at f e s two compare it with copper indium s e, then if you compare it with c s i, which is crystalline silicon a s I is amorphous silicon gallium arsenide is g a a

s cadmium telluride is c d t e, if you compare all of them you will see comparatively for producing same amount of output using these kind of photovoltaic material.

You need minimum amount with iron pyrite this is its phenomenal ability to transform sunlight into electrical energy into photovoltaic energy, and this is the inspiration point for generation of scientist that in a era when we are really running out of the the petiole, and all other sources what will be other other alternative when sun is there your option is. So, there is lot of research is going on the on these iron sulfide, because it is lubricators it is it is not going to really you know it is non-toxic, and by this time must have one during that it has remaining integral part of our whole evolution. So, so coming back how they look like these are some of the crystals of iron pyrite a, if you look at them.

So, now here I will pause an actually, but before I close in I will leave a something for you guys to think over it why I kind of you know started this an ancient molecule with rich heritage it is indeed a very ancient molecule, and if you believe the iron sulfur theory of evolution, then possibly this has remain integral part of the evolution itself, and just like chlorophyll f e s two owls has ability to transform solar energy. So, could these molecule which are biologically benign, and they are not going to you know create pollution could these kind of molecules be the answer for tomorrows energy requirement, and that is why I took up a totally different molecule, and I am not getting to this solar energy conversion, and all those things in you know m, and p type all those things.

I will leave it I will give you certain references you can go through it, but to give you an idea why people have interest on molecule, and what is its genesis from the biological perspective, because we are talking about bioelectricity. So, this is the whole biological perspective biochemical or you know chemical perspective which ever call its whichever you left to call it is how f e s two a molecule, which is ancient molecule has such a rich heritage that you know this could be one of the s answer to our ever increasing demand for energy.

Thank you.