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Lecture-09
Inorganic Soil Components (Contd.)

Welcome students to this fourth lecture of week 2 of the NPTEL course environmental soil chemistry and in this week we are talking about different inorganic components of soil. So, in the previous 3 lectures of this week we have talked about in details about different primary minerals and different types of coordination structures, we have learned about Pauling's rules, we have talked about 5 different Pauling's rules, we then we have talked about different coordination compound, coordination amount number.

And then no rattling limit and then how this coordination structure changes depending on the ratio of radius ratio of cations and anions, then we have started talking about primary minerals, I have give I have showed you different examples of primary minerals and also we have started talking about the secondary minerals. In the secondary minerals as you know we have started with 1 is to 1 type of mineral.

In the 1 is 1 type of mineral we have talked about 1 is to 1 di-octahedral kaolinite, we have discussed their structure and also we have discussed the halloysite which has the similar structure as kaolinite. But within interlayer water molecule, so today's lecture will be starting with this 1 is to 1 trioctahedral serpentines. Now in this 1 is to 1 trioctahedral serpentines that basically you know 2 trioctahedral serpentine that are 1 is to 1 type of clay.

Or you know their most important are antigorite and chrysotile and these clay have all 3 octagonal position fields with magnesium because these are trioctahedral you know that in that trioctahedral structure 3 out of the 3 octahedral positions are filled. And in that case magnesium is the major cation, so in this case all 3 octagonal positions are filled by magnesium and there is no substitution in either the tetrahedral or octahedral sheet and does they have no permanent negative charge, the permanent negative charge always developed due to the isomorphous substitution, whether there is no isomorphous substitution just like in kaolinite there will be no negative charge development.

Similarly in case of this 1 is to 1 trioctahedral serpentine as you can see I have shown you in the picture of antigorite and chrysotile, both of them does not have both of them do not show any kind of isomorphic substitution. As a result they are having no permanent negative charge.

So, we have completed 1 is to 1 type of clay mineral. Now let us move to 2 is to 1 type of clays, at first in the 2 is to 1 type of clay let us talk about the pyrophyllite talc group, now pyrophyllite is a 2 is to 1 di-octahedral clay and it belongs to this pyrophyllite talc group. So, if you see it has the chemical formula of these $Al_2Si_4O_{20}OH_2$ and it had it does not show any kind of isomorphous substitution.

So, there is a characteristic feature of the pyrophyllite and as a result of that it is electrically neutral and since it is electrically neutral it has the layer charge per half-cell formula unit 0. So, it has 0 layer charge per cell formula unit. So, in case of terminal we generally use half cell formula unit to define its chemical composition and layer charge. So, in this case in case of pyrophyllite we are having 0 layer charge.

So, there is also no interlayer space, however, the edge sides play a major role in various physical properties and retention of metals. So, although they do not have any kind of you know negative your permanent charge development due to the absence of isomorphous substitution, they do play some roles in different various physical you know various physical and retention physical properties and retention of metals.

So, if we move ahead and see the structure of the pyrophyllite, it is becoming more clear that these the 2 is to 1 type of structure as we have discussed 2 silica tetrahedral sheet and 1 octahedral sheet, sandwich in this in-between these 2 tetrahedral sheet and it is basically a di-octahedral structure because aluminum is present. So, this is the structure of pyrophyllite and as you can see among the 2 layer the interlayer space is almost 0. So, this is the structure of pyrophyllite and this is the actual pyrophyllite you know mineral.

So, let us go move ahead and see what is the another important mineral in this group. Another important mineral in this group is talc which is also a 2 is to 1 tri-octahedron clay. So, again it is a tri-octahedral clay that means it has magnesium in its structure. So, as you can see in this chemical formula magnesium is present and also it does not show any type of isomorphous substitution just like a pyrophyllite and interlayer space and it has also the 0 layer charge per half cell formula unit. However. the edge sites may play a major role in various physical and retention of metal. Just like we have seen in case of pyrophyllite.

So, let us move ahead and see what are the other important 2 is to 1 type of mineral. Let us discard the serpentine smectite serpentine group, this is one of the major you know one of the very important group and this group consists of di-octahedral smectite and tri-octahedral saponites and it has a layer charge of 0.2 to 0.6 per half cell formula unit and an example of this di-octahedral smectite is montmorillonite.

It is a most one of the most important mineral clay mineral we are going to talk about and other dioxide the smectite are beidellite and nontronite and as far as the tri-octahedral saponites are concerned the examples are saponite and hectorite. Among all of these this montmorillonite plays a very important role in soil physical and chemical properties.

So, if we move ahead and see in details about the montmorillonite, this is this montmorillonite clay mineral basically looks like. So, the layer charge basically in case of montmorillonite originates from the substitution of magnesium for aluminium in the octahedral sheet. So, here the mainly isomorphous substitution goes on in the octahedral sheet, it is highly nutrient rich.

Because it generates high negative charge or permanent charge and it has very high shrink swell capacity, why we will discuss, that means this clay can shrink during dehydration and if you if you rehydrate that soil it will swell. So, this is one of the major property of this type of clay mineral, it is shrink it will shrink and swell. So, it is also very unstable under low pH and high moisture condition.

So, if we go ahead and see the structure of montmorillonite, this is the structure of montmorillonite looks like. So, basically if you see this is 1 layer, this is 1 layer and this is another layer and in this 2 is to 1 type of layer you can see at the octahedral layer 1 aluminium, so basically it is a di-octahedral structure. So, in the di-octahedral structure when aluminum gets replaced by this magnesium then this negative charge develops.

And in the interlayer space, this inter layer space between 2 layer is basically occupied by calcium, magnesium and water. So, basically miscellaneous cations and water molecules occupied in the middle and as a result there is a large gap between the 2 adjacent layers and it is that is why it is showing high or maximum swelling okay. So, I hope this is now clear to you. If we move ahead.

And see what is the reason behind that. Now as I have told you in the last slide that isomorphous substitution occurred only nocturnal sheet, negative charge develops and when the negative charge develops in the surface of these clay mineral or a surface of these layers there is always a natural repulsion between the negative charges when they when the 2 layers come very close.

Because similar charge you know they repel each other. As a result of that there is a high space in between and it causes cations to move into the interlayer space where they can replace by other cations. So, this is the reason that this montmorillonite show is high swell and shrink property.

So, this is in details about the structure of the montmorillonite, remember this the d axis spacing is 1 to 2 nanometer, it is highly you know it is highly expanding type of mineral. So, here the d axis spacing is 1 to 2 nanometer. Now what is the d axis spacing. D axis spacing is basically the distance between 2 repeating layers of atoms. So, here if you see these are 2 adjacent layers.

And in this adjacent layer if we consider this is the top layer of oxygen sorry this is the top layer of oxygen. So, the repeating top layer of oxygen will be found here in the next adjacent layer and this linear distance between these 2 repeating you know similar layer of atoms is called the d axis spacing. Now the d axis spacing is highest one of the highest in this case that means in the montmorillonite clay mineral among all the mineral.

So, this is the electron microscope view of montmorillonite you can see it is irregular flake like structure and the clay in India which is mostly dominated by this montmorillonite type of soil where clay mineral is the black cotton soil which you can see in the peninsula region specially in Maharashtra. So, here you can see this type of soil and as a result of swelling and shrinkage these soil looks like this.

They basically develop these large cracks during the summer season where there is no water and water will be dehydrated from the soil as a result there will be large cracks as you can see and during the monsoon season when there will be further water movement then these cracks will be closed. So, this is called periodic swelling shrinkage property of montmorillonite.

So other 2 is to 1 type of clay in the smectite saponite groups are you know beidellite, nontronite. So, in case of beidellite and nontronite isomorphous substitution occurs in the tetrahedral sheet, we have seen that in case montmorillonite the the isomorphous substitution was occurring in the octahedral sheet. Now in case of beidellite, nontronite these isomorphous substitution occurs in the tetrahedral sheet.

Remember nontronite is iron-rich and saponite is you know is a mineral where isomorphous substitution occurs in the tetrahedral sheet, hectorite is basically lithium bearing mineral and also in case of hectorite substitution occurs in the octahedral sheet. So, depending upon which particular iron is dominant and where the isomorphous substitution is going on we can differentiate different types of clay mineral.

Another 2 is to 1 type of mineral is mica, remember in case of mica it has a layer charge of 1 per half cell formula unit, it is basically di-octahedral in nature that means aluminum is dominated in their octahedral sheet. Examples are muscovite and paragonite, also there are some tri-octahedral micas, examples are biotite, phlogopite, lepidolite. Now except paragonite other micas have potassium ions in the interlayer space.

This potassium ion is very, very small and it basically comes in the interlayer space and lock the structure and as a result these micas are the major potassium bearing minerals in the soil, when these micas weather they basically converts into partially expansible 2 is to 1 type of clay like illite and vermiculite. We will be discussing those 2 clay minerals in the next slides. So, mica is a 2 is to 1 type of clay mineral.

It has both di-octahedral and tri-octahedral variants and di-octahedral one of the major di-octahedral variant is a muscovite, where there the one of the major tri-octahedral variant is biotite, it has got potassium ions in their interlayer space and as the result is a major potassium bearing minerals in the soil and as a result of weathering it can convert into partially expandable or partially expensable 2 is to 1 type of clay like illite and vermiculite.

So, this is the structure of muscovite as well as phlogopite, you can see that how this potassium ions are in between these layers, these are the small potassium ions and this is the basically 2 is to 1 type of structure and this is the phlogopite structure. Now in case of muscovite it is basically di-octahedral and in case of the phlogopite you can see it is basically tri-octahedral structure.

Since magnesium is present in the octahedral shaped. We have already discussed that in the previous slide. Now let us move ahead and see another very important mineral called 2 is to 1 type of 2 is to one of the major important 2 is to 1 type of clay minerals that is illite, the another means another name of illite is you know fine mica I mean it is basically water product of the mica and it has a layer charge of 0.8 per half cell formula unit which is intermediate between smectite and mica.

And just like you know in just like mica it interlayer space is also dominated by potassium, it is the predominant inter layer ion, and it has more silica magnesium and water this less tetrahedral aluminum and potassium and water then mica as you can see here there is a structure of the illite as you can see this is the 2 is to 1 type of structure and interlayer space is occupied by potassium making it a locked and collapse structure. And here the D axis spacing is only 1 nanometer.

So, this is basically in details about the illite structure, the interlayer space is occupied by these potassium ions and since it is a basically weathered product of mica it is also known as the fine-grained mica, it is non expanding type of mineral, it shows minimum swelling because of this interlayer potassium ions which basically collapse the structure. Since this potassium ions are very, very small in size.

Now one of the basic feature of this illite structure is the isomorphous substitution always occurs in the tetrahedral sheet and as a result of this isomorphous substitution the tetrahedral sheet K+ or potassium ion comes into the interlayer space to satisfy the charge. So, as a result of tetrahedral substitution isomorphous substitution there is negative charge developed in the surface and this negative charge which develops in the surface is occupied or satisfied by this potassium ions which comes into the interlayers making it is a lock structure.

As a result of that this is a illite is basically known as a non expandable or non you know minimum swelling type of mineral. So, this is illite electron microscopic picture you can see it basically appears like you know fibrous under the electron microscope. Now another important mineral is vermiculite, now vermiculite is basically where the product of illite when illite goes further weathering it basically converts to vermiculite.

So, it is basically weathered mica product because mica is the you know mica is the major mineral from where the illite has been formed and then further down these vermiculite group is formed. So, this is the way that mica products were the potassium ions between the molecular sheets are replaced by magnesium.

And so this is the one of the major distinguishing characteristics and difference from illite. So, in illite the interlayer space was occupied by potassium and however when further weathering going on this potassium and get replaced by water molecules as well as magnesium and other ions. So, there is a dominance of magnesium in the interlayer space in case of vermiculite.

And it has a layer charge of 0.6 to 0.9 per half cell formula unit. Di-octahedral vermiculite obviously you can see the substitution in both the tetrahedral and octahedral sheet. However, in the tri-octahedral variants of vermiculite you will see substitution only in the tetrahedral sheet and all 3 of the octahedral cations position are filled with magnesium.

So, if we go ahead and see the detailed structure of vermiculite it becomes very clear that the why it is having high negative charge development, because it shows the isomorphous substitution both in the tetrahedral sheet as well as in the octahedral sheet. So, you can see in the tetrahedral sheet silica get replaced by this aluminum, whereas in the octahedral sheet aluminum gets a aluminum gets replaced by magnesium as well as iron.

Irons are denoted by these blue dots, whereas green dots are basically magnesium. So, as a result you can see the lot you know in both the sheets octahedral sheet and tetrahedral sheet the isomorphous substitution going on. As a result of that there is lots of charge imbalance developed in this both sheets and as a result of that high nutrient supplying you know charge imbalance occurs.

And as a result this charge imbalance negative charge developed as a result of high negative charge it this vermiculite has the capacity to attract the nutrient cations and as a result this type of soil can supply a high amount of nutrients to the plants. So, if we move ahead and see the electron microscopic view of vermiculite you will see that this is the electron microscope view of vermiculite.

It has the highest cation exchange capacity because of huge amount of substitution going on in the tetrahedral sheet as well as in octahedral sheet, it has less swelling capacity than smectite but more than kaolinite and it is nutrient rich why it is nutrient rich we have already discussed and it is stable under low pH conditions.
So, the another very important mineral is known as the chloride and the structure of the chlorite is a specific you know we designate the structure of the chlorite as 2 is to 1 is to 1 type of clay, sometimes we call it 2 is to 2 type of clay also. So, what are the features of chloride. So, basically it has the 2 is to 1 type of layer octahedral sheet sandwich within 2 tetrahedral sheet just like any other 2 is to 1 type of clay mineral.

However, in the interlayer space is basically dominated by a hydroxide sheet. So, as you can see 2 is to 1 type of clay with continuous hydroxide interlayer and this iron and magnesium occupy this octahedral sheet. So, you can see this octahedral sheet are basically dominated by either iron or magnesium and in this hydroxide octahedral sheet in the interlayer space maybe it is a tri-octahedral or it may be di-octahedral.

If it is a di-octahedral it is known as the brucite layer where the hydroxide sheet is dominated by magnesium, whereas if it is a di-octahedral hydroxide sheet then it is known as gibbsite. So, in the di-octahedral the it is dominated by basically aluminum. So, these are 2 types of hydroxide layer which can come in the interlayer space of the chlorite clay mineral. Now in the di tri-octahedral I mean you know there is another called di-tri-octahedral.

So, di-octahedral in the 2 is to 1 type of layer and tri-octahedral in the interlayer octahedral hydroxide sheet. In this condition it will be called a di-tri-octahedral chlorite. Another condition is tri, tri-octahedral, that means tri-octahedral in the octahedral sheet of the 2 is to 1 layer as well as the interlayer octahedral hydroxide sheet. So, both the hydroxide sheet as well as the octahedral layer will be dominated by magnesium.

In case of tri, tri-octahedral, however in case of di, tri-octahedral the interlayer space will be dominated by tri-octahedral hydroxides like brucite, however in the 2 is to 1 type of layer the octahedral layer will be di-octahedral that means dominated by aluminum. So, I hope now it is clear to you.

So, if I move ahead and see that is you know structure in details obviously this shows the detailed structure of chlorite as you can see that this is the you know oxygen atom followed by either silicon and aluminum because here some tetrahedral substitution is also occurring in the octahedral sheet either it is dominated by aluminum then we call it is a di-octahedral if it is dominated by magnesium then it is a tri-octahedral.

And similarly when it is dominated by Fe2+ it is also tri-octahedral and in the interlayer space it is basically occupied by this hydroxide interlayer. So, this is how this chlorite structure will look like okay.

Now chlorite shows the restricted swelling due to locked interlayer structure since there is a magnesium or aluminum hydroxide layer in the interlayer it shows the lock structure and as a result it is very nutrient poor because there is no space for nutrients to get adsorbed and it is very common in sedimentary rocks and the soil derives from them.

So, if you see a visual comparison between different types of clay minerals it will be more clear. So, we start with the kaolinite which is a 1 is to 1 type of non expanding or non swelling the d axis spacing is low is 0 point only 0.7 nanometer because of the presence of the strong hydrogen bonding in the interlayer space, it is also a we call a structure and then we go to montmorillonite where there is huge interlayer space.

And the isomorphous substitution occurs in the octahedral sheet and the interlayer space is occupied by water molecules and miscellaneous cations, the d axis spacing is highest 1 to 2 nanometer, vermiculite also 2 is to 1 type of expending some swelling it is not as much it does not give as much as swelling as montmorillonite, but it also gives some amount of swelling in term you know it is basically the interlayer space is dominated by water molecules magnesium and other ions.

The d axis spacing is 1 to 1.5 nanometer, similarly illite which is a fine-grained mica, it is basically weathered product of mica, the interlayer space is dominated by potassium and it is showing the restricted swelling the d axis spacing is only 1 nanometer. In case of 2 is to 1 type of clay chlorite it is basically dominated by the hydroxide layer a hydroxide sheet in the interlayer space giving a you know locked structure.

So, this is a visual comparison of different types of different important clay minerals showing their structural differences. So, if we see how this clay mineral basically develops or converts from one very you know one type of clay mineral to another type of clay mineral we have to see this you know this diagram. So, this diagram basically shows how this primary mineral ultimately goes to the iron and aluminum oxide which is the highest you know which is the highest form of degradation or chemical weathering or highest chemical weathering products.

So, the primary minerals first develops to illite and then chlorite and then by removing the potassium from the interlayer space of the illite it develops into vermiculite and also in case of chlorite when the magnesium interlayer the hydroxy interlayer sheet is removed due to weathering process chemical weathering, it collapsed into vermiculite and in the vermiculite when the interlayer magnesium gets depleted it develops into smectite which is a still it is a 2 is to 1 type of mineral.

Then this smectite goes further weathering and then you know remove 1 silica tetrahedral layer. So, there is a loss of silica and it remove it converts into the kaolinite which is a 1 is to 1 type of mineral and from there 1 is to 1 type of kaolinite when there is a further degradation further chemical weathering, high intensity chemical weathering warm and humid climate then there will be further loss of silica ultimately it will be developed into the iron aluminum oxide.

So, you can see that in this direction there is an increased weathering rate. So, obviously the illite and chlorite will appear in the initial stage of weathering however kaolinite and iron all aluminum oxide will appear in the final or you know that or the later stages of weathering. So, guys we have covered the basic the major important 2 is to 1 type of mineral and 1 is to 1 type of mineral clay mineral in this lecture.

The next lecture we will be talking about some other important secondary clay minerals and second other secondary minerals, different integrated mineral, inter stratified mineral and also we will be talking about different methods to identify different clay minerals, thank you let us meet in the next lecture.