Biological Inorganic Chemistry
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Lecture 54
Sulfur and Selenium

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Concepts to be Covered

- Sulfur bearing proteins
- Different sulfur based donors for metal ion coordination
- Metalloenzymes having sulfur coordination
- Selenium in biological world
- Selenocysteine in animals

Hello, everybody so very good morning to all of you. So, we will be starting today on lecture 54. So, of these all these nonmetallic species what we are talking about so today we will be talking about sulfur as well as selenium. How these two elements can help us in understanding biology from their point of view? So, definitely we should know about the sulfur bearing proteins, we all know about the sulfur bearing amino acids.

So, different Salford based donors which are available we all know that for beautiful metal ion coordination like your pyridoxin and rubredoxins. Then definitely, all these metalloenzymes have very defined sulfur coordinations from the different points that means preserving the coordination number. Then other part of this class basically is devoted to selenium in the biological world, and corresponding system analog of selenium is selenocysteine, how it is present in different animals including us.

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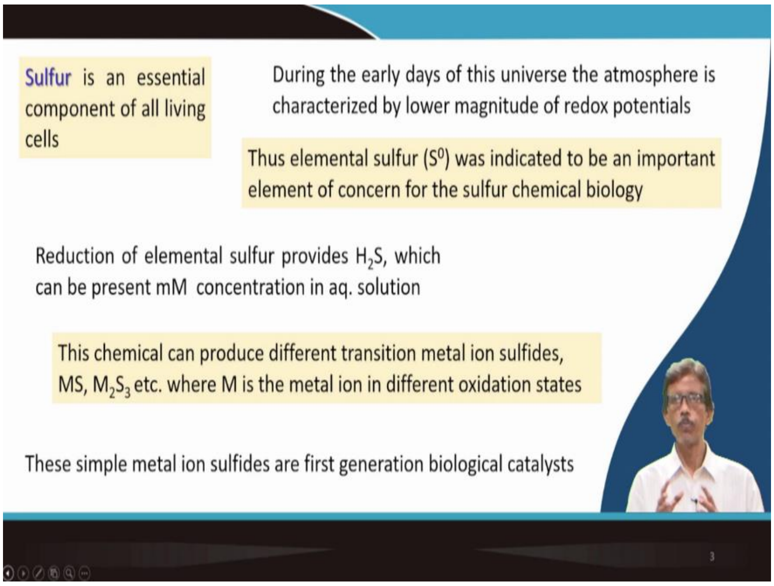

Sulfur is an essential component of all living cells

During the early days of this universe the atmosphere is characterized by lower magnitude of redox potentials

Thus elemental sulfur (S^0) was indicated to be an important element of concern for the sulfur chemical biology

Reduction of elemental sulfur provides H_2S, which can be present mM concentration in aq. solution

This chemical can produce different transition metal ion sulfides, MS, M_2S_3 etc. where M is the metal ion in different oxidation states

These simple metal ion sulfides are first generation biological catalysts

So, going back to the basic understanding about the sulfur, probably from your school days you are learning your sulfur. There are atomic number, atomic weight and its corresponding the activity and other patterns. But for the living cells, we also know that these are the essential component. So, during the early days of this universe, when the atmosphere is characterized by lower magnitude of redox potential, that means, we do not have much amount of oxygen, photosynthesis was also not known that time what was happening at that particular time.

If you have some mineral deposit or the old deposit of typical elemental sulfur, yellow sulfur the sulfur powders those were indicated for element of concert for the sulfur chemical biology. So, how we can have that? That sulfur, then sulfur bearing different anions and even the elemental sulfur, how it can go for producing something very interesting molecules.

So, if your environment is of lower magnitude of E0 value, then the reduction of the elemental sulfur, which can be available to us, so S0 we can produce S2 minus which is after protonation gives you H2S. So, how much we can have so it is only in millimolar concentration level in solution because the solubility is very less, otherwise you will have the deposition or the crystallization.

So, this chemical basically the sulfur S0 can produce different transient metal ion sulfides. All we know that if you go to excavate the earth crust with the help of a metallurgist or geologist will get some many metal ion sulfides. And in your school days or college days, what do we know that the different metal ions the cationic species can be identified nicely by knowing the color and the appearance of the different sulfides, the copper sulfide, the nickel sulfide, so, the group saver is not able to handled also, depending upon the different sulfides.

So, if we have the metal ions, so, if we have the metal ion in bivariant and the trivalent state, we can have MS the typical sulfide or M2S3 depending upon the two different oxidation states which are plus 2, as well as plus 3. Then, if the system is available, if the biological world is smart enough, whether they can use this particular assembly or aggregate. When you talk about the iron sulfur protein, what you write iron, FE-S or FE oblique S, so these are our ns helper proteins. So, these are not typical ferrous or ferric sulfides, but these are iron sulfur proteins. And we know that two different types of sulfur we can have in all these electron transport proteins.

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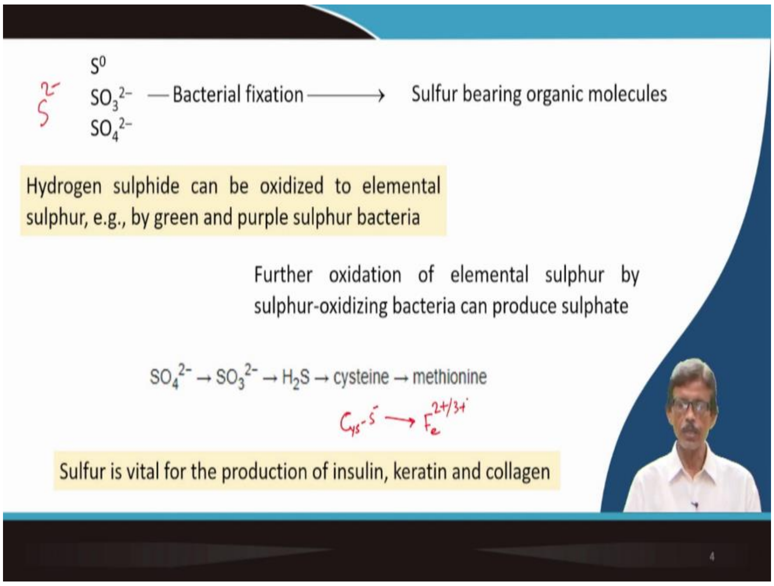

S^{2-}

S^0

SO_3^{2-} — Bacterial fixation ⟶ Sulfur bearing organic molecules

SO_4^{2-}

Hydrogen sulphide can be oxidized to elemental sulphur, e.g., by green and purple sulphur bacteria

Further oxidation of elemental sulphur by sulphur-oxidizing bacteria can produce sulphate

$SO_4^{2-} \rightarrow SO_3^{2-} \rightarrow H_2S \rightarrow$ cysteine $\rightarrow$ methionine

$Cys\text{-}S^- \rightarrow Fe^{2+/3+}$

Sulfur is vital for the production of insulin, keratin and collagen

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So, if we start from the reduced form, that means, the is S0 form, and the other oxidized form the sulfide and the sulfate, what we can have? That bacterias are very smart enough for us for doing these chemical reactions. So, bacteria can also come into the play, giving rise to the fixation of sulfur. We know that like nitrogen cycle or the oxygen cycle or the hydrogen cycle, sulfur can have therefore the cycle, which can cycle between starting from S0 and ending again with S0 by giving many important species like your sulfite and sulfate.

So, sulfur ion bearing organic molecules you can have. What are those organic molecules? The simplest possible known organic molecules, which will be useful for our discussion our understanding is your amino acids. So, what are those amino acids? Where you have the sulfur group present. So, those, whether the bacteria can produce those things, and how our body can also produce those minuses because, when those amino acids are coupled together forming your peptides, dipeptides, tripeptides, tetrapeptides and polypeptides and finally, to the proteins. So, proteins will have several those sulfur groups appended on the chain on the seat or on the helix.

Then one most important reagent, the laboratory reagent we use from our, again, from our school days that H2S we use cape separators for the production of H2S how we produce that also you know from the ferrous sulfide sticks, and sulfuric acid. So, if you had two chambers in the Kipp's separators, one you filled with acid and another you filled with the solid ferrous sulfide and continuous supply of H2S, as you open the stopcock like your water tap, if you open it up, you will be able to get H2S, but nowadays for the maintenance for not knowing and not using these things, we are slowly discarding that very simple equipment.

I call it the equipment basically, it is a very useful equipment when people introduce first time, as and when required supply of H2S can be available to us. Now, if we go for the biological world, we find that this similar smell is a rotten egg smell we call, the smell of the H2S we can also get from the rotten egg, that means, egg is a biological stuff, so that biological material through degradation can have something where it can produce the H2S to you.

So, when H2S we have it can be oxidized again back to your elemental sulfur, which can be done by some bacteria again. So, your H2S can be substrate for your green or purple sulfur bacteria and those bacteria can oxidize your H2S that means the reduced form is not collected over at the top, so it is not there. So, if you can have, so that particular thing that if you can have H2 minus also.

So, what we can have? The reduction as well as oxidation for all these things can happen together. So, only thing that what is that biological stuff you are using so bacteria what you are using. So, sulfur oxidizing bacteria can have, and we tackle with that of your S0. So, S0, we try to oxidize it and if you say produce some sulfate via sulfide, you can fix it. But why, how and when we can have that?

So, if the fully oxidized form of sulfate is available to us, we know is a very simple anion like sodium sulfate, potassium sulfate, we are using for many years. So, that sulfate one-step reduction to sulfide then finally, it can definitely go through S0 and then S2 minus. So, these are the most common oxidation states of sulfide from S2 minus to S plus 6. Then whether these species can be available to us for giving the very useful amino acid system or the methionine, methionine has S methyl function only. Because the cysteine residues are available to us and we can use those cysteine residues to get not only the introduction or getting that particular very useful molecules like insulin, keratin and collagen.

So, the introduction of the sulfur in very different forms is important. But if we see that the cystine is available, so what do we know that the cystine S minus, cysteine S minus is available, it is a very good ligand, and we all know that it can bind to FE2 plus or FE3 plus in your rubredoxins or Ferredoxin system. So, that is why our body or our system should be well matched to produce these system molecules from say sulfur 0 or the sulfate such that it can further be utilized for your rubredoxins or ferredoxin molecule.

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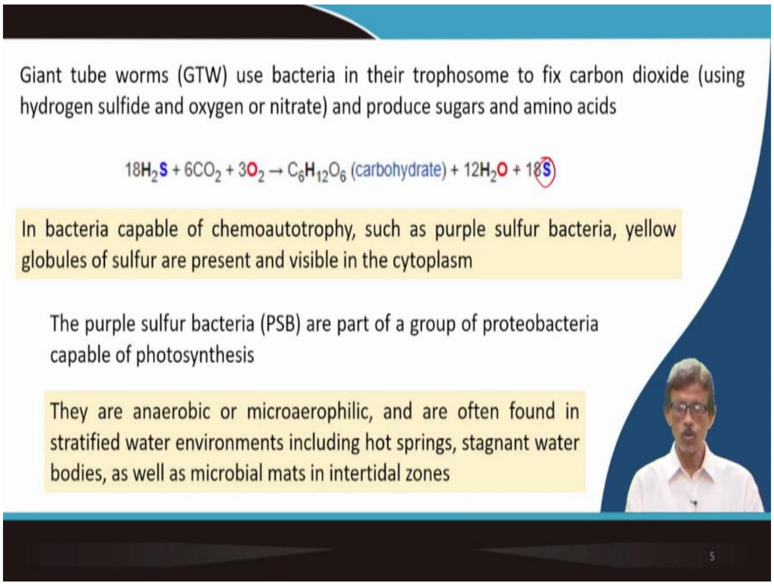

Giant tube worms (GTW) use bacteria in their trophosome to fix carbon dioxide (using hydrogen sulfide and oxygen or nitrate) and produce sugars and amino acids

$$18H_2S + 6CO_2 + 3O_2 \rightarrow C_6H_{12}O_6 \text{ (carbohydrate)} + 12H_2O + 18S$$

In bacteria capable of chemoautotrophy, such as purple sulfur bacteria, yellow globules of sulfur are present and visible in the cytoplasm

The purple sulfur bacteria (PSB) are part of a group of proteobacteria capable of photosynthesis

They are anaerobic or microaerophilic, and are often found in stratified water environments including hot springs, stagnant water bodies, as well as microbial mats in intertidal zones

So likewise, not only bacteria, but also worms. Giant tube worms, GTW also use some bacteria in their trophosome to fix the carbon is not chromosome is chromosome, carbon dioxide using hydrogen sulfide and oxygen or nitrate and produce sugars and amino acids. So, it is a very beautiful chemical conversion can take place and can happen by bacteria only such that it can produce sugar and amine acid.

So, what should be the reaction? The chemical reaction, what we can think of you take H2S. What we are taking is a very simple thing that we are not taking H2O like water. When you use H2O for our photosynthesis, we know we will be able to produce dioxygen molecule that is why we are surviving also. We take oxygen, plants are producing that oxygen for us through photosynthesis.

But here if you have H2S and if you go for similar type of reaction, you see, you will be able to produce carbohydrate or carbohydrate-based some glucose molecules then some water molecules will be freed because no water molecules are there on the left hand side, but along with that of your 18 sulfur molecules you will able to produce, so that is important. That elemental sulfur you can also produce by this process. Then when the bacteria is available and chemoautotrophs, the bacteria can do the process which is known as chemoautotrophy, such as purple sulfur bacteria, yellow globules of sulfur are formed and which are visible on the cytoplasm of those bacteria or the bacteria residing on some plants or somewhere.

So, very beautiful powders of sulfur can be seen because they are producing continuously the elemental sulfur as these 18S. This S they are producing so, this is S0, elemental sulfur. So, PSB is abbreviated as your corresponding bacteria or part of the group of bacteria which are proteobacteria capable of doing photosynthesis type of activity like cyanobacteria.

But they are an aerobic in nature they do not require oxygen microaerophilic then they are often found in stratified water environment because this contaminated water from the hot spring or from the industry or some stagnant water also we call is the water and water bodies as well as microbial mats in intertidal zones.

The tide we know the ocean tides or the sea tides we have. So, you have certain tidal intertidal zones where you can have the corresponding these bacteria are there so, these are basically of marine origin. So, that is why the marine chemistry is also so rich and the deposition can take place below marine or the marine seashore or the ocean seashore.

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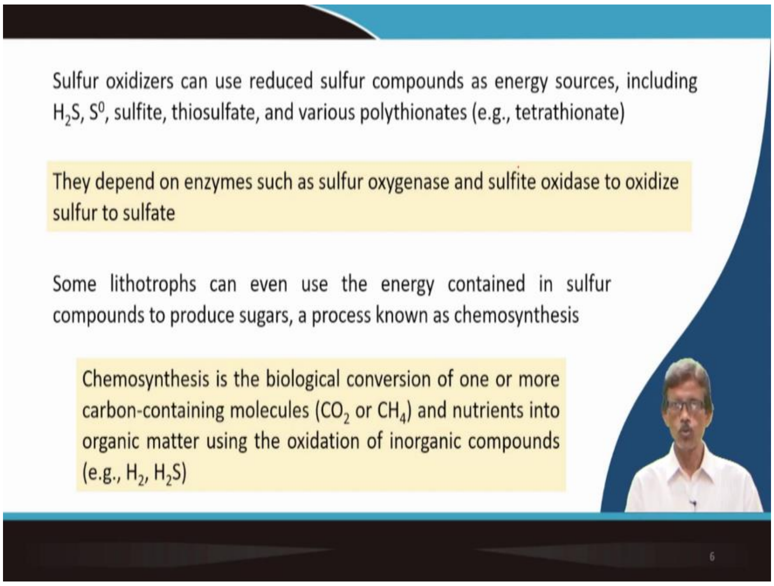

Sulfur oxidizers can use reduced sulfur compounds as energy sources, including H_2S, S^0, sulfite, thiosulfate, and various polythionates (e.g., tetrathionate)

They depend on enzymes such as sulfur oxygenase and sulfite oxidase to oxidize sulfur to sulfate

Some lithotrophs can even use the energy contained in sulfur compounds to produce sugars, a process known as chemosynthesis

Chemosynthesis is the biological conversion of one or more carbon-containing molecules (CO_2 or CH_4) and nutrients into organic matter using the oxidation of inorganic compounds (e.g., H_2, H_2S)

So, when you have the oxidizing agent or the oxidizers can use all these reduced form, not the sulfide, not the corresponding sulfate, but it can use H2S, that means, H2 minus H0 sulfide because you can go further oxidation or thiosulfate H2O32 minus, and various other polythionates tiredness that means tetrathionate. So, these are all the reduced form.

So, if you have the reduced form in your hand you can go for oxidation, that means, sulfur oxidizer there, oxidation can take place on the sulfur atom, if it is sulfur 0. So, some enzymes can come, so sulfur oxygenase. So, is not oxidation only is oxygenation reaction that means you can put some oxygen or you can have some new sulfur oxygen bonds, and sulfite oxidase to oxidize sulfur to sulfate. Finally, we find that is to the sulfate.

Similarly, some lithotrophs can even use the energy because you must have not only the chemical reaction, but we all know the free energy change which is easily accessible energy for the transformation or for the conversion or for the making of new molecules. So, we will be making new sulfur compounds, which can ultimately produce sugars a process known as chemosynthesis. So, try to know by definition only what is chemosynthesis.

So, we will be producing new chemicals or new compounds through some synthetic process but is the living synthesis. What is that? Is a biological conversion of one or more carbon containing molecules. So, if you have C1 system that means C1 one carbon containing molecule is carbon dioxide or methane and any other nutrients more than one or single carbon containing molecule, organic matter we can produce using oxidation of inorganic compounds that means, oxidation of H2 we know hydrogenases are there or the oxidation of H2S.

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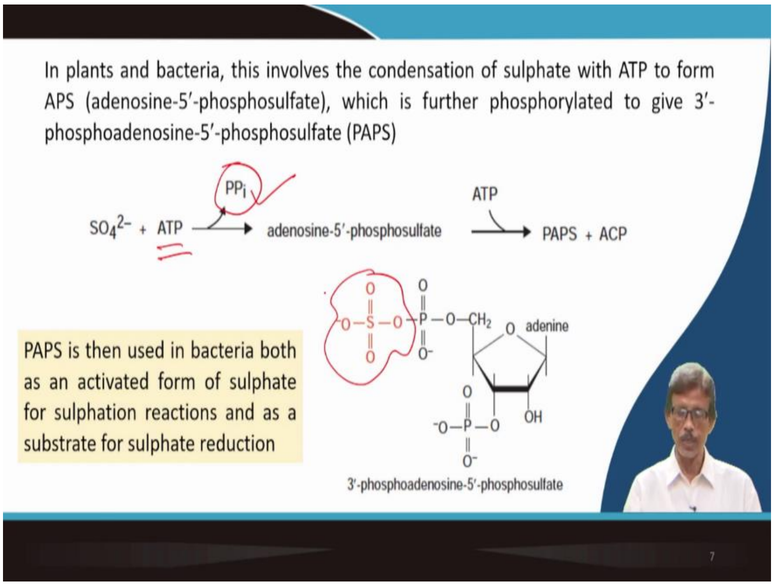

In plants and bacteria, this involves the condensation of sulphate with ATP to form APS (adenosine-5′-phosphosulfate), which is further phosphorylated to give 3′-phosphoadenosine-5′-phosphosulfate (PAPS)

SO_4^{2-} + ATP $\xrightarrow{PP_i}$ adenosine-5′-phosphosulfate $\xrightarrow{ATP}$ PAPS + ACP

PAPS is then used in bacteria both as an activated form of sulphate for sulphation reactions and as a substrate for sulphate reduction

So, many useful molecules we can produce. So, what are those molecules basically? So, we go further, let us think or talk about the plants also. So, in case of plants also the condensation of sulfate like phosphate, whether these two are not similar is that you will have only the phosphate chains like the triphosphate chain like in ATP to AMP molecules, but sometime it can so happen that sulfate can give rise to a similar reactivity pattern that means it can attach to the phosphate end of the ADP or AMP molecule.

So, when it is attaching sulfate with ATP to form the APS adenosine 5 prime phosphorsulfate, which can further be phosphorylated to give 3 prime phosphoadenosine 5 prime phosphatesulfate. Do not worry about the big name and all these things because you will already know about the ATP molecules ADP molecules and AMP molecule. So, now instead of phosphate we have seen also, we have studied in detail about the phosphate chemistry or the phosphorus chemical biology, how the different phosphate groups can be attached.

Now, instead of phosphate if you can have the sulfate only, so that is the basic idea of knowing this particular thing. So, you take that ATP molecule that mean triphosphate you are taking a biological triphosphate you are using. So, the bacteria or the plant can use that thing also and being the sulfate and try to see some reaction, what is happening then, the inorganic diphosphate an ion is living PPI.

PI is the mono phosphate, inorganic monophosphate PPI is your inorganic diphosphate. So, out of these triphosphate system this biological triphosphate a diphosphate is moving out and sulfur is entering. What is the product therefore? So, you will get a phosphorsulfate species a organic or nucleobase dependent or adenosine-based phosphosulfate thing, then that can further be phosphorylated.

So, how that can also be phosphorylated such that you get a molecule known as PAPS and ACP. What are these? So, PAPS, PAPS, so, PAPS is this particular molecule. So, we have taken out, basically you are having three phosphate links so, one, two of them is going out like this then one sulfate is entering and sulfate is entering here.

Then if you go for this particular reaction with another ATP molecule, so, you can phosphorylate further, so that basically gives you that particular reaction, that means, corresponding one phosphoadenosine 5 prime phosphate sulfate PAPS is their particular molecule, so this ultimately what you are getting is your PAPS molecule.

So, you can have some similarity in terms of the anion the inorganic anion or nonmetallic anion what we are talking about having some role in the biological world. So, once it is formed the bacteria will come now can activate the activated form of sulfate for sulfation reaction because it is a very good reagent for sulfate transfer reaction. Like the phosphorylation reaction we have seen, you can transfer the phosphate group to some organic molecules, some alcohol, some sugar. Similarly, this particular molecule can be used for sulfation reaction, and you see, you transfer this particular sulfate group which is red in color to some organic molecule.

So, you can go for that reaction, as a substrate for sulfate reduction. So, that can also be substrate for sulfate reduction because you can tackle the sulfate and you can transfer that sulfate to other organic molecule. So, it is initially reduced to sulfide in a reaction involving thioredoxin.

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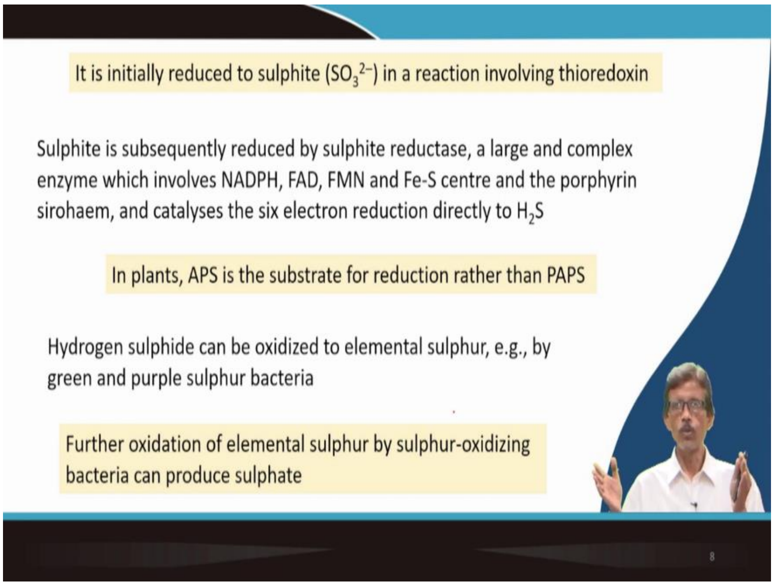

It is initially reduced to sulphite (SO_3^{2-}) in a reaction involving thioredoxin

Sulphite is subsequently reduced by sulphite reductase, a large and complex enzyme which involves NADPH, FAD, FMN and Fe-S centre and the porphyrin sirohaem, and catalyses the six electron reduction directly to H_2S

In plants, APS is the substrate for reduction rather than PAPS

Hydrogen sulphide can be oxidized to elemental sulphur, e.g., by green and purple sulphur bacteria

Further oxidation of elemental sulphur by sulphur-oxidizing bacteria can produce sulphate

So, now will being another molecule which is thioredoxin. So, that thioredoxin if it is coming and you are having sulfate and we are talking about attachment of sulfate to your ATP molecule or in some other way you can go for the phosphate in some other parts also for your ATP molecule. So, is adenine sugar and the triphosphate so it is ATP molecule, but you can go for further phosphorylated form of phosphoadenosine, phosphor sulfate. So, you are going for some other part of phosphate, so may have, you can think of in this particular point that you can have some extra sulfate molecule attached to it, or you can have the extra phosphate.

So, the molecule having some burden of sulfate or burden of phosphate. So, if we can utilize this molecule nicely the PAPS can be utilized for this corresponding sulfation reaction, as well as phosphorylation reaction. And when this sulfur is transferred, and we can further reduce their sulfate to sulfide because the sulfide is also a very good reagent. Nonmetallic reagent for many other type of reaction, but we bring now other enzyme or molecule for that particular purpose involving thioredoxin.

So, this sulfide is subsequently reduced to sulfide reductase. So, sulfite reductase can further reduce this sulfide in large and a complex enzyme. We are not talking all these things, but what are the systems involved over there from NADPH to iron sulfur ferredoxin or rubredoxins molecule is available or for porphyrin sirohaem is there, so another porphyrin based system is also available, and catalyzed is a 6 electron reduction directly to H2S.

So, you have the sulfide, SO32 minus having sulfide in the oxidation state of 4 plus that will be immediately reduced to H2 minor, so you will have 6 electron transfer reaction for the production of not elemental sulfur that we are not producing S0, but we are producing S2 minus. Then in plants this APS is the substrate for reduction rather than PAPS. So, this APS basically if we can have and APS is basically in the different plants.

So, another molecule you can have for this corresponding reduction reaction, unlike your PAPS molecule or PAPS molecule. Then once it is produced is going through for that particular reduction process, but not we are able to trap that S0 or the elemental sulfur, but can be oxidized by purple sulfur bacteria. So, because for all these systems what bacteria is working, what enzyme is working, you know the substrate E is coming to trap the S and you are producing P. So, as most of the cases these are very simple step reaction, but we no need to know the corresponding catalytic cycle if there are different steps for proton transfer, for electron transfer and for any other SIP type of 1 to SIP type of thing can happen.

So, then this oxidation, so reduction oxidation, all these things are going together. As we have seen also in case of your iron sulfur proteins, because these are to and fro movements. So, whenever you have the electron demand the system, that iron sulfur proteins are getting oxidized, but when you require to port electron it will be reduced, so this is a to and for reaction. So, if we go for this use of these H2S so, further oxidation of the elemental sulfur S2 minus two S0, then we bring the sulfur oxidizing bacteria which can produce finally again back to sulfate. So, this is the window basically for the different oxidation states of sulfur S2 minus to S plus 6 in sulfate.

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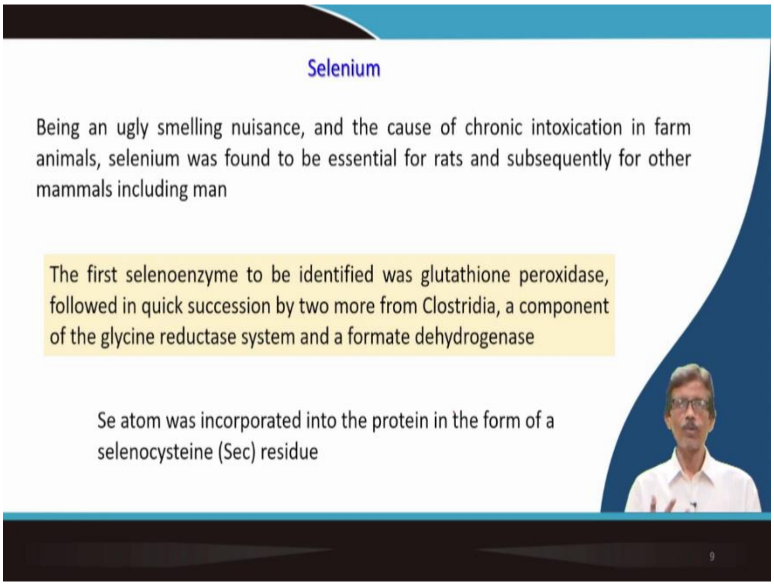

Selenium

Being an ugly smelling nuisance, and the cause of chronic intoxication in farm animals, selenium was found to be essential for rats and subsequently for other mammals including man

The first selenoenzyme to be identified was glutathione peroxidase, followed in quick succession by two more from Clostridia, a component of the glycine reductase system and a formate dehydrogenase

Se atom was incorporated into the protein in the form of a selenocysteine (Sec) residue

Now, we slowly see, a little bit about the corresponding selenium thing. So, which is very much similar to that of our sulfur. So, sulfur, we are having, we have seen that we can have the amino acids, we can have the corresponding iron sulfur proteins and many things. But what about selenium? It is a newest member in all this biological world, is a newest member in the amino acid family also.

So, we should know about element wise. From the periodic table also you see how we can compare sulfur, selenium and tellurium also. So, side by side how sulfur and the Selenium property and all the basic property for these because we are having something where we are just simply instead of capital S as the elemental sulfur you put one E only. It is not like that you are having a difference in the elemental composition from sulfur to selenium.

So, when people identified the composition of the elemental selenium its smell is very bad. And that particular point is ugly smelling nuisance people call it, and cause chronic intoxication of farm animals like the poultry animals like the chicken, hen and all other. So, the farm animals are suffering so there will be toxication or intoxication by this particular element where you can have the source of selenium, as the corresponding ore or mineral.

And if some bacteria is available now, it is clear to us to everybody also that the bacteria can do some marvel. Bacteria can produce something in the elemental form, bacteria can produce the sulfur in the S0 state, the sulfur powder it can produce. Similarly, if the bacteria is available, which can be active on the substrate material, which is your mineral to produce the free or SE0 that means elemental selenium.

But finally, we have seen that is not only very bad in terms of its odder, in terms of its toxicity, but also it can be very much useful for rats and subsequently for other mammals, animals including us. So, what is that enzyme? If we think that selenium is a very important component for our survival for our life process, so we must have some selenoenzyme.

So, if we consider, the statement is given to you is reported to you that okay we know say selenoenzyme giant. So, definitely we must have selenium bearing protein, polypeptide or selenium bearing amino acid. So, where it has been identified? So, selenoenzyme are there for the function of glutathione peroxidase.

Again, handling of peroxidase molecule that means peroxidase activity, so we have to reduce the corresponding reactive oxygen species level in our level in our body, so we know that peroxide concentration can be diminished can be reduced by the catalyst activity and peroxidase activity.

So, similarly, it is glutathione based, glutathione is a very useful, very simple tripeptide molecule and that tripeptide molecule can be very useful in other purpose also that it can that corresponding peroxidase activity. So, two more clostridia, we can have followed by a quick succession by two more clostridia a component of glycine reductase.

So, one glycine reductase you must have which is there and which is the glutathione and peroxidase type of activity we can find due to the selenoenzyme, and another is your format dehydrogenase. So, these are by name only. We are not going to study all these things, but only thing you know that where we can find this Selenium. So, it can be incorporated via that amino acid to this protein molecule you get that Sec. So, cysteine we know CYS we abbreviate but it is Sec is a selenocysteine residue. So, amine acid is abbreviated also in that way.

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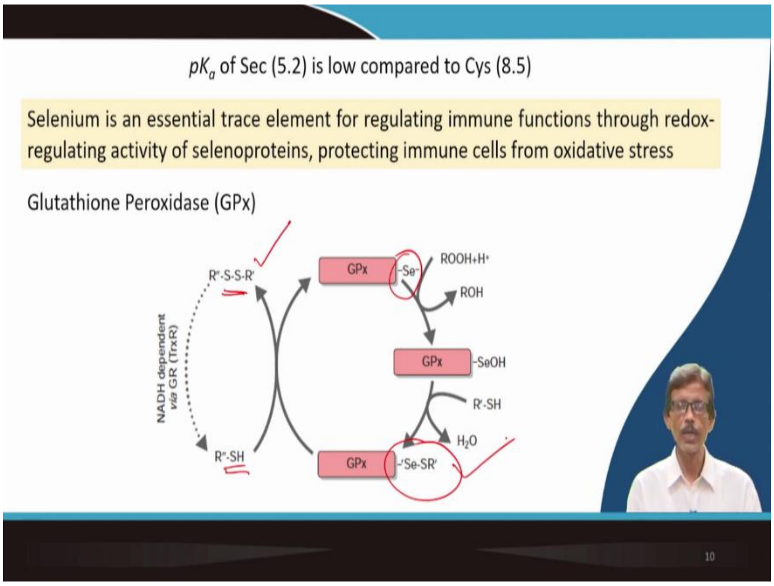

pK_a of Sec (5.2) is low compared to Cys (8.5)

Selenium is an essential trace element for regulating immune functions through redox-regulating activity of selenoproteins, protecting immune cells from oxidative stress

Glutathione Peroxidase (GPx)

So, the selenocysteine has a PK value is lower of 5.2 compared to your cysteine, which is 8.5. So, definitely the property wise everything will be different. It is a tress essential element to us regulating the immune function which is very important. Through redox regulating activity that means it can reduce the ROS concentration in our body and protecting our immune cells also for oxidative stress because we slowly we are oxidizing with time.

So, what is that glutathione peroxidase? Only the basic block diagram we will see the catalytic cycle we will see how the glutathione peroxidase can work. No detail, nothing do not worry for that. So, this is the thing, that GPx is there, and if this GPx is cycling between these forms basically and one is the oxidized form and another is the reduced form and we can have NH-dependent other GR residues so thyroxin reductase we will find.

And what is happening therefore, that if you have the thiol residue on one part or the protein part we will ending with the disulfide bond, so disulfide bond formation is important. And selenium can be there for your, this, glutathione peroxide unit that is the corresponding active side. Instead of S miners you can have the Se minus thing, and which can, again it can form a disulfide bond like this, this disulfide bond and silly no sulfide bond is important for all these activities. Sometimes we form the selenol, selenol can react with thiol, so selenol, thiol all these things are involved.

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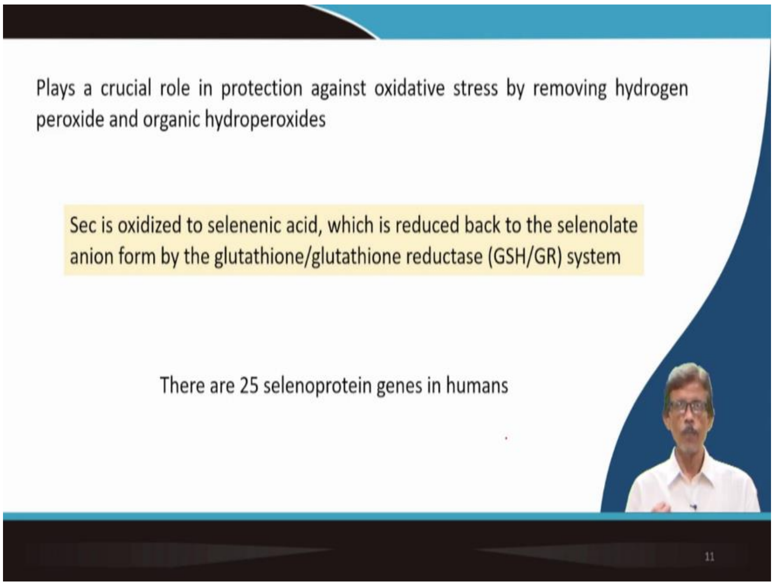

Plays a crucial role in protection against oxidative stress by removing hydrogen peroxide and organic hydroperoxides

Sec is oxidized to selenenic acid, which is reduced back to the selenolate anion form by the glutathione/glutathione reductase (GSH/GR) system

There are 25 selenoprotein genes in humans

So, that is why along with all sulfur bearing important molecules selenium can take part in the biological world because it can be incorporated in the corresponding amino acid. So, that is why it is very useful for our protection against oxidative stress, removing hydrogen peroxide and organic hydroperoxides.

It is oxidized to selenenic acid and the corresponding selenolate that means corresponding alcohol function then glutathione and glutathione reductase. There are altogether 25 selenoprotine genes in our body also humans’ gene are there. So, once you know the protein, know the amine acid you should also be able to identify and that has been identified that you can have so many numbers of genes.

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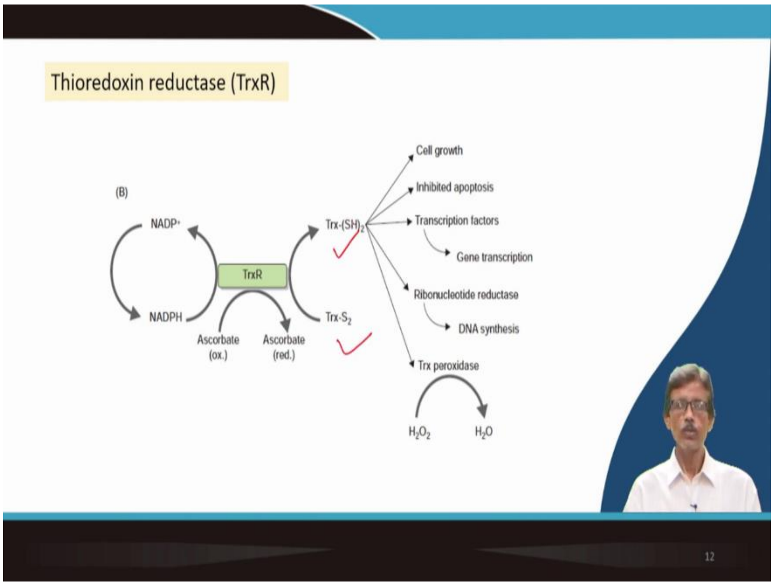

Thioredoxin reductase (TrxR)

Then lastly, we will see what is thioredoxin reductase because it will be correlated to our next class where we will talk about the corresponding chloride or iodide in the biology. So, how this is there? So, you can have the corresponding Trx that means the thioredoxin, thioredoxin and thioredoxin reductase. It can also superoxidase activity by degrading H2O to water. So, it can also settle between these two forms that means the reduced form and the oxidized form, and in the oxidized form you have the disulfide linkage which we call as the S2 and the reduced forms that SH.

Where we require? We require this for cell growth, inhibited apoptosis, transcription factor gene transcription, ribonucleotide reductase reaction, DNA synthesis and finally the Trs peroxidase activity. So, not only knowing the Trs peroxidase activity, but we should also know about the different types of activities, what thioredoxin reductase can help us in doing all these this reaction, so we will know about when we talk about the corresponding things in all these enzymes.

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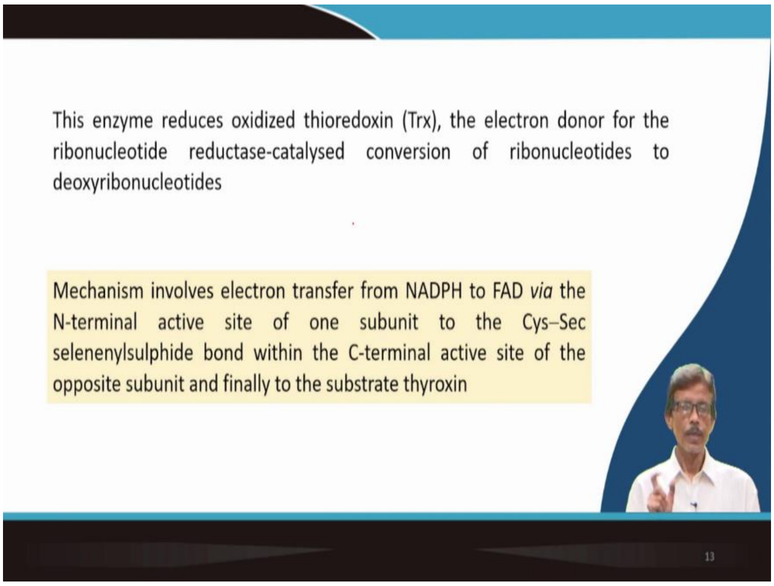

This enzyme reduces oxidized thioredoxin (Trx), the electron donor for the ribonucleotide reductase-catalysed conversion of ribonucleotides to deoxyribonucleotides

Mechanism involves electron transfer from NADPH to FAD *via* the N-terminal active site of one subunit to the Cys–Sec selenenylsulphide bond within the C-terminal active site of the opposite subunit and finally to the substrate thyroxin

So, thyroxin is the enzyme reduces the oxidized form of it, and electron donor for the ribonucleotide reductase that just now, we have seen, to give you the corresponding deoxyribonucleotide. So, it is another route basically, ribonucleotide reductase as always we know for the DNA synthesis. So, we will have the electron transfer involving NADPH or FAD to FAD also because you have a different E0 values for these two molecules. Then the link between Cys and Sec, that means, selenenylsulphide bond SS bond instead of SS bond you have Se bond. And that is useful for all these reactivities.

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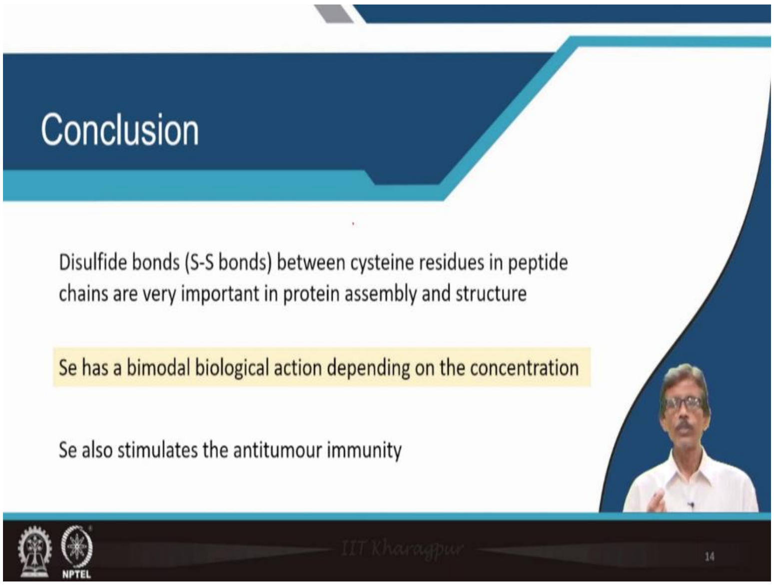
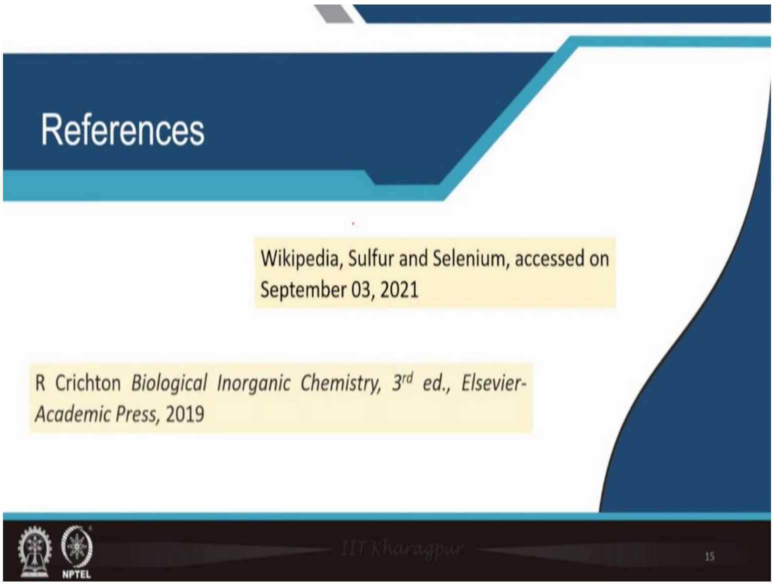


Conclusion

Disulfide bonds (S-S bonds) between cysteine residues in peptide chains are very important in protein assembly and structure

Se has a bimodal biological action depending on the concentration

Se also stimulates the antitumour immunity



References

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So, like the disulfide bond the S-S bond formation within the cystine reduce, we can modify the structure of the peptide chain and many such disulfide bonds are important for the assembly process of the protein giving a particular type of structure. Selenium can function as a bimodal two types, the bimodal role, biological action depending on the concentrations at lower concentration. It can show one type of reaction at higher concentration and so another type of reaction that is called bimodal.

It also finally is a new finding. People are working right now about whether it can show something or it can stimulate the anti-tumor immunity of the human body. So, references starting from your selenium page to then before that you can have the sulfur page for Wikipedia and the book have Crichton. Thank you very much, for your kind attention.