Soil Science and Technology
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Lecture – 22
Silicate Clays (Contd.)

Welcome friends to this new lecture of Soil Science and Technology and in the previous lecture we talk about what is soil colloid and what are the different classes of soil colloids. And, then we distinguish about we distinguish between the inorganic soil colloids and organic colloids. We talked about what are the different types of inorganic soil colloids.

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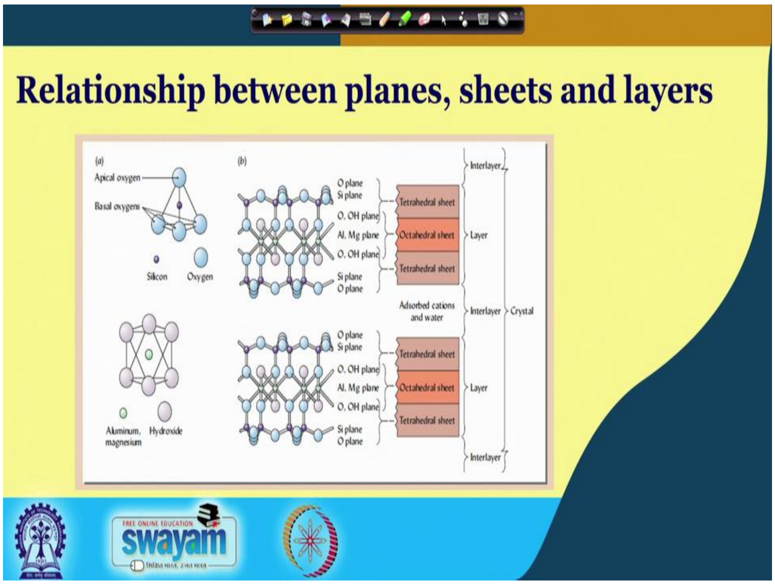

Relationship between planes, sheets and layers

And then we started about silicate clays and we distinguish silicate clays into several categories starting from nesosilicates, then sorosilicates, then cyclosilicates, inosilicates, then phyllosilicates and tectosilicates. And, we specifically started talking about phyllosilicate, because that represents soil clay minerals and.

We started talking about the basic building blocks of phyllosilicates that is silicate tetrahedral. We talked about their structure and we talked about how they linked each other linked with each other to form a silicate tetrahedral sheet. And, then we also talked about aluminium octahedral and how aluminium octahedral sheets are formed. And, then how they are sandwiched between you know one octahedral you know one octahedral sheets sandwiched between two tetrahedral sheet to form a 2 is to 1 structure and what is 1 is to 1 structure.

What is unit cell and what is inter layer, what is layer and what is you know what is crystal and then what are the different types of plates. So, we stop there and let us start and let us go from the here. And, in today's lecture we will be discussing in details about mineral structure of different clay minerals.

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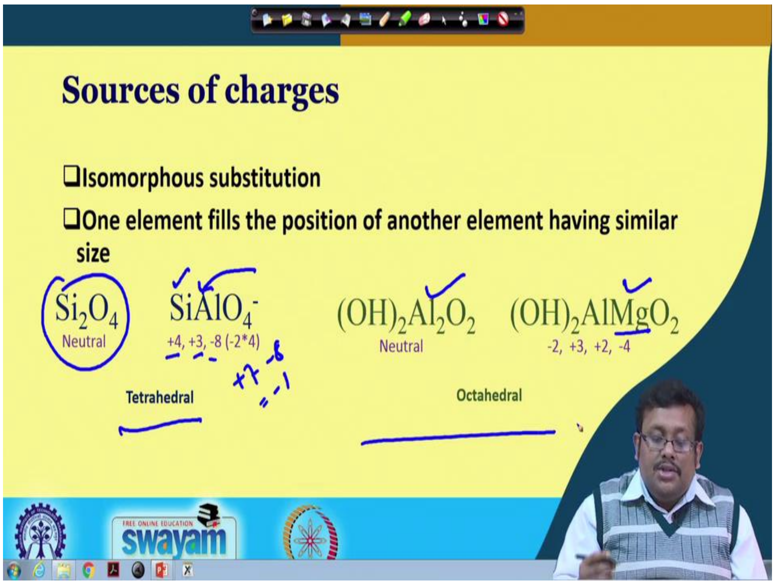

Sources of charges

❑Isomorphous substitution

❑One element fills the position of another element having similar size

Si_2O_4 Neutral

$SiAlO_4^-$ +4, +3, -8 (-2*4)

+7 -8 = -1

Tetrahedral

$(OH)_2Al_2O_2$ Neutral

$(OH)_2AlMgO_2$ -2, +3, +2, -4

Octahedral

So, before going to the structure of the clay minerals let us discuss what are the major sources of charge. Now, we will be discussing the sources of charges in details in our forthcoming lecture. But let me tell you that there are two major source of charge sources of charges which developed within the clay minerals.

So, one of them is isomorphous substitution and in case of isomorphous substitution what happens: one element face the position of another element having similar size. So, you can see here one in a here there is a tetrahedra silicate tetrahedral which is basically neutral. And, then one silica in the tetrahedral you know is basically you know replaced by in the tetrahedral sheet basically.

This is the tetrahedral sheet and one silica in the tetrahedral sheet is getting replaced by aluminium which are which is having the similar sizes as that of silica. And, as a result of that there is an excess of negative charge. So, because silica you know that plus 4 aluminium is plus 3 and O 4 minus 8. So, here plus 7 minus 8; that means, minus 1. So, there is a negative charge generation. So, as a result of this type of substitution we call it isomorphous iso stands for similar morphous stands for size.

So, since silica and aluminium has almost similar size they this aluminium can substitute this silicon not only that they you know, another major prerequisite for this type of substitution is that there should be there should be difference in valency of 1 not more than 1. So, you can see plus 4 valency of silica is getting replaced by plus 3 valency you know of aluminium. So, this is call silica this is example of a isomorphous substitution in case of tetrahedral layer. However, in case of octahedral layer you can see aluminium is getting replaced by magnesium because both of them are having the similar size.

So, remember that in case of silica tetrahedral layer a silica tetrahedral sheets silica get replaced by aluminium whereas, in case of octahedral layer aluminium generally got replaced by either magnesium or iron. So, these isomorphous substitution is one of the major source of charges which develop in the clay minerals; that is why clay is very active. There are other charges you know there are other sources of charges also we will discuss them later on.

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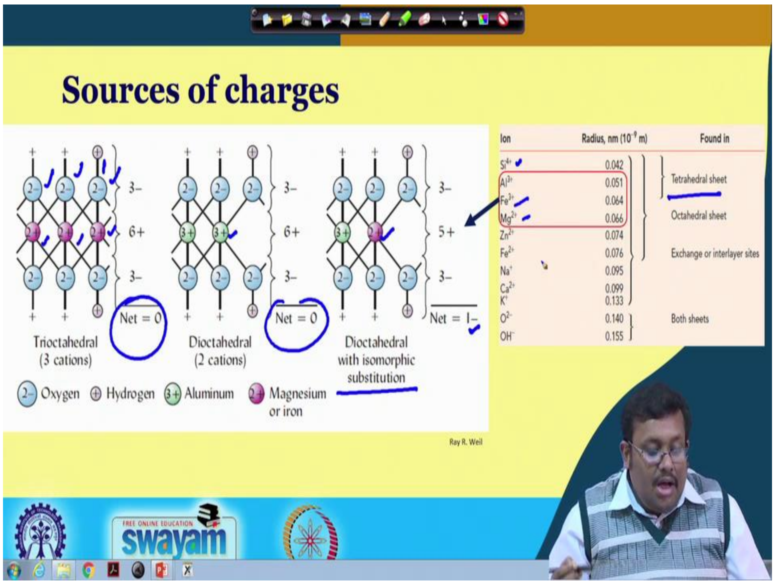

Sources of charges

Ion	Radius, nm (10^{-9} m)	Found in
Si^{4+}	0.042	
Al^{3+}	0.051	Tetrahedral sheet
Fe^{3+}	0.064	
Mg^{2+}	0.066	Octahedral sheet
Zn^{2+}	0.074	
Fe^{2+}	0.076	Exchange or interlayer sites
Na^{+}	0.095	
Ca^{2+}	0.099	
K^{+}	0.133	
O^{2-}	0.140	Both sheets
OH^{-}	0.155	

Ray R. Weil

So, let us move ahead and see in details you know this isomorphous substitution, you can see here in this tetrahedra three cations obviously, minus 3 stands for 3 you know oxygen group. And so, we are getting minus 3 because, one of their minus charge is getting shared with the adjacent silica. And, here in the trioctahedral layer obviously, you remember the tetrahedral layer where all the 3 octahedral positions are filled by cations.

Now, in case of trioctahedral layer if you remember the octahedral positions are basically dominated by magnesium because, it has 2 valency plus 2. So, you can see this is plus 2 plus 2 plus 2 so, it is plus 6. So, we are we are getting a net charge of 0. However, when we are replacing also I am in here also this is the dioctahedral layer where we are getting the total net charge of 0. However, if in these you know dioctahedral sheet if we replace 1 aluminium with 1 magnesium then you can see there is a generation of net 1 negative charge.

So, this is an example of dioctahedral with isomorphic substitution. You can see what are the different ions which can replace you know among themselves. So, silica get already replaced by aluminium and this type of silica replacement by aluminium occurs in tetrahedral sheet. Whereas, in case of octahedral sheet you can see generally aluminium get replaced by either iron or magnesium or sometimes zinc. So, these are some results these are some examples of isomorphic substitution or isomorphous substitution.

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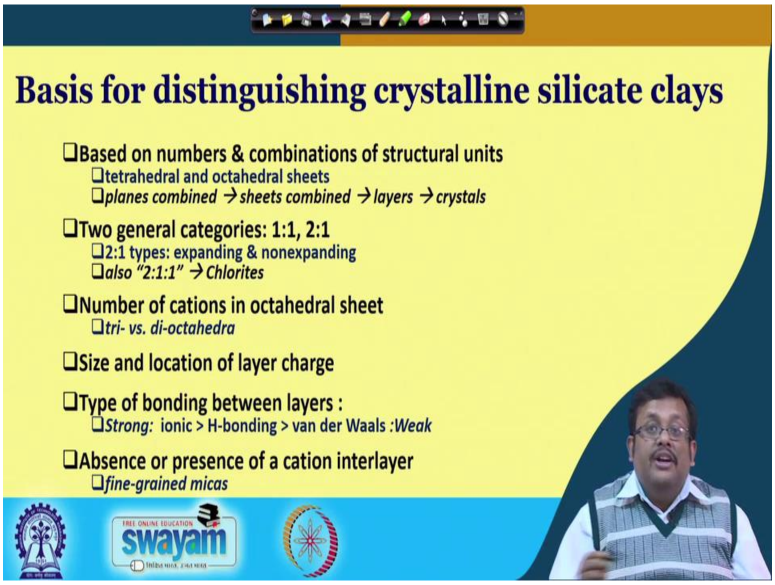

Basis for distinguishing crystalline silicate clays

- ☐Based on numbers & combinations of structural units
  - ☐tetrahedral and octahedral sheets
  - ☐*planes combined → sheets combined → layers → crystals*
- ☐Two general categories: 1:1, 2:1
  - ☐2:1 types: expanding & nonexpanding
  - ☐*also "2:1:1" → Chlorites*
- ☐Number of cations in octahedral sheet
  - ☐*tri- vs. di-octahedra*
- ☐Size and location of layer charge
- ☐Type of bonding between layers :
  - ☐*Strong:* ionic > H-bonding > van der Waals :*Weak*
- ☐Absence or presence of a cation interlayer
  - ☐*fine-grained micas*

So, in summary what are the basis for distinguishing crystalline silicate clays; obviously, based on the numbers and combine combination of structural units we already know that you know how these crystals are formed. And each crystals are formed with in the form of layers and obviously, there are two general categories: 1 is to 1 and 2 is to 1. We have already discussed this and obviously, by the number of cations in the octahedral sheet trioctahedral structure and dioctahedral structure we have already covered this.

Then size and location of layer charge and then type of bonding of layers; obviously, remember that there are different types of you know bonding occurs between the layers. Obviously, ionic is ionic bonding is the most you know ionic bonding has a more strength followed by hydrogen bonding and then van der Waals force which is very weak in nature. And obviously, you know we can distinguish clay in a crystalline silicate clays based on the present or you know presence of a cationic interlayer. Like in case of fine grained mica or like, we will discuss that in later.

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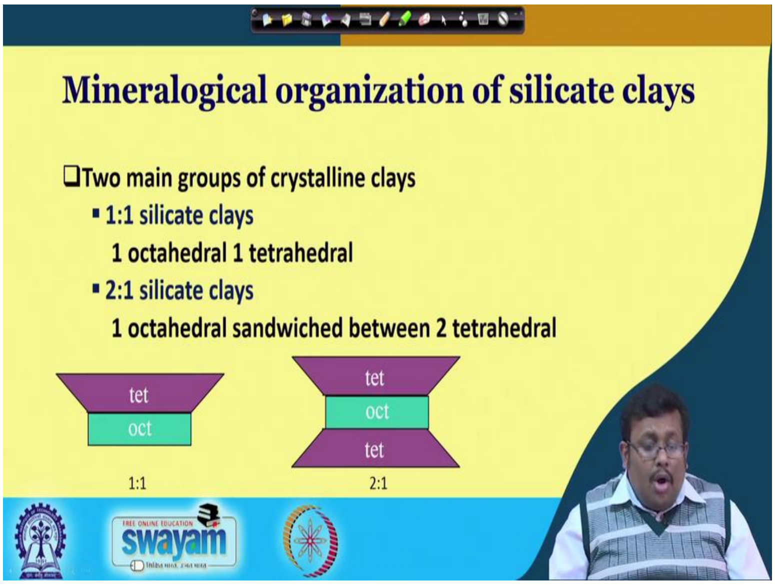

Mineralogical organization of silicate clays

☐ Two main groups of crystalline clays

- 1:1 silicate clays

  1 octahedral 1 tetrahedral

- 2:1 silicate clays

  1 octahedral sandwiched between 2 tetrahedral

So, mineralogical organization of silicate clays we already it covered that in last lecture that is 1 is to 1 type of silicate clays and 2 is to 1 type of silicate clays. I am not going to discuss that in details. Obviously, in case of 2 is to 1 type of layer 1 octahedral layer is sandwiched between 2 tetrahedral sheet. And so, this is the basic you know organizational difference between this 1 is 1 and 2 is to 1 type of layer.

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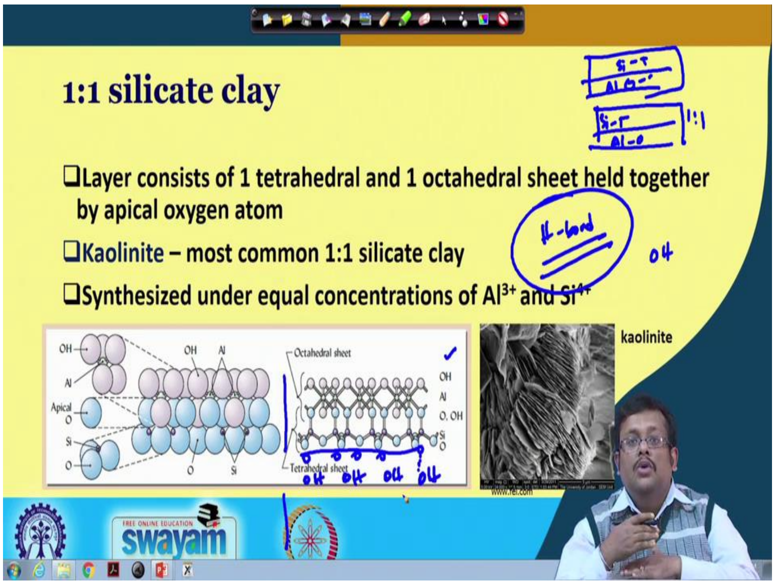

1:1 silicate clay

- ☐ Layer consists of 1 tetrahedral and 1 octahedral sheet held together by apical oxygen atom
- ☐ **Kaolinite** – most common 1:1 silicate clay
- ☐ Synthesized under equal concentrations of Al^{3+} and Si^{4+}

Now, let us start with 1 is to 1 silicate clays. So, you can see here the basically if this type of silicate clays it layer consists of 1 tetrahedral and 1 octahedral sheet held together by apical oxygen atom. Obviously, you can see there are certain planes of atoms; obviously, here you can see hydroxyl and aluminium which are snugly fitted in the holes and also oxygen and silica in between. So, there are several layers of atoms and if we see a two-dimension display we can see. Obviously, there will be hydroxyl plane followed by aluminium plane and then again oxygen and hydroxyl plane followed by silica plane and then oxygen plane.

So, this example of 1 is to 1 I will layer of 1 is to 1 type of clay because there is only 1 silica tetrahedral sheet and 1 aluminium octahedral sheet. What is the major you know clay mineral? Kaolinite is the most common 1 is to 1 type of clay. This is most one of the most prevalent 1 is to 1 type of clay. I remember that this kaolinite is the major ingredient of the porcelain and these kaolinite got its name because, it was first invented in the kaolin province of China. And, it is synthesized under equal concentration of aluminium and silicon.

And this is the actual silica structure you can see these are basically hexagonal flex layer. These are basically hexagonal, this individual layers are hexagonal in shape and this is how this kaolinite will look under the electron microscope.

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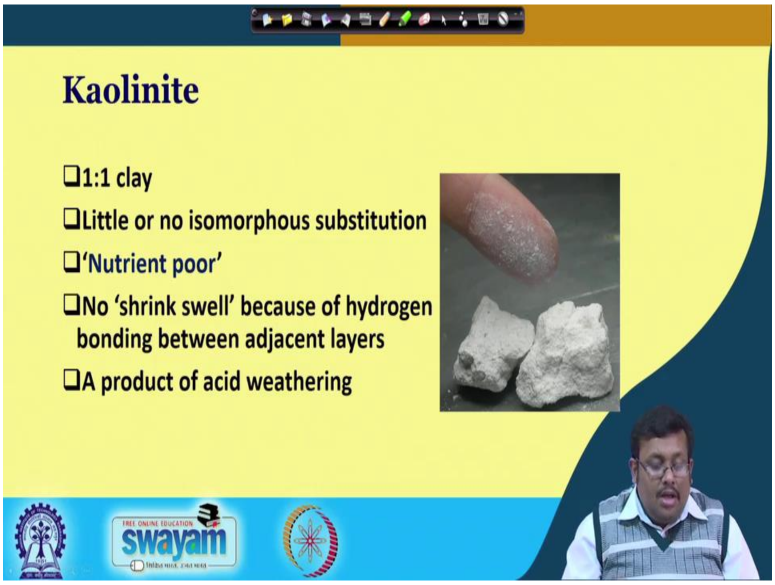

Kaolinite

- ❑1:1 clay
- ❑Little or no isomorphous substitution
- ❑'Nutrient poor'
- ❑No 'shrink swell' because of hydrogen bonding between adjacent layers
- ❑A product of acid weathering

So, let us go ahead and see the some properties of kaolinite. Obviously, in case of kaolinite there is no isomorphous substitution remember that this is very important in case of kaolinite we cannot see any isomorphous substitution. So, due to the due to the absence of isomorphous substitution; obviously, there is very little chance of development of negative charge. There is very little chance of development of negative charge at their surface and as a result of that they are very nutrient poor.

Because no cationic nutrient can absorb at the surface because, of these low you know lower low negative charge development. And obviously, it has got no shrink well potential because of hydrogen bonding between the adjacent layer. So, let me show you if what is that mean. So, if we consider 1 you know tetrahedral you know 1 1 is to 1 kaolinite; obviously. So, this will be silica tetrahedra and this will be aluminium octahedra.

So, similarly another adjacent layer will consists the similar repeating units. So, it will be silica tetrahedra followed by aluminium octahedra. So, in the aluminium octahedra as you can see at the base of aluminium octahedral; obviously, there will be hydroxyl ions and just below these alluminium hydroxyl ions you will see the oxygen plane. So, if you consider this is as a layer single layer and you consider another repeating layer here; obviously, there will be hydroxyl atoms here. So, here we are getting oxygen and here their adjacent hydroxyl.

So obviously, there will be a bond formation between this oxygen and hydroxyl, this is the hydrogen bonding or hydrogen bond. And, due to the presence of this hydrogen bond between these two adjacent layer; this 1 is to 1 type of layer clay or kaolinite cannot show any swelling shrinkage property. Because, of this hydrogen bonding between that two repeating layers. So, that the reason that these I mean kaolinite cannot show any swelling shrinkage properties and obviously, it is a product of acid weathering. And, this is how we kaolinite will look like, it is white in colour. Pure kaolinite is basically white in colour.

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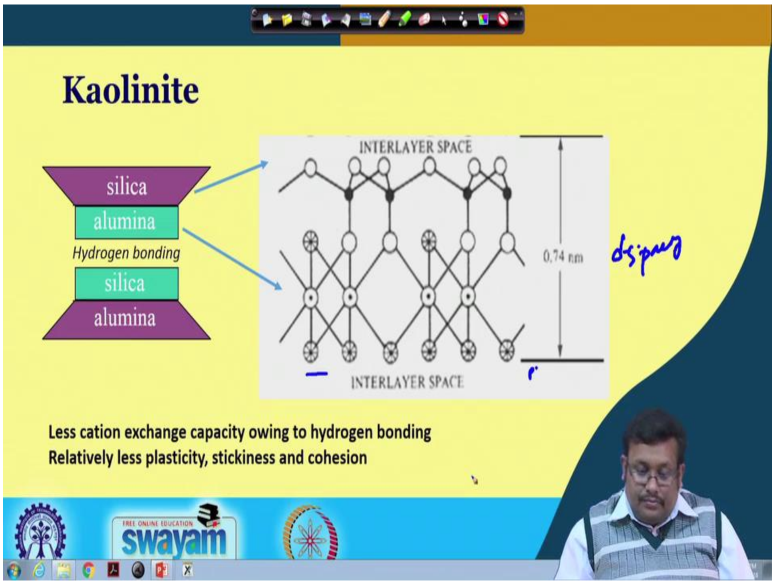

Kaolinite

Less cation exchange capacity owing to hydrogen bonding
Relatively less plasticity, stickiness and cohesion

And this is the interlayer structure; obviously, this is the layer structure of kaolinite. Obviously, you can see the d axis spacing; that means the spacing between. If we consider this is a if we consider this is a plane of layer of atom and; obviously, the adjacent or that very next similar plane layer of atoms the distance is called d axis spacing or d spacing.

And, this d spacing in case of kaolinite is 0.74 nanometer. So, again the d axis spacing in case of kaolinite is 0.74 nanometer or 7.2 Armstrong. So, less cation exchange capacity owing to hydrogen bonding and relatively it is less and this kaolinite shows relatively less plasticity stickiness and cohesion.

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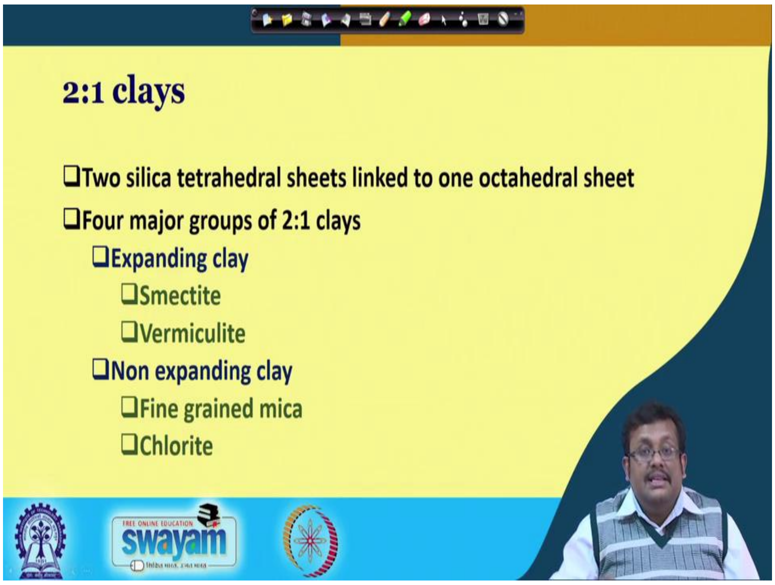

2:1 clays

- Two silica tetrahedral sheets linked to one octahedral sheet
- Four major groups of 2:1 clays
  - Expanding clay
    - Smectite
    - Vermiculite
  - Non expanding clay
    - Fine grained mica
    - Chlorite

So, we have finished the kaolinite; I hope then let us go ahead and see what are 2 is to 1 type of clays. Well, as the name suggest 2 is to 1 is basically 2 will silica tetrahedral sheets linked with 1 octahedral sheet. And, you can see four major groups of 2 is to 1 type of clays: one is expanding clay and the you know non-expanding clay.

Among the expanding clay you can see smectite and then vermiculite. And however, in case of non-expanding clay there are fine grained mica or illite and then clorite.

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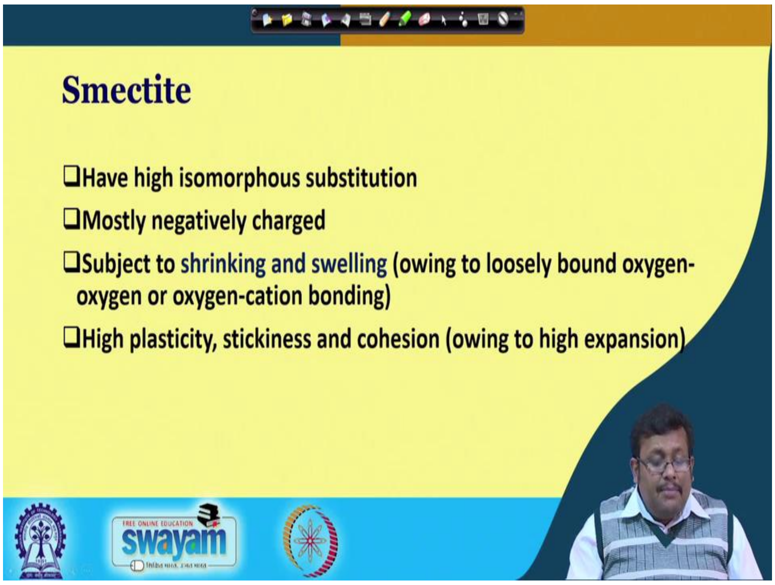

Smectite

- Have high isomorphous substitution
- Mostly negatively charged
- Subject to shrinking and swelling (owing to loosely bound oxygen-oxygen or oxygen-cation bonding)
- High plasticity, stickiness and cohesion (owing to high expansion)

So, these are four I would say these are four major types of I would say these are four major types of 2 is to 1 type of clays and we will discuss them in details not groups, but in the types. So, let us start with the smectite. So, in case of smectite; obviously, in there will be in case of smectite there is a high amount of isomorphous substitution and they are mostly negatively charged because of this high amount of isomorphous substitution. And as a result of interlayer molecules and interlayer water and cations they are subjected to shrinking and swelling.

When owing to loosely bound oxygen to oxygen or oxygen cation bonding we will we will see it in a bit. And, remember that it also shows high plasticity stickiness and cohesion owing to high expansion. So, the one of the major you know example of this smectite is a montmorillonite. And, this smectite type of clay can be found in the black cotton soil of India special in Maharashtra region, where you will see the development of cracks. And swell during the wet, during the monsoon as well as in rises in ellipse; I will show you.

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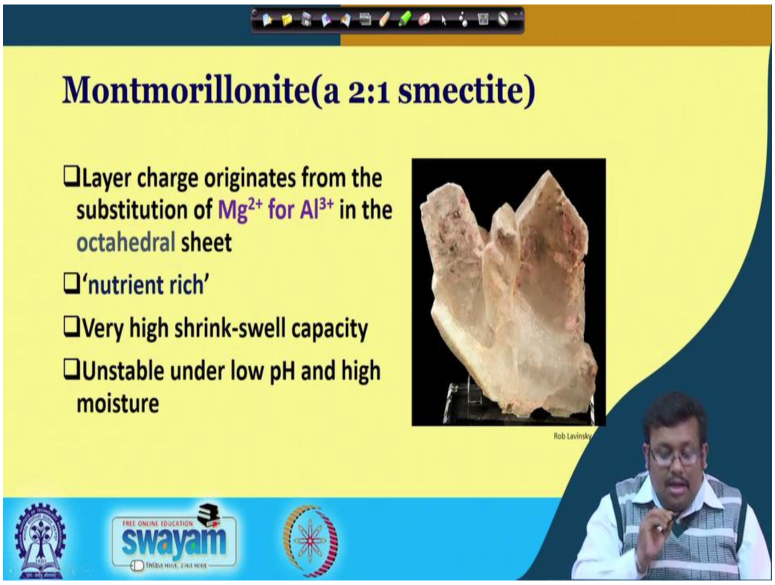

Montmorillonite(a 2:1 smectite)

- ❑Layer charge originates from the substitution of Mg^{2+} for Al^{3+} in the octahedral sheet
- ❑'nutrient rich'
- ❑Very high shrink-swell capacity
- ❑Unstable under low pH and high moisture

Rob Lavinsky

So, let us see the montmorillonite. Montmorillonite is 2 is to 1 type of smectite; obviously, a layer charge originates from the substitution of magnesium from alumina in the octahedral sheet. Remember these are nutrient rich and they show very high shrink swell capacity and they are very unstable on the low pH. And, high moisture and this is how the pure montmorillonite you know will look like.

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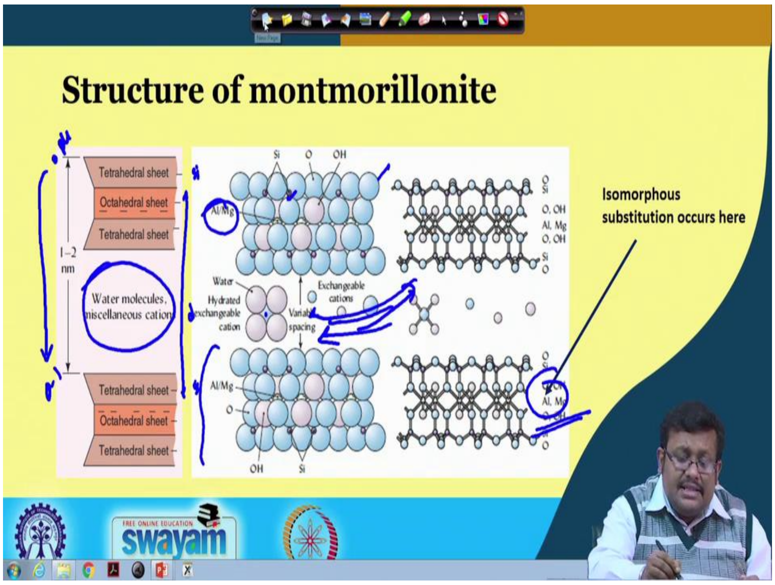

Structure of montmorillonite

Isomorphous substitution occurs here

So, let us see the structure of montmorillonite. So, this is structure of the montmorillonite; obviously, the d axis spacing that is if we consider this is a oxygen plane and this is another repeating oxygen plane. So, the distance is d axis spacing. So, similarly if we consider this is a silica plane, and here is a also silica plane. So, the distance between these two similarity repetitive layer is basically the d axis spacing. So, do not get confused about d axis spacing.

So, montmorillonite the d axis spacing varies from 1 to 2 nanometer and because, in the interlayer space there is a high amount of water molecules and miscellaneous cations. Why there are high molecules in interlayer cation, because you can see this is a structure of montmorillonite. Obviously, there will be hydroxyl, there will be oxygen atoms and there will be silica atoms followed by then hydroxyl then aluminium and magnesium because aluminium and magnesium.

Because of isomorphous substitution and the similar repeatating layer you can see here. So obviously, due to the variable spacing between these two repeatating layer, there will be chance for exchangeable cations to enter. And; obviously, there will be hydrated exchangeable cation inside this interlayer space and as a result of this there will be variable you know distance or there will be variable d axis spacing. As you can see it is varying from 1 to 2 nanometer and remember that isomorphous substitution is occurring in the octahedral layer. So, again in case of montmorillonite the isomorphous substitution occurring the octahedral layer and as a result of this substitution, you know there will be generation of the negative charge.

Negative charge repulse themselves as a result there will be; obviously, you know different hydrated exchangeable cations enter into the interlayer space and as a result there will be variable spacing. And, as a result of this variable spacing they will show shrink and swell property. Because in the dry season; obviously, the interlayer water will evaporate and these two layer will collapse to each other and then it will shrink. And, during the wet season or monsoon season the water will go inside, and then it will create the swelling. So, this is how montmorillonite shows the swelling and shrinkage property.

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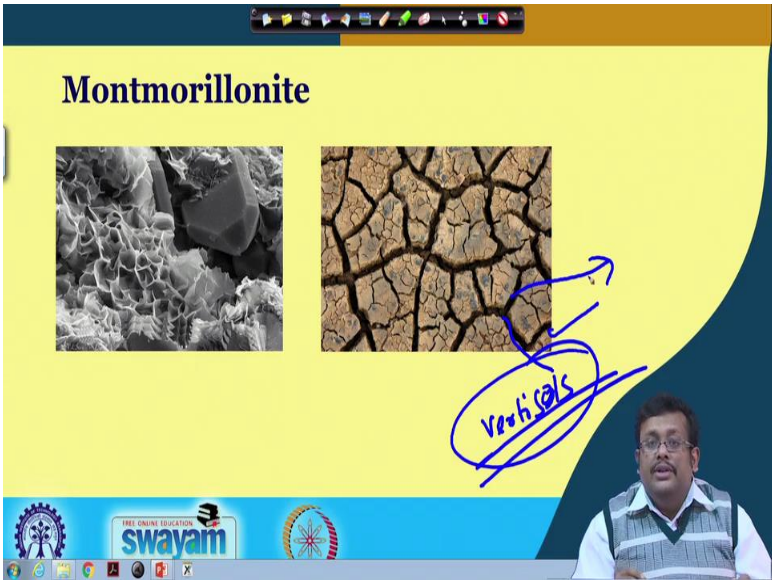

Montmorillonite

And this is how montmorillonite looks like under electro microscope and you can see this is very common black cotton soil in India. And, you can see you know this is an example vertisals; obviously, you know about the vertisal also. Vertisals are like that I mean they are dominated by the smectite and montmorillonite and they shows this deep cracks during the dry season, because of this swelling and shrinkage property.

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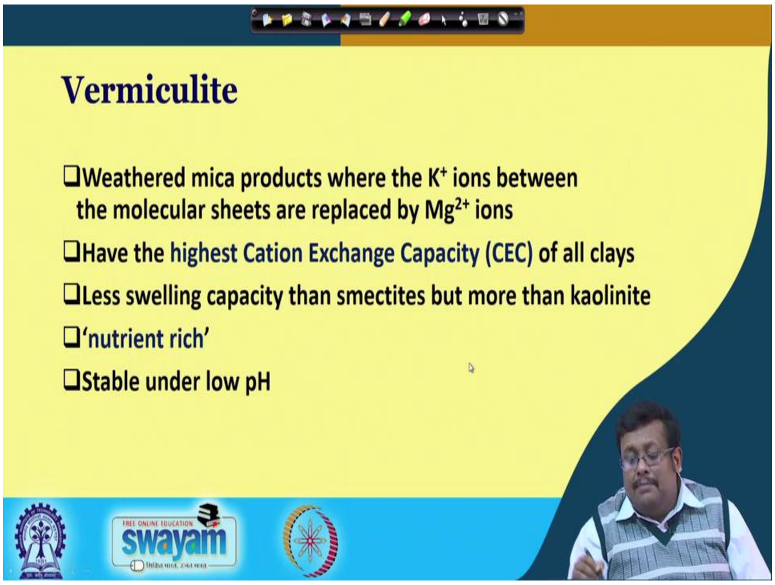

Vermiculite

- Weathered mica products where the K^+ ions between the molecular sheets are replaced by Mg^{2+} ions
- Have the highest Cation Exchange Capacity (CEC) of all clays
- Less swelling capacity than smectites but more than kaolinite
- 'nutrient rich'
- Stable under low pH

So, let us go to another one vermiculite. Remember that it is weathered mica product where potassium ions between the molecular sheets are replaced by magnesium ions. And, they have highest cation exchange capacity we will discuss: what is cation exchange capacity later on among all the clay. And, less swelling capacity than smectite, but more than kaolinite; remember they are very very nutrient rich and stable under low pH. Now, this is important less swelling capacity than smectite, but more than kaolinite we will discuss why.

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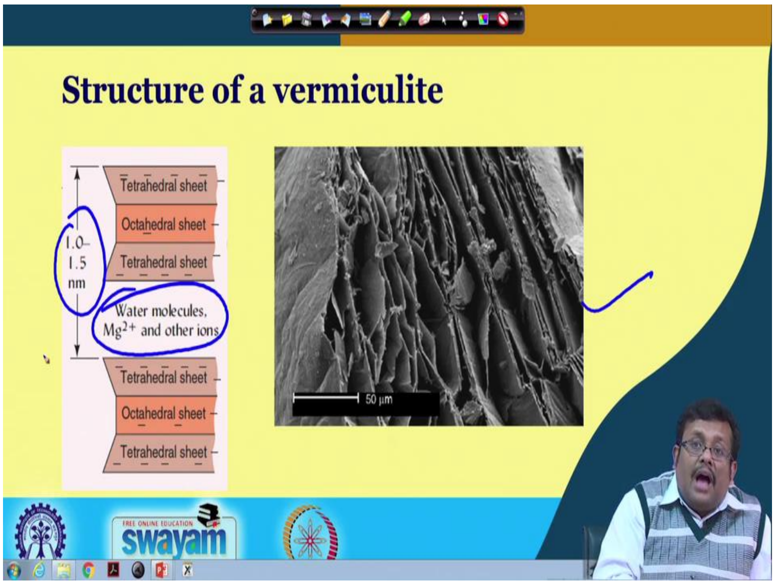

Structure of a vermiculite

So, again this is a structure of vermiculate you can see. This is the right most structure is basically the electro micrograph of vermiculite. And the left one you can see you know the actual structure of vermiculite. The interlayer d axis spacing varies from 1 to 1.5 nanometer. And obviously, in the interlayer space there will be dominance of water molecules magnesium and other ions. So, this is about vermiculite.

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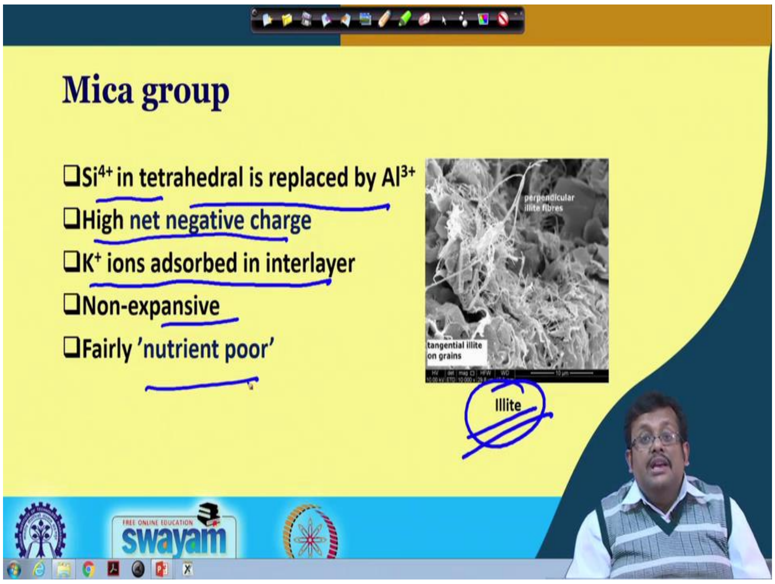

Mica group

❑Si^{4+} in tetrahedral is replaced by Al^{3+}
❑High net negative charge
❑K^+ ions adsorbed in interlayer
❑Non-expansive
❑Fairly 'nutrient poor'

So, let us see what we have; the next group is mica group. Mica group is you know a basically you know represented by this mineral call illite and illite will look like fibrous. Illite will show fibrous nature under electro microscope and in case of illite; obviously, there will be only isomorphous substitution in the tetrahedral layer. In the tetrahedral layer silica 4 or silica atom get replaced by aluminium atom or aluminium ions.

Silica get replaced by aluminium and as a result of that there will be a high net negative charge. Although the interlayer space will be dominated by potassium and which get adsorbed in the interlayer. And, as a result of that they will lock the structure these potassium ions are very small in size as a result of that there will be very less space in the interlayer. And, a as a result will be there will be non-expanding there are non-expensive and they are fairly nutrient poor in nature.

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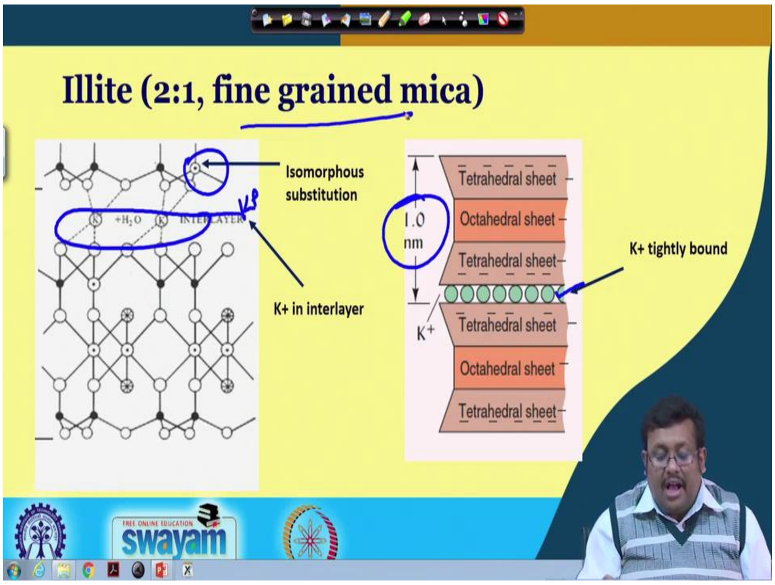

Illite (2:1, fine grained mica)

So, this is a structure of illite; obviously, you can see the isomorphous substitution only occurring in the tetrahedral layer. And obviously, whatever negative charge develop is getting satisfied by this interlayer K plus and K plus is very small as a result of that they are almost collapse. And, as a result of that they are very much tightly bound and as a result their collapse only the d axis spacing is 1 nanometer. And, that is why these are non-expanding in nature; another name of illite is fine grained mica alright.

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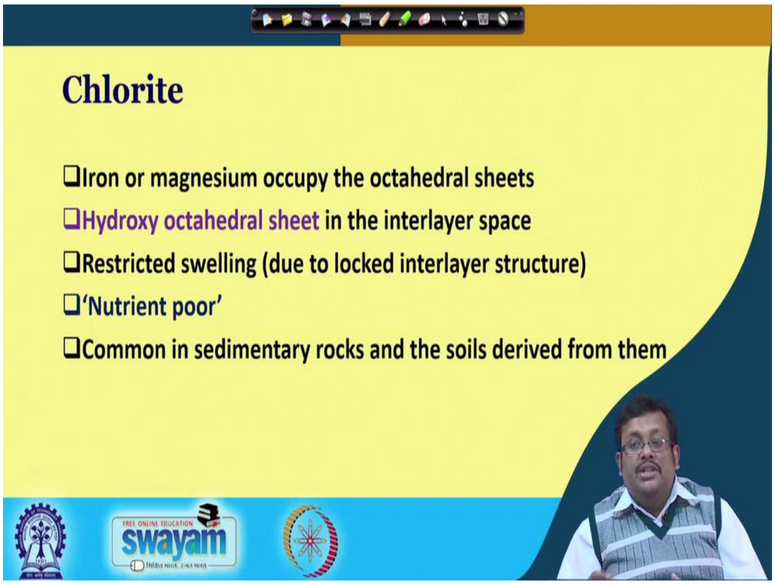

Chlorite

- ☐ Iron or magnesium occupy the octahedral sheets
- ☐ Hydroxy octahedral sheet in the interlayer space
- ☐ Restricted swelling (due to locked interlayer structure)
- ☐ 'Nutrient poor'
- ☐ Common in sedimentary rocks and the soils derived from them

So, the final one chlorite; chlorite is basically also having the similar structure as the other 2 is to 1 type of mineral. However, in the interlayer space there are iron and magnesium occupy, in the there will be you know interlayer octahedral sheet which will be either occupied by iron or either occupied by magnesium. We talked about that in our last class; obviously, when there will be magnesium hydroxide interlayer that will be considered as brucite layer.

When there will be alluminium hydroxide interlayer that will be considered as gibbsite layer. So, hydroxy octahedral sheet in the interlayer space and they; obviously, due to the presence of this hydroxy octahedral interlayer space they shows restricted swelling. Due to the locked interlayer structure they are nutrient poor and there very much common in sedimentary rocks and the soils derived from them.

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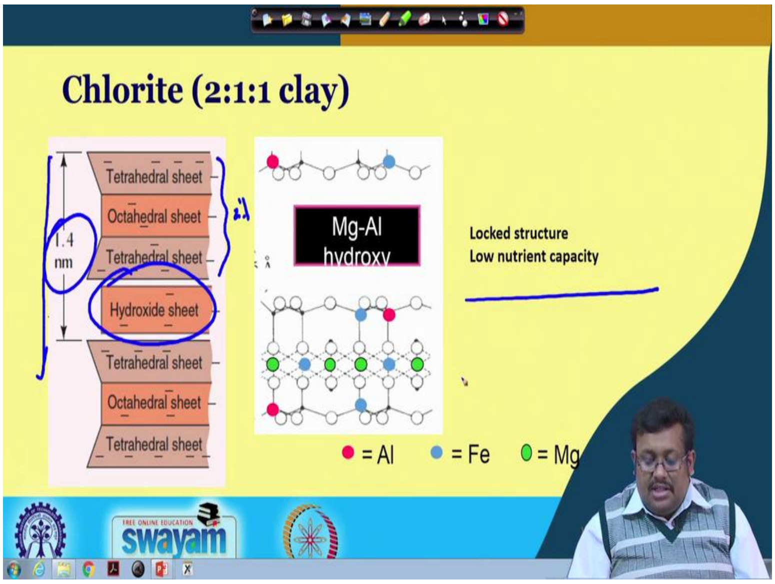

Chlorite (2:1:1 clay)

Locked structure

Low nutrient capacity

So, this is a structure of the chlorite you can see; obviously, they are almost similar than that you know that with the 2 is to 1 type of mineral. However, in the interlayer space there is a hydroxide sheets based on the dominance of hydroxide, based on the dominance of the cations of the hydroxide they are named differently.

Obviously, you know either it is magnesium hydroxide or ammonium hydroxide. The interlayer or d axis spacing is 1.4 nanometer and as a result of the presence of this hydroxide sheet their locked structure and they have low nutrient capacity.

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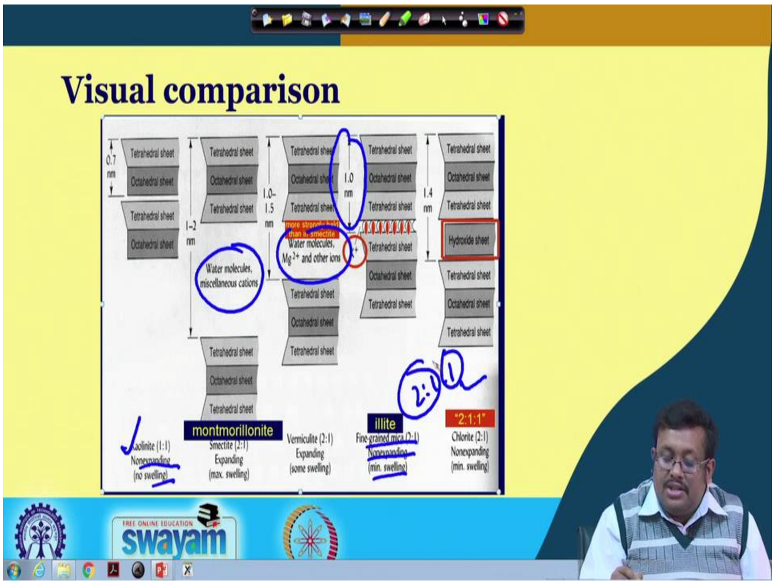

Visual comparison

So, let us see visual comparison between all the different types of you know clay minerals some major clay minerals. Remember that there are 100’s of different clay minerals; however, we are only focusing on 4 to 5 major ones. So, let us see what are their visually how can separate them. So, you can say let us start with the simplest one. So, the kaolinite, kaolinite is the simplest one, it is non-expanding and non-swelling, it is 0.5 you know 1 is to 1 type of layer; with the d axis spacing of 0.7 nanometer followed by montmorillonite.

Montmorillonite is you know one is you know 1 to 2 nanometer interlayer or d axis spacing and water molecules. So, you know the interlayer space is dominated by either water molecules or miscellaneous cations. And, in case of vermiculite the interlayer space is dominated by water molecules and magnesium and other ions. And, the d axis spacing is little bit lower than that of montmorillonite; it is one point 1 to 1.5 nanometer.

And then find in mica or non expanding illite; obviously, due to the presence of interlayer potassium they are locked in nature. And, the d axis spacing is also very less followed by these chlorite which is 2 is to 1 1 is to 1. We by the way we call to a chlorite as 2 is to 1 is to 1 because 2 is to 1 we already know and 1 stands for another magnesium or aluminium hydroxide sheet, and these are also non-expanding on minimum swelling. So, this is the visual you know visual comparison between these major clay minerals.

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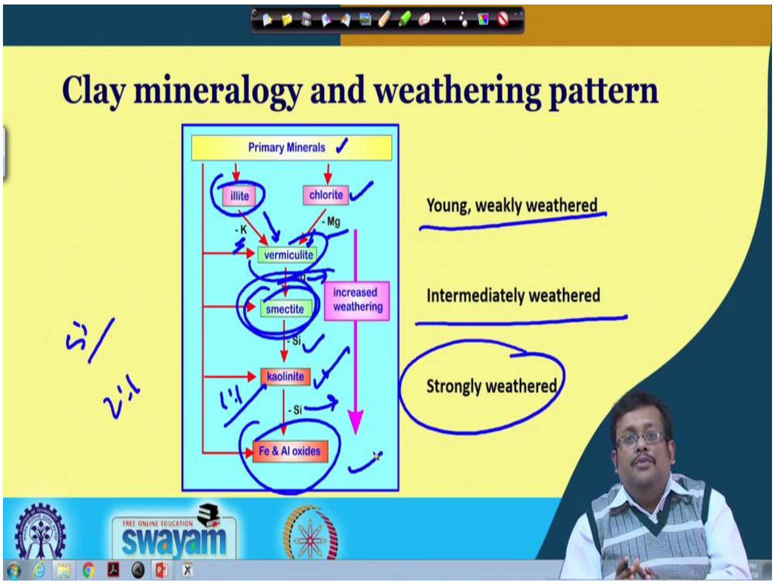

Clay mineralogy and weathering pattern

So, let us see what how clay mineralogy and weathering patterns are linked. So, this is very interesting diagram. So, that you know secondary minerals or clay minerals basically forms from weathering of the primary minerals. So, let us see what are the sequence of different secondary minerals when they are formulating, when they are generating from the primary minerals. So, let if you see the primary minerals these are the first or precursor of secondary minerals or clay minerals.

So, at first from the primary minerals; obviously, there will be the formation of illite or chlorite. And in the next step; obviously, the interlayer potassium of the chlorite interlayer potassium of illite will be replaced. Because, as the weathering is going on all the interlayer you know interlayer ions will be getting replaced by other ions which are present in the soil environment. Obviously, you will see that illite will be converted to vermiculite because the only difference between illite and vermiculite is the interlayer potassium. So, when the interlayer potassium get replaced they will be ultimately converted to the vermiculite.

Similarly, in case of chlorite when the magnesium will be replaced magnesium will be you know magnesium will be weathered or magnesium will be removed; ultimately it will be producing the vermiculite. And, from the vermiculite when the interlayer magnesium will be further reduced or removed ultimately it will produce a smectite, from the smectite remember that this is the 2 is to 1 type of mineral. So, we are having more dominance of silica tetrahedral than alluminium octahedral 2 is to 1 you know. So, there will be further weathering, further weathering will remove the silica further ultimately we will be producing 1 is to 1 type of kaolinite. And, further and extreme weathering condition there will be further removal silica ultimately producing the iron aluminium oxide.

So, you can see in case of young and weakly weathering soil you will see the dominance of illite and chlorite. And, in case of intermediate weathering you will see the dominance of smectite in sometime vermiculite. And obviously, in case of strong weathering condition you will see the dominance of kaolinite and iron and alluminium oxides. So, this is how weathering and intensity of weathering and help in changing one clay mineral to another clay mineral.

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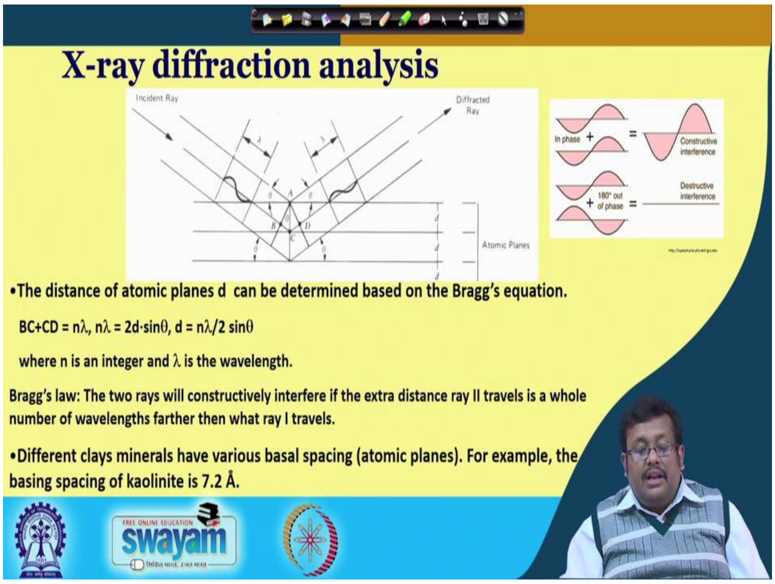

X-ray diffraction analysis

•The distance of atomic planes d can be determined based on the Bragg's equation.

$BC+CD = n\lambda$, $n\lambda = 2d \cdot \sin\theta$, $d = n\lambda/2 \sin\theta$

where n is an integer and λ is the wavelength.

Bragg's law: The two rays will constructively interfere if the extra distance ray II travels is a whole number of wavelengths farther then what ray I travels.

•Different clays minerals have various basal spacing (atomic planes). For example, the basing spacing of kaolinite is 7.2 Å.

This is the so, we have covered the basic structure of clay minerals and we have discuss about their d axis spacing and all these important parameters which are you know. And, then we made the visual comparison between different clay minerals and we distinguish them based on their d axis spacing and also based on the interlayer cations and interlayer other molecules.

So, let us rap up here and in the next lecture we will be finishing these silicate clays. And, then we will go ahead and see: what are the different sources of charge which are of different sources of charges which basically develop within the clay mineral.

So, till then thank you.