Environmental Chemistry and Microbiology
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Module - 11
Lecture - 57
Metabolic Diversity - II

Welcome everyone to lecture number 57 of module 11. This is the second part of Metabolic Diversity.

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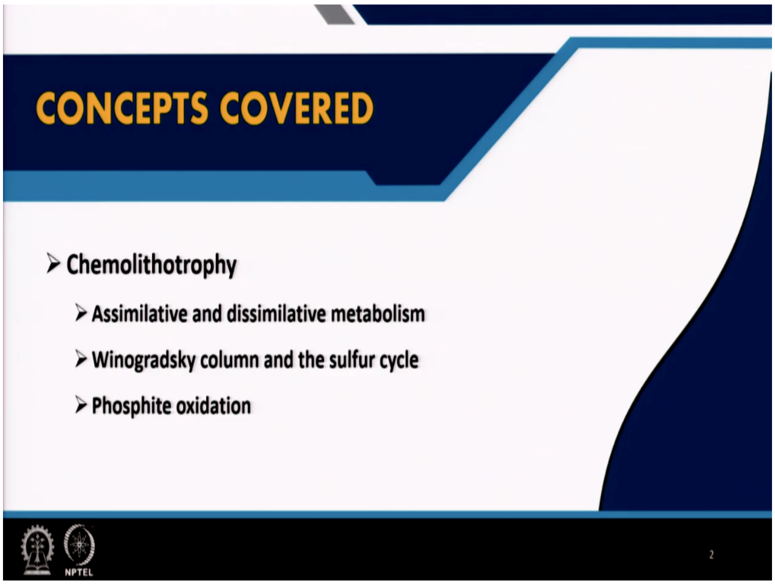

CONCEPTS COVERED

- Chemolithotrophy
  - Assimilative and dissimilative metabolism
  - Winogradsky column and the sulfur cycle
  - Phosphite oxidation

So, in this particular lecture, we are going to look at chemolithotrophy after having seen phototrophy. So, chemolithotrophy is a very large part of the metabolic diversity that we are going to be looking at. So, I will first define assimilative and dissimilative metabolism. And then, we will take a look at the Winogradsky column, the sulphur cycle and phosphite oxidation which is also part of the sulphur cycle.

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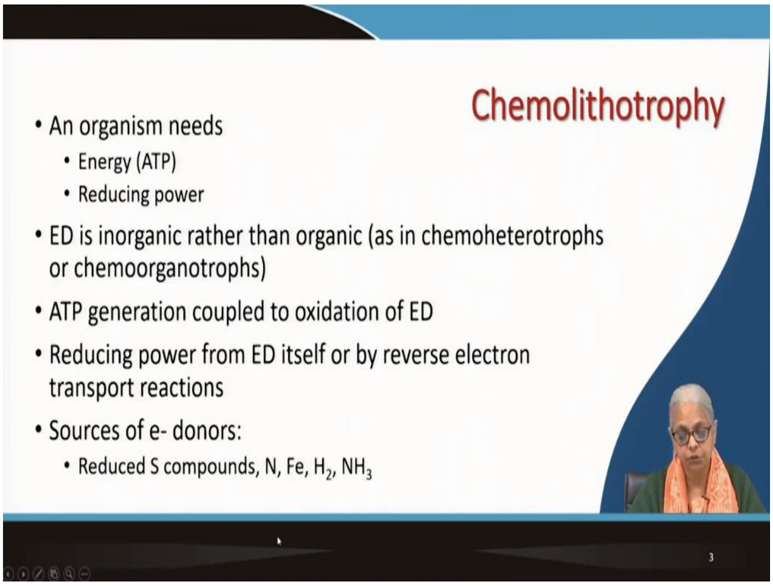

Chemolithotrophy

- An organism needs
  - Energy (ATP)
  - Reducing power
- ED is inorganic rather than organic (as in chemoheterotrophs or chemoorganotrophs)
- ATP generation coupled to oxidation of ED
- Reducing power from ED itself or by reverse electron transport reactions
- Sources of e- donors:
  - Reduced S compounds, N, Fe, H_2, NH_3

So, what is chemolithotrophy? Any organism needs 2 things. It needs ATP which is the chemical energy and it needs reducing power (the passing of electrons from one compound to another until it is taken up by an electron acceptor; this process is tied to the generation of PMF – proton motive force). So, this has to be obtained by coupling certain oxidation reactions with other reduction reactions. So, the coupling of the electron donors and electron acceptors is how the organism derives its energy as well as reducing power. ED stands for electron donor. It can be inorganic rather than (or) organic.

You can have organic chemoheterotrophs or chemoorganotrophs, or you can have chemoautotrophs as well. Then we have ATP generation which is coupled to the oxidation of the electron donor. So, as they are donating their electrons, they are being oxidised. And that is the source of energy for the organism. Reducing power from the electron donor itself can be utilised or by reverse electron transport reactions.

We have seen an example of reverse electron transport reactions in the photosynthetic case. What are the different sources of electron donors that are available? You can have any number of reduced sulphur compounds. Remember that sulphur can exist in several different oxidation states. Only sulphate is the most oxidised form. So, below that, you have thiosulphate, you have elemental sulphur, you have sulphide; all these are reduced sulphur compounds.

Similarly, you have reduced nitrogen compounds, ferrous, hydrogen and ammonia, these are all reduced forms of inorganic compounds. Any of them can serve as electron donors. And in the process, they will get oxidised.

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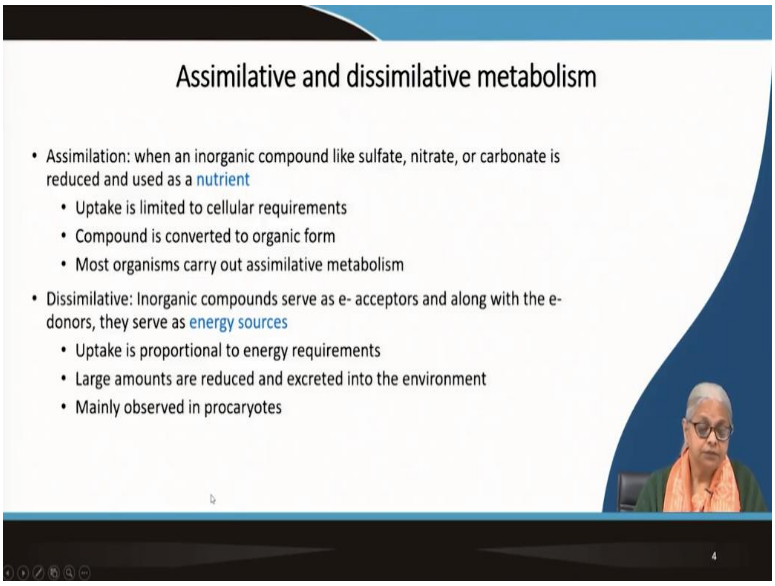

Assimilative and dissimilative metabolism

- Assimilation: when an inorganic compound like sulfate, nitrate, or carbonate is reduced and used as a nutrient
  - Uptake is limited to cellular requirements
  - Compound is converted to organic form
  - Most organisms carry out assimilative metabolism
- Dissimilative: Inorganic compounds serve as e- acceptors and along with the e- donors, they serve as energy sources
  - Uptake is proportional to energy requirements
  - Large amounts are reduced and excreted into the environment
  - Mainly observed in procaryotes

Let us define assimilative and dissimilative metabolism clearly over here. So, assimilation is when an inorganic compound like sulphate, nitrate or carbonate is reduced and it is utilized as a nutrient. Remember what I said about macronutrients and micronutrients. So, sulphate, nitrate, carbonate, are macronutrients. They have to be reduced, turned into organic carbon, organic biomass; and that is why they are macronutrients.

Their uptake is limited to the cellular requirement. So, if you were to do an elemental analysis of the cell, you would find that the cell will utilise only what is required for its functions. The compound has to be converted to organic form. So, whether it comes in organic form or in inorganic form, it goes into the cell and becomes an organic compound. Most organisms have to carry out assimilative metabolism. Whether they are microorganisms, whether they are bacteria or human beings or anything else, they all have to carry out assimilative metabolism. This is essential to all life forms.

Then we come to dissimilative metabolism. So, what is dissimilative metabolism? That is, inorganic compounds are not serving as nutrients, they are serving as electron acceptors along with electron donors.

So, as I said, the coupling of electron donors with electron acceptors is where you get a release of energy and that is dissimilative metabolism. This uptake is no longer proportionate to the cell requirement. It is proportionate to the energy requirement. Large amounts of the end products of these reactions are going to be reduced and excreted into the environment. This is typically seen in prokaryotes or bacteria.

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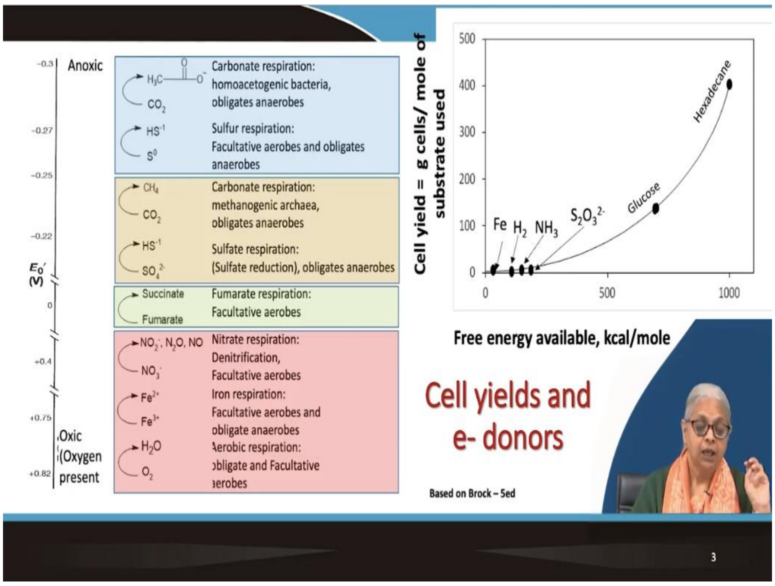

Cell yields and e- donors

Based on Brock – 5ed

So, just to let you know; I have already explained a little bit about assimilative and dissimilative metabolism, but we are going to go a little further with that. What you see here are 2 graphics.

One is the cell yield with different electron donors and oxygen as the terminal electron acceptor. So, before we go into assimilation and dissimilation, I want to talk about cell yield.

Remember what I said in previous topics that when you have different electron donors; it can be organic compounds, it can be inorganic compounds; depending on the nature of the electron donor, when you couple it with oxygen, you get the highest possible energy yield. So here, the highest amount of free energy available is with Hexadecane. So, that is a C16 molecule. Then you have a C6 molecule, thiosulphate, ammonia, hydrogen and iron. Now, as we go down, from right to left, you will find that the cell yield, the number of cells per mole of substrate is going down. So, this is basically considered to be a simple correlation between ΔG values that can be derived by coupling different electron donors with oxygen as the electron acceptor. And you get a direct correlation between the ΔG values and the cell yield.

On the left-hand side are various examples of anaerobic respiration. So, starting with anoxic conditions at the top, ending with oxic conditions at the bottom, you can see you have fermentation reactions where the ΔE_0 is going to be the lowest. So, you have carbonate respiration, homoacetogenic bacteria, which I will talk about a little bit later; obligate anaerobes. So, that is where the cell yield is the poorest. And the graphic on the right-hand side is with oxygen as the terminal electron acceptor. It has the highest energy yield for that combination of electron donor and acceptor. All the others are going to be below that.

Then you have sulphur respiration. We have already seen examples of sulphur respiration and the dissimilation and assimilation of sulphur. Some of them are facultative aerobes, others are obligate anaerobes, we have seen examples of all of them.

Then you have methanogenic bacteria which are completely obligate anaerobes; you have sulphate respiration, those are also obligate anaerobes. Then you have fermentative bacteria which can be facultative. You also have nitrate respiration, iron respiration and finally aerobic respiration.

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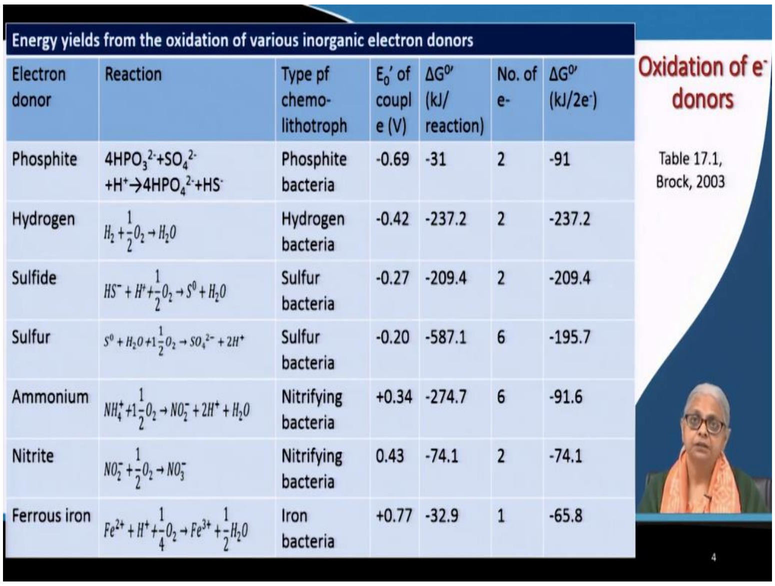

Energy yields from the oxidation of various inorganic electron donors

Electron donor	Reaction	Type pf chemo-lithotroph	E_0' of couple (V)	$\Delta G^{0\prime}$ (kJ/ reaction)	No. of e-	$\Delta G^{0\prime}$ (kJ/2e$^-$)
Phosphite	$4HPO_3^{2-}+SO_4^{2-}+H^+ \rightarrow 4HPO_4^{2-}+HS^-$	Phosphite bacteria	-0.69	-31	2	-91
Hydrogen	$H_2+\frac{1}{2}O_2 \rightarrow H_2O$	Hydrogen bacteria	-0.42	-237.2	2	-237.2
Sulfide	$HS^- + H^+ + \frac{1}{2}O_2 \rightarrow S^0 + H_2O$	Sulfur bacteria	-0.27	-209.4	2	-209.4
Sulfur	$S^0 + H_2O + 1\frac{1}{2}O_2 \rightarrow SO_4^{2-} + 2H^+$	Sulfur bacteria	-0.20	-587.1	6	-195.7
Ammonium	$NH_4^+ + 1\frac{1}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O$	Nitrifying bacteria	+0.34	-274.7	6	-91.6
Nitrite	$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$	Nitrifying bacteria	0.43	-74.1	2	-74.1
Ferrous iron	$Fe^{2+} + H^+ + \frac{1}{4}O_2 \rightarrow Fe^{3+} + \frac{1}{2}H_2O$	Iron bacteria	+0.77	-32.9	1	-65.8

Oxidation of e$^-$ donors

Table 17.1, Brock, 2003

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Now, here is a table that summarises many of these reactions and it gives you the ΔG^0 values for these reactions. Other than the first one, in all other cases, oxygen is the terminal electron acceptor. Remember what I said; you have to have a combination of electron donor with the electron acceptor and the 2 together, when they come together, there has to be a negative ΔG value for the organism to derive energy, convert it to ATP and therefore, survive.

So, here you have; let us ignore the first one. You have $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ the second case; $HS^- + H^+ + \frac{1}{2}O_2 \rightarrow S^0 + H_2O$. That is done by sulphur bacteria. And you can see, the number of; the ΔG values are all negative, which means there is sufficient energy for the cell to survive. And elemental sulphur can be further oxidised to $SO_4{}^{2-}$. Again, that is done by sulphur bacteria.

You have ammonia $(NH_4{}^+)$ which is being converted to nitrite $(NO_2{}^-)$ and nitrate $(NO_3{}^-)$ by nitrifying bacteria. Again, these are autotrophic bacteria. Then you have ferrous iron (Fe^{2+}) being converted to ferric iron (Fe^{3+}). I have already said a little bit about that in the iron cycle. So, these are all examples of the utilisation of inorganic electron donors, their combination with oxygen as the terminal electron acceptor.

Now, let us take a look at the first one. The first one is phosphite ($HPO_3{}^{2-}$). Phosphite is rarely found in the environment, because it gets easily converted in the presence of air, to phosphate ($HPO_4{}^{2-}$). Now, if phosphite bacteria are present and sulphate ($SO_4{}^{2-}$) is also present in the environment, then sulphate ($SO_4{}^{2-}$) is reduced to sulphide (HS^-) and phosphite ($HPO_3{}^{2-}$)is oxidised to phosphate ($HPO_4{}^{2-}$). This is also an energy-producing reaction. And it is the only known example where phosphorus exists in an oxidation state different from phosphate. There is only 1 example.

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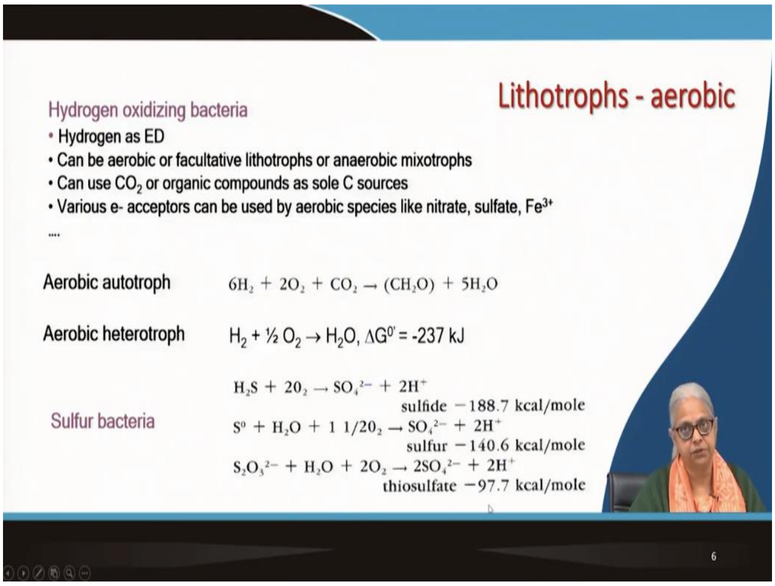

Lithotrophs - aerobic

Hydrogen oxidizing bacteria

- Hydrogen as ED
- Can be aerobic or facultative lithotrophs or anaerobic mixotrophs
- Can use CO_2 or organic compounds as sole C sources
- Various e- acceptors can be used by aerobic species like nitrate, sulfate, Fe^{3+}

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Aerobic autotroph $6H_2 + 2O_2 + CO_2 \rightarrow (CH_2O) + 5H_2O$

Aerobic heterotroph $H_2 + ½\, O_2 \rightarrow H_2O,\ \Delta G^{0'} = -237$ kJ

Sulfur bacteria

$H_2S + 2O_2 \rightarrow SO_4{}^{2-} + 2H^+$

sulfide -188.7 kcal/mole

$S^0 + H_2O + 1\ 1/2O_2 \rightarrow SO_4{}^{2-} + 2H^+$

sulfur -140.6 kcal/mole

$S_2O_3{}^{2-} + H_2O + 2O_2 \rightarrow 2SO_4{}^{2-} + 2H^+$

thiosulfate -97.7 kcal/mole

So, then we come to lithotrophs that exist under oxygen conditions or aerobic conditions. I was talking about hydrogen oxidising bacteria where hydrogen (H_2) is the electron donor. Now, this electron donor can be coupled with oxygen (O_2) under aerobic conditions. And if the source of carbon is carbon dioxide (CO_2), it is being converted to organic carbon. Then we have aerobic autotrophic bacteria.

If on the other hand, the electron donor and acceptor are both inorganic, and they are utilising organic carbon as the source of carbon which is possible, then it is an aerobic heterotroph. So, here you can have aerobic or facultative lithotrophs, anaerobic mixotrophs. They are capable of utilising CO_2 or organic compounds as the sole carbon source. And they can use various electron acceptors, not just oxygen but also nitrate, sulphate, ferric iron and so on.

So, here we have examples of sulphur bacteria, which I have already explained in the previous slide. You can have $H_2S + 2O_2 \rightarrow SO_4{}^{2-} + 2H^+$. You can see the amount of energy released. $S^0 + H_2O + \frac{3}{2}O_2 \rightarrow SO_4{}^{2-} + 2H^+$, slightly less energy is released. In this case, in all of these cases, oxygen is the terminal electron acceptor. And it is being combined with different electron donors, sulphide, elemental sulphur or thiosulphate. In all cases, energy is released; the ΔG values are negative; and therefore, the organism can survive under aerobic conditions.

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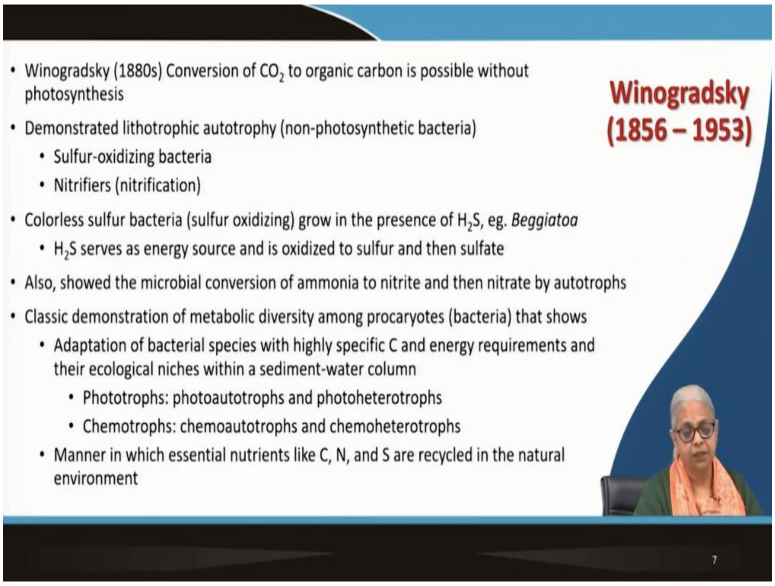

Winogradsky (1856 – 1953)

- Winogradsky (1880s) Conversion of CO_2 to organic carbon is possible without photosynthesis
- Demonstrated lithotrophic autotrophy (non-photosynthetic bacteria)
  - Sulfur-oxidizing bacteria
  - Nitrifiers (nitrification)
- Colorless sulfur bacteria (sulfur oxidizing) grow in the presence of H_2S, eg. *Beggiatoa*
  - H_2S serves as energy source and is oxidized to sulfur and then sulfate
- Also, showed the microbial conversion of ammonia to nitrite and then nitrate by autotrophs
- Classic demonstration of metabolic diversity among procaryotes (bacteria) that shows
  - Adaptation of bacterial species with highly specific C and energy requirements and their ecological niches within a sediment-water column
    - Phototrophs: photoautotrophs and photoheterotrophs
    - Chemotrophs: chemoautotrophs and chemoheterotrophs
  - Manner in which essential nutrients like C, N, and S are recycled in the natural environment

Let us take a look at the Winogradsky column and what it tells us. So, Winogradsky has contributed in a big way to our understanding of microbial diversity in the environment. And way back in the 1880s, he was able to show that CO_2 can be converted to organic carbon without photosynthesis, which even today seems like a radical idea. Because even in high school, we are taught that CO_2 can be converted to organic carbon only by the photosynthetic process.

But here we will take a look at some of the reactions that can happen in the environment without photosynthesis. And he also showed that lithotrophic autotrophy by non-photosynthetic bacteria is possible. What are these bacteria? They are sulphur-oxidising bacteria as well as nitrifying bacteria. And we are all; those of us who are in civil engineering or environmental engineering, we are all familiar with the fact that ammonia in the wastewater is converted to nitrite and nitrate. So, those are nitrifying bacteria.

So, those are simple examples of non-photosynthetic bacteria. We also have colourless sulphur bacteria. They are the ones that are sulphur oxidising bacteria that can grow in the presence of hydrogen sulphide (H_2S). So, *Beggiatoa* is an example of that. H_2S is the energy source and it is converted to sulphur (S) and then sulphate ($SO_4{}^{2-}$).

We also see the microbial conversion of ammonia to nitrite and then nitrate by autotrophs. Classic demonstration of metabolic diversity in the water sediment column is going to be shown in the next slide. So, this was the reason why it is called the Winogradsky column.

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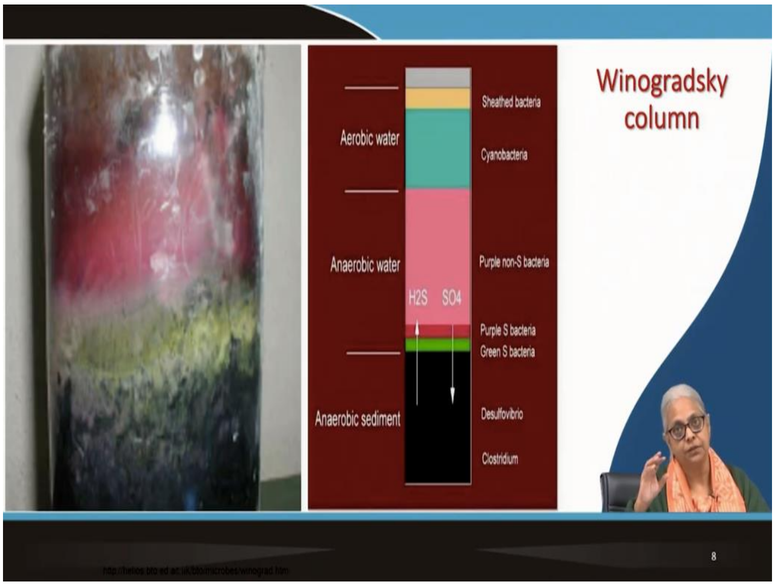

Winogradsky column

http://helios.bto.ed.ac.uk/bto/microbes/winograd.htm

Let me show it to you. So, this is a typical Winogradsky column in both photographic as well as schematic form. And I will go through the entire process of how you have various groups or various species that coexist in the water-sediment column, and are responsible for recycling sulphur through the aquatic system. So, this was demonstrated by Winogradsky. It is a classic demonstration of the metabolic diversity amongst bacteria.

It shows the adaptation of bacterial species with very specific carbon and energy requirements, and their ecological niche within the water-sediment column. You have phototrophs, both photoautotrophs and photoheterotrophs. You have chemotrophs, both autotrophic as well as heterotrophic. All of them coexist in this entire column. And you can do it; you can do a demo in your own lab. You can take a long plastic bottle, fill it with sediment and water with all the essential nutrients and perhaps a little surplus of sulphur; and you may be able to recreate it in the lab. This is the way nature recycles nutrients like carbon, nitrogen and sulphur in the environment.

So, here we have an aerobic zone at the top. Remember, it is in contact with the atmospheric air. So, the top part of this column is aerobic. As you go deeper into the column, it becomes more and more anaerobic. And at the bottom, we consider it to be completely anaerobic. And I will show you each part of this column.

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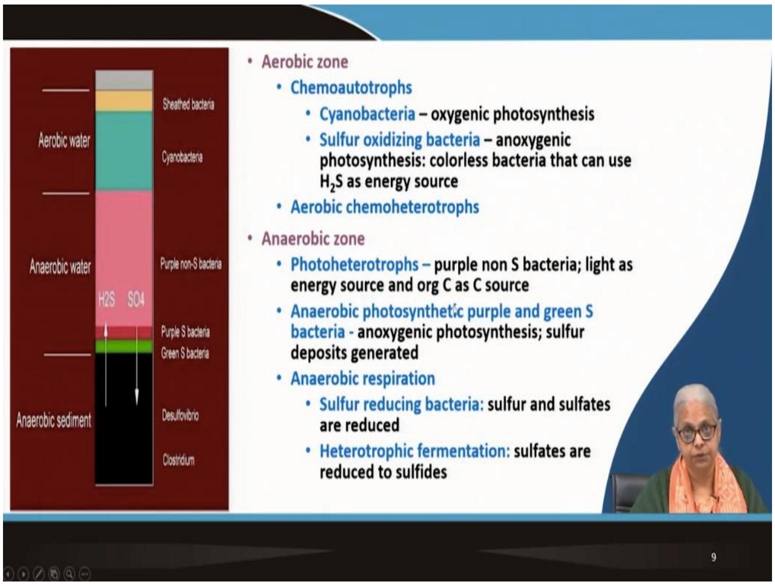

- Aerobic zone
  - Chemoautotrophs
    - Cyanobacteria – oxygenic photosynthesis
    - Sulfur oxidizing bacteria – anoxygenic photosynthesis: colorless bacteria that can use H_2S as energy source
  - Aerobic chemoheterotrophs
- Anaerobic zone
  - Photoheterotrophs – purple non S bacteria; light as energy source and org C as C source
  - Anaerobic photosynthetic purple and green S bacteria - anoxygenic photosynthesis; sulfur deposits generated
  - Anaerobic respiration
    - Sulfur reducing bacteria: sulfur and sulfates are reduced
    - Heterotrophic fermentation: sulfates are reduced to sulfides

So, what is existing in the aerobic zone? The first thing that is going to obviously takeover is chemoautotrophs. So, the chemoautotrophs include cyanobacteria. These are our blue-green algae. They are responsible for oxygenic photosynthesis. So, what you see directly with your eye, anytime you go by a pond or a puddle of water which has a green layer on it, these are all cyanobacteria or blue-green algae. They are responsible for oxygenic photosynthesis.

You can also have sulphur oxidising bacteria. How are these sulphur oxidising bacteria going to thrive in the same environment? They are responsible for anoxygenic photosynthesis. They are colourless bacteria, so you cannot see them visibly. And they are capable of utilising hydrogen sulphide (H_2S) as the energy source. And where is the hydrogen sulphide coming from? It is coming up; it is a gas; it comes upwards. So, it is being generated at the bottom of the column. Whether it is a lake or a pond or any other place, you will find that it has a lot of dark sediment at the bottom and H_2S is being generated in that sediment. And because of its gaseous nature, it will come to the top. And these sulphur oxidising bacteria are capable of utilising it as their energy source.

Then we have aerobic chemoheterotrophic bacteria. Now, aerobic chemoheterotrophic bacteria are capable of utilising organic carbon, and they will exist just like all the other bacteria in your activated sludge process. They are all aerobic chemoheterotrophs.

Then we have anaerobic; then we have the lower layers have this column. In the lower layers of this column where oxygen is either completely gone or at very low levels, you can have several other species. So, in the anaerobic zone, we have photoheterotrophs. Purple non-sulphur bacteria can exist. Light is the energy source and organic carbon is the carbon source. Then you also have photosynthetic purple and green sulphur bacteria. So, you can see the colours. The normal bacteria at the top, these are aerobic photoheterotrophs. As you go further down, you get purple non-sulphur bacteria, purple sulphur bacteria; you can see the colours; and the green sulphur bacteria.

And as you go further down, you get completely black coloured sediment because of the anaerobic nature of the material. So, you have anaerobic photosynthetic purple and green sulphur bacteria, anoxygenic photosynthesis. Sulphur is deposited over here. You remember, elemental sulphur will precipitate; it will get deposited. This elemental sulphur will be reduced further. You get reduction of elemental sulphur and sulphates by sulphur reducing bacteria. And you get heterotrophic fermentation where sulphates are reduced to sulphides. And these sulphides, because they are in gaseous form, will come upwards in the column.

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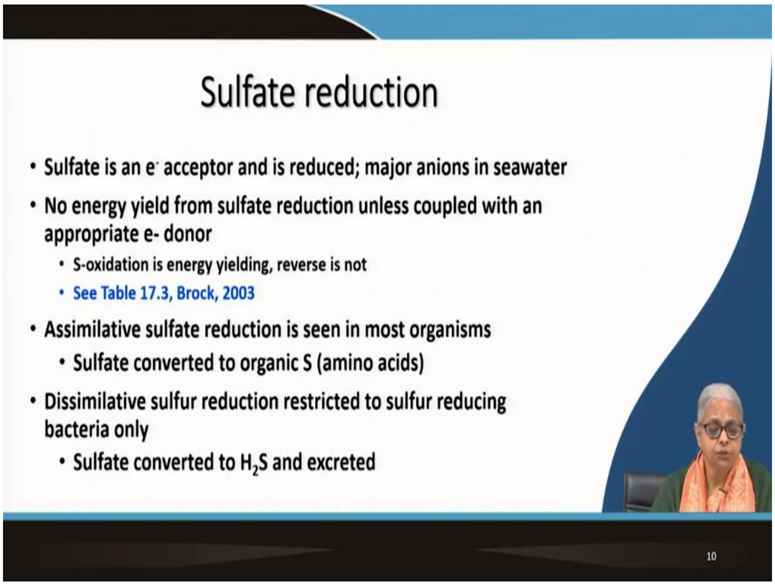

Sulfate reduction

- Sulfate is an e^- acceptor and is reduced; major anions in seawater
- No energy yield from sulfate reduction unless coupled with an appropriate e- donor
  - S-oxidation is energy yielding, reverse is not
  - See Table 17.3, Brock, 2003
- Assimilative sulfate reduction is seen in most organisms
  - Sulfate converted to organic S (amino acids)
- Dissimilative sulfur reduction restricted to sulfur reducing bacteria only
  - Sulfate converted to H_2S and excreted

So, let us take a look at sulphate reduction. In sulphate reduction, sulphate is an electron acceptor; it gets reduced; and the major anion; it is also a major anion in seawater. By itself, sulphate reduction is not capable of providing energy. For the organism to derive energy using sulphate as the electron acceptor, it has to be coupled with the appropriate electron donor. So, sulphur oxidation is energy yielding, but the reverse reaction is not an energy yielding reaction. You can refer to another table.

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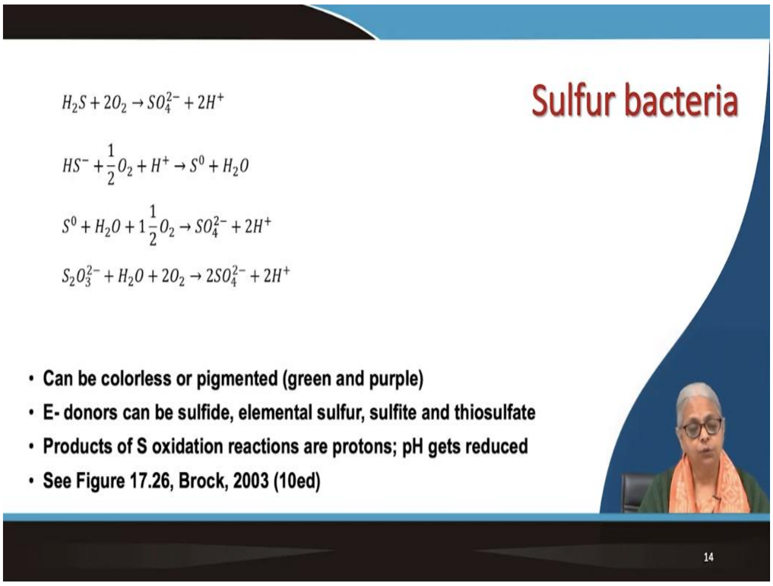

Sulfur bacteria

$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$

$HS^- + \frac{1}{2}O_2 + H^+ \rightarrow S^0 + H_2O$

$S^0 + H_2O + 1\frac{1}{2}O_2 \rightarrow SO_4^{2-} + 2H^+$

$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow 2SO_4^{2-} + 2H^+$

- Can be colorless or pigmented (green and purple)
- E- donors can be sulfide, elemental sulfur, sulfite and thiosulfate
- Products of S oxidation reactions are protons; pH gets reduced
- See Figure 17.26, Brock, 2003 (10ed)

So, if I were to show you this particular set of reactions, $H_2S \rightarrow SO_4{}^{2-}$ has a ΔG that is negative. It is a high number and it is a negative ΔG. So, energy can be obtained. But $SO_4{}^{2-} \rightarrow H_2S$ is going to be positive, and therefore it is not an energy yielding reaction. So, it has to be coupled with the right electron donor. And I will show you, I think I have examples, later.

Assimilative; so, now there is another thing that I need to talk about and that is assimilative versus dissimilative sulphur or nitrogen reduction, oxidation, all of that. Assimilative means, where the element is taken up as an organic compound. So, assimilation into the organic biomass of the organism is what we call assimilative sulphate reduction. And that is common in almost all organisms, whether they are microorganisms or higher organisms.

This sulphate is converted to organic sulphur. And you know that organic sulphur is present in at least 2 amino acids; yes, cysteine and methionine. So, these are the 2 amino acids that contain organic sulphur. And then we have dissimilative sulphur reduction, where sulphur reducing bacteria are the only ones that are capable of utilising sulphate and converting it to sulphide. And that sulphide is excreted. And that is what I showed you in the Winogradsky column.

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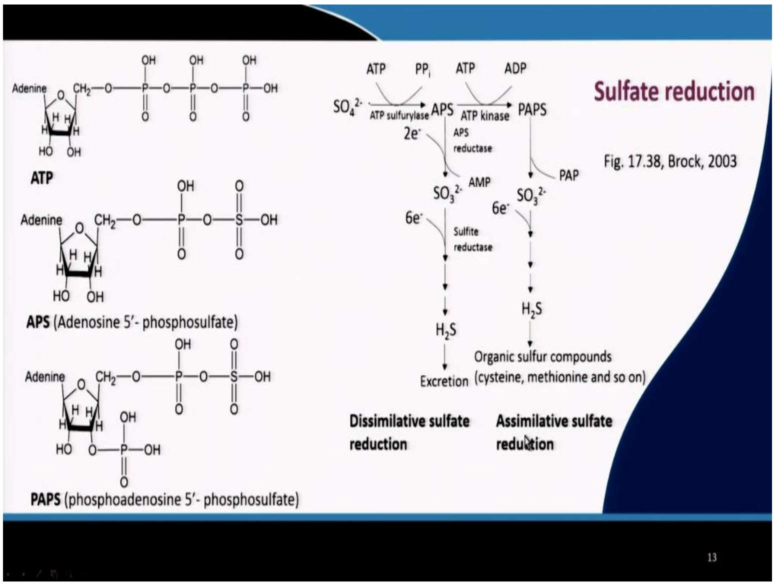

Sulfate reduction

Fig. 17.38, Brock, 2003

So, what we have here are some of the compounds that are involved in sulphate reduction. As we know, sulphate is going to be reduced to hydrogen sulphide. Now, this is an 8 electron transfer and it goes through a series of reactions before it is completed. One of the major compounds that is involved in this reduction of sulphate is called APS, and that is adenosine 5 phosphosulphate.

So, if you look at ATP, 2 of the phosphates in ATP have been replaced by a single sulphate. And that is what APS is, that is adenosine-5-phosphosulphate. Now, this adenosine-5-phosphosulphate is used to activate the sulphate molecule. The 2 phosphates are released; APS is formed; 2 electrons are transferred to form sulphite; and AMP, adenosine monophosphate is released.

Sulphite picks up 6 electrons and is converted through a series of reactions mediated by sulphite reductase to form H_2S. Now, this H_2S is excreted into the environment through the pathway of dissimilative sulphate reduction. There is another possibility and that is assimilative sulphate reduction. So, in assimilative sulphate reduction, sulphate again has to donate 8 electrons and give them to hydrogen sulphide.

In this case, another compound is formed, and that is phosphoadenosine-5-phosphosulphate. So, here you have our ATP molecule. It has already been formed as APS. So, that is adenosine-5-phosphosulphate. Another phosphate is added at the C2 position to get phosphoadenosine-5-phosphosulphate. And that is PAPS for short. Now, ATP is being converted to ADP and a PAPS molecule is generated. The mediating enzyme is ATP kinase.

And when PAPS is converted to sulphide, PAP is released; the sulphate is converted to sulphite; it picks up 6 electrons and is then converted to hydrogen sulphide or organic sulphur compounds. So, we know that organic sulphur compounds especially in the amino acids are cysteine and methionine. So, these are examples of organic sulphur compound. And they have been assimilated into the biomass of the bacteria or other organisms. And that is why we call it assimilative sulphate reduction.

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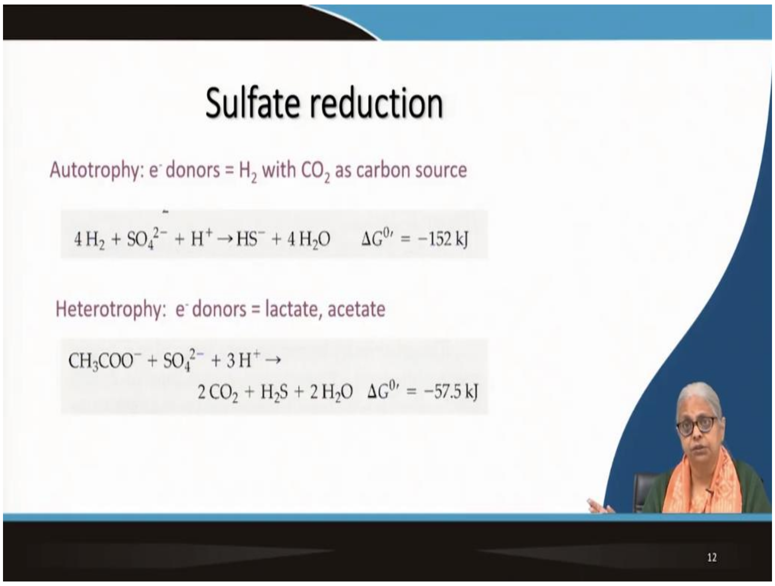

Sulfate reduction

Autotrophy: e^- donors = H_2 with CO_2 as carbon source

$$4\,H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\,H_2O \qquad \Delta G^{0\prime} = -152\ kJ$$

Heterotrophy: e^- donors = lactate, acetate

$$CH_3COO^- + SO_4^{2-} + 3\,H^+ \rightarrow 2\,CO_2 + H_2S + 2\,H_2O \qquad \Delta G^{0\prime} = -57.5\ kJ$$

Let us come to sulphate reduction. So, like I said, sulphate reduction by itself does not yield any energy. It has to be combined with the right electron donor. Now, if it is an autotrophic organism, the right electron donor can be hydrogen and CO_2 can be the carbon source. So, in this case, $4\,H_2 + SO_4{}^{2-} + H^+ \rightarrow HS^- + 4H_2O$. And the net $\Delta G^{0\prime}$ for this reaction is -152 kilojoules per electron equivalent; and that is sufficient for the organism to survive.

Heterotroph is for heterotrophic organisms, they can use sulphate along with any organic compound. These organic compounds can be lactate, acetate, any number of compounds are possible. They will convert the organic compound to CO_2. Sulphate will be converted to sulphide. And that is what we see around us. When you think about wastewater, what happens? Whether you have sulphide or sulphate, if you have sulphate, it is going to get converted to sulphide. So, that is what is possible. So, these are some of those examples.

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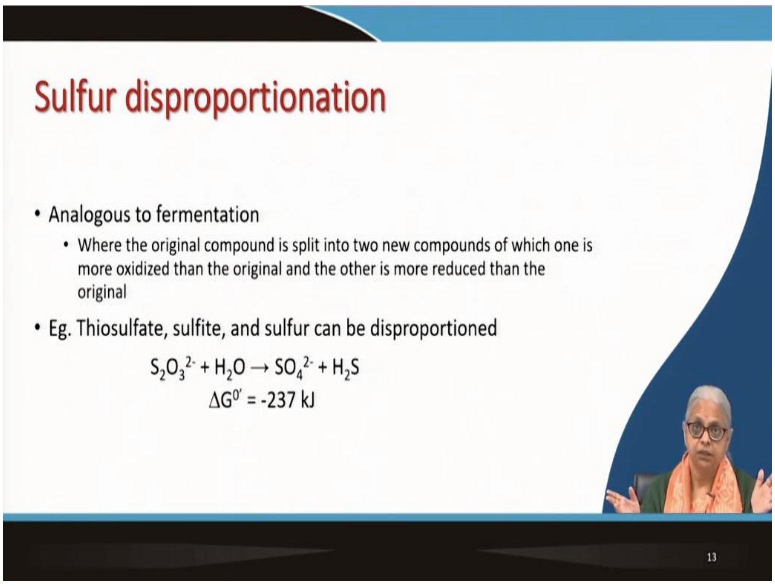

Sulfur disproportionation

- Analogous to fermentation
  - Where the original compound is split into two new compounds of which one is more oxidized than the original and the other is more reduced than the original
- Eg. Thiosulfate, sulfite, and sulfur can be disproportioned

$$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2S$$

$$\Delta G^{0'} = -237 \text{ kJ}$$

Then, we have sulphur disproportionation. So, sulphur disproportionation means, it is somewhat similar to fermentation. If you remember what I said about fermentation; your starting compound, let us say is glucose; it will get converted to methane and CO_2. Now, we are assuming, just for the electron balance; we will say that, for each molecule of glucose, you will get 3 molecules of methane CH_4 and 3 molecules of CO_2; just to maintain the electron balance.

It is a very simplistic way of looking at things. Similarly here, at the reduced end of the sulphur oxidation states, you have sulphides (HS^-) at the most oxidised end, you have sulphate ($SO_4{}^{2-}$). What is in between? We have thiosulphate ($S_2O_3{}^{2-}$) and elemental sulphur S^0that are in between. So, either of them, thiosulphate, sulphite and elemental sulphur can be disproportioned. So, disproportioned means, part of it will be oxidised and part of it will be reduced. So, that is called disproportionation. It is similar to what we saw in fermentation.

Then we come to sulphur bacteria. So, here we have; I have already said a lot about sulphur bacteria, but these are different reduced forms of sulphur. Hydrogen sulphide, elemental sulphur, thiosulphate, in combination with oxygen can convert it to more oxidised forms of sulphur. So, sulphur bacteria are fairly common all around you.

They can be both colourless or pigmented. They can be green or purple. And the electron donors can be sulphide, like I have already said that. Products of the sulphur oxidation reactions are protons and the pH gets reduced.

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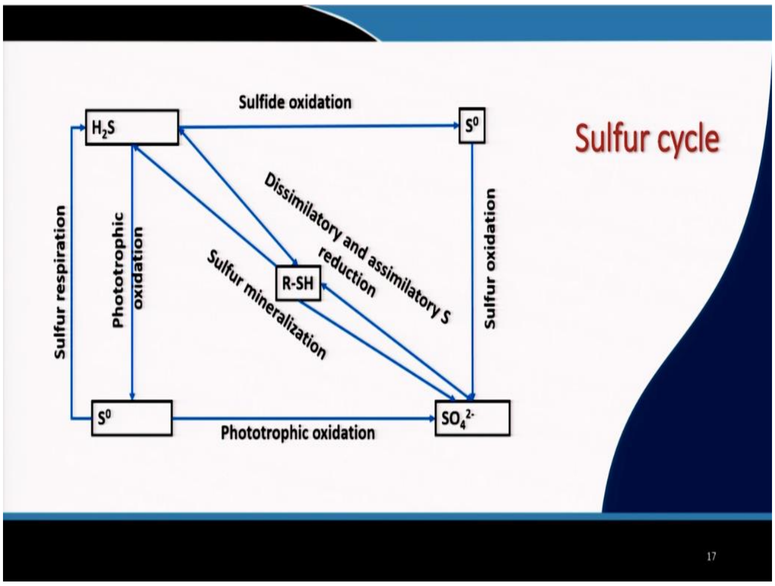

Sulfur cycle

So, I have already covered the sulphur cycle or will be covering the sulphur cycle in the biogeochemical cycles. So, here we have a schematic that explains the different forms of sulphur that are present in the environment. So, what you see here are 3 major inorganic forms. So, hydrogen sulphides (H_2S), elemental sulphur (S^0) and sulphate ($SO_4{}^{2-}$); these are the 3 major inorganic forms of sulphur.

And then you also have the organic form of sulphur. So, SH stands for the sulphydryl group, and this represents the sulphur that is part of the biomass. Now, you can see from the sulphur; this is a very simple schematic that shows you how sulphur changes its oxidation state through various processes. So, let us start with hydrogen sulphide, H_2S. It gets converted to elemental sulphur (S^0) by sulphide oxidation, and then to sulphate ($SO_4{}^{2-}$) by sulphur oxidation.

Now, this sulphate is going to be taken up, either hydrogen sulphide or sulphate or even elemental sulphur; we have seen some examples of that; they can be taken up as either nutrients or they can serve as energy sources. So, if organic sulphur is being converted to these inorganic forms, we call it sulphur mineralization; and it is also part of the dissimilatory sulphur reduction pathway.

Now, there are 2 pathways dissimilatory and assimilatory sulphur reduction. So, assimilatory means, it becomes, the inorganic forms are being converted to organic sulphur, and they are becoming a part of the biomass of the organism. And dissimilatory is when the inorganic forms are serving as either; they are serving as energy sources and other inorganic forms are being excreted into the environment. So, we are going to go into some of these details.

Now, we also have another thing that; another process that we have; I think we have already covered it; and that is phototrophic oxidation of the reduced forms of sulphur. So, just like we have oxygenic photosynthesis where water is converted to oxygen ($H_2O \rightarrow O_2$) , in the same way, anoxygenic photosynthesis where hydrogen sulphide can be converted to elemental sulphur as well as sulphate ($H_2S \rightarrow S^0 \ / \ SO_4{}^{2-}$). So, those are the phototrophic oxidation pathways.

When these inorganic forms are converted back to hydrogen sulphide, that is called sulphur respiration. So, you can see the number of different processes that are present in the environment, which allow complete recycling of sulphur in the environment.

I will be talking about that a little bit more. I have also mentioned in previous topics that certain cells can create storage granules of the nutrient that is essential for energy generation. So, for sulphur bacteria, they have storage granules either inside the cell or outside the cell.

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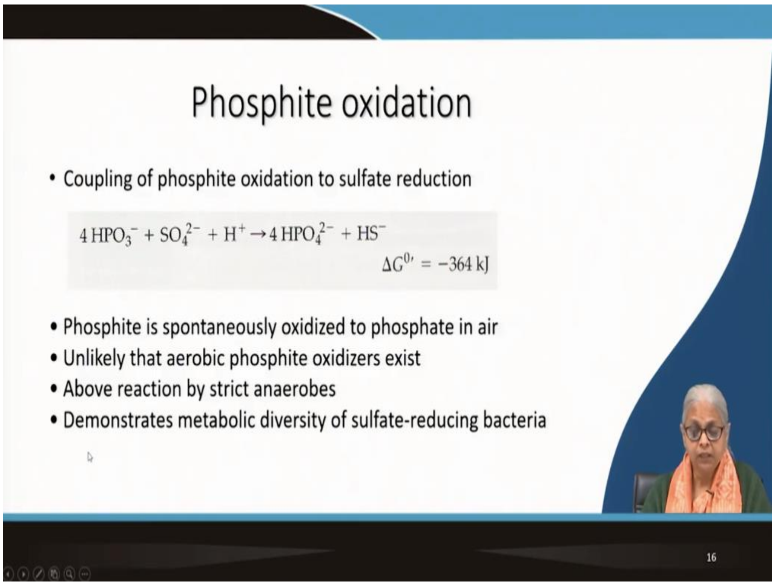

Phosphite oxidation

- Coupling of phosphite oxidation to sulfate reduction

$$4\,HPO_3^{-} + SO_4^{2-} + H^{+} \rightarrow 4\,HPO_4^{2-} + HS^{-}$$
$$\Delta G^{0\prime} = -364\ kJ$$

- Phosphite is spontaneously oxidized to phosphate in air
- Unlikely that aerobic phosphite oxidizers exist
- Above reaction by strict anaerobes
- Demonstrates metabolic diversity of sulfate-reducing bacteria

I also mentioned that phosphite oxidation is something that is coupled to sulphate reduction. So, this is the same example. Phosphite ($HPO_3{}^{-}$) under aerobic conditions is spontaneously oxidised to phosphate ($HPO_4{}^{2-}$). And because this spontaneous oxidation is a chemical reaction, it is unlikely that any aerobic phosphite oxidisers exist. Like I said, there is only 1 species that has been found that is capable of utilising phosphite and sulphate and converting both of them to phosphate and sulphide. So, this is a reaction that is mediated by strictly anaerobic bacteria. And it also shows the metabolic diversity of sulphate reducing bacteria.

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I will stop at this point. Thank you.